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Atom/Bond Analysis of Conformational Properties of Molecules (PCILO-CNDO)

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Abstract: A methodology to analyze the conformational properties of molecular systems in terms of local energy contributions is presented. The energy partitioning proposed here is based on a theoretical additive expansion in terms of one-bond. two-bond, three-bond, etc., contributions. The additive structure of the energy is built using fully localized bond MO's and a perturbation expansion. This methodology has been applied to the study of internal rotation barriers of the following molecular series: CH_3XH_n, $CH_3XH_{n-1}CH_3$ (X = C,N,O), and $X_3B{\cdot}NY_3$ (X,Y = H,F). The energy analysis is made in terms of one-, two-, and three-body contributions at the zeroth-, second-, and third-order perturbative corrections within the PCILO-CNDO scheme. The role of vicinal, geminal. and long-range interactions (third-neighbor bonds) is considered. the transferability of similar contributions from one series to the other, and the effects of substitutions. Our method confirms directly the important role of the delocalization tails. but also the nonnegligible role of the zeroth-order repulsive effects and intramolecular van der Waals dispersion energies.

The conformational properties and especially the internal rotation barriers represent a very good test of the accuracy of quantum chemical methods. since they concern changes of a few kilocalories per mole in a total energy of 10^5 to 10^7 kcal/mol. A theoretical approach such as the Hartree-Fock approximation provides the accurate values for the internal rotation barriers in numerous molecules;[2] the barrier is calculated by subtracting the total energies evaluated for each appropriate conformation of the molecule, but this procedure itself provides no information about the origin of the barrier.

The explanation of the sources of such barriers is a very interesting problem. In the past many different theoretical approaches have been carried out. Among them, Lowe[3] qualitatively explained the barriers about single bonds, comparing the results obtained with the following type of approaches: i.e., (1) using a decomposition of the total energy change with rotation into nonlocal physical components,[4] (2) using delocalized or canonical molecular orbitals, and (3) using localized MO's.

Approach 1 presents the following serious defects: (a) the qualitative description of a barrier (as repulsive or attractive dominant) can change depending on whether the calculation is carried out in the rigid-rotor or the geometry-optimized approximation,[5,6] and (b) for two calculations based on identical geometries, the use of different basis sets can change a calculated barrier from attractive to repulsive dominant.[4-7] Moreover, this approach does not allow a direct relation with the local geometry changes of the nuclear skeleton. With respect to approach 2, the delocalized nature of the canonical Hartree-Fock orbitals does not allow us to analyze the phenomena explicitly in terms of bonds or atomic interactions. Hence, we think that a local analysis in terms of local contributions is more promising; it may refer to atoms or to bonds.

The expression of the Hartree-Fock energy in the LCAO approximation allows a partition in one-, two-, three-, and four-atom terms; it is reduced to one- and two-atom contributions in the CNDO approximation.[8] Section IA briefly recalls this partition and illustrates its limitations in the analysis of a few energy conformational changes.[9-11] The important contributions to the energy changes sometimes concern monatomic or diatomic contributions between atoms whose relative positions are unchanged during the conformational change. Such contributions may come from some changes in the density matrix which are not explained.

In section IB, one considers the analysis of SCF results, referring to bonds (use of bond-like SCF localized MO's[12]). This methodology gives very interesting information about the local origin of the barriers, showing the dominant role of the tails of the SCF-MO's on vicinal groups, as well as the important role of the monoelectronic part of the CNDO (or INDO)

Table I. Bonded and Nonbonded Atomic Contributions to the Total Energy of F_3NO[a]

∠ONF	ΔE_{tot}	ΔE(O)	ΔE(N)	$3\Delta E$(F)	ΔE(N·O)	$3\Delta E$(N·F)	$3\Delta E$(O·F)	$3\Delta E$(F·F)
118°/110°	−13.04	4.30	5.17	−8.50	0.03	−13.15	−12.19	11.30

[a] Reference 10. Values in table given in kcal/mol.

Hamiltonian. This kind of analysis may be performed to a high degree of accuracy upon the wave function (and the tails of localized MO's),[13] but it is not satisfactory to explain the physical origin of the tails (i.e., through space delocalization or step by step delocalization processes).

The local approach of Sovers et al.[14] avoids the SCF step. They used a crude wave function built with fully localized MO's on the bonds. This ab initio method represents an a priori analysis; it gives information about the role of short-range repulsion effects in the ethane and methanol barriers.[14,15] This zeroth description might be improved through an appropriate perturbation expansion.

A further local decomposition in terms of one-bond, two-bond, three-bond, etc., effects is possible.[16,17] The methodology proposed in this paper to the study of conformational problems constitute a construction of an additive structure of the energy in terms of one-bond, two-bond, etc., contributions, using localized bond MO's and a perturbation expansion. It is briefly described in part II. Some applications are presented in part III. The analysis of internal rotation barriers has been done within a semiempirical scheme (differential PCILO method[18]) using a CNDO Hamiltonian.

Our approach constitutes a many-body construction of the energy (and energy change) in terms of completely localized fragments and their interactions, instead of an a posteriori analysis of the exact or refined variational wave function. It allows a better understanding of some paradoxical results obtained with the atom decomposition, it confirms directly and explicitly the conclusions of England et al. about the internal rotation barriers,[12,19,20] and it allows us to follow the building up of the tails of the MO's from fully localized MO's.

Results and Discussion

IA. An Atomic Partition of the Total Energy. A natural partition of the total molecular energy for a closed-shell system within the LCAO-MO scheme is implicitly given by the energy decomposition in terms of atomic integrals. The energy of a Slater determinant (for instance the SCF Slater determinant) is written as:

$$E_{\text{T}} = \sum_{\mu\nu} P_{\mu\nu}H_{\mu\nu} + \tfrac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu}P_{\lambda\sigma}[(\mu\nu,\lambda\sigma) - \tfrac{1}{2}(\mu\lambda,\nu\sigma)] + \sum_{\text{A}}\sum_{<\text{B}} Z_{\text{A}}Z_{\text{B}}R_{\text{AB}}^{-1} \quad (1)$$

where indices μ, ν, λ, σ refer to the atomic orbitals and A and B to the nuclei, $P_{\mu\nu}$, $H_{\mu\nu}$ are respectively the density matrix elements and the matrix elements of the core Hamiltonian with respect to atomic orbitals (kinetic operator and attraction operator by the nuclei), Z_{A} and Z_{B} are the atomic charges of atoms A and B and R_{AB} the internuclear distance.

It is possible in general to express the terms of eq 1 in one-atom, two-atom, up to four-atom contributions according to the type of matrix elements $H_{\mu\nu}$ and $(\mu\nu,\lambda\sigma)$. This general decomposition has been frequently used within the CNDO[8] assumptions for the atomic integrals as suggested by Pople and Beveridge. Every term in the CNDO total energy expression is associated with one or two atoms because of the ZDO hypothesis, so that an energy breakdown into monatomic and diatomic contributions is possible,[8]

$$E_{\text{T}} = \sum_{\text{A}} \epsilon_{\text{A}} + \sum_{\text{A<B}} \epsilon_{\text{AB}} \quad (2)$$

where

$$\epsilon_{\text{A}} = \sum_{\mu}^{\text{A}} P_{\mu\mu}U_{\mu\mu} + \tfrac{1}{2} \sum_{\mu}^{\text{A}} \sum_{\nu}^{\text{A}} (P_{\mu\mu}P_{\nu\nu} - \tfrac{1}{2} P_{\mu\nu}^{2})\gamma_{\text{AA}} \quad (2a)$$

and

$$\epsilon_{\text{AB}} = \sum_{\mu}^{\text{A}} \sum_{\nu}^{\text{B}} (2P_{\mu\nu}\beta_{\mu\nu} - \tfrac{1}{2} P_{\mu\nu}^{2}\gamma_{\text{AB}}) + (Z_{\text{A}}Z_{\text{B}}R_{\text{AB}}^{-1} - P_{\text{AA}}V_{\text{AB}} - P_{\text{BB}}V_{\text{BA}} + P_{\text{AA}}P_{\text{BB}}\gamma_{\text{AB}}) \quad (2b)$$

where Σ_{μ}^{A} means sum over all orbitals on A, $U_{\mu\mu} = (\mu| - \tfrac{1}{2}\cdot\nabla^2 - V_{\text{A}}|\mu)$ is the energy associated with the orbital μ in the bare field of the core of its own atom, $\gamma_{\text{AB}} = (\mu\mu,\nu\nu)$, $\mu \in \text{A}$ and $\nu \in \text{B}$, $\beta_{\mu\nu}$ is the nondiagonal element of the one-electron Hamiltonian and is supposed to depend only on A and B, $P_{\text{AA}} = \Sigma_{\mu}^{\text{A}} P_{\mu\mu}$ is the total electron density associated with atom A, and V_{AB} is the attraction of one valence electron on A by the core of B. This energy partitioning has been used by Labarre and co-workers for numerous conformational studies[9-11] with the use of an analogous decomposition,

$$E_{\text{tot}} = E_{\text{b}} + E_{\text{nb}} \quad (3)$$

with

$$E_{\text{b}} = \sum_{\text{A}} \epsilon_{\text{A}} + \sum_{\text{A<B}} \epsilon_{\text{AB}} \qquad \text{(A and B bonded)} \quad (3a)$$

$$E_{\text{nb}} = \sum_{\text{A<B}} \epsilon_{\text{AB}} \qquad \text{(A and B nonbonded)} \quad (3b)$$

One may hope that the energy variations will come from pairs of atoms whose relative positions have been modified during the conformational change. Labarre and co-workers actually found in general in their rotation barriers analysis that the dominant factor in the variation of the total energy with a change of conformation is ΔE_{nb}.

