Beyond the MNDO Model: Methodical Considerations and Numerical Results

Matthias Kolb and Walter Thiel*

Theoretische Chemie, Universität GH Wuppertal, D-5600 Wuppertal 1, Germany

It is suggested to improve the MNDO model by the explicit inclusion of valence-shell orthogonalization corrections, penetration integrals, and effective core potentials (ECPs) in the one-center part of the core Hamiltonian matrix. Guided by analytic formulas and numerical *ab initio* results, the orthogonalization corrections are expressed in terms of the resonance integrals that are represented by a new empirical parametric function. All two-center Coulomb interactions and ECP integrals are evaluated analytically in a Gaussian basis followed by a uniform Klopman–Ohno scaling. One particular implementation of the proposed NDDO SCF approach is described and parameterized for the elements H, C, N, O, and F. In a statistical evaluation of ground-state properties, this implementation shows slight but consistent improvements over MNDO, AM1, and PM3. Significant improvements are found for excited states, transition states, and strong hydrogen bonds. Possible further enhancements of the current implementation are discussed. © 1993 by John Wiley & Sons, Inc.

INTRODUCTION

MNDO,[1] AM1,[2] and PM3[3] are widely used in theoretical studies of molecular structure and reactivity.[4-6] These three semiempirical SCF methods are based upon the same theoretical model of electronic structure because they employ identical formulas for the Fock matrix elements. They differ in the treatment of the core repulsion function, which is more flexible and highly parameterized in AM1 and PM3. Given the considerable effort that has gone into the parameterization of these methods, it seems likely that further overall improvement will not be found by a mere reparameterization of MNDO-type methods but will require a more refined theoretical model that goes beyond MNDO.

It is generally agreed that the semiempirical integral approximations are best justified when using a Loewdin orthogonalized basis set.[7,8] In this case, the NDDO approximation for the two-electron integrals is valid through second order in overlap,[9-11] and numerical calculations have confirmed that the third-order corrections of the two-electron integrals are small.[12] However, the situation is less favorable for the one-electron integrals[10,11,13-19] because the transformation from the usual nonorthogonal basis to the Loewdin orthogonalized basis leads to substantial changes in the core Hamiltonian matrix. The orthogonalization corrections are not treated explic-

itly in MNDO, AM1, or PM3, where they are taken into account only indirectly through the neglect of penetration integrals and the parameterization of the core repulsion functions and the resonance integrals. An approximate treatment of these one-electron corrections has been introduced both at the CNDO and INDO levels[20-22] (CNDO-S^2, SINDO1). In view of the importance of such orthogonalization effects,[9-22] it seems desirable to incorporate them explicitly also at the NDDO level.

The present article reports a methical study of the one-electron orthogonalization terms and proposes parametric formulas for their representation in the context of the NDDO approximation. Based upon these ideas, a new semiempirical NDDO SCF method is outlined that features several other enhancements[5] to MNDO and related methods. A preliminary parameterization and a survey of numerical results are given to demonstrate the validity of the new approach.[23]

THEORETICAL DEVELOPMENT

Ab initio SCF methods solve the following eigenvalue problem:

$$^\lambda\mathbf{F}^\lambda\mathbf{C} = {}^\lambda\mathbf{C}\mathbf{E} \tag{1}$$

$$^\lambda\mathbf{F} = \mathbf{S}^{-1/2}\mathbf{F}\mathbf{S}^{-1/2} \tag{2}$$

$$^\lambda\mathbf{C} = \mathbf{S}^{1/2}\mathbf{C} \tag{3}$$

where $^\lambda\mathbf{F}$ and $^\lambda\mathbf{C}$ denote the Fock matrix and the eigenvector matrix in the Loewdin orthogonalized basis ($^\lambda\Phi$), respectively. $\mathbf{F}$ and $\mathbf{C}$ are the correspond-

ing matrices in the basis of the nonorthogonal atomic orbitals (Φ), **S** is the overlap matrix, and **E** the diagonal eigenvalue matrix.

Semiempirical SCF methods solve an eigenvalue problem analogous to eq. (1). The semiempirical integrals can therefore be associated with theoretical integrals in the $^\lambda\Phi$-basis. In the case of the two-electron integrals, this provides a justification for the NDDO approximation[9–12]: Because the three- and four-center two-electron integrals are small in the $^\lambda\Phi$-basis, they may be neglected. Among the remaining NDDO-type integrals, the one-center two-electron integrals are usually derived from experimental atomic data,[1,2,24] and the resulting empirical values agree well with those obtained from high-level *ab initio* calculations employing an effective valence-shell Hamiltonian.[25,26] In current implementations,[1–3,27,28] the two-center two-electron NDDO integrals adopt their classic electrostatic values in the limit of large internuclear distances ($R_{AB} \to \infty$) and are smoothly connected to the corresponding empirical values in the one-center limit ($R_{AB} = 0$) by applying the Klopman–Ohno scaling.[29,30] Compared with the analytic values in the $^\lambda\Phi$-basis, this scaling leads to a reduction of the two-center two-electron NDDO integrals at intermediate distances that is consistent with the changes caused by the orthogonalization transformation ($\Phi \to {}^\lambda\Phi$)[9–12] but may also reflect the influence of dynamic electron correlation.[5] Hence, current MNDO-type methods account for major orthogonalization effects on the two-electron integrals in that they neglect integrals that are small in the $^\lambda\Phi$-basis and employ reduced values for the nonzero two-electron integrals at intermediate distances. In an *ab initio* calculation for a given molecule, there will be additional structure-dependent orthogonalization effects on the two-electron integrals, of course. Such more involved corrections to the two-electron integrals will not be attempted in the present study because this would tend to sacrifice the computational efficiency that is essential for practical implementations of semiempirical methods. Instead, for the reasons given above, we shall rely upon the NDDO approximation for the two-electron integrals with Klopman–Ohno scaling, similar as in the established MNDO-type models.[1–3]

The orthogonalization transformation ($\Phi \to {}^\lambda\Phi$) for the one-electron integrals leads to significant changes in the core Hamiltonian matrix:

$$^\lambda\mathbf{H} = \mathbf{S}^{-1/2}\mathbf{H}\mathbf{S}^{-1/2} \qquad (4)$$

From a computational point of view, $^\lambda\mathbf{H} - \mathbf{H}$ could easily be evaluated analytically (*ab initio*) and then be added to the semiempirical core Hamiltonian matrix. This procedure, however, introduces an imbalance between the one- and two-electron parts of the Fock matrix as long as the two-electron integrals are not subjected to the same exact transformation ($\Phi \to {}^\lambda\Phi$), which is computationally not feasible in

semiempirical methods (see above). Despite this expectation, we investigated the use of $^\lambda\mathbf{H} - \mathbf{H}$ (*ab initio*) in several reasonable variants,[17,23] as a correction for the full core Hamiltonian matrix as well as only for its one-center part, but without much success. We therefore concluded that it is mandatory to avoid such an imbalance and represent the major orthogonalization corrections to the one-electron integrals by suitable parametric functions that are numerically less sensitive than $^\lambda\mathbf{H} - \mathbf{H}$ (*ab initio*), e.g., with respect to parameter and geometry variations.

The choice of such parametric functions is guided by the analytic expressions for $^\lambda\mathbf{H}$ in simple two-orbital systems, by power series expansions for $^\lambda\mathbf{H}$ according to eq. (4), and by numerical results from *ab initio* SCF calculations. In the case of a homonuclear diatomic molecular with two orbitals (Φ_μ at atom A, Φ_λ at atom B, overlap $S_{\mu\lambda}$), the matrix elements of $^\lambda\mathbf{H}$ can be written as

$$^\lambda H_{\mu\mu} = H_{\mu\mu} - S_{\mu\lambda}M_{\mu\lambda}/(1 - S^2_{\mu\lambda}) \qquad (5)$$

$$^\lambda H_{\mu\lambda} = M_{\mu\lambda}/(1 - S^2_{\mu\lambda}) \qquad (6)$$

$$M_{\mu\lambda} = H_{\mu\lambda} - S_{\mu\lambda}(H_{\mu\mu} + H_{\lambda\lambda})/2 \qquad (7)$$

The approximate expressions from a second-order expansion of the $\mathbf{S}^{-1/2}$ matrix[7–11] have the same structure but neglect the denominators $(1 - S^2_{\mu\lambda})$ in eqs. (5) and (6), which approach 1 for small overlap. The diagonal and offdiagonal elements of $^\lambda\mathbf{H}$ are obviously related by

$$^\lambda H_{\mu\mu} = H_{\mu\mu} - S_{\mu\lambda}{}^\lambda H_{\mu\lambda} \qquad (8)$$

In the case of a heteronuclear diatomic molecule with two orbitals,[18] $^\lambda H_{\mu\lambda}$ is again given by eqs. (6) and (7) whereas $^\lambda H_{\mu\mu}$ can be expressed as

$$^\lambda H_{\mu\mu} = H_{\mu\mu} - S_{\mu\lambda}{}^\lambda H_{\mu\lambda} \\ + 1/2(H_{\mu\mu} - H_{\lambda\lambda})[(1 - S^2_{\mu\lambda})^{-1/2} - 1] \qquad (9)$$

Expanding the term in the square brackets yields

$$^\lambda H_{\mu\mu} = H_{\mu\mu} - S_{\mu\lambda}{}^\lambda H_{\mu\lambda} \\ + 1/4S^2_{\mu\lambda}(H_{\mu\mu} - H_{\lambda\lambda})[1 - 3/4S^2_{\mu\lambda} + \ldots] \qquad (10)$$

Numerical calculations for the hydrogen molecule with a minimal basis show that $H_{\mu\mu}$ and $^\lambda H_{\mu\mu}$ are of the same order of magnitude whereas $H_{\mu\lambda}$ and $^\lambda H_{\mu\lambda}$ differ strongly.[31] Therefore, $^\lambda H_{\mu\mu} - H_{\mu\mu}$ may be regarded as a relatively small correction whereas a qualitatively correct description of $^\lambda H_{\mu\lambda}$ requires the use of the Mulliken function[32] $M_{\mu\lambda}$ [see eq. (7)].[31]

For larger molecules, analytic formulas for $^\lambda\mathbf{H}$ are no longer available so that the orthogonalization transformation in eq. (4) is commonly analyzed by a power series expansion of the $\mathbf{S}^{-1/2}$ matrix.[9–19,21,33] This expansion may diverge in the general case[33] but there is a formal procedure to make the expansion convergent by a shift of origin.[11] In the following, we shall use the expansion formulas only as a guideline for defining parametric functions to represent orthogonalization corrections.

The power series expansion of eq. (4) is carried out in terms of the matrix $\tilde{\mathbf{S}}$, which contains the offdiagonal elements of the overlap matrix $\mathbf{S}$ and thus differs from $\mathbf{S}$ by the unit matrix $\mathbf{1}$.

$$\mathbf{S}^{-1/2} = (\mathbf{1} + \tilde{\mathbf{S}})^{-1/2}$$

$$= \mathbf{1} - 1/2\tilde{\mathbf{S}} + 3/8\tilde{\mathbf{S}}^2 - 5/16\tilde{\mathbf{S}}^3$$
$$+ 35/128\tilde{\mathbf{S}}^4 - \ldots \tag{11}$$

$$\tilde{\mathbf{S}}_{\mu\lambda} = \mathbf{S}_{\mu\lambda} \quad \text{for } \mu \neq \lambda \tag{12}$$

Inserting eq. (11) into eq. (4) and collecting terms up to order n in the overlap yields approximations ${}^\lambda\mathbf{H}^{(n)}$:

$$\tag{13} {}^\lambda\mathbf{H}^{(0)} = \mathbf{H}$$

$$\tag{14} {}^\lambda\mathbf{H}^{(1)} = {}^\lambda\mathbf{H}^{(0)} - 1/2(\tilde{\mathbf{S}}\mathbf{H} + \mathbf{H}\tilde{\mathbf{S}})$$

$$\tag{15} {}^\lambda\mathbf{H}^{(2)} = {}^\lambda\mathbf{H}^{(1)} + 3/8(\tilde{\mathbf{S}}^2\mathbf{H} + \mathbf{H}\tilde{\mathbf{S}}^2) + 1/4\tilde{\mathbf{S}}\mathbf{H}\tilde{\mathbf{S}}$$

$$\begin{aligned} {}^\lambda\mathbf{H}^{(3)} = {}^\lambda\mathbf{H}^{(2)} &- 5/16(\tilde{\mathbf{S}}^3\mathbf{H} + \mathbf{H}\tilde{\mathbf{S}}^3) \\ &- 3/16(\tilde{\mathbf{S}}^2\mathbf{H}\tilde{\mathbf{S}} + \tilde{\mathbf{S}}\mathbf{H}\tilde{\mathbf{S}}^2) \end{aligned} \tag{16}$$

$$\begin{aligned} {}^\lambda\mathbf{H}^{(4)} = {}^\lambda\mathbf{H}^{(3)} &+ 35/128(\tilde{\mathbf{S}}^4\mathbf{H} + \mathbf{H}\tilde{\mathbf{S}}^4) \\ &+ 5/32(\tilde{\mathbf{S}}^3\mathbf{H}\tilde{\mathbf{S}} + \tilde{\mathbf{S}}\mathbf{H}\tilde{\mathbf{S}}^3) + 9/64\tilde{\mathbf{S}}^2\mathbf{H}\tilde{\mathbf{S}}^2 \end{aligned} \tag{17}$$

Equations (14)–(17) may alternatively be written as

$$\tag{18} {}^\lambda\mathbf{H}^{(n)} = \mathbf{H} + \mathbf{\Delta}^{(n)} + \mathbf{R}^{(n)}$$

$$\tag{19} \mathbf{\Delta}^{(n)} = -1/2(\tilde{\mathbf{S}}{}^\lambda\mathbf{H}^{(n-1)} + {}^\lambda\mathbf{H}^{(n-1)}\tilde{\mathbf{S}})$$

$$\tag{20} \mathbf{R}^{(1)} = 0$$

$$\tag{21} \mathbf{R}^{(2)} = \mathbf{R}^{(1)} + 1/8(\tilde{\mathbf{S}}^2\mathbf{H} + \mathbf{H}\tilde{\mathbf{S}}^2) - 1/4\tilde{\mathbf{S}}\mathbf{H}\tilde{\mathbf{S}}$$

$$\begin{aligned} \mathbf{R}^{(3)} = \mathbf{R}^{(2)} &- 1/8(\tilde{\mathbf{S}}^3\mathbf{H} + \mathbf{H}\tilde{\mathbf{S}}^3) \\ &+ 1/8(\tilde{\mathbf{S}}^2\mathbf{H}\tilde{\mathbf{S}} + \tilde{\mathbf{S}}\mathbf{H}\tilde{\mathbf{S}}^2) \end{aligned} \tag{22}$$

$$\begin{aligned} \mathbf{R}^{(4)} = \mathbf{R}^{(3)} &+ 15/128(\tilde{\mathbf{S}}^4\mathbf{H} + \mathbf{H}\tilde{\mathbf{S}}^4) \\ &- 3/32(\tilde{\mathbf{S}}^3\mathbf{H}\tilde{\mathbf{S}} + \tilde{\mathbf{S}}\mathbf{H}\tilde{\mathbf{S}}^3) - 3/64\tilde{\mathbf{S}}^2\mathbf{H}\tilde{\mathbf{S}}^2 \end{aligned} \tag{23}$$

Comparison between eqs. (15)–(17) and (21)–(23) indicates that the remainders $\mathbf{R}^{(n)} - \mathbf{R}^{(n-1)}$ introduced in nth order ($n = 2$–4) are expected to be much smaller than the corresponding differences ${}^\lambda\mathbf{H}^{(n)} - {}^\lambda\mathbf{H}^{(n-1)}$ because each of the contributing terms has a smaller prefactor and because there are alternating signs for the terms of each order. In fact, if the matrices $\tilde{\mathbf{S}}$ and $\mathbf{H}$ would commute (which they do not) the remainders $\mathbf{R}^{(n)}$ would vanish [see eqs. (21)–(23)]. Hence, even though the expression $\mathbf{H} + \mathbf{\Delta}^{(n)}$ formally looks like a first-order expansion [see eq. 19)] it should converge well because it includes many higher-order terms. The most accurate corrections $\mathbf{\Delta}^{(n)}$ should be obtained in the limit $n \to \infty$, i.e., when using the exact matrix ${}^\lambda\mathbf{H}$ in eq. (19):

$$\tag{24} {}^\lambda\mathbf{H} = \mathbf{H} + \mathbf{\Delta}^{(\infty)} + \mathbf{R}^{(\infty)}$$

$$\tag{25} \mathbf{\Delta}^{(\infty)} = -1/2(\tilde{\mathbf{S}}{}^\lambda\mathbf{H} + {}^\lambda\mathbf{H}\tilde{\mathbf{S}})$$

which is consistent with the analytic formulas for the two-orbital cases discussed above [see eqs. (8) and (9)].

Semiempirical approaches will focus on the inclusion of the dominant orthogonalization corrections and avoid the explicit evaluation of elaborate high-order corrections. In view of the preceding discussion, an expression of the form

$$\tag{26} {}^\lambda\mathbf{H}^{(s)} = \mathbf{H} + \mathbf{\Delta}^{(s)} + \mathbf{R}^{(s)}$$

$$\tag{27} \mathbf{\Delta}^{(s)} = -1/2(\tilde{\mathbf{S}}\mathbf{H}^{(s)} + \mathbf{H}^{(s)}\tilde{\mathbf{S}})$$

appears to be an attractive semiempirical ansatz (superscripts s for semiempirical). We first consider orthogonalization corrections to the one-center one-electron matrix elements $H_{\mu\nu}$ (Φ_μ and Φ_ν at the same atom A):

$$\Delta_{\mu\nu}^{(s)} = -1/2 \sum_{\lambda \neq \mu,\nu} (S_{\mu\lambda}H_{\lambda\nu}^{(s)} + H_{\mu\lambda}^{(s)}S_{\lambda\nu}) \tag{28}$$

Because the semiempirical methods employ a minimal valence basis set where all orbitals at a given atom are orthogonal, $\Delta_{\mu\nu}^{(s)}$ consists of two-center contributions only (i.e., ϕ_λ is located at a different atom B). Hence, if a realistic representation of the two-center one-electron matrix elements ("resonance integral") is available it may be used to calculate the dominant orthogonalization corrections $\Delta_{\mu\nu}^{(s)}$ to the one-center one-electron matrix elements. The remainder $R_{\mu\nu}^{(s)}$ may be defined on the basis of eqs. (21)–(23). In a semiempirical context, it should certainly be sufficient to consider only the second-order contributions from eq. (21). In general, these contributions will contain terms of three-center character (in the triple matrix product) that do not appear elsewhere in NDDO-type methods and should therefore be neglected to avoid an internal imbalance. Thus, the simplest semiempirical expression for $R_{\mu\nu}^{(s)}$ includes only those terms of two-center character from eq. (21) that involve diagonal core Hamiltonian matrix elements:

$$R_{\mu\nu}^{(s)} = 1/8 \sum_{\lambda \neq \mu,\nu} S_{\mu\lambda}S_{\lambda\nu}(H_{\mu\mu} + H_{\nu\nu} - 2H_{\lambda\lambda}) \tag{29}$$

It should be noted that the semiempirical orthogonalization corrections for a heteronuclear diatomic molecule with two orbitals are thus given by

$$\Delta_{\mu\mu}^{(s)} + R_{\mu\mu}^{(s)} = -S_{\mu\lambda}H_{\mu\lambda}^{(s)} + 1/4S_{\mu\lambda}^2(H_{\mu\mu} - H_{\lambda\lambda}) \tag{30}$$

which is compatible with the analytic expression [see eq. (10)] up to the fourth order in the overlap.

To assess the magnitude of the various correction terms discussed, the relevant integrals were calculated analytically (ab initio) for a set of about 20 molecules[23] using a minimal valence basis of contracted Gaussian functions (see the next section). The test molecules included typical hydrocarbons ranging in size from CH_2 to C_6H_{12} and small molecules containing heteroatoms (Li, N, O, F).[23] The ex-

act orthogonalization corrections from eq. (4) were used as reference:

$$\Delta^\lambda H_{\mu\nu} = {}^\lambda H_{\mu\nu} - H_{\mu\nu} \tag{31}$$

The following conclusions emerge from the available analytic results[23]: The differences ${}^\lambda H_{\mu\nu}^{(1)} - H_{\mu\nu}$ and ${}^\lambda H_{\mu\nu}^{(2)} - {}^\lambda H_{\mu\nu}^{(1)}$ [see eqs. (14) and (15)] are huge and normally of opposite sign. Both ${}^\lambda H_{\mu\nu}^{(1)} - H_{\mu\nu}$ and ${}^\lambda H_{\mu\nu}^{(2)} - {}^\lambda H_{\mu\nu}$ are unsuitable as approximations to $\Delta^\lambda H_{\mu\nu}$ because they are usually much larger in absolute value and sometimes even show the wrong sign (in the case of ${}^\lambda H_{\mu\nu}^{(2)} - {}^\lambda H_{\mu\nu}$). By contrast, the corrections $\Delta_{\mu\nu}^{(\infty)}$ [see eq. (25)] generally have the correct sign and a reasonable order of magnitude, and the agreement with $\Delta^\lambda H_{\mu\nu}$ is further improved by adding the remainders $R_{\mu\nu}^{(s)}$ [see eq. (29)], which provide a significant contribution and should therefore not be neglected. For example, in the case of the diagonal elements involving hydrogen s orbitals ($\mu = s_H$) $\Delta_{\mu\mu}^{(\infty)}$ is typically between 6–9 eV, $R_{\mu\mu}^{(s)}$ between 4–7 eV, $\Delta_{\mu\mu}^{(\infty)} + R_{\mu\mu}^{(s)}$ between 11–14 eV, and $\Delta^\lambda H_{\mu\mu}$ between 13–15 eV. Likewise, in the case of the carbon s orbitals ($\mu = s_C$) $\Delta_{\mu\mu}^{(\infty)}$ normally lies between 15–21 eV, $R_{\mu\mu}^{(s)}$ between -3 and -10 eV, $\Delta_{\mu\mu}^{(\infty)} + R_{\mu\mu}^{(s)}$ between 8–13 eV, and $\Delta^\lambda H_{\mu\mu}$ between 7–12 eV. In these and other examples, the deviations $\Delta^\lambda H_{\mu\nu} - (\Delta_{\mu\nu}^{(\infty)} + R_{\mu\nu}^{(s)})$ are usually around 2 eV and the matrix elements $\Delta^\lambda H_{\mu\nu}$ and the corresponding sums ($\Delta_{\mu\nu}^{(\infty)} + R_{\mu\nu}^{(s)}$) often show similar qualitative trends and relative magnitudes. The diagonal matrix elements involving $p\pi$ orbitals exhibit special behavior in that the corresponding $\Delta^\lambda H_{\mu\mu}$ values are small (below 1 eV) and reproduced by ($\Delta_{\mu\mu}^{(\infty)} + R_{\mu\mu}^{(s)}$) either exactly (HCCH, $H_2C=CH_2$) or almost exactly (HCN, H_2CO, LiF), as expected from eqs. (8)–(10). In summary, the numerical results[23] indicate that ($\Delta_{\mu\nu}^{(\infty)} + R_{\mu\nu}^{(s)}$) provides a useful approximation to the exact one-center orthogonalization corrections $\Delta^\lambda H_{\mu\nu}$ if all integrals are evaluated analytically (*ab initio*).