In Table I one reports the results obtained by Labarre et al. in the analysis of the total energy of ONF_3 referring to the stabilization of the energy with respect to the ∠ONF angle, with the CNDO/2 energy partitioning.[11]

The ΔE_{nb} contribution ($3\Delta E$(O·F) + $3\Delta E$(F·F)) is only −0.89 kcal/mol. The bonded interactions $3\Delta E$(N·F) are much more important, and the atomic contributions are far from being negligible.

In the conformational analysis of $(CH_3)_2SO_2$[9] referring to the variation of the energy as a result of mutual rotation of the two methyl groups, they always found with the bicentric energy partitioning a contribution to the variation in the total energy of 70% from the single sum, ΣE(S···H), of the spatial interaction terms between sulfur and the six hydrogens. On the contrary, the contribution of terms which change during the rotation, that is, ΣE(O···H) + ΣE(H···H) is only 30%.

The atomic and bonded contributions, which we hoped to be negligible, sometimes play the leading role in the conformational property. Since the corresponding atoms do not change their relative position, the integrals are constant and the variation of the energy contribution must come from a change in the density matrix elements appearing in eq 2. Unfortunately, the variations of the density matrix elements cannot be explicitly derived from the geometry change, since they result from the iterative procedure and the mystery about the energy change is converted into a mystery about the density matrix variations.

IB. SCF Energy Partition in Terms of Bonds. If one wants to derive an energy partition in terms of bonds, one faces immediately a difficulty concerning the nuclear repulsion energy and the nuclear attraction operator, since both are expressed in terms of atoms. In order to obtain a homogeneous partition of the total energy in terms of one-bond and two-bond contributions, one must do a partition of the nuclear charge into bond nuclear distributions.

If Z_A is the charge of atom A (total charge in an ab initio case) the elementary charge $q_i^A = Z_A/(n_V^A + 2n_D^A)$, where n_V^A represents the number of bonds involving A and n_D^A the lone pairs on A. Each chemical bond will have one q_i^A charge and a lone pair, $2q_i^A$ (for a neutral atom $q_i^A = 1$). The bond nuclear charge for a neutral molecule will be a $(+1 \cdots +1)$ distribution on the two atoms of the bond, which compensates the two-electron distribution *ii*. In that manner, the nuclear field is decomposed into bond-nuclear fields,

$$\sum_A Z_A/r_A = \sum_i h_i \tag{4}$$

where

$$h_i = (q_i^A/r_A) + (q_i^B/r_B) \tag{4a}$$

for a bond *i* and

$$h_i = 2q_i^A/r_A \tag{4b}$$

for a lone pair on A.

The nuclear repulsion energy can be written as a sum of nuclear repulsions between nuclear bond distributions,

$$E_N = \sum_A \sum_{<B} \frac{Z_A Z_B}{R_{AB}} = \sum_i N_{ii} + \sum_i \sum_{<j} N_{ij} \tag{5}$$

where

$$N_{ii} = q_i^A q_i^B / R_{AB} \tag{5a}$$

for a bond *i* and

$$N_{ii} = 0$$

for a lone pair.

The off-diagonal terms N_{ij} represent the repulsion between the two nuclear charges of bond *i* with the two nuclear charges of bond *j*.

The ab initio energy can be expressed in terms of bond energy and bond interaction energy,

$$E = \sum_i \mathcal{E}_i + \sum_i \sum_{<j} \mathcal{E}_{ij} \tag{6}$$

with

$$\mathcal{E}_i = 2\langle i|\nabla^2/2|i\rangle + 2\langle i|h_i|i\rangle + J_{ii} + N_{ii} \tag{6a}$$

$$\mathcal{E}_{ij} = 2\langle i|h_j|i\rangle + 2\langle j|h_i|j\rangle + 4J_{ij} - 2K_{ij} + N_{ij} \tag{6b}$$

The one-body term $\mathcal{E}_i$ involves the kinetic energy, the intrabond electrostatic interactions of the two electrons, and the two nuclear charges of the bond. The two-body term $\mathcal{E}_{ij}$ contain the electrostatic interactions between the two electrons and two nuclear charges of bond *i* with the similar distribution of bond *j* plus the exchange term.

This kind of two-body partition of the total energy was suggested by England and Gordon,[12] referring to localized SCF MO's practically obtained through the use of the localization criterion of Edmiston and Ruedenberg.[21] Most of their applications used the INDO[22] Hamiltonian. Within the framework of INDO Hamiltonian, except on monocentric bielectronic interactions, the overlap distribution only plays a role through the monoelectronic terms, because of neglect of differential overlap.

Table II. INDO Barriers[a]

Molecule	ΔE	ΔI
CH_3CH_3[b]	2.20	2.22
CH_3OH[c]	0.78	0.64
CH_3NH_2[c]	1.56	1.40
BH_3NH_3[d]	1.97	1.89

[a] Energies in kcal/mol; $\Delta E = E$(least stable) − E(most stable rotamer), using a standard geometry. [b] W. England and M. S. Gordon, *J. Am. Chem. Soc.*, **93**, 4649 (1971). [c] M. S. Gordon and W. England, *ibid.*, **95**, 1753 (1973). [d] Optimized geometry calculation by M. S. Gordon and W. England, *Chem. Phys. Lett.*, **15**, 59 (1972).

When going from one conformation to another, all one-bond and two-bond $\mathcal{E}_i$ and $\mathcal{E}_{ij}$ quantities may vary, since the SCF localized MO's depend on the conformation. The main coefficients on the concerned bond may change, and the tails on the adjacent, vicinal, and further bonds also vary. In a recent detailed analysis of 33 INDO SCF calculations with standard geometries, England et al.[13] showed that an SCF localized MO may be built from (a) an invariant contribution on the two hybrids of the main bond plus the environment-dependent increments on these hybrids, and (b) the position- and environment-dependent tails on the adjacent, vicinal, . . . bonds. This work shows therefore a transferability of position- and environment-dependent tails.

This fine analysis has not been performed with respect to the energy. To understand the variations of $\mathcal{E}_i$ and $\mathcal{E}_{ij}$, England and Gordon decompose the *ii* distribution into a contribution on the bond itself and contributions involving the tails. This decomposition might be performed in terms of fully localized MO's, but the analysis has been done in terms of atoms.

They distinguished the atomic charge distributions $\mu\mu$, where μ is an atomic orbital, and the diatomic interference (or overlap) distribution $\mu\nu$ ($\mu \in$ A, $\nu \in$ B) according to the Rudenberg's partition suggested in his paper on the nature of the chemical bond.[23]

This quantity defined as,

$$\beta_i(A,B) = \sum_{\mu \in A} \sum_{\nu \in B} P_{\mu\nu}{}^i \langle \mu| - (\nabla^2/2) + h_A + h_B|\nu\rangle \tag{7a}$$

with

$$P_{\mu\nu}{}^i = C_{\mu i} C_{\nu i} \tag{7b}$$

represents the kinetic and nuclear attraction energy of the overlap $\mu\nu$ distribution of the MO *i*.

This definition of β_i(A,B) assumes implicitly that the integral

$$\left\langle \mu \middle| - (\nabla^2/2) + \sum_A h_A \middle| \nu \right\rangle = (S_{\mu\nu}/2)\,(\beta_0{}^\mu + \beta_0{}^\nu) \tag{8}$$

is a rather obscure quantity in the CNDO[8] approximations.

It is expected that the only effects we can obtain with this approach in the rotational barrier analysis must appear through the interactions of the tails of the localized orbitals, taking account of the nonexistence of the overlap effects.

England and Gordon explained the origin of the rotational barriers[12,19,20] in terms of changes in one-electron two-center interference interactions in the LMO's adjacent to the axial bond, the vicinal interference barrier ($\Delta I = \Sigma_i \Delta I_i$) reproducing the calculated INDO barrier. They confirmed, of course, the preponderant role of the tails of the localized orbitals.

In Table II one sees some results obtained by these authors for some molecules which we will consider later in part 111 of this paper.

II. A Local Interpretation of Energetic Properties Based on a Many-Body Partition of the Molecular Energy in Terms of

Bonds. Our procedure constitutes a construction of the energy through a many-body expansion; that is, a theoretical systematic which gives the energy as a sum of one-body, two-body, . . . etc., contributions. It allows us to explain the deviations from additivity, the effects of substitutions, and the conformational changes.

In order to explain the energy changes, we isolate invariant contributions during the conformational change and we refer to: (1) Transferable fragments. The total exact energy is expressed in terms of matrix elements between these fragments; the matrix elements are transferable if they involve transferable fragments in the same relative positions. (2) The classical invariants, which are the atoms and/or bonds. Because a quantal description cannot be built directly in terms of atoms, we tried to join the intuitive interpretations and build the transferable fragments on the bonds. (3) An additive expansion in terms of one-body, two-body, three-body contributions. The perturbative N-body expansion appears to be a natural choice.

In view of carrying out the construction of such a method it is necessary

(1) To do a partition of the nuclear field and nuclear repulsion energy, as suggested in part IB.

(2) To build fully localized molecular orbitals on the bonds. To do that, the bond MO's are defined from the atomic orbitals of only two atoms, and of only one atom if they represent the core or lone pairs. According to the hybridization process of Del Re[24] used in our method, (a) the hybrid orbitals of the same atom are orthogonal, (b) the overlap between the hybrids of the same bond is maximum, and (c) the overlap between hybrids of different bonds are small.