Most semiempirical methods do not make explicit use of the two-center one-electron matrix elements ${}^\lambda H_{\mu\lambda}$ [see eq. (4)] that enter the evaluation of $\Delta_{\mu\nu}^{(\infty)}$ [see eq. (25)]. Therefore, the question arises whether there are other theoretical matrix elements that are easily available and can replace ${}^\lambda H_{\mu\lambda}$ in the calculation of the orthogonalization corrections. An obvious candidate is the Mulliken function $M_{\mu\lambda}$ [see eq. (7)], which may be regarded as the simplest reasonable approximation to ${}^\lambda H_{\mu\lambda}$ [see eq. (6)] or, more precisely, to ${}^\lambda H_{\mu\lambda}^{(1)}$ while neglecting the contributions of three-center character. In diatomic molecules, $M_{\mu\lambda}$ closely approximates ${}^\lambda H_{\mu\lambda}$ at large internuclear distances, is appreciably smaller around the equilibrium distance (often by a factor of about 2), and is much smaller at shorter distances. We evaluated the Mulliken orthogonalization corrections $\Delta^{(M)}$ from eq. (27) with $H_{\mu\lambda}^{(s)} = M_{\mu\lambda}$ and compared the numerical results with those for $\Delta^{(\infty)}$ (see above). As expected,

the corrections $\Delta_{\mu\nu}^{(M)}$ are considerably smaller than $\Delta_{\mu\nu}^{(\infty)}$ for all test molecules considered and the deviations from $\Delta^\lambda H_{\mu\nu}$ are significantly higher for ($\Delta_{\mu\nu}^{(M)} + R_{\mu\nu}^{(s)}$) than for ($\Delta_{\mu\nu}^{(\infty)} + R_{\mu\nu}^{(s)}$). This latter point is illustrated in Figure 1 for the atom pair C—H, which emphasizes the importance of high-order terms at short distances. Hence, a purely theoretical evaluation of the orthogonalization corrections with the use of $M_{\mu\lambda}$ cannot be recommended.

On the basis of the preceding discussion, we propose that the semiempirical orthogonalization corrections to the one-center core Hamiltonian matrix elements are determined from eq. (26), with the following modifications for $\Delta^{(s)}$ and $R^{(s)}$: The computation of $\Delta_{\mu\nu}^{(s)}$ [see eq. (28)] employs the semiempirical resonance integral $\beta_{\mu\lambda}$ (see below) instead of the theoretical integrals such as ${}^\lambda H_{\mu\lambda}$ or $M_{\mu\lambda}$. This has the advantage of a balanced treatment of attractive and repulsive interactions: On the one hand, the resonance integrals represent the two-center core Hamiltonian matrix elements, which are mainly responsible for the bonding; on the other, they enter the core Hamiltonian matrix elements in an antibonding manner because the orthogonalization corrections are normally repulsive. Hence, in this formulation the role of the resonance integrals $\beta_{\mu\lambda}$ in semiempirical methods is the same as that of the matrix elements ${}^\lambda H_{\mu\lambda}$ in *ab initio* methods (see eqs. (8)–(10), (24) and (25)]. The parameterization of $\beta_{\mu\lambda}$ (see below) will thus affect both attractive and repulsive interactions, which is expected to be "safer" than a completely independent parameterization of these interactions. It may, however, be too restrictive to insist on a completely fixed relation, and we shall therefore allow for a scaling of the semiempirical orthogonalization corrections [see eqs. (27) and (28)] by a factor of the order 1, which will be determined by the parameterization. Turning to the remainder $R^{(s)}$, eq. (29) contains differences $H_{\mu\mu} + H_{\nu\nu} - 2H_{\lambda\lambda}$) of one-electron energies (Φ_μ and Φ_ν at atom A, Φ_λ at atom B) that are related to the polarity of
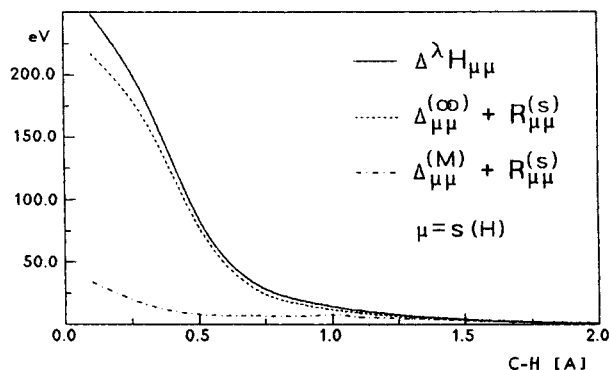

Figure 1. Orthogonalization corrections in C—H for the diagonal matrix element involving the hydrogen $1s$ orbital (ECP-3G basis, $\zeta^C = 1.0$, $\zeta^H = 1.24$). See text for definition of symbols.

$A - B$. The *ab initio* evaluation of $(H_{\mu\mu} + H_{\nu\nu} - 2H_{\lambda\lambda})$ includes contributions from all atoms of the molecule (via the nuclear attraction integrals). Because the major part of the differences $(H_{\mu\mu} + H_{\nu\nu} - 2H_{\lambda\lambda})$ is expected to originate from atoms A and B, it seems justified to include only this diatomic part $(H_{\mu\mu}^{AB} + H_{\nu\nu}^{AB} - 2H_{\lambda\lambda}^{AB})$ in a semiempirical evaluation of eq. (29). This will introduce some error, of course, as well as the neglect of higher-order contributions to $\mathbf{R}^{(s)}$ in eqs. (21)–(23), so it would seem advisable to allow for a slightly scaling of $\mathbf{R}^{(s)}$ by a factor of the order 1, which will be optimized in the parameterization. Based upon these considerations, the semiempirical orthogonalization corrections to the one-center core Hamiltonian matrix elements take the following final form:

$$^A H_{\mu\nu}^{(s)} = H_{\mu\nu} + \sum_B V_{\mu\nu,B}^{ORT(s)} \qquad (32)$$

$$V_{\mu\nu,B}^{ORT(s)} = \gamma_1^A \Delta_{\mu\nu,B}^{(s)} + \gamma_2^A R_{\mu\nu,B}^{(s)} \qquad (33)$$

$$\Delta_{\mu\nu,B}^{(s)} = -1/2 \sum_{\lambda(B)} (S_{\mu\lambda}\beta_{\lambda\nu} + \beta_{\mu\lambda}S_{\lambda\nu}) \qquad (34)$$

$$R_{\mu\nu,B}^{(s)} = 1/8 \sum_{\lambda(B)} S_{\mu\lambda}S_{\lambda\nu}(H_{\mu\mu}^{AB} + H_{\nu\nu}^{AB} - 2H_{\lambda\lambda}^{AB}) \qquad (35)$$

with Φ_μ and Φ_ν at atom A, Φ_λ at atom B, and adjustable atomic parameters γ_1^A and γ_2^A [see eqs. (36) and (46) below for further definitions].

At this point, we turn to the determination of $\beta_{\mu\lambda}$. It is clear from the previous discussion that the semiempirical resonance integrals $\beta_{\mu\lambda}$ should mimic the theoretical two-center one-electron matrix elements $^A H_{\mu\lambda}$ in the orthogonal $^A\Phi$-basis as closely as possible if one wants to maximize the correspondence between semiempirical and *ab initio* methods. Figure 2 shows plots of the analytic integrals $H_{\mu\lambda}$, $^A H_{\mu\lambda}$, $M_{\mu\lambda}$, and $S_{\mu\lambda}$ for a C—C atom pair at distances from 0–3 Å, and Figure 3 compares some of these integrals at distances between 1.0 and 3.5 Å. Figure 2 illustrates the well-known fact that the orthogonalization transformation $(\mathbf{H} \rightarrow {}^A\mathbf{H})$ introduces drastic changes in the two-center core Hamiltonian matrix elements:

Compared with $H_{\mu\lambda}$, the $^A H_{\mu\lambda}$ integrals are much smaller in absolute value at all relevant distances, they fall off faster with increasing distance, the maxima for the $s\sigma$ and $\sigma\sigma$ integrals occur at smaller distances, a new maximum appears for the ss integral, and the relative magnitude of the different integrals changes. These orthogonalization effects are so pronounced that it would be hopeless to absorb them into semiempirical corrections to the integrals $H_{\mu\lambda}$ in the nonorthogonal basis.

This has been recognized in current semiempirical methods,[1–6] of course, where the resonance integrals $\beta_{\mu\lambda}$ are taken to be proportional to the overlap in-
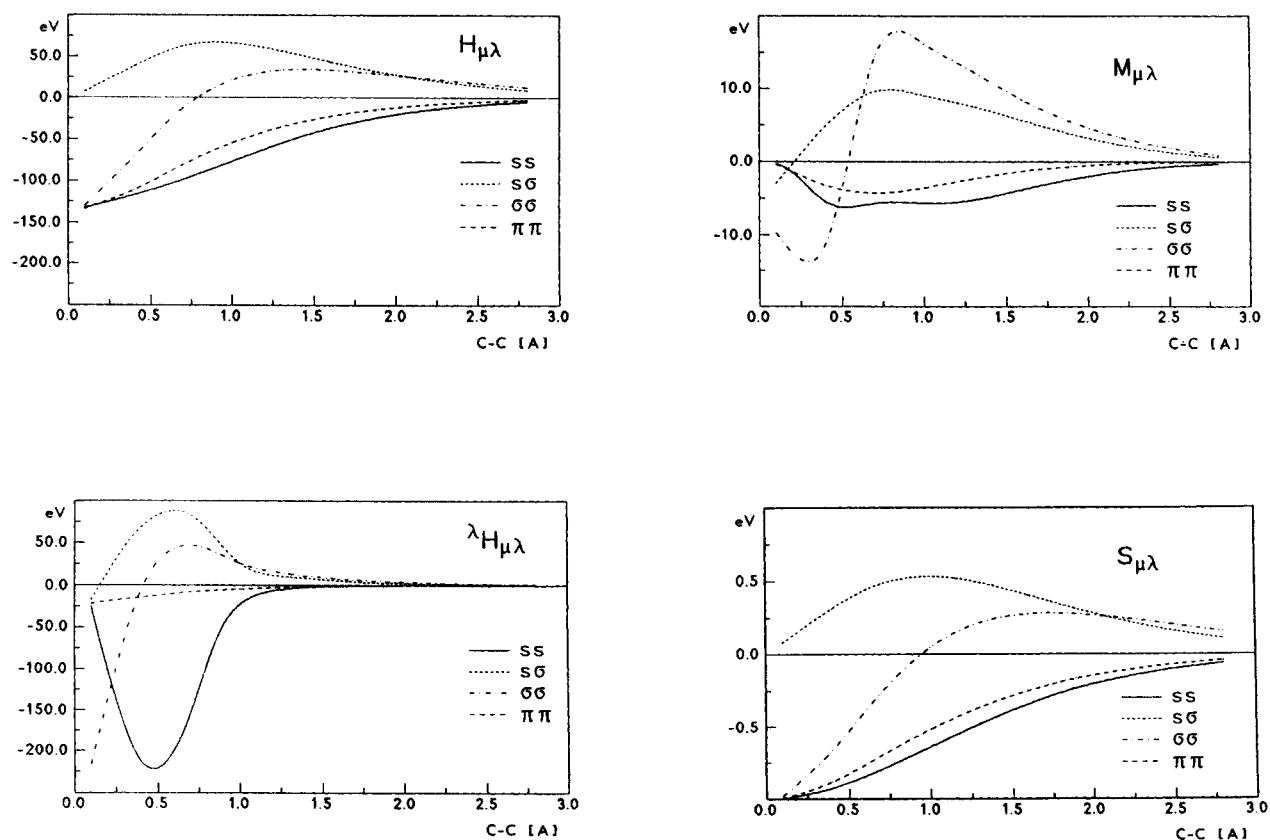

Figure 2. Two-center one-electron matrix elements for C—C at distances between 0 and 3 Å (ECP-3G basis, $\zeta^C = 1.0$). See text for definition of symbols.
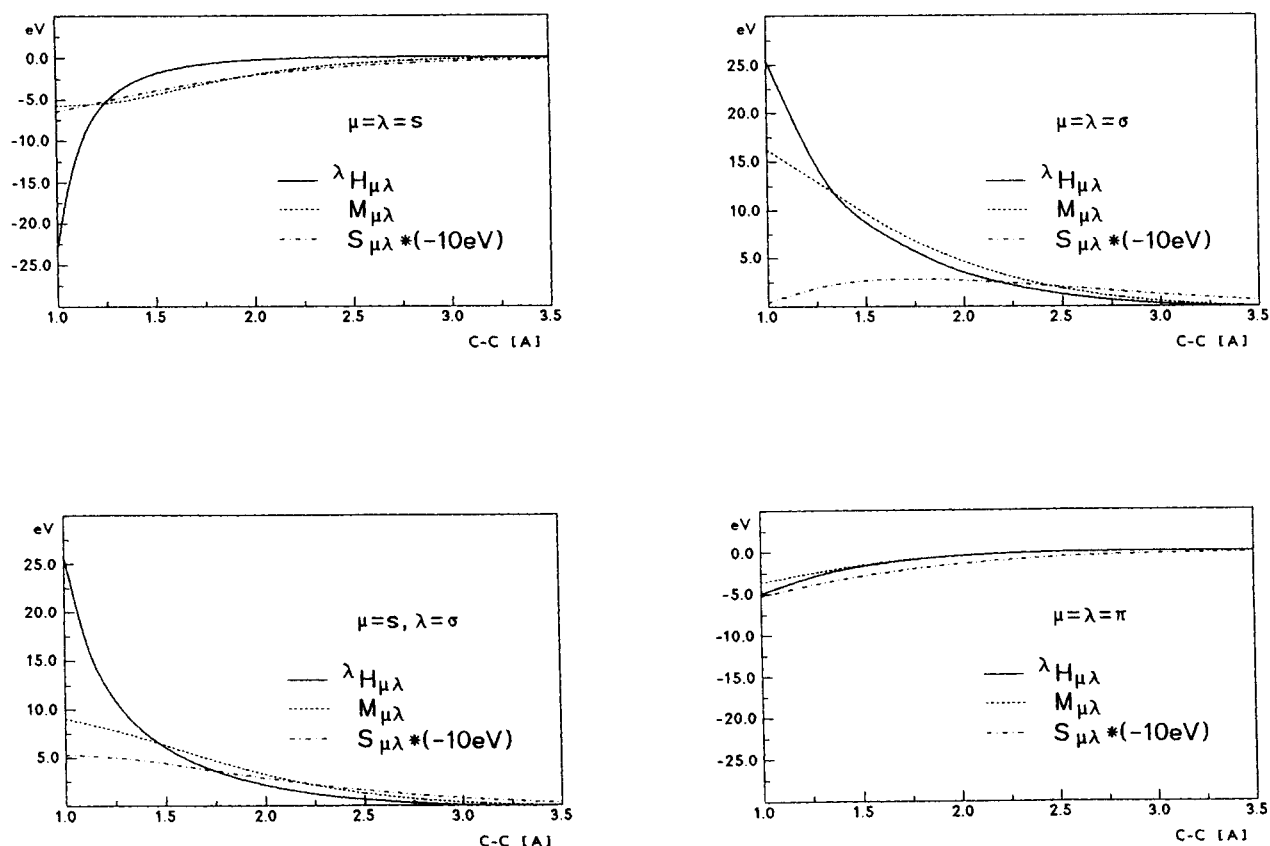
Figure 3. Two-center one-electron matrix elements for C—C at distances between 1.0 and 3.5 Å (ECP-3G basis, $\zeta^C = 1.0$). See text for definition of symbols.

tegral $S_{\mu\lambda}$. The proportionality constants are determined by the parameterization and turn out to be such that the resulting $\beta_{\mu\lambda}$ values are much smaller than $H_{\mu\lambda}$ and of the same order of magnitude as $^\lambda H_{\mu\lambda}$, as expected. Inspection of Figure 2 indicates, however, that the overlap integrals $S_{\mu\lambda}$ show a distance dependence which resembles more that of $H_{\mu\lambda}$ than that of $^\lambda H_{\mu\lambda}$. In particular, the falloff of $S_{\mu\lambda}$ with increasing distance is generally not steep enough when compared with $^\lambda H_{\mu\lambda}$. To some extent, the parameterization of current methods[1-6] has apparently attempted to overcome this problem by producing orbital exponents that are higher than expected and therefore yield steeper overlaps than expected, but naturally there are limits on what the parameterization can achieve due to the imposed functional form $\beta_{\mu\lambda} \sim S_{\mu\lambda}$. From this point of view, it appears that the established MNDO-type methods[1-6] might not describe the resonance integrals in the optimum manner when choosing $\beta_{\mu\lambda} \sim S_{\mu\lambda}$. This choice has been criticized before,[15,16] and different approximations have been proposed and implemented at the INDO level.[21,34]

In general, we have not found a clearcut theoretical preference for a particular functional form to represent the semiempirical resonance integral. For the reasons given above, they should "somehow"

resemble the theoretical integrals $^\lambda H_{\mu\lambda}$ with respect to their absolute magnitude and distance dependence and should reproduce the relative magnitudes of different integrals $^\lambda H_{\mu\lambda}$ for a given atom pair. We illustrated these arguments in the case of the C—C atom pair (see Figs. 2 and 3) and checked several other atom pairs in a similar manner without finding a compelling argument in favor of a particular representation. Moreover, one has to worry about multicenter effects on $^\lambda H_{\mu\lambda}$ in polyatomic molecules and also about the possible influence of electron correlation on the resonance integrals. In view of this situation, we decided to define a number of reasonable parametric functions for the resonance integrals (see below), run a complete parameterization for each of these functions (at least for hydrocarbons, see the fourth section), and select the "best" parametric function empirically (simply based upon the overall accuracy of the final results). As documented elsewhere in more detail,[23] one type of parametric function contained a theoretical integral (i.e., $S_{\mu\lambda}$, $M_{\mu\lambda}$, or $^\lambda H_{\mu\lambda}$ in a local diatomic system) multiplied by a factor to adjust the magnitude of the integral and possibly also by a function to modify its steepness, whereas the second type of parametric function was purely empirical. The best results were indeed obtained with the second alternative, i.e., with

an empirical resonance integral that assumes the following form in a local diatomic coordinate system:

$$\beta_{\mu\lambda}^{loc} = (-1)^{l_\lambda + m_\lambda}[(\beta_\mu^A + \beta_\lambda^B)/2](R_{AB}/au)^{1/2}$$
$$\exp[-(\alpha_\mu^A + \alpha_\lambda^B)R_{AB}^2] \quad (36)$$

The resonance integrals $\beta_{\mu\lambda}$ in the molecular coordinate system are obtained from the $\beta_{\mu\lambda}^{loc}$ values by the usual rotational transformation. In eq. (36), the phase factor $(-1)^{l_\lambda + m_\lambda}$ ensures the correct sign of $\beta_{\mu\lambda}^{loc}$ under our standard conventions.[27] The factor in square brackets contains the parameters β_μ^A and β_λ^B, which adjust the magnitude of $\beta_{\mu\lambda}^{loc}$ in the parameterization, in complete analogy to the established methods.[1-3] The distance dependence in eq. (36) is empirical: The Gaussian exponential function with the adjustable parameters α_μ^A and α_λ^B provides a fast falloff with increasing distance R_{AB} whereas the factor $R_{AB}^{1/2}$ produces extrema of $\beta_{\mu\lambda}^{loc}$ at diatomic distances below 1 Å that are also found for $^\Lambda H_{\mu\lambda}$ in a similar region (see Fig. 2). Other distance dependences for $\beta_{\mu\lambda}^{loc}$ were tested (e.g., with a simple exponential rather than a Gaussian function) and discarded because they led to less accurate results.[23]

It should be emphasized that the empirical resonance integral $\beta_{\mu\lambda}$ is considered to contain any orthogonalization corrections so that it corresponds to the theoretical integral $^\Lambda H_{\mu\lambda}$ conceptually. Hence, in our approach the orthogonalization corrections to the core Hamiltonian matrix are handled differently for the one- and two-center matrix elements. They are treated explicitly in the one-center case [see eqs. (32)–(35)] and implicitly in the two-center case [see eq. (36)].

Many semiempirical methods that do not explicitly include the repulsive orthogonalization corrections to the one-center core Hamiltonian matrix elements also neglect the contributions from the attractive penetration integrals[35,36] to these matrix elements (i.e., the part of the core-electron attractions that exceeds the corresponding electron–electron repulsions in absolute magnitude). This type of error compensation is exploited, e.g., in CNDO/2,[36] MNDO,[1] AM1,[2] and PM3,[3] and it works reasonably well because the two terms involved are roughly of comparable magnitude and show a similar falloff with increasing distance.[5,19] Because the repulsive terms are usually somewhat larger than the attractive terms, MNDO,[1] AM1,[2] and PM3[3] add an empirical exponential term to the core repulsion function that is parameterized to adjust the balance between attractive and repulsive terms in more detail.