As a result, for a rotation around an AB single bond, one may isolate three groups of bonds. A group I composed only by the rotor bond AB, and the groups II and III composed by the bonds linked to atoms A and B on opposite sides. The hybrids of groups II and III keep their relative positions during the rotational change, but the bonds and hybrids of group II move with respect to those of group III. Groups II and III are composed of transferable pairs of hybrids, defining invariant bonds. As concerning the AB rotor bond, if the surrounding of A (and/or B) is anisotropic (different substituents), the orthogonal hybrid of A (and/or B) along the AB bond is no longer directed along the AB axis, and the overlap between the two orthogonalized hybrids of the AB bond may change. The AB bond is not transferable, except if the surroundings of A and B are isotropic.

The fully localized bond MO's i are built from the two-hybrid χ_μ of the two atoms A and B.

$$i = c_i\chi_\mu{}^{(\mathrm{A}_i)} + d_i\chi_\nu{}^{(\mathrm{B}_i)} \tag{9}$$

The MO i is invariant if and only if $\chi_\mu{}^{(\mathrm{A}_i)}$ and $\chi_\nu{}^{(\mathrm{B}_i)}$ are in the same relative position and if c_i and d_i are kept constant (fixed polarities). The use of the ZDO approximation (PCILO-CNDO scheme[18]) simplifies the normality condition for the localized MO i to the expression

$$c_i{}^2 + d_i{}^2 = 1 \tag{9a}$$

Equation 9a concerns the orthogonality between the bonding MO i and the antibonding MO i^* on the same bond.

$$i^* = c_i'\chi_\mu{}^{(\mathrm{A}_i)} + d_i'\chi_\nu{}^{(\mathrm{B}_i)} \tag{9b}$$

The orthogonality condition can be written,

$$c_ic_i' + d_id_i' = 0 \tag{9c}$$

and one obtains the expression for the antibonding MO's,

$$i^* = -d_i\chi_\mu{}^{(\mathrm{A}_i)} + c_i\chi_\nu{}^{(\mathrm{B}_i)} \tag{9d}$$

which are orthogonal to the whole set of bonding and antibonding MO's. The coefficients c_i and d_i are calculated by an iterative optimization process of bond polarities. They are evaluated for the first conformation (reference conformation) and kept constant for all conformations.

In this iterative process a rotational transformation is done on the bonding and antibonding MO's of the same bond. With these new orbitals,

$$\begin{aligned} i' &= i + \alpha_i i^* \\ i'^* &= i - \alpha_i i^* \end{aligned} \tag{9e}$$

the new determinant ϕ_0' may be expressed,

$$\phi_0' = \phi_0 + \alpha_i\phi\binom{i^*}{i}$$

if one only keeps the first-order coefficient α_i. $\phi({}_i{}^{i*})$ represents the monoexcited determinant corresponding to the i bond.

The expression for the corresponding energy E_0' is

$$E_0' = \langle\phi_0'|H|\phi_0'\rangle/\langle\phi_0'|H|\phi_0'\rangle$$

$$E_0' = E_0 + 2\sum_i \alpha_i\left\langle\phi_0|H|\phi\binom{i^*}{i}\right\rangle + \ldots \tag{9f}$$

and

$$\partial E_0'/\partial\alpha_i = 2\left\langle\phi_0|H|\phi\binom{i^*}{i}\right\rangle = 2\langle i|F^0|i^*\rangle \tag{9g}$$

If F^0 is the Fock operator for the reference conformation, a local Brillouin's theorem is iteratively achieved,

$$\langle i|F^{(0)}|i^*\rangle = 0 \tag{9h}$$

That implies a minimization of the energy without authorizing any delocalization.

(3) To decompose the zeroth order energy E^0 of the fully localized determinant

$$\phi_0 = A(1\bar{1}\ldots i\bar{i}\ldots n\bar{n}) \tag{10}$$

in terms of one-bond and two-bond energy contributions

$$E_0 = \sum_i \epsilon_i + \sum_i\sum_{<j} \epsilon_{ij} \tag{11}$$

where the one-bond energy

$$\epsilon_i = 2\langle i|(\nabla^2/2) + h_i|i\rangle + J_{ii} + N_{ii} \tag{12}$$

depends only on the bond i and does not change if the bond is invariant. For the cases of the rotation around the AB bond, the one-bond energy ϵ_i relative to the AB bond may vary if the surroundings are not isotropic because the change of relative orientation of the two atomic hybrids defining the bond. The two-body energy contribution ϵ_{ij},

$$\epsilon_{ij} = -2\langle i|h_j|i\rangle + 2\langle j|h_i|j\rangle + 4J_{ij} - 2K_{ij} + N_{ij} \tag{13}$$

depends on the relative position of bonds i and j. If i and j belong to the same group, the contribution ϵ_{ij} is invariant and transferable from one molecule to the other if standard geometries are used.

(4) To perturb the zeroth order description under its interaction with the "excited determinants" built from the set of local bonding and antibonding MO's, as done in the classical excitonic[25] and PCILO schemes.[26] This process represents a perturbative research of the lowest eigenvalue of the CI matrix built from localized MO's, and must be done according to *the Rayleigh Schrödinger expansion* to obtain the correct behavior of the energy corrections with the number of particles.[27] The correction corresponding to each order of the perturbation expansion only involves some MO's, and may be referred to this subset of body. If this subset is invariant in the geometry change (all the concerned bonds belonging to part I for instance), it would be advantageous to obtain a corresponding

invariant correction. This invariance is verified with a proper choice of the unperturbed Hamiltonian $\mathcal{H}_0$, which ensures the energy denominators to be constant. $\mathcal{H}_0$ will keep the same spectrum whatever the conformation is. For the pth conformation,

$$\mathcal{H}_0{}^{(P)} = \sum_I \langle \phi_I{}^{(0)} | \mathcal{H}^{(0)} | \phi_I{}^{(0)} \rangle | \phi_I{}^{(P)} \rangle \langle \phi_I{}^{(P)} | \qquad (14)$$

where (P) and (0) represent the pth and reference conformations, respectively, the $\phi_I{}^{(P)}$'s (resp. $\phi_I{}^{(0)}$) represent the determinants spanning the CI matrix in the pth (resp. zeroth) conformation, in the basis of fully localized bonding and antibonding MO's. This definition ensures that

$$\begin{aligned} \langle \phi_I{}^{(P)} | \mathcal{H}_0{}^{(P)} | \phi_I{}^{(P)} \rangle - \langle \phi_J{}^{(P)} | \mathcal{H}_0{}^{(P)} | \phi_J{}^{(P)} \rangle \\ = \langle \phi_I{}^{(0)} | \mathcal{H}_0{}^{(0)} | \phi_I{}^{(0)} \rangle \\ - \langle \phi_J{}^{(0)} | \mathcal{H}_0{}^{(0)} | \phi_J{}^{(0)} \rangle \text{ for each } P, I, \text{ and } J \qquad (15) \end{aligned}$$

It represents an adaptation of the Epstein–Nesbet definition of the unperturbed Hamiltonian.[28] It introduces some small diagonal terms of the perturbation Hamiltonian $\mathcal{V}^{(P)} = \mathcal{H}^{(P)} - \mathcal{H}_0{}^{(P)}$

$$\begin{aligned} \langle \phi_I{}^{(P)} | \mathcal{V}^{(P)} | \phi_i{}^{(P)} \rangle = \langle \phi_I{}^{(P)} | \mathcal{H}^{(P)} | \phi_I{}^{(P)} \rangle \\ - \langle \phi_I{}^{(P)} | \mathcal{H}_0{}^{(P)} | \phi_I{}^{(P)} \rangle \qquad (15\text{a}) \end{aligned}$$

These matrix elements introduce some supplementary third-order corrections. One may understand the physical significance of these elements by referring to the diagonal Fock operator matrix elements; for i belonging to a group I, invariant in the conformational change,

$$\langle i | F^{(P)} | i \rangle - \langle i | F^{(0)} | i \rangle = \left\langle i \middle| \sum_{j \notin I} \Delta(h_j + 2J_j) \middle| i \right\rangle \qquad (16)$$

where $\Delta(h_j + 2J_j)$ represents the *change* (under the conformational change) of the nuclear attraction plus electronic repulsion exerted on the electrons of bond i, by the nuclear plus electronic distribution of bonds belonging to the other parts of the molecule, with respect to the reference conformation (0). The electrostatic neutrality of bonds j, for neutral molecules, guarantees that the changes of the external fields on bond i are small, and the modifications of the diagonal Fock matrix elements are actually small.