In our present formalism, the repulsive orthogonalization corrections to $H_{\mu\nu}$ are evaluated explicitly according to eqs. (32)–(35). Hence, there is no justification for neglecting the penetration integrals and introducing additional exponential terms in the core repulsion functions. Therefore, we shall calculate the core–electron attractions $(\mu^A \nu^A, B)$ and the core–

core repulsions E_{AB}^{core} without such additional assumptions and approximations but in a manner that is compatible with the calculation of the electron–electron repulsion integrals $(\mu^A \nu^A, \lambda^B \rho^B)$ to ensure a balanced treatment of all two-center Coulomb interactions. For the reason given above, a Klopman–Ohno scaling[29,30] is employed for the two-center two-electron integrals. For the simplest case of the integral $(s^A s^A, s^B s^B)$, a Klopman–Ohno scale factor may be defined as

$$f_{KO} = (s^A s^A, s^B s^B)^{(s)}/(s^A s^A, s^B s^B)^{(a)} \quad (37)$$

where the superscripts s and a refer to a semiempirical and analytic evaluation, respectively. The factor f_{KO} depends upon the internuclear distance. It will always approach 1 for large distances and is normally around 0.7–0.8 in the region of the equilibrium distances (for an MNDO-type semiempirical evaluation[27-30] and an analytic evaluation with a reasonable minimal basis). A balanced semiempirical treatment of all two-center Coulomb interactions can be achieved by the following uniform scaling of the analytic integrals:

$$(\mu^A \nu^A, \lambda^B \sigma^B)^{(s)} = f_{KO}(\mu^A \nu^A, \lambda^B \sigma^B)^{(a)} \quad (38)$$

$$(\mu^A \nu^A, B)^{(s)} = f_{KO}(\mu^A \nu^A, B)^{(a)} \quad (39)$$

$$E_{AB}^{core} = f_{KO} Z_A Z_B e^2 R_{AB}^{-1} \quad (40)$$

Several reasonable alternatives to eqs. (38)–(40) were considered[23] but none led to significantly better results. Therefore, we adopt eqs. (38)–(40) in the present study as the conceptually simplest representation of the two-center Coulomb interactions.

The core electrons are treated in MNDO-type methods[1-3] as point charges located at the respective nucleus, i.e., each core electron is assumed to reduce the effective nuclear charge by 1. Extensive ab initio work has shown, however, that in addition to this zero-order effect the core electrons produce an effective repulsive potential acting on the valence electrons that is mainly due to exchange repulsion and orthogonality constraints (see ref. 37 for a review). In view of the fact that we include orthogonalization corrections within the valence shell [see eqs. (32)–(35)], it would seem logical to incorporate similar interactions between the core and valence electrons into our model, too. This can be done by using one of the ab initio effective core potentials (ECPs)[38,39] that have proven to be realistic in ab initio studies. When adding these ECPs to the one-center core Hamiltonian matrix elements, their analytic values $V_{\mu\nu,B}^{ECP(a)}$ should be scaled in the same manner as the two-center Coulomb interactions to keep a balance between all contributions. Hence, we represent the semiempirical ECP contributions by

$$V_{\mu\nu,B}^{ECP(s)} = f_{KO} V_{\mu\nu,B}^{ECP(a)} \quad (41)$$

Other choices seem possible but were not yet tested. Semiempirical pseudopotentials of a different form[40] are used in SINDO1.[21] The ECP contributions lead to an additional steep short-range repulsion between atoms with core electrons that is expected to be especially important for second-row and heavier atoms with a large core but less so for the first-row atoms considered presently.

In summary, based upon the discussion in this section we propose to improve MNDO-type models by explicitly including the following terms into the one-center core Hamiltonian matrix elements:

1. Orthogonalization corrections.
2. Penetration integrals.
3. Effective core potentials.

The reasoning in favor of these improvements suggests the following additional changes:

4. Introduction of a new parametric function for the resonance integrals;
5. Removal of exponential correction terms from the core repulsion function.

Explicit formulas for all relevant new terms are outlined in eqs. (32)–(41), which have been chosen on the basis of theoretical arguments, comparisons with analytic *ab initio* integrals, and extensive parameterizations.[23]

It should be noted that many of the ideas discussed in this section are not new but build on previous theoretical work.[7–22,31,33] Some of the suggestions above have already been implemented in one or another form, particularly at the INDO level in the SINDO1 method.[21,22] Our present work differs from such previous studies in that it refers to the more refined and more accurate NDDO integral approximation. Moreover, guided by *ab initio* considerations, our theoretical development has led to semiempirical formulas for the two-center interactions [see eqs. (32)–(41)] that differ from previous choices.

IMPLEMENTATION

In the remainder of this article, we describe one particular implementation of our new NDDO SCF approach.[23] The basic equations for the Fock matrix elements are the same as in MNDO[1]:

$$F_{\mu\mu} = U_{\mu\mu} + \sum_B V_{\mu\mu,B}$$
$$+ \sum_{\nu}^{A} P_{\nu\nu}[(\mu\mu, \nu\nu) - 1/2(\mu\nu, \mu\nu)]$$
$$+ \sum_{B} \sum_{\lambda,\sigma}^{B} P_{\lambda\sigma}(\mu\mu, \lambda\sigma) \quad (42)$$

$$F_{\mu\nu} = \sum_B V_{\mu\nu,B} + 1/2 P_{\mu\nu}[3(\mu\nu, \mu\nu) - (\mu\mu, \nu\nu)]$$
$$+ \sum_{B} \sum_{\lambda,\sigma}^{B} P_{\lambda\sigma}(\mu\nu, \lambda\sigma) \quad (43)$$

$$F_{\mu\lambda} = \beta_{\mu\lambda} - 1/2 \sum_{\nu}^{A} \sum_{\sigma}^{B} P_{\nu\sigma}(\mu\nu, \lambda\sigma) \quad (44)$$

Equations (42)–(44) refer to closed-shell molecules and employ the usual notation.[1] Here and in the following, the atomic orbitals (AOs) Φ_μ and Φ_ν are centered at atom A and the AOs Φ_λ and Φ_σ at atom B ($A \neq B$). If necessary, superscripts A or B assign a particular symbol to atom A or B, respectively.

The self-consistent solution of the secular equations[1] provides the molecular orbitals (MOs) ψ_i and the electronic energy E_{el}. The total energy E_{tot} is the sum of the electronic energy E_{el} and the repulsions E_{AB}^{core} between the cores of atom A and B.

$$E_{tot} = E_{el} + \sum_{A<B}\sum E_{AB}^{core} \quad (45)$$

The total energy of a molecule can be converted into its heat of formation ΔH_f in the usual way.[1]

The one-center terms in the Fock matrix are treated in the same manner as in MNDO.[1] The one-center one-electron energies $U_{\mu\mu}$ are adjustable parameters that are optimized in the parameterization. The one-center two-electron integrals $(\mu\mu, \nu\nu)$ and $(\mu\nu, \mu\nu)$ are constants determined from experimental atomic data.[1,24]

The two-center terms in the Fock matrix are evaluated in the usual local coordinate system[27] and then transformed to the molecular coordinate system. Their representation differs from MNDO. As discussed in the previous section, the two-center one-electron resonance integrals $\beta_{\mu\lambda}$ are described by an empirical parametric function in local coordinates [see eq. (36)]. The two-center one-electron terms $V_{\mu\nu,B}$ that enter the one-center part of the Fock matrix [see eqs. (42) and (43)] are sums of the Coulomb contribution $(\mu\nu, B)^{(s)}$, an ECP contribution $V_{\mu\nu,B}^{ECP(s)}$, and an orthogonalization contribution $V_{\mu\nu,B}^{ORT(s)}$, which are defined in eqs. (39), (41), and (32)–(35), respectively. In eq. (35), the diatomic part of the diagonal core Hamiltonian matrix elements is given by

$$H_{\mu\mu}^{AB} = U_{\mu\mu} + (\mu\mu, B)^{(s)} + V_{\mu\mu,B}^{ECP(s)} \quad (46)$$

with analogous formulas for $H_{\nu\nu}^{AB}$ and $H_{\lambda\lambda}^{AB}$. The two-center two-electron integrals $(\mu\nu, \lambda\sigma)$ and the core–core repulsions E_{AB}^{core} are determined from eqs. (38) and (40), respectively.

The calculation of the semiempirical two-center terms in the Fock matrix requires the analytic evaluation of overlap integrals [see eqs. (34) and (35)], two-center two-electron integrals [see eqs. (37) and (38)], two-center core–electron attraction integrals

[see eq. (39)], and ECP integrals[41,42] [see eq. (41)]. In these calculations, we use a minimal basis set of contracted Gaussian functions for all elements and a published effective core potential for the first-row elements.[38] The recommended ECP basis set[38] consists of four primitives with shared s and p exponents (elements Li–Ne) and may thus be designated as ECP-4G in its fully contracted form. To minimize the computational effort in our semiempirical approach, we derived an ECP-3G basis with three Gaussian primitives by a least-squares fit to the published ECP-4G basis[38] following established procedures[43] and employing analytic first and second derivatives in this fit.[23] The resulting ECP-3G basis is listed in Table I. Parameterizations with the ECP-4G and ECP-3G basis show that the quality of the semiempirical results is not affected significantly by changing between these two basis sets. Therefore, we decided to use the ECP-3G basis for Li–Ne (see Table I) along with the standard STO-3G basis for hydrogen[44] in our approach. The integral calculations reported in the previous section were carried out with this basis. Because atomic orbitals may contract upon bond formation,[44] we allow for one adjustable parameter ζ per element that scales the exponents of all Gaussian primitives in the usual manner (multiplication by ζ^2). These scale factors ζ are optimized in the parameterization but are expected to remain close to 1 as in the ab initio case.

The current computational implementation of our approach is fully specified by eqs. (32)–(46) and the additional information given in this section and in Table I. It should be emphasized that there are alternative possible representations for most two-center interactions, within the general framework of our approach. As indicated in the previous section, many such alternatives to eqs. (32)–(40) and (46) have been investigated in extensive parameterization work documented elsewhere.[23] The current implementation has been chosen on the basis of more than 300 parameterization runs with different combinations of alternative options.[23] Therefore, it should be close to the best one possible within the given theoretical framework, even though certain technical

enhancements may still be feasible (see the discussion).

PARAMETERS

In analogy to MNDO,[1] the adjustable parameters were determined by a nonlinear least-squares optimization procedure that minimizes the sum of squares (SSQ) of the weighted errors for a chosen set of properties in the reference molecules[23] (see below). The available optimization program[45] was improved by adding the option to calculate the Jacobi matrix numerically to generate better search directions.[23] Such evaluations of the Jacobi matrix (typically in the first, second, and every tenth of the following iterations) led to a significant speedup of the parameterization[23] and allowed us to avoid the sidesteps applied previously.[1]

The initial parameterizations made use of the same set of reference properties and reference molecules as in MNDO.[1] Later parameterizations employed increasingly larger sets, up to 300 reference properties in the final runs.[23] In this stage, the overall quality of the results was judged not only from the final SSQ value in the parameterization but mainly from survey calculations on a larger number of molecules.[23]

The current implementation of our approach (see the previous section) requires the following parameters for a given element: The scale factor ζ for the Gaussian basis functions, the one-center one-electron energies U_{ss} and U_{pp}, the prefactors γ_1 and γ_2 in the orthogonalization corrections [see eq. (33)], and the parameters α_μ and β_μ for the resonance integrals [see eq. (36)]. In the latter case, we associate different resonance interactions with different parameters and therefore distinguish between α_s, $\alpha_{p\sigma}$, $\alpha_{p\pi}$, β_s, $\beta_{p\sigma}$, and $\beta_{p\pi}$ in the evaluation of $\beta_{\mu\lambda}^{loc}$ [see eq. (36)]. Hence, there are normally 11 adjustable parameters for a first-row element (compared with 5–7 in MNDO, 13–16 in AM1, and 18 in PM3). The current parameterization focuses on the resonance interactions (normally 6 parameters for first-row ele-

Table I. ECP-3G basis for first-row elements.[a]

	Li	Be	B	C	N	O	F	Ne
α_1	0.44227	1.06039	1.72427	2.64486	3.68849	4.78449	6.01783	7.47831
α_2	0.07847	0.20785	0.35009	0.54215	0.77534	0.99860	1.25315	1.55488
α_3	0.02434	0.05933	0.09394	0.14466	0.20498	0.25687	0.31760	0.39057
c_1^s	−0.18805	−0.18525	−0.19359	−0.19188	−0.19269	−0.19248	−0.18850	−0.18692
c_2^s	0.66552	0.52418	0.61497	0.61628	0.61888	0.66952	0.69800	0.70988
c_3^s	0.47762	0.62320	0.54976	0.54896	0.54926	0.50270	0.47427	0.46248
c_1^p	0.11671	0.15121	0.18292	0.20259	0.22281	0.24158	0.25667	0.26586
c_2^p	0.52628	0.55940	0.54437	0.55830	0.56032	0.55890	0.56013	0.56134
c_3^p	0.52282	0.47765	0.48303	0.45514	0.43859	0.43160	0.42139	0.41439

Exponents α_i (au); contraction coefficients c_i^s and c_i^p for s and p orbitals, respectively.

Table II. Optimized parameters.

	H	C	N	O	F
ζ	1.20949	1.13551	1.16082	1.10190	1.16498
U_{ss}	-12.83852	-50.15945	-71.33505	-93.04159	-121.69518
U_{pp}		-38.76257	-56.58315	-77.59793	-106.37311
α_s	0.09654	0.09325	0.10186	0.10892	0.19375
α_p		0.05399	0.08541	0.09667	0.13035
α_π		0.10477	0.14351	0.15255	0.22034
α_s (X—H)			0.07515	0.07953	
α_p (X—H)			0.11556	0.12909	
β_s	-4.89312	-7.58632	-12.00586	-6.22224	-5.73558
β_p		-4.49894	-9.64950	-9.94029	-16.36168
β_π		-5.91210	-10.16406	-11.29343	-17.22482
β_s (X—H)			-8.08332	-6.45961	
β_p (X—H)			-11.48923	-12.47451	
γ_1	0.54129	0.50384	0.63476	0.68193	1.19939
γ_2	0.84669	0.66944	0.31136	0.47653	0.49484

ζ and α_μ in atomic units, $U_{\mu\mu}$ and β_μ in eV; for notation, see text.

ments) whereas the AM1 and PM3 approaches emphasize a flexible description of the core–core repulsions (7–13 parameters per first-row element).

Table II lists the optimized parameters. In the case of nitrogen and oxygen, a slight improvement of the results (particularly with regard to bond lengths) was obtained when using separate α_μ and β_μ parameters for the X—H resonance interactions (X = N, O). We adopted these additional parameters in view of the fact that there is also a special treatment of the N—H and O—H atom pairs in the MNDO core repulsion function.[1] Hence, Table II contains 15 optimized parameters for N and O, 11 for C and F, and 6 for H. The optimized values of these parameters generally appear to be reasonable.

RESULTS

In this section, we present a survey of results to assess the merits and shortcomings of our new approach. Detailed numerical results for individual molecules are documented and described else-

where.[23] Here, we stress overall comparisons with MNDO, AM1, and PM3, which employ established sets of reference molecules and reference properties from previous evaluations of semiempirical methods.[1,46-50]

Table III lists the mean absolute errors in the calculated heats of formation, bond lengths, bond angles, ionization potentials, and dipole moments for the standard MNDO reference molecules.[1,46] Compared with the previous evaluations,[1,46] the experimental reference data have been updated[23] if more accurate experimental values have become available in recent years. Inspection of Table III shows that our new approach offers slight but consistent improvements over MNDO, AM1, and PM3 for ground-state properties. In particular, for the complete CHNOF set of 176 reference molecules the mean absolute error in the computed heats of formation is reduced to 3.9 kcal/mol (MNDO 7.3 kcal/mol, AM1 5.8 kcal/mol, PM3 4.8 kcal/mol).

Table IV contains similar results for radicals and radical cations.[47] The new approach is again superior to MNDO, AM1, and PM3 in that it leads to lower

Table III. Mean absolute errors for ground-state properties.

	Group[a]	n[b]	This Work	MNDO	AM1	PM3
ΔH_f (kcal/mol)	CHNO	133	3.49	6.26	5.52	4.23
	F	43	5.17	10.51	6.76	6.45
R (Å)	CHNO	228	0.012	0.015	0.017	0.011
	F	124	0.020	0.037	0.027	0.022
Θ (°)	CHNO	92	1.88	2.69	2.01	2.22
	F	68	1.96	3.04	3.11	2.72
IP (eV)	CHNO	51	0.32	0.47	0.36	0.43
	F	40	0.25	0.34	0.54	0.40
μ (D)	CHNO	57	0.25	0.32	0.25	0.27
	F	40	0.27	0.38	0.31	0.29

Heats of formation ΔH_f, bond lengths R, bond angles Θ, first vertical ionization potentials IP (Koopmans' theorem), dipole moments μ.

[a]Group of test molecules, CHNO-containing molecules from ref. 1, F-containing molecules from ref. 46. Five molecules from the original CHNO set for ΔH_f have been disregarded because there are conflicting experimental values in the literature (diacetylene, fulvene, diazomethane, diimine, and diazirene; see ref. 23).

[b]Number of comparisons.

Table IV. Mean absolute errors for properties of radicals and radical cations.

	Group[a]	n^b	This Work	MNDO	AM1	PM3
ΔH_f (kcal/mol)	All	38	6.70	11.08	9.73	9.41
	CH	21	5.53	10.95	8.28	8.16
	CHNO	17	8.15	11.24	11.54	10.96
IP (eV)	All	25	0.43	0.87	0.72	0.83
	CH	17	0.37	0.89	0.71	0.80
	CHNO	8	0.56	0.82	0.75	0.90

Heats of formation ΔH_f (from half-electron SCF calculations), first vertical ionization potentials IP (Koopmans' theorem with the appropriate half-electron corrections).

[a]Test molecules taken from ref. 47.

[b]Number of comparisons.

errors in the calculated heats of formation and ionization potentials (even though these errors are generally somewhat higher than in the case of closed-shell ground states; see Table III).

Tables V and VI list vertical and adiabatic excitation energies, respectively, for a number of electronic transitions (mostly $\pi\pi^*$ and $n\pi^*$) that have previously been studied at the MNDOC and MNDO levels.[49] The excitation energies were obtained from PERTCI[51] calculations using the same computational procedure as before.[49] Our new approach tends to underestimate the vertical excitation energies slightly (see Table V) but much less so than the established semiempirical methods. The mean absolute error for 33 $\pi\pi^*$ and $n\pi^*$ transitions is only 0.28 eV compared with 1.39, 1.20, 1.18, and 0.95 eV in MNDO, AM1, PM3, and MNDOC, respectively.

Similar results are found for the adiabatic excitation energies (see Table VI). The geometries of the excited states are calculated reasonably well,[23] with an accuracy similar to MNDOC.[49] Hence, it is clear from the available comparisons[23] with experimental data[49,52,53] that excited states are described much better by our new approach than by previous MNDO-type methods.[1-3,48,49]

To test the performance for transition states, we studied a set of 24 organic reactions[50] for which high-level correlated ab initio results are available. These reactions include 1,1- and 1,2-eliminations, hydrogen shifts, and other intramolecular rearrangements on the potential surfaces of ethylene, formaldehyde, methanol, ketene, propene, formic acid, and glyoxal.[50] The new approach yields transition structures[23] that are generally close to the corresponding ab initio structures and of similar quality as those from MNDOC.[23] For the calculated activation energies,[23] the mean absolute deviation from the best ab initio reference data[50] is 5.5 kcal/mol (7%) compared with 21.9, 12.1, 14.2, and 8.7 kcal/mol in MNDO, AM1, PM3, and MNDOC, respectively, which indicates a substantial improvement over the established methods.

Table VII contains the activation energies for selected other reactions, i.e., pericyclic and hydrogen

transfer reactions. Two competing pathways have been discussed in the literature for pericyclic reactions: Ab initio calculations[54] normally favor a concerted mechanism via an aromatic transition state, whereas previous semiempirical calculations[55-57] provide arguments for a biradicaloid mechanism via unsymmetrical transition states, particularly with substituted molecules. Our present results for pericyclic reactions are still incomplete because we only studied the concerted mechanisms. The new approach yields genuine transition states for the concerted pathways in all cases studied (see Table VIII), with one negative eigenvalue of the force constant matrix. The calculated activation energies are generally close to the available experimental data[58-63] and to ab initio reference values,[64-68] both with regard to their absolute magnitude and their ordering for related systems. In the case of the Diels–Alder reaction, we investigated the effect of cyano substitution[23]: When, in the reaction with butadiene, ethylene is replaced by acrylonitrile, fumaronitrile, or maleonitrile, the calculated barriers[23] are lowered by 1–2 kcal/mol, which may be compared with a lowering of 2–5 kcal/mol in ab initio SCF calculations and an increase of 1–3 kcal/mol in AM1 and PM3. Upon this cyano substitution, the calculated transition structures[23] for the Diels–Alder reaction are not distorted much compared with the unsubstituted case, in analogy to the ab initio results.[54] For the hydrogen transfer reactions in Table VII, the new approach predicts activation energies that are considerably lower than in MNDO, AM1, or PM3 and closer to available experimental[69] and ab initio[70,71] data. Similar improvements have also been found when applying the new approach to another set of intramolecular hydrogen transfer reactions.[72]

Table VIII lists hydrogen bond energies. Excellent results are obtained for strong hydrogen bonds involving cations, with experimental hydrogen bond energies in the range of 16–23 kcal/mol, which are reproduced by our approach with an accuracy of typically 2 kcal/mol. The results for weak hydrogen bonds between neutral molecules are less satisfactory because the bifurcated form of the water dimer

Table V. Vertical excitation energies (eV).

Molecule	State[a]	Exp.[b]	This Work	Errors		
				New	AM1	PM3
Ethylene	$^3B_{3u}$	4.4	4.23	−0.17	−1.44	−1.44
	$^1B_{3g}$		7.43			
	$^1B_{3u}$	7.65	7.73	0.08	−1.25	−1.37
Acetylene	$^3\Sigma_u^+$	5.2	4.98	−0.22	−1.39	−1.39
	$^3\Delta_u$	6.0	6.15	0.15	−1.15	−0.79
	$^1\Sigma_u^-$		7.04			
	$^1\Delta_u$	7.4	7.28	−0.12	−1.25	−0.42
Propene	$^3A'$		4.00			
	$^1A''$		6.49			
	$^1A'$	7.19	7.11	0.08	−1.21	−1.20
2-Butene	^3B_u	4.2	3.78	−0.42	−1.58	−1.55
	^1B_u	7.08	6.64	−0.44	−1.48	−1.40
Butadiene	^3B_u	3.2	3.19	−0.01	−0.92	−0.84
	^1B_g		6.68			
	^1A_u		6.63			
	^1B_u	5.92	6.12	0.20	−0.73	−0.68
	^1A_g	5.80	6.16	0.36	−1.29	−1.15
	^3A_g	4.95	4.65	−0.30	−1.70	−1.65
Cyclopropene	$^3B_2$	4.16	3.63	−0.53	−1.50	−1.45
	$^1B_2$	7.19	6.04	−1.15	−2.07	−1.87
Benzene	$^1B_{2u}$	4.89	4.56	−0.33	−1.70	−1.66
	$^1B_{1u}$	6.2	5.93	−0.27	−1.54	−1.50
	$^1E_{1u}$	6.95	6.91	−0.04	−1.38	−1.35
	$^3B_{1u}$	3.89	3.79	−0.10	−1.37	−1.35
	$^3E_{1u}$	4.85	4.59	−0.26	−1.58	−1.54
	$^3B_{2u}$	5.69	5.65	−0.04	−1.30	−1.24
Pyridine	$^1B_1$	4.51	4.43	−0.08	−0.55	−0.78
	$^1B_2$	5.00	4.69	−0.31	−1.50	−1.54
	$^1A_1$	6.45	6.03	−0.42	−1.61	−1.65
	$^1B_2$	7.23	6.98	−0.25	−1.52	−1.39
	$^1A_1$	7.23	7.17	−0.08	−1.32	−1.48
Formaldehyde	$^3A_2$	3.50	3.32	−0.18	−0.93	−1.10
	$^1A_2$	3.79	3.53	−0.26	−1.02	−1.30
	$^3A_1$	5.82	6.07	0.25	−0.15	−0.54
Ketene	$^3A_2$		2.60			
	$^1A_2$	3.84	2.65	−1.19	−1.83	−1.81
	$^3A_1$		3.61			
Propynal	$^3A''$	2.99	3.53	0.54	−0.08	−0.20
	$^1A''$	3.56	3.74	0.18	−0.40	−0.66
Glyoxal	^3A_u	2.38	2.26	−0.12	−0.38	−0.17
	^1A_u	2.73	2.56	−0.17	−0.45	−0.48
Mean absolute error (33 comparisons)				0.28	1.20	1.18

See ref. 49 for MNDO and MNDOC results.