In a semiempirical framework, using the CNDO hypothesis,[8] the ZDO approximation and the full localization of the MO's make possible an exact transferability of the nondiagonal Fock matrix elements, F_{mn}, between two bonds belonging to the same group,

$$\begin{aligned} F_{mn} = \langle m | (\nabla^2/2) + h_m + h_n + 2J_m - K_m + 2J_n - K_n | n \rangle \\ + \sum_{j \neq m,n} \langle m | h_j + 2J_j - K_j | n \rangle \qquad (17\text{a}) \end{aligned}$$

since

$$\langle m | h_j + 2J_j - K_j | n \rangle = 0, \qquad F_{mn}{}^{(P)} = F_{mn}{}^{(0)} \qquad (17\text{b})$$

Then the excitations appearing in the second-order correction are:

(a) The intrabond single excitations (or polarization contributions) $i \rightarrow i^*$. The corresponding contribution is, $2\Sigma_i (F_{ii^*}{}^P)^2/\Delta E({}_i^{i^*})$, where

$$\begin{aligned} F_{ii^*} = \langle i | (\nabla^2/2) + h_i + J_{i^*} | i^* \rangle \\ + \sum_j \langle i | h_j + 2J_j - K_j | i^* \rangle \qquad (18) \end{aligned}$$

represents the matrix element of the total field on the ii^* transition distribution, and $-\Delta E({}_i^{i^*}) = F_{i^*i^*}{}^{(0)} - F_{ii}{}^{(0)} - (ii,i^*i^*)^{(0)} + 2(ii^*,ii^*)^{(0)}$. After the initial optimization of bond polarities, F_{ii^*} is zero for the reference conformation; then, in the passage to another conformation, F_{ii^*} will change according to the variation of the field exerted by the moving bonds j (or new bonds when one goes from one molecule to another). If $F_{ii^*}{}^{(0)} = 0$,

$$\begin{aligned} F_{ii^*}{}^{(P)} = \sum_j \langle i | (h_j + 2J_j - K_j)^P \\ - (h_j + 2J_j - K_j)^0 | i^* \rangle \qquad (19) \end{aligned}$$

where the modification of the field exerted by the nuclear plus electronic distribution of bond j is represented by δ_j,

$$\delta_j = (h_j + 2J_j - K_j)^P - (h_j + 2J_j - K_j)^0$$

Three-body terms appear in the second-order correction as

$$\sum_j \sum_k \frac{\langle i | \delta_j | i^* \rangle \langle i^* | \delta_k | i \rangle}{e_i - e_{i^*}}$$

where e_i represents the diagonal element of the Fock operator. This is a well-known result of intermolecular theory; the polarization energies deviate from pairwise additivity.

(b) The delocalization single excitations $i \rightarrow j^*$ $(j \neq i)$ from a bonding MO to an antibonding MO of another bond. In this contribution the transfer of the electrons from one bond to another is authorized. The sum of these contributions gives the delocalization energy $E_{\text{del}} = 2\Sigma_i \Sigma_{j \neq i} F_{ij^*}{}^2/\Delta E({}_i^{i^*})$ (where $-\Delta E({}_i^{i^*}) = F_{j^*j^*}{}^{(0)} - F_{ii}{}^{(0)} - (ii,j^*j^*)^{(0)}$), which is responsible for most of the SCF energy lowering and plays a very important role in the conformational energy. Moreover, these delocalization single excitation $i \rightarrow j^*$ effects may be viewed in terms of Lowe's hyperconjugation effects when i and j^* are at opposite ends of the rotor bond; the important role of these effects may be anticipated using the Lowe's arguments about the molecular orbital explanation for the internal rotation barriers about single bonds[29] in ethane-like molecules.

(c) The intrabond double excitations $(i \rightarrow i^*)^2$ provide an intrabond correlation energy,

$$E_{\text{intracorrel}} = \sum (ii^*,ii^*)^2/\Delta E \begin{pmatrix} i^* & i^* \\ i & i \end{pmatrix}$$

where (ii^*,ii^*) represents an intrabond doubly excited determinant, and

$$\begin{aligned} \Delta E \begin{pmatrix} i^* & i^* \\ i & i \end{pmatrix} = 2F_{i^*i^*}{}^{(0)} - 2F_{ii}{}^{(0)} \\ - 2(ii,i^*i^*)^{(0)} + (ii,ii)^{(0)} + (i^*i^*,i^*i^*)^{(0)} \end{aligned}$$

These contributions concern one-body terms; the only important contributions to the conformational energy come from the variable bonds belonging to the variable groups.

(d) The interbond double excitations $i \rightarrow i^*$, $j \rightarrow j^*$ are responsible for the attractive van der Waals dispersion energies between bonds i and j; they provide the interbond correlation energy,

$$E_{\text{intercorrel}} = 4 \sum_i \sum_{j \neq i} \frac{(ii^*,ii^*)^2}{\Delta E \begin{pmatrix} i^* & j^* \\ i & j \end{pmatrix}}$$

The second-order energy correction is therefore a sum of one-body, two-body, and three-body contributions.

The numerically important contributions in a conformational change arising from the third-order correction are: (a) the delocalization–delocalization interactions which give three-body contributions; (b) the delocalization–interbond correlation (two-bond contributions); (c) the interbond-interbond correlation contributions which involve three bonds i, j, and k; (d) the intrabond–interbond correlation, which is a special case $(k = i)$ of the preceding contribution involving only two bonds. The explicit decomposition of the energy obtained with a perturbative N-body expansion in terms of local

Table III. Geometries for the $(CH_3)_2XH_{n-1}$ series (X = C,N,O)

Molecule	d(C–H), Å	d(C–X), Å	d(X–H), Å	∠CXC, deg	∠HXH, deg
$CH_3CH_2CH_3$	1.09	1.54		111.5	109.47
CH_3NHCH_3	1.08	1.46	1.014	108	
CH_3OCH_3	1.094	1.416		111.5	

and transferable fragments (bonds) allows an analysis with respect to the $i, j, k, \ldots p, \ldots$ bond contributions (where $i, j, k, \ldots, p, \ldots$ represent the bonds) on one hand, and with respect to the nth order correction of the perturbation expansion on the other. With the use of this double expansion, the total energy can be expressed,

$$E = \sum_n \left(\sum_i \epsilon_i{}^{(n)} + \sum_i \sum_{<j} \epsilon_{ij}{}^{(n)} + \ldots \right. \\ \left. + \sum_i \sum_{<j} \ldots \sum_{<p} \epsilon_{i,j,\ldots,p\ldots}{}^{(n)} + \ldots \right) \quad (20)$$

where $\Sigma_n \Sigma_i\ \epsilon_i{}^n$ represents the one-body contributions up to the nth order correction. the same meaning for the two-body, the three-body. etc., terms.

The conformational energy change will be written as,

$$\Delta E^{(n,p)} = \sum_n \left(\sum_i \Delta\epsilon_i{}^n + \sum_i \sum_{<j} \Delta\epsilon_{ij}{}^n + \ldots \right. \\ \left. + \sum_i \sum_{<j} \ldots \sum_{<p} \epsilon_{i,j,\ldots,p}{}^n \right) \quad (21)$$

where $\Delta E^{(n,p)}$ means the energy change up to the nth order correction involving one-body, two-body, up to p-body contributions. ($\Delta E^{(3,3)}$, for instance, means the energy change due to one-body, two-body, and three-body contributions at the zeroth-, second-, and third-order correction).

III. DPCILO Calculations Applied to the Analysis of Rotational Barriers around Single Bonds in the Series of Molecules: CH_3XH_n and Their Superior Homologous $(CH_3)_2XH_{n-1}$ (X = C, N, O). The internal rotation barriers of the series of molecules CH_3XH_n and $(CH_3)_2XH_{n-1}$ (X = C, N, O) have been investigated within the framework of DPCILO-CNDO approximation.[18] One used the geometrical data given by Labarre et al. for the molecular series $(CH_3)_2XH_{n-1}$[31] (see Table III) and a minimal basis of Slater atomic orbitals. All the calculations have been done in the rigid rotator hypothesis.[31]

The choice of the two series of molecules is based on a double purpose: (1) to do an analysis of the origin of barriers in the CH_3XH_n molecules (X = C, N, O) and understand which specific effects are responsible for the decrease of the barriers in the CH_3XH_n series (substitution effects),

$$CH_3CH_3 > CH_3NH_2 > CH_3OH$$

and (2) to investigate the transferability of contributions in the passage from reference systems (CH_3XH_n) to their corresponding superior homologous $(CH_3)_2XH_{n-1}$ and the role of vicinal, geminal, and long-range interactions in the considered series.

As a first step, we consider the effects of bond polarities on the energies and on the internal rotation barriers for the molecular series CH_3XH_n (X = C, N, O). The calculations were carried out taking two reference conformations, the eclipsed ($\varphi = 0$) and the staggered ($\varphi = 60$) ones. The bond polarities were optimized for the reference conformation and were kept fixed for the other conformations. Next we did calculations with optimized bond polarities for each conformation. The results are listed in Table IV. One sees that in ethane the energies and its barrier are insensitive to the reference conformation polarities, the barrier height with fixed polarities is the same as that with optimized polarities for each conformation (2.05 kcal/mol). Analogous results are obtained for the methylamine and methyl alcohol, the hybrid coefficients for the eclipsed and staggered conformation differ at most by 10^{-3}, but this difference does not affect sensibly the barrier. The corresponding barriers taking the eclipsed and staggered conformations as reference conformations are respectively 1.539 and 1.532 kcal/mol for methylamine and 0.786 and 0.773 for methyl alcohol, to compare respectively to values of 1.532 and 0.782, corresponding to optimized polarities for each conformation.

Next, we proceed to analyze the rotational barriers of the CH_3XH_n series. The various contributions to the barrier from the zeroth, second, and third orders are listed in Table V.