[a] $\pi\pi^*$ transitions, except $^1B_1$ in pyridine, $^3A_2$ and $^1A_2$ in formaldehyde, $^3A''$ and $^1A''$ in glyoxal ($n\pi^*$).

[b] Experimental values from ref. 49 except for formaldehyde (ref. 52).

is slightly more stable than the linear form in the current implementation and the dimers of formic acid and acetic acid are not stable enough. It would clearly be desirable to describe such weak hydrogen bonds more accurately, but this may require a specific parameterization[73,74] in view of the fact that the corresponding *ab initio* potential surfaces are rather flat and show complicated features.[75]

We conclude this survey by summarizing some other typical results[23]: Similar as in the established MNDO-type methods,[1–3] the new approach underestimates the stability of large aromatic hydrocarbons,[76] of nonclassic (vs. classic) carbonium ions, and of small anions where the extra charge is localized.[77] The accuracy of the calculated proton af-

finities and deprotonation enthalpies is similar as in AM1.[78] The rotational barriers around C—C single bonds are still underestimated, whereas the relative energies of gauche/anti conformers and of equatorial and axial isomers in compounds with six-membered rings are often well reproduced. Realistic results are obtained for several standard applications[48] including methylene, where the calculated singlet/triplet splitting of 10.7 kcal/mol is close to the experimental value of 9.0 kcal/mol.[79]

DISCUSSION

The survey of the results in the preceding section shows that the current implementation of our new

Table VI. Adiabatic excitation energies (eV).

Molecule	State	This Work	Exp.[a]	Error
C_2H_4	$^1B_1$ N	2.42	2.82	−0.40
	$^3A_2$ T	2.56		
	$^1A_1$ Z	4.53		
	$^1B_2$ V	4.75	4.96	−0.21
C_2H_2	^1A_u Ã	5.08	5.23	−0.15
HCN	$^1A''$ Ã	6.42	6.45	−0.03
	2 $^1A'$	6.52	6.83	−0.31
	3 $^1A'$	7.86	8.03	−0.17
$(CN)_2$	$^3\Sigma_u^+$ ã	4.23	4.13	0.10
	$^3\Delta_u$ b̃	5.01	4.94	0.07
	$^1\Sigma_u^-$ Ã	5.68	5.63	0.05
	$^1\Delta_u$ B̃	5.95	5.99	−0.04
CO_2	$^1B_2$ Ã	4.60	5.70	−1.10
H_2CO	$^3A''$ ã	2.86	3.00	−0.14
	$^1A''$ Ã	3.20	3.35	−0.15
CH_2CO	$^3A''$ ã	1.54	2.39	−0.85
	$^1A''$ Ã	1.83	2.65	−0.82
HC≡C—CHO	$^3A''$ ã	3.21	2.99	0.22
	$^1A''$ Ã	3.41	3.24	0.17
HNO	$^1A''$ Ã	1.78	1.63	0.15
	$^3A''$ ã	1.05	0.85	0.20
Glyoxal	^3A_u ã	2.17	2.38	−0.21
	^1A_u Ã	2.44	2.72	−0.28

See ref. 49 for MNDO and MNDOC results.

[a]Experimental values from ref. 49 except for HCN (ref. 53) and H_2CO (ref. 52).

approach offers slight but consistent improvements over MNDO, AM1, and PM3 for ground-state properties and significant improvements in the treatment of excited states, transition states, and strong hydrogen bonds. Despite this satisfactory overall performance, we do not yet recommend general use of the current implementation for the following two reasons.

First, even though the computational effort for MNDO and for our new NDDO approach must be essentially the same in the limit of large molecules (due to the dominance of matrix operations of order N^3 over integral evaluations of order N^2 for N basis functions), MNDO calculations are still faster by a factor of about 2 for smaller molecules. This is mainly due to the time spent in the analytic evaluation of the two-center two-electron integrals and the ECP integrals in the new approach [see eqs. (38) and (41)]. It would therefore seem worthwhile to check whether simpler semiempirical representations of these integrals can be found to reduce the computational effort without sacrificing accuracy.

Second, despite the large number of results available already,[23] it would seem advisable to carry out additional applications for further checking. Moreover, the parameterization of the new method should be extended to other elements, including second-row and heavier elements. Based upon our experience with the MNDO/d method,[28,80] it is planned to include d orbitals for such elements from the beginning. The current implementation of our approach would then require analytic integral evaluations over d orbitals that are relatively complicated and expensive. This prospect provides additional impetus to look for simple semiempirical representations of these integrals that can be extended to d orbitals. One such scheme for two-center two-electron integrals has been suggested[28] and will be tested in the context of our new approach. If such a scheme is adopted, it should clearly be used for all elements (including H, C, N, O, and F). In this case, a minor reparameterization (for H, C, N, O, and F) will be necessary that will change the numerical results for individual mole-

Table VII. Activation energies (kcal/mol) for selected reactions.

Reaction	Exp.	Ab Initio	This Work	AM1	PM3
Diels–Alder reaction: trans-butadiene + ethylene	27.5[a]	32.0[b]	29.0	23.8	27.0
Electrocyclic reaction: cis-butadiene → cyclobutene	32.9[c]	37.6[d]	40.9	35.3	40.6
Cope rearrangement					
1,5-Hexadiene, chair TS	33.5[e]	28.3[f]	36.2	37.9	41.8
1,5-Hexadiene, boat TS	44.6[g]		47.1	48.6	50.2
2,5-Dicyano-1,5-hexadiene, chair TS		20.1	29.5	30.0	34.4
Claisen rearrangement					
Allyl vinyl ether, chair TS	29.8[h]	24.6[i]	29.3	30.8	33.4
Allyl vinyl ether, boat TS		31.2	35.6	37.4	38.8
1,3-Dipolar cycloaddition					
Ethylene + HCNO		18.2[j]	19.9	22.4	41.4
Acetylene + HCNO		15.3	17.7	16.0	36.9
Acetylene + H_2CNOH		11.9	17.5	17.9	32.2
Ene reaction					
Propene + ethylene	35[k]	31.2[k]	40.1	37.6	33.8
Propene + formaldehyde	26.4	27.5	33.3	40.6	43.3
Hydrogen transfer reaction					
Malonaldehyde, enol	4.0–5.2[l]	4.3[m]	7.0	22.1	25.7
Methanol + formaldehyde		31.2[n]	44.9	50.8	54.8

See ref. 23 for more detail. [a]Ref. 58. [b]Ref. 64. [c]Ref. 59. [d]Ref. 65. [e]Ref. 60. [f]Ref. 66. [g]Ref. 61. [h]Ref. 62. [i]Ref. 67. [j]Ref. 68. [k]Ref. 63. [l]Ref. 69. [m]Ref. 70. [n]Ref. 71.

Table VIII. Hydrogen bond energies (kcal/mol).

	This Work	Exp.	Error			Ref.
			New	AM1	PM3	
$(H_2O)_2$	−4.3	−3.6	−0.7	−1.5	0.1	81
$(NH_3)_2$	−3.6	−4.5	0.9	2.1	3.6	82
$(HCOOH)_2$	−6.7	−14.8	8.1	8.4	6.1	83
$(CH_3COOH)_2$	−6.7	−14.6	7.9	8.2	5.5	84
Phenol-acetone	−4.2	−4.2	0.0	−0.1	0.3	85
Phenol-dimethylether	−3.3	−5.4	2.1	1.9	2.4	85[a]
H_3O^+—OH_2	−35.1	−35.0	−0.1	9.4	8.5	86
H_3O^+—$(OH_2)_2$	−19.1	−20.2	1.1	−0.7	−0.8	86
H_3O^+—$(OH_2)_3$	−14.8	−17.6	2.8	1.4	0.5	87
$CH_3OH_2^+$—OH_2	−29.4	−27.3	−2.1	6.2	6.8	88
$(CH_3)_2OH^+$—OH_2	−25.5	−24.0	−1.5	7.8	5.8	88
$(CH_2)_2OH^+$—$O(CH3)_2$	−25.2	−29.5	4.3	14.5	11.8	88
NH_4^+—OH_2	−18.2	−20.6	2.4	5.3	7.1	88
$CH_3NH_3^+$—OH_2	−16.8	−18.4	1.6	4.0	5.6	88
NH_4^+—NH_3	−23.5	−24.8	1.3	6.1	7.4	88
$CH_3NH_3^+$—NH_3	−21.0	−21.4	0.4	4.6	5.0	88
$N(C_2H_5)_3H^+$—NH_3	−14.3	−16.3	2.0	4.1	5.0	88
$HCNH^+$—OH_2	−27.2	−27.4	0.2	13.2	12.0	89
$HCNH^+$—NCH	−27.0	−26.1	−0.9	12.2	4.2	89
$C_5H_5NH^+$—OH_2	−14.1	−16.1	2.0	4.3	5.1	90
$C_5H_5NH^+$—NH_3	−17.2	−17.3	0.1	3.7	2.6	88
CO_2H^+—OCO	−19.8	−20.1	0.3	7.6	5.9	91
$HCOOH_2^+$—OH_2	−24.7	−24.1	−0.6	7.1	7.0	88
H_2COH^+—OH_2	−31.4	−28.5	−2.9	9.8	9.2	88
H_2O—OH^-	−31.1	−27.0	−4.1	4.8	0.7	92
H_2O—OCH_3^-	−15.3	−23.9	8.6	7.4	4.8	92
H_2O—CN^-	−19.8	−14.6	−5.2	−0.3	−6.4	93
H_2O—$OOCH^-$	−14.9	−16.0	1.1	0.4	0.1	92
CH_3OH—$OOCH^-$	−12.0	−17.6	5.6	5.6	2.4	92
H_2O—CCH^-	−21.4	−16.2	−5.2	−0.8	−6.4	93

See ref. 23 for more detail.
[a]Experimental value for diethylether.

cules slightly without affecting the statistical evaluations much.

From a methodical point of view, however, the current implementation is sufficient to demonstrate that the proposed improvements to the MNDO model (see the second section) lead to an overall improvement in the quality of the numerical results (see the previous section) that supports the validity of the underlying theoretical considerations.