Table IV. Effects of Bond Polarities on the Energies[a] and on the Rotation Barrier[b] for the Molecular Series CH_3HX_n (X = C,N.O)[d]

		Hybrid coefficients						
		Eclipsed ($\varphi = 0°$)			Staggered ($\varphi = 60°$)			
	Bond	$\varphi = 0°$	$\varphi = 60°$	ΔE^b	$\varphi = 60°$	$\varphi = 0°$	ΔE^b	ΔE^c
X = C	CC	0.707107	0.707107		0.707107	0.707107		
	CH	0.713266	0.700894		0.713277	0.700882		
	E^0	−11768.227	−11768.460	0.233	−11768.460	−11768.227	0.233	0.233
	$E^0 + \epsilon^2$	−11841.165	−11843.014	1.849	−11843.011	−11841.163	1.849	1.846
	$E^0 + \epsilon^2 + \epsilon^3$	−11841.912	−11843.960	2.048	−11843.948	−11841.893	2.055	2.036
X = N	CN	0.684836	0.728697		0.684830	0.728703		
	CH	0.712917	0.701248		0.713978	0.700168		
	NH	0.738647	0.674092		0.738647	0.674093		
	$N_{\text{lone pair}}$	1.0	0.0		1.0	0.0		
	E^0	−14130.096	−14130.319	0.224	−14130.323	−14130.092	0.232	0.227
	$E^0 + \epsilon^2$	−14198.683	−14199.971	1.288	−14199.962	−14198.681	1.288	1.286
	$E^0 + \epsilon^2 + \epsilon^3$	−14198.122	−14199.622	1.539	−14199.654	−14198.117	1.537	1.532
X = O	CO	0.660416	0.750899		0.660407	0.750908		
	CH	0.713402	0.700755		0.714701	0.699430		
	OH	0.762076	0.647487		0.762055	0.647513		
	$O_{\text{lone pair}}$	1.0	0.0		1.0	0.0		
	E^0	−17892.419	−17892.541	0.122	−17892.555	−17892.405	0.149	0.149
	$E^0 + \epsilon^2$	−17954.307	−17954.913	0.606	−17954.913	−17954.305	0.608	0.608
	$E^0 + \epsilon^2 + \epsilon^3$	−17953.998	−17954.784	0.786	−17954.780	−17954.008	0.773	0.773

[a] The zeroth-, second-, and third-order energies are calculated with bond polarities optimized for the reference conformation, in au. [b] The barrier $\Delta E = E(\text{eclipsed}) - E(\text{staggered})$ is given in kcal/mol. [c] Rotation barrier calculated with bond polarities optimized for each conformation. [d] The bond polarities refer to the eclipsed and staggered conformations.

Table V. DPCILO Rotational Barrier Contributions[a] of the CH_3XH_n (X = C, N, O) Molecular Series

	CH_3CH_3[b]	CH_3NH_2[b]	CH_3OH[b]
ΔE_0[a] (zeroth order) barrier	0.23	0.22	0.12
Second-order correction	1.62	1.06	0.48
ΔE polarization	0.0	0.0	0.0
ΔE delocalization	1.86	1.24	0.56
ΔE intrabond-correlation	0.0	0.0	0.0
ΔE interbond-correlation	−0.25	−0.18	−0.09
ΔE[a] (zeroth + second order) barrier	1.85	1.29	0.61
Third-order correction	0.20	0.25	0.18
ΔE del–del	0.29	0.28	0.17
ΔE inter–del	−0.19	−0.10	−0.03
ΔE intra–inter	0.08	0.06	0.03
ΔE inter–inter	0.03	0.02	0.01
ΔE[a] (zeroth + second + third order) barrier	2.05	1.54	0.79

[a] All barriers and contributions are given in kcal/mol; $\Delta E = E$ (least stable) − E(most stable rotamer). [b] Experimental barriers in kcal/mol are 2.875, 1.97, and 1.07 for CH_3CH_3, CH_3NH_2, and CH_3OH respectively: the corresponding references are, W. J. Lafferty and E. K. Plyler. *J. Chem. Phys.*, 37, 2688 (1962): T. Nishikawa, T. Itoh. and K. Shimada. *ibid.*. 23. 1735 (1955); E. V. Ivash and D. M. Dennison, *ibid.*. 21 1804 (1953).

The DPCILO-CNDO approximation gives a small zeroth-order contribution to the barrier; the preponderant contributions arise essentially from the second-order correction due to the delocalization ($i \rightarrow i^*$) single excitations. At this stage, the first-order corrected wave function may be expressed as a modified single determinant

$$\phi_0 + \langle i|F|j^*\rangle/(\epsilon_i - \epsilon_j{}^*)\left(\phi\begin{pmatrix} j^* \\ i \end{pmatrix} + \phi\begin{pmatrix} \bar{j}^* \\ \bar{i} \end{pmatrix}\right) \simeq |1\bar{1}\ldots i'\bar{i}'\ldots n\bar{n}| + \mathcal{O}(2)$$

where $\phi({}_i{}^{j^*})$ represents a delocalized ($i \rightarrow j^*$) single excited determinant $a_j{}^+a_i\phi_0$, and the localized MO's $i' = i + (\langle i|F|j^*\rangle/\epsilon_\mathrm{i} - \epsilon_{\mathrm{j}*})\,j^*$ have tails on the other bonds. This result gives a direct confirmation of the results obtained by England and Gordon in an SCF scheme; the CNDO barrier arises from the delocalization effects introducing the tails. In that case it is clear that the only contribution to the barrier comes from the delocalization between vicinal CH bonds, the other pairs being geminal pairs and therefore invariant. Moreover, in the CNDO approximation the matrix element $\langle i|F|j^*\rangle$ between nonoverlapping MO's reduces to $\langle i|h|j^*\rangle$; i.e., a purely monoelectronic effect called interference energy by Ruedenberg.[23] In spite of the smallness of the zeroth-order contribution, the repulsive effects are not negligible as well as the interbond correlation contributions, this van der Waals dispersion energy diminishes the barrier to a nonnegligible extent. In the third-order correction the delocalization effects are also preponderant, the global third-order correction coming almost entirely from the delocalization–delocalization interactions, which involve three bonds.

One can do an analysis of the preponderant contributions arising from the zeroth-, second-, and third-order corrections with respect to the one-bond, two-bond, and three-bond contributions, with the help of the explicit energy decomposition expression given in eq 20 and 21.

The barrier analysis reveals that the one-body contributions to the barrier are zero ($\sum_i \Delta\epsilon_i = 0$) in both the zeroth- and second-order barriers because the one-body terms remain constant ($\Delta_i\epsilon_\mathrm{i} = cte$) from one conformation to the other, as implied by the definition of the process; one may notice, however, that the bond defining the rotation axis which might have a varying one-body contribution is constant enough to be considered a nonvarying bond. The barrier is then given by the two-bond and three-bond contributions (at zeroth-, second-, and third-order corrections),

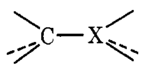
Table VI. Two Body Vicinal Contributions to the Energy[a] of the Eclipsed and Staggered (in parentheses) Forms of the CH_3XH_n (X = C, N, O) Molecular Series[b]

Molecule	Type of interactions	No. of interactions	Zeroth order	Delocalization
CH_3CH_3	c(CH,CH) (t)	3	8.994 (8.739)	−3.832 (−6.534)
	γ(CH,CH) (g)	6	8.752 8.841	−1.869 −0.829
CH_3NH_2	c(CH.N_{1p}) (t)	1	14.841 (14.841)	−3.581 (−4.811)
	c(CH,NH) (t)	2	8.705 (8.274)	−3.092 (−5.884)
	γ(CH,N_{1p}) (g)	2	14.841 (14.841)	−1.366 (−0.776)
	γ(CH,NH) (g)	4	8.306 (8.465)	−1.762 (−0.671)
CH_3OH	c(CH.O_{1p}) (t)	2	13.243 (13.243	−3.213 (−3.878)
	c(CH,OH) (t)	1	8.385 (7.828)	−2.876 (−5.077)
	γ(CH,O_{1p}) (g)	4	13.243 (13.243)	−1.053 (−0.735)
	γ(CH,OH) (g)	2	7.883 (8.100)	−1.581 (−0.733)

[a] All contributions are given in kcal/mol. [b] Zeroth- and second-order terms.

$$\Delta E^{(3,3)} = \sum_{n=0}^{3}\left(\sum_i\sum_{<j}\Delta\epsilon_{ij}{}^n + \sum_i\sum_{<j}\sum_{<k}\Delta\epsilon_{ijk}{}^n\right)$$

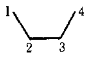
In principle, the two-body terms may be divided into geminal, vicinal, and long-range interactions, according to the relative position of the concerned bonds. The geminal interactions remain constant during the rotation if both bonds and their relative positions are constant. The only possible exception in our case must involve the



bond, which may change if the X atom is anisotropic. For instance, the geminal H–C–N (resp. O) interaction only varies by 0.02 kcal/mol (resp. 0.04). The only significant two-body interactions are therefore the vicinal ones.

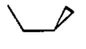
Different types of vicinal interactions appear in the considered rotational conformations (eclipsed and staggered conformers). One can distinguish these interactions making use of Ito's[32] conventional nomenclature proposed in his empirical additive systematic. For the vicinal two-bond interactions one uses four symbols c, t, γ, and g (cis, trans, "gamma", and gauche, respectively) which define the type of interaction

For

$\varphi = 0°$ ⟶ cis interaction


$\varphi = 180°$ ⟶ trans interaction


$\varphi = \pm120°$ ⟶ "gamma" interaction


$\varphi = \pm60°$ ⟶ gauche interaction


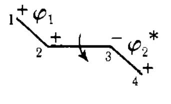
according to the relative position of the two involved bonds, defined by the dihedral angle φ(123,234). Positions c and γ occur in the eclipsed conformations, while t and g occur in the staggered ones. The same symbols are used for the three-body interactions; the geminal interactions are represented by "gem".

IIIA (1). Role of the Vicinal Interactions (Eclipsed and Staggered Conformations) in the CH_3XH_n (X = C, N, O)

Molecular Series. The various zeroth- and second-order two-body vicinal interactions have been reported in Table VI. One may notice that the zeroth-order contributions are larger in absolute value, but poorly stereospecific, especially when lone pairs are involved. (This conclusion is only valid for the CNDO approximation.)

Although smaller in absolute values, the second-order delocalization two-body terms present strong variations and are responsible for the barrier. For instance, the (CH, XH) interactions become twice as large when going from cis to trans positions.

The variation of the delocalization two-body correction is easily understood from the simplified case of two nonpolar bonds. With the arbitrary choice of the phase factor of $\varphi_2{}^*$, one obtains



$$\langle\varphi_1|h|\varphi_2{}^*\rangle = \tfrac{1}{2}\,[-\langle X_1|h|X_3\rangle + \langle X_1|h|X_4\rangle - \langle X_2|h|X_3\rangle + \langle X_2|h|X_4\rangle] \quad (22a)$$

which reduces to

$$\langle\varphi_1|h|\varphi_2{}^*\rangle = +\tfrac{1}{2}\,(\langle X_1|h|X_4\rangle - \langle X_2|h|X_3\rangle) \quad (22b)$$

if the bonds are similar ($\langle X_1|h|X_3\rangle \simeq \langle X_2|h|X_4\rangle$). In eq 22b, $\langle X_1|h|X_4\rangle$ and $\langle X_2|h|X_2\rangle$ occur with opposite signs and the molecular integral will be larger if $\langle X_1|h|X_4\rangle$ is smaller; therefore, the second-order correction increases when φ varies from 0 to 180°,

$$\frac{\langle\varphi_1|h|\varphi_2{}^*\rangle^2}{|\epsilon_1 - \epsilon_2{}^*|}\,t > \frac{\langle\varphi_1|h|\varphi_2{}^*\rangle^2}{|\epsilon_1 - \epsilon_2{}^*|}\,c$$

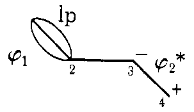
The delocalization is stronger by 3 kcal/mol when the bonds are trans and therefore more distant from each other. The decrease by 1 kcal/mol of the (CH, XH) interaction when going from γ to g positions does not compensate the stabilization due to the trans position.

The second-order dispersion two-body terms are less important in absolute value (in full agreement with ab initio calculations[33]) and less stereospecific. The transition dipole-transition dipole interaction (ii^*,jj^*) may be written within the same hypothesis

$$(ii^*,jj^*) = \tfrac{1}{4}\,(g_{13} - g_{24} - g_{14} - g_{23})$$

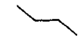
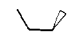
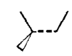
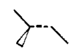
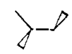
where g_{pq} is the Coulombic integral $\langle pq|pq\rangle$ between the atomic orbitals p and q. In this integral the $(g_{14} + g_{23})$ integrals are slightly larger than $(g_{13} + g_{24})$ and favor the compact cis form, in agreement with the expected dependence of a dipole-dipole interaction on the distance.

In the heteroatomic compounds, two essential modifications occur with respect to ethane: (i) one or two CH bonds are replaced by an XH bond (X = O or N); and (ii) two or one CH bonds are replaced by a lone pair. The vicinal (CH, XH) two-body terms do not differ strongly from the corresponding (CH, CH) two-body terms, especially at the zeroth-order level (for instance, c(CH, CH), c(CH, NH), and c(CH, OH) are respectively equal to 8.99, 8.71, and 8.39 kcal/mol). The delocalization two-body terms are more different (3.83, 3.09, and 2.88 kcal/mol) for the same series. Their changes in the rotation from cis to trans position are, respectively, 2.70, 2.79, and 2.20 kcal/mol, which cannot explain the decrease of the total delocalization contribution to the barrier (1.86, 1.24, 0.56 kcal/mol). This decrease is due to the lone pairs. The (CH,X_{lp}) delocalization two-body terms involving the lone pairs are much smaller and less stereospecific, as appears from Table VI (in the c → t transformation, (CH,N_{lp}) goes from −3.58 to −4.81 kcal/mol, (CH,O_{lp}) goes from −3.21 to −3.88 kcal/mol, while (CH,CH) varies from −3.82 to −6.53 kcal/mol). This decrease of stereospecificity may be understood, since in that case: (i) $\langle\varphi_2|h|\varphi_1{}^*\rangle$ disappears if φ_1 is the lone pair; there is no delocalization towards the lone pair. (ii) $\langle\varphi_1|h|\varphi_2{}^*\rangle$ reduces to $\langle\varphi_1|h|\varphi_2{}^*\rangle = (1/\sqrt{2})\,[-\langle X_2|h|X_3\rangle + \langle X_2|h|X_4\rangle]$. and $\langle X_2|h|X_4\rangle$ is less stereospecific than $\langle X_1|h|X_4\rangle$ in the (CH,CH) case. The introduction of lone pairs explains the decreases of the barrier when going from ethane to methylamine and methyl alcohol.



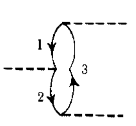
IIIA (2). Role of Three-Body Terms. The role of three-body terms is exemplified in the case of ethane. They practically reduce to the delocalization-delocalization third-order correction. The only varying three-body terms must imply two vicinal CH bonds; the third bond may be the CC bond or another CH bond. One gets, therefore, four types of three-body terms for each conformation, which are given in Table VII.

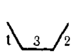
Table VII. Three-Body Terms Involved in the Rotational Barrier of Ethane[a]

	Eclipsed form			Staggered form		
	Type of interaction	Energy	No.	Type of interaction	Energy	No.
(CH.CC,CH)		−0.070	3		−0.055	3
		−0.039	6		−0.036	6
(CH,CH,CH)		−0.450	12		−0.424	12
		0.271	6		0.174	6

[a] In kcal/mol.

One may notice that (i) the intermediate C–C bond is less important than the CH bonds, (ii) the trans interactions are less stabilizing than the cis ones, contrary to the two-body terms, (iii) the final stabilization of the staggered form by the three-body terms (by 0.29 kcal/mol) is essentially due to the difference between g,g,gem (0.174) and γ,γ,gem (0.271) (CH,CH,CH) interactions (last line of Table VII). One may easily explain why the trans interactions are less stabilized than the cis ones by considering the corresponding third-order corrections. In the following diagram,





and its contribution

$$-\frac{\langle\varphi_2|h|\varphi_3{}^*\rangle\langle\varphi_2|h|\varphi_1\rangle\langle\varphi_1|h|\varphi_3{}^*\rangle}{(\epsilon_2 - \epsilon_3{}^*)(\epsilon_1 - \epsilon_3{}^*)}$$

the stereospecific element is $\langle\varphi_1|h|\varphi_2\rangle$. Turning back to the AO's, as in eq 22a,

$$\langle\varphi_1|h|\varphi_2\rangle = \tfrac{1}{2}\,[\langle X_1|h|X_3\rangle - \langle X_1|h|X_4\rangle + \langle X_2|h|X_3\rangle + \langle X_2|h|X_4\rangle]$$

which is larger for the cis position.

IIIA (3). Transferability of Vicinal Interactions from the CH_3XH_n to the $CH_3XH_{n-1}CH_3$ Series. In such compounds the empirical potentials of the Westheimer type[34] frequently assume that in the rotation around a single bond, the energy change is equal to the sum of the rotational barrier of the basic compound CH_3XH_n, plus the variation of the long-range in-

Table VIII. DPCILO Barrier Contributions[a] of the $(CH_3)_2XH_{n-1}$ (X = C,N,O) Molecular Series

	$CH_3CH_2CH_3$		CH_3NHCH_3		CH_3OCH_3	
Rotation	(0.0) → (60,0)	(0,0) → (60,60)	(0,0) → (60,0)	(0,0) → (60,60)	(0,0) → (60,0)	(0,0) → (60,60)
ΔE_0 (zeroth order) barrier	0.42	1.36	0.74	2.83	0.54	2.26
	(0.21 + 0.21)[b]	(0.43 + 0.95)[b]	(0.23 + 0.50)[b]	(0.52 + 2.36)[b]	(0.11 + 0.43)[b]	(0.26 + 2.02)[b]
Second-order correction	1.71	3.87	1.11	3.31	0.46	2.05
ΔE polarization	0.0	0.0	0.01	0.01	0.01	0.02
ΔE delocalization	1.88	4.49	1.20	3.93	0.45	2.45
	(1.97 − 0.08)[b]	(4.0 + 0.50)[b]	(1.33 − 0.13)[b]	(2.66 + 1.25)[b]	(0.57 − 0.12)[b]	(1.20 + 1.29)[b]
ΔE intrabond-correlation	0.0	0.0	0.0	0.0	0.0	0.0
ΔE interbond-correlation	−0.18	−0.62	−0.10	−0.63	0.0	−0.42
ΔE (zeroth + second order) barrier	2.13	5.23	1.84	6.13	1.00	4.31
Third-order correction	0.08	0.01	0.14	−0.25	0.11	−0.41
ΔE del–del	0.17	0.10	0.17	−0.33	0.12	−0.53
ΔE inter–del	−0.16	−0.33	−0.06	−0.14	0.0	−0.02
ΔE intra–inter	0.33	0.19	0.03	0.19	0.0	0.13
ΔE inter–inter	0.02	0.06	0.01	0.05	0.0	0.03
ΔE (zeroth + second + third order) barrier	2.21	5.24	1.97	5.88	1.11	3.90

[a] All barriers and contributions are given in kcal/mol: $\Delta E = E$(least stable) $- E$(most stable rotamer). [b] The two numbers between parentheses represent, respectively, the vicinal and long-range contributions.