References

1. M.J.S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4899, 4907 (1977).
2. M.J.S. Dewar, E. Zoebisch, E.F. Healy, and J.J.P. Stewart, *J. Am. Chem. Soc.*, **107**, 3902 (1985).
3. J.J.P. Stewart, *J. Comp. Chem.*, **10**, 209, 221 (1989).
4. M.J.S. Dewar, *J. Phys. Chem.*, **89**, 2145 (1985).
5. W. Thiel, *Tetrahedron*, **44**, 7393 (1988).
6. J.J.P. Stewart, In *Reviews in Computational Chemistry*, vol. 1, K.B. Lipkowitz and D.B. Boyd, Eds., VCH Publishers, New York, 1990, pp. 45–81.
7. P.O. Loewdin, *J. Chem. Phys.*, **18**, 365 (1950).

8. P.O. Loewdin, *Adv. Quant. Chem.*, **5**, 185 (1970).
9. K.R. Roby, *Chem. Phys. Lett.* **11**, 6 (1971); *Chem. Phys. Lett.*, **12**, 579 (1972).
10. R.D. Brown and K.R. Roby, *Theor. Chim. Acta*, **16**, 175 (1970).
11. G.S. Chandler and F.E. Grader, *Theor. Chim. Acta*, **54**, 131 (1980).
12. D.B. Cook, P.C. Hollis, and R. McWeeny, *Mol. Phys.*, **13**, 553 (1967).
13. I. Fischer-Hjalmars, *J. Chem. Phys.*, **42**, 1962 (1965).
14. I. Fischer-Hjalmars, *Adv. Quant. Chem.*, **2**, 25 (1965).
15. S. de Bruijn, In *Studies in Physical and Theoretical Chemistry*, vol. 21, R. Carbo, Ed., Elsevier, Amsterdam, 1982, p. 251.
16. S. de Bruijn, *Int. J. Quant. Chem.*, **25**, 367 (1984).
17. J. Spanget-Larsen, *Theor. Chim. Acta*, **55**, 165 (1980).
18. P. Coffey and K. Jug, *J. Am. Chem. Soc.*, **95**, 7575 (1973).
19. P. Coffey, *Int. J. Quant. Chem.*, **8**, 263 (1974).
20. M.J. Filatov, O.V. Gritsenko, and G.M. Zhidomirov, *Theor. Chim. Acta*, **72**, 211 (1987).
21. D.N. Nanda and K. Jug, *Theor. Chim. Acta*, **57**, 95 (1980).
22. K. Jug, R. Iffert, and J. Schulz, *Int. J. Quant. Chem.*, **32**, 265 (1987).
23. M. Kolb, PhD dissertation, Wuppertal, 1991.
24. L. Oleari, L. Di Sipio, and G. De Michelis, *Mol. Phys.*, **10**, 97 (1966).

25. D.L. Yeager, H. Sun, K.F. Freed, and M.F. Herman, *Chem. Phys. Lett.*, **57**, 490 (1978).
26. K. Freed and H. Sun, *Isr. J. Chem.*, **19**, 99 (1980).
27. M.J.S. Dewar and W. Thiel, *Theor. Chim. Acta*, **46**, 89 (1977).
28. W. Thiel and A. Voityuk, *Theor. Chim. Acta*, **81**, 391 (1992).
29. G. Klopman, *J. Am. Chem. Soc.*, **86**, 4550 (1964).
30. K. Ohno, *Theor. Chim. Acta*, **2**, 219 (1964).
31. W. Kutzelnigg, *Einführung in die Theoretische Chemie*, vol. 2, Verlag Chemie, Weinheim, 1978.
32. R.S. Mulliken, *J. Chim. Phys.*, **46**, 497 (1949).
33. M. Scholz and H.J. Köhler, *Quantenchemie III*, Hüthig, Heidelberg, 1981.
34. M.C. Böhm and R. Gleiter, *Theor. Chim. Acta*, **59**, 127 (1981).
35. M. Goeppert-Meyer and A.L. Sklar, *J. Chem. Phys.*, **6**, 645 (1938).
36. J.A. Pople and G.A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).
37. M. Krauss and W.J. Stevens, *Annu. Rev. Phys. Chem.*, **35**, 357 (1984).
38. W.J. Stevens, H. Basch, and M. Krauss, *J. Chem. Phys.*, **81**, 6026 (1984).
39. W.R. Wadt and P.J. Hay, *J. Chem. Phys.*, **82**, 284 (1985).
40. M.C. Zerner, *Mol. Phys.*, **23**, 963 (1972).
41. L.R. Kahn, P. Baybutt, and D.G. Truhlar, *J. Chem. Phys.*, **65**, 3826 (1976).
42. J. Breidung, W. Thiel, and A. Komornicki, *Chem. Phys. Lett.*, **153**, 76 (1988).
43. R.F. Stewart, *J. Chem. Phys.*, **50**, 2485 (1969).
44. W.J. Hehre, R.F. Stewart, and J.A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
45. P.K. Weiner, PhD dissertation, University of Texas, Austin, TX, 1975.
46. M.J.S. Dewar and H.S. Rzepa, *J. Am. Chem. Soc.*, **100**, 58 (1978).
47. D. Higgins, C. Thomson, and W. Thiel, *J. Comp. Chem.*, **9**, 702 (1988).
48. W. Thiel, *J. Am. Chem. Soc.*, **103**, 1413, 1420 (1981).
49. A. Schweig and W. Thiel, *J. Am. Chem. Soc.*, **103**, 1425 (1981).
50. S. Schröder and W. Thiel, *J. Am. Chem. Soc.*, **107**, 4422 (1985); *J. Am. Chem. Soc.*, **108**, 7985 (1986).
51. H.L. Hase, G. Lauer, K.-W. Schulte, and A. Schweig, *Theor. Chim. Acta*, **48**, 47 (1978).
52. K.N. Walzl, C.F. Koerting, and A. Kuppermann, *J. Chem. Phys.*, **87**, 3796 (1987).
53. R. Rianda, R. Frueholz, and A. Kuppermann, *J. Chem. Phys.*, **80**, 4035 (1984).
54. K.N. Houk, Y. Li, and J.D. Evansek, *Angew. Chem.* **10**, 711 (1992), and literature cited therein.
55. M.J.S. Dewar, *J. Am. Chem. Soc.*, **106**, 209 (1984).
56. M.J.S. Dewar, S. Olivella, and J.J.P. Stewart, *J. Am. Chem. Soc.*, **108**, 5771 (1986).
57. M.J.S. Dewar and C. Jie, *J. Am. Chem. Soc.*, **109**, 5893 (1987).
58. D. Rowley and H. Steiner, *Discuss. Faraday Soc.*, **10**, 198 (1951).
59. R.W. Carr and W.D. Walters, *J. Phys. Chem.*, **69**, 1073 (1965).
60. W.v.E. Doering, V.G. Toscano, and G.H. Beasley, *Tetrahedron*, **27**, 5299 (1971).
61. M.J. Goldstein and M.S. Benzon, *J. Am. Chem. Soc.*, **94**, 7147 (1972).
62. F.W. Schuler and G.W. Murphy, *J. Am. Chem. Soc.*, **72**, 3155 (1950).
63. R.J. Loncharich and K.N. Houk, *J. Am. Chem. Soc.*, **109**, 6947 (1987).
64. F. Bernardi, A. Bottoni, M.J. Field, M. Guest, I.H. Hillier, M.A. Robb, and A. Venturine, *J. Am. Chem. Soc.*, **110**, 3050 (1988).
65. D.C. Spellmeyer and K.N. Houk, *J. Am. Chem. Soc.*, **110**, 3412 (1988).
66. M.J. Goldstein and M.S. Benzon, *J. Am. Chem. Soc.*, **94**, 7147 (1972).
67. R.L. Vance, N.G. Rondan, K.N. Houk, F. Jensen, W.T. Borden, A. Komornicki, and E. Wimmer, *J. Am. Chem. Soc.*, **110**, 2314 (1988).
68. J.J.W. McDouall, M.A. Robb, U. Niazi, F. Bernardi, and H.B. Schlegel, *J. Am. Chem. Soc.*, **109**, 4642 (1987).
69. S.L. Baughcum, Z. Smith, E.D. Wilson, and R.W. Duerst, *J. Am. Chem. Soc.*, **106**, 2260 (1984).
70. M.J. Frisch, A.C. Scheiner, H.F. Schaefer, and J.S. Binkley, *J. Chem. Phys.*, **82**, 4194 (1985).
71. M. McKee, P.B. Shevlin, and H.S. Rzepa, *J. Am. Chem. Soc.*, **108**, 5793 (1986).
72. M.A. Rios and J. Rodriguez, *J. Comp. Chem.*, **13**, 860 (1992).
73. A.A. Voityuk and A.A. Bliznyuk, *J. Mol. Struct.* (*THEOCHEM*), **164**, 343 (1988).
74. A. Goldblum, *J. Comp. Chem.*, **8**, 835 (1987).
75. S. Scheiner, In *Reviews in Computational Chemistry*, vol. 1, K.B. Lipkowitz and D.B. Boyd, Eds., VCH Publishers, New York, 1991, pp. 165–218.
76. P. Scano and C. Thomson, *J. Comp. Chem.*, **12**, 172 (1991).
77. M.J.S. Dewar and H.S. Rzepa, *J. Am. Chem. Soc.*, **100**, 784 (1978).
78. M.J.S. Dewar and K.M. Dieter, *J. Am. Chem. Soc.*, **108**, 8075 (1986).
79. A.R.W. McKellar, P.R. Bunker, T.J. Sears, K.M. Evenson, R.J. Saykally, and S.R. Langhoff, *J. Chem. Phys.*, **79**, 5251 (1983).
80. W. Thiel and A. Voityuk, *Int. J. Quant. Chem.*, **44**, 807 (1992).
81. L.A. Curtiss, D.J. Frurip, and M. Blander, *J. Chem. Phys.*, **71**, 2703 (1979).
82. K.D. Cook and J.W. Taylor, *Int. J. Mass Spectrosc. Ion. Phys.*, **30**, 345 (1979).
83. H.J. Bernstein and A.D.H. Clague, *Spectrochim. Acta*, **25**, 593 (1969).
84. D.J. Frurip, L.A. Curtiss, and M. Blander, *J. Am. Chem. Soc.*, **102**, 2610 (1980).
85. T. Zeegers-Huiskens, *J. Mol. Struct.* (*THEOCHEM*), **135**, 93 (1986).
86. K. Hiraoka, H. Takimoto, and S. Yamabe, *J. Phys. Chem.*, **90**, 5910 (1986).
87. M. Meot-Ner and C.V. Speller, *J. Chem. Phys.*, **90**, 6616 (1986).
88. M. Meot-Ner, *J. Am. Chem. Soc.*, **106**, 1257, 1265 (1984).
89. M. Meot-Ner and C.V. Speller, *J. Phys. Chem.*, **89**, 5217 (1985).
90. M. Meot-Ner and L.W. Sieck, *J. Am. Chem. Soc.*, **105**, 2956 (1983).
91. W.R. Davidson, J. Summer, and P. Kebarle, *J. Am. Chem. Soc.*, **101**, 1675 (1979).
92. M. Meot-Ner and L.W. Sieck, *J. Am. Chem. Soc.*, **108**, 7525 (1986).
93. M. Meot-Ner, *J. Am. Chem. Soc.*, **110**, 3858 (1988).