Table IX. Two-Body Vicinal Contributions to the Energy[a] of the Eclipsed and Staggered (in parentheses) Forms of the $(CH_3)_2XH_{n-1}$ (X = C,N.O) Molecular Series[b]

Molecule	Type of interaction	No. of interactions	Zeroth order	Delocalization
CH_3CH_2CH	c(CH,CC) (t)	1	8.49 (8.36)	−2.60 (−6.46)
	c(CH.CH) (t)	2	9.04 (8.97)	−3.82 (−6.50)
	γ(CH.CC) (g)	2	8.37 (8.40)	−2.03 (−0.46)
	γ(CH,CH) (g)	4	8.78 (8.87)	−1.85 (−0.83)
CH_3NHCH_3	c(CH.N_{1p}) (t)	1	14.84 (14.84)	−3.54 (−4.76)
	c(CH,NC) (t)	1	8.04 (7.72)	−2.56 (−6.16)
	c(CH,NH) (t)	1	8.68 (8.26)	−3.06 (−5.81)
	γ(CH,N_{1p}) (g)	2	14.84 (14.84)	−1.36 (−0.76)
	γ(CH,NC) (g)	2	7.74 (7.83)	−2.02 (−0.58)
	γ(CH,CH) (g)	2	8.29 (8.44)	−1.75 (−0.67)
CH_3OCH_3	c(CH,O_{1p}) (t)	2	13.24 (13.24)	−3.25 (−3.89)
	c(CH.CO) (t)	1	7.34 (7.01)	−2.74 (−5.43)
	γ(CH.O_{1p}) (g)	4	13.24 (13.24)	−1.05 (−0.75)
	γ(CH,CO) (g)	2	7.04 (7.14)	−1.87 (−0.79)

[a] All contributions are given in kcal/mol. [b] Zeroth- and second-order terms.

teratomic interactions; for two simultaneous rotations, the energy change would be the sum of the two elementary barriers plus the change in long-range interactions between the terminal methyl groups. Our methodology may check the validity of these assumptions. When going from CH_3XH_n to $CH_3XH_{n-1}CH_3$, (i) one should find some interactions already involved in the former compounds (for instance, the (CH,XH) interaction which played the key role in the rotational barrier), and one may verify their transferability; (ii) an XH bond is replaced by an XC bond and one may hope that due to similar polarities their interactions are not too much different, allowing a global transfer of vicinal interactions and therefore of the basic rotational barrier; and (iii) the method gives explicitly the long-range interactions, the role of which may be discerned.

Three conformations have been studied, the fully staggered one (0,0) which is the most stable, the eclipsed staggered one (0,60) corresponding to a (60,0) single rotation around a C–X bond, and the fully eclipsed form (60,60) corresponding to two simultaneous rotations around the C–X bonds, and which should be the highest energy conformation. The (0,0) → (0,60) and (0,0) → (60,60) energy differences are given in Table VIII as well as the different contributions from the zeroth-, second-, and third-order corrections. With respect to the reference series (CH_3XH_n), the contributions from the zeroth order are significantly larger, and represent 30–50% of the final energy change. A new zeroth-order repulsive effect appears in these compounds, which will be attributed to the repulsion between the methyl groups through a detailed analysis of two-body terms. The other essential contribution arises from the second-order correction, essentially from the delocalization effect (although the dispersion interbond correlation energies are not negligible). The third-order correction diminishes the barrier to some extent.

Turning back to a many-body analysis, one may verify first the *transferability* of the two body (CH,XH) terms which appeared in the basic compounds. Comparing Tables VI and IX, one sees that this transferability is almost perfect. For instance, the zeroth- and second-order delocalization two-body terms are, respectively, 8.99 and −3.83, 9.04 and −3.82 for the cis (CH,CH) interactions in ethane and propane, 8.74 and −6.53, 8.77 and −6.50 for the trans interactions in the same compounds, 8.71 and −3.09, 8.68 and −3.06 for cis (CH,NH) interactions in methyl- and dimethylamines, 14.84 and −1.37, 14.84 and −1.36 kcal/mol for the γ (CH,N_{1p}) interactions in the same compounds.

One may wonder whether the X–C and X–H bonds are approximately equivalent in the vicinal two-body terms as implicitly assumed by empirical systematics with transfer rotation barriers. Again the comparison of Tables VI and IX show that this equivalence is only approximate. For instance, the zeroth- and delocalization second-order two-body terms are 8.49 and −2.60 for cis (CH,CC) instead of 8.99 and −3.83 kcal/mol for cis (CH,CH), 8.04 and −2.56 for cis (CH,NC) instead of 8.71 and −3.09 for cis (CH,NH). However, some cancellations occur and the final sum of all vicinal interactions are almost the same in basic and heavier compounds. For in-

Table X. Two-Body Long-Range (CH,CH) Interactions for the $(CH_3)_2XH_{n-1}$ Molecular Series[a]

Molecular conformation	Type of interaction	No. of interactions	X = C Zeroth order	X = C Del	X = N Zeroth order	X = N Del	X = O Zeroth order	X = O Del
(0,0)	tt	1	0.13	−0.09	0.29	−0.08	0.33	−0.11
	gg	2	0.28	−0.06	0.64	−0.21	0.65	−0.28
	gg′	2	0.21	−0.0	0.46	−0.01	0.48	−0.02
	gt	4	0.17	−0.31	0.37	−0.59	0.40	−0.55
(0,60)	ct	1	0.25	−0.88	0.56	−1.65	0.57	−1.52
	tγ	2	0.14	−0.01	0.30	−0.001	0.33	−0.01
	gc	2	0.40	−0.06	0.90	−0.23	0.88	−0.30
	gγ	2	0.18	−0.003	0.39	−0.01	0.41	−0.01
	gγ′	2	0.17	−0.25	0.37	−0.47	0.40	−0.45
(60,60)	cc	1	1.14	−0.003	2.81	−0.05	2.55	−0.12
	γγ	2	0.14	−0.04	0.30	−0.08	0.34	−0.09
	γγ′	2	0.14	−0.07	0.30	−0.16	0.33	−0.17
	cγ	4	0.26	−0.18	0.58	−0.28	0.58	−0.24

[a] Zeroth- and second-order terms in kcal/mol.

stance, at the zeroth order,

$$\Delta E_0{}^{v}(CH_3NHCH_3) = 0.26\ \text{kcal/mol}$$

$$\Delta E_0{}^{v}(CH_3NH_2) = 0.22\ \text{kcal/mol}$$

and at the second order.

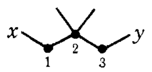
$$\Delta E_{2,\text{del}}{}^{v}(CH_3NHCH_3) = 1.33\ \text{kcal/mol}$$

$$\Delta E_{2,\text{del}}{}^{v}(CH_3NH_2) = 1.25\ \text{kcal/mol}$$

The transfer of the basic rotation barrier into larger compounds may therefore introduce an error of a few tenths of a kilocalorie per mole.

IIIB. The Role of Long-Range (Third Neighbor Bonds) Interactions in the Rotational Barriers of the $CH_3XH_{n-1}CH_3$ Series. Table X gives the various types of (CH,CH) long-range interactions, which are distinguished using the symbols appearing in the vicinal interactions. The reference plan is this which involves the three heavy atoms.

The couple of bonds (1-*x*) and (3-*y*) attached to atoms 1 and 3, for instance. will be defined by the position of (1-*x*)



bond with respect to (2-3), and (3-*y*) bond with respect to (2-1). For the two bonds not placed on the plane (123), one must distinguish whether they are located on the same side of the (123) plane or on opposite sides. The prime (′) symbol will be attached to the couple of bonds placed on opposite sides.

The relative role of the long-range interactions with respect to the vicinal interactions have been summarized in Table X, showing (i) that these effects are of the same order of magnitude. and (ii) that the long-range effects are mainly zeroth-order repulsive effects, while the vicinal interactions are essentially due to the delocalization. The detailed values of two-body long-range interactions given in Table X follow the expected dependence on the relative position of the concerned bonds.

The stronger interaction concerns the (c,c) couple occurring for the (60,60) conformation (1.14 kcal/mol) in propane at the zeroth order, the (t.t) interaction is the lowest one (for the


(c, c)


(c, t)


(t. t)

(0,0) conformation of propane, 0.13 kcal/mol), while the (c,t) interaction presents an intermediate value (0.25 kcal/mol).

One may also verify from this theoretical approach the additivity of rotation barriers in a Westheimer potential systematic. If one keeps only two-body terms, one may write

$$\Delta E[(0,0) \rightarrow (60,60)] = \sum_{ij} \Delta E_{ij}{}^{v}\,[(0,0) \rightarrow (60,60)]$$
$$+ \sum_{ij} \Delta E_{ij}{}^{l}[(0,0) \rightarrow (60,60)]$$

But,

$$\sum_{ij} \Delta E_{ij}{}^{v}[(0,0) \rightarrow (60,60)] = \sum_{ij} \Delta E_{ij}{}^{v}[(0,0) \rightarrow (0,60)]$$
$$+ \sum_{ij} \Delta E_{ij}{}^{v}[(0,60) \rightarrow (60,60)]$$

The vicinal interactions around the X(2)-C(3) bond do not depend on the rotation around the C(1)-X(2) bond, and therefore,

$$\sum_{ij} \Delta E_{ij}{}^{v}[(0,60) \rightarrow (60,60)] = \sum_{ij} \Delta E_{ij}{}^{v}[(0,0) \rightarrow (0,60)]$$

Hence,

$$\Delta E[(0,0) \rightarrow (60,60)] = 2 \sum_{ij} \Delta E_{ij}{}^{v}[(0,60) \rightarrow (60,60)]$$
$$+ \sum_{ij} \Delta E_{ij}{}^{l}[(0,0) \rightarrow (60,60)]$$

since $\Sigma_{ij}{}^{v}\Delta E_{ij}[(0,60) \rightarrow (60,60)]$ is almost the rotation barrier ΔE(basic) for the basic compounds. As verified previously, one has,

$$\Delta E[(0,0) \rightarrow (60,60)] = 2\Delta E(\text{basic})$$
$$+ \sum_{ij} \Delta E_{ij}{}^{l}[(0,0) \rightarrow (60,60)]$$

At the second-order level this is almost perfectly verified.

IIIC. Rotation Barriers in the Series X_3B–NY_3 (X, Y = H, F). As a further example, we have chosen the series of borazane and the perfluoro derivatives, since the analysis in terms of atoms and atomic interactions[10] gives a rather strange role to the bonded interactions and to the X···Y, N···X, and B···Y interactions. Table XI reproduces the various contributions of the perturbation series, showing a small zeroth-order contribution as in the basic barriers studied before; the main contribution again arises for all compounds from the second-order correction and essentially from the delocalization effect.

The role of vicinal and "long-range" interactions have been reported in Table XI (long range meaning only the interactions with the lone pairs which play the role of bonds besides the vicinal bonds). One sees that the lone pairs play a very important role. the $F_{lp} \rightarrow BH^*$ or BF^* delocalization increases the barrier in F_3N-BH_3 and F_3N-BF_3, while the $F_{lp} \rightarrow NH^*$

Table XI. DPCILO Rotational Barrier Contributions[a] of the BH_3NH_3 and Its Perfluoro Derivatives BH_3NF_3, F_3BNH_3, and F_3NBF_3

Molecule	BH_3NH_3	F_3BNH_3	F_3NBH_3	F_3NBF_3
ΔE_0 (zeroth order) barrier	0.17 $(0.17 + 0.00)^b$	0.18 $(-0.30 + 0.48)^b$	0.25 $(0.09 + 0.16)^b$	0.05 $(0.05 + 0.00)^b$
Second-order correction	1.39	0.57	1.56	0.54
ΔE pol	0.0	0.0	0.0	0.0
ΔE del	1.64 $(1.64 + 0.00)^b$	0.77 $(1.20 - 0.43)^b$	1.80 $(1.29 + 0.51)^b$	0.77 $(0.42 + 0.35)^b$
ΔE intrabond-correlation	0.0	0.01	0.0	0.0
ΔE interbond-correlation	0.0	−0.21	−0.25	−0.23
ΔE (zeroth + second order) barrier	1.56	0.74	1.81	0.58
Third-order correction	0.26	0.09	−0.40	−0.20
ΔE del–del	0.28	−0.09	−0.35	−0.20
ΔE inter–del	−0.13	−0.05	−0.20	−0.12
ΔE intra–inter	0.08	0.06	0.10	0.09
ΔE inter–inter	0.04	0.03	0.05	0.04
ΔE (zeroth + second + third order) barrier	1.82	0.83	1.41	0.38

[a] The energies in kcal/mol; the CNDO/2 barriers are 1.94, 0.94, 1.48, and 0.70, respectively. See M. C. Bach, F. Crasnier, J. F. Labarre, and C. Leibovici, *J. Mol. Struct.*, **16**, 89 (1973). [b] The two numbers in parentheses represent respectively the vicinal and long-range interactions.

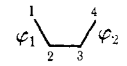
delocalization decreases it in $F_3B{-}NH_3$. The anomalous behavior of that compound in Labarre's analysis appears at this level in our scheme. The third-order correction also plays an important role, decreasing the $F_3N{-}BH_3$ barrier under the value for $BH_3{-}NH_3$ and giving finally the sequence obtained from a variational SCF-CNDO calculation. The important third-order correction is again a delocalization effect (del-del correction) involving three-bond contributions which are rather difficult to analyze. This series shows both the already noticed leading role of the delocalization effects (mainly between vicinal bonds) and the importance of long-range interactions and three-body effects.

Conclusions

(1) The choice of bond MO's and of a perturbative calculation of the energy allows one to study through a quantum mechanical approach the theoretical foundations of the empirical additive systematics and refined empirical potentials. The PCILO scheme in its differential version allows a many-body partition of the energy in terms of bonds and exhibits one-body bond energies, two-body interactions between vicinal or long-distance bonds, three-body corrections, etc. The numerical values are not expected to give the values of the empirical systematics for several reasons. (a) The empirical values and the theoretical choices have some arbitrariness;[16] one may, for instance, include two-body terms between adjacent bonds (or geminal atoms) into the one-body terms relative to these bonds (or the central atom) in a series of compounds for which these adjacent bonds always occur. The same is true for the three-body terms, which may be converted into two-body terms (the three-body H-C-C-H interaction may be attributed to the (CH_2CH) two-body terms). (b) The empirical systematics work besides the sum of the atomic energies, while the theoretical systematics do not exhibit the atomic energies. However, the theoretical approach reveals that the one- and two-body terms are well transferable from one molecule to another and the sum of the vicinal interactions, which give rise to the rotation barriers in the elementary compounds CH_3XH_n, is almost exactly equal to the sum of the vicinal interactions occurring in the heavier compounds $CH_3XH_{n-1}CH_3$. These results validate the transfer of rotation barriers if one adds the new "long-range" two-body interactions, as done in the Westheimer type potentials. It is possible, if one carefully examines the content of a quantum mechanical energy, to find a hidden structure which parallels the well-known intuitive systematics of the chemist. For the wave functions and electronic density, the concept of localized electron pairs has received a full confirmation from theoretical studies.[35] A detailed analysis of transferable environment-dependent tails of MO's is even possible.[13] An analogous justification is possible for the energy.

(2) The a posteriori decomposition of the quantum mechanical energy in terms of atoms does not bring much information for an understanding of conformational energy, since it requires the knowledge of the variational density matrix, which a priori depends on the whole molecule. The perturbative-bond localized approach does not meet with the difficulties of the atomic partition; the rotation barrier, for instance, essentially appears from delocalization effects between vicinal bonds as may be expected from intuition, since the moving elements are the vicinal bonds.

If one decomposes the $\langle \varphi_1 | F | \varphi_2^* \rangle$ matrix element in terms of atoms, one will get contributions from the vicinal atoms



(1-4) (which move), but also from the geminal (1-3, 2-4) and bonded atoms (2-3), which have constant relative positions. But the contribution due, for instance, to a (2-3) diatomic integral may go through the *bond* matrix element $\langle \varphi_1 | F | \varphi_2^* \rangle$ without involving the intermediate bond. Our bond analysis attributing the phenomenon to the vicinal bond interactions explains the puzzling role of "bonded" and geminal atomic interactions exemplified by Labarre and co-workers in a large series of compounds.

This perturbative (additive) calculation of the energy supports the conclusions of Christiansen and Palke[36] concerning the orthogonality effects between the CH bond orbitals on opposite ends of the molecules. It confirms also the conclusion reached by Gordon and England through an a posteriori analysis of the SCF variational result; the CNDO rotational barriers are due to the delocalization effects between vicinal bonds, and to the monoelectronic part of the Hamiltonian. Our approach does not require either the first variational SCF procedure or the relocalization variational step. Moreover, it allows us to distinguish between the various physical phenomena which may occur between the bonds, in a language derived from the theory of intermolecular forces. Whatever the limits of the CNDO Hamiltonian are, we think it is interesting to see through a localized approach the detail content and building up of the CNDO energy (and energy changes)[37] and the ways followed to reproduce experiment. Moreover, the exploit of cheap semiempirical methods in view of obtaining qualitative information about conformational problems may be helpful for their physical understanding.

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Ab Initio Valence-Bond Calculations. 5. Benzene

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Abstract: π-Electron ab initio valence-bond calculations for ground and singlet and triplet excited states of benzene have been performed using two minimal basis sets (STO. GTO). Vertical ionization potentials. atomization. and resonance energies have also been computed. By means of a population analysis the results have been interpreted and discussed in terms of individual and symmetry VB structures. Comparisons with previous semiempirical and ab initio calculations are presented.

1. Introduction

In a recent paper by Norbeck and Gallup[1] ab initio valence-bond (VB) results on benzene were interpreted as strongly different from those obtained by means of previous semiempirical treatments.[2,3] In particular, the question of the validity of the qualitative bonding theories commonly used by experimental chemists was raised. Our interest in performing a new VB calculation on benzene was to study to what extent the conclusions contained in that paper were dependent on the particular choice of the basis functions. To this aim we performed calculations using optimized Slater type orbitals (STO's) and a less sophisticated, but widely used basis set of Gaussian type orbitals (GTO's, ref 4). These two basis sets, in addition to the atomic SCF functions based on Gaussian lobes[5] used in ref 1, should be adequate to show up any dependence of the general results on the kind of basis functions used. It was also our interest to explore the capabilities of the VB method in studying the π-electron excited states (singlet and triplet) of such an important aromatic system as benzene, even when restricted to the use of a minimal basis set. The good agreement with experiment obtained for the ionization potentials (IP's) of H_2S[6] prompted us to perform theoretical calculations on the IP's of benzene. The next section briefly describes the method of calculation. Section 3 is concerned with the results obtained for the ground state; a comparison with the results of Norbeck and Gallup[1] is also given. In section 4 the results for the excited states and the ionization potentials are presented and discussed. General conclusions are contained in the last section.