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Fast NDDO Method for Molecular Structure Calculations Based on Strictly Localized Geminals

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The problem of constructing fast computational schemes has been attacked by using the antisymmetrized product of strictly localized geminals (APSLG) form of the trial wave function instead of the Slater determinant. The procedure is implemented on the semiempirical neglect of diatomic differential overlap (NDDO) level with three well-known parametrizations—modified neglect of diatomic overlap (MNDO), first-Austin method (AM1) and third-parametric method (PM3). Heats of formation and geometry structures calculated are compared for self-consistent field (SCF) and APSLG approaches. Specific APSLG electronic structure parameters—bond characteristics and hybridization matrices—obtained on the ground of variational principle are proven to correspond to chemical intuition. The advantages and limitations of the scheme proposed are discussed.

1. Introduction

Almost 40 years ago, the series of seminal papers by R. Hoffmann[1−3] has launched the enterprise of all valence semiempirical calculations of organic molecules using the single-determinant approximation for the many-electron trial wave function. The progress of this enterprise in the fields of semiempirical and ab initio quantum chemistry was enormous, and success in calculation of small molecules achieved by modern ab initio methods is impressive. At the same time, a vast number of real molecular systems of chemists' interest remain practically unaccessible by quantum chemistry because of huge computational costs. The reason for this is an unacceptable growth of computational resources required by ab initio techniques with the size growth of the system ($N^4 \div N^7$, where N is the dimension of the one-electron basis involved in the calculation). In the case of semiempirical self-consistent field (SCF) methods, the computational resources also grow as N^3 because of matrix diagonalizations involved in the procedure. Therefore, even the application of semiempirical methods to construct potential energy surfaces (PESs) for large systems (especially those of biological significance) may well become problematic.

Two principal types of solutions to the above problems are proposed in the literature. The first one is to construct the methods with a weaker dependence of the required computational resources on the system size. The construction of such schemes is based on the localization of electronic degree of freedom, which exploits the "principle of nearsightedness"[4] or the exponential decay of the one-electron density matrix elements in real (coordinate) space.[5] It was shown that for large molecules calculation time should increase as slowly as $N^{1.3}$.[6] Different strategies to achieve the optimal scaling properties are proposed in the literature. In the "divide-and-conquer" methods,[7−10] the system is divided on disjoint parts and local Hamiltonians are given by projection of the Hamiltonian on subsystems and the local density matrix is usually obtained by direct diagonalization of the local Hamiltonians. The Fermi operator expansion methods[11,12] replace the density operator by the Fermi operator at a finite temperature. A truncated Tchebycheff polynomial is used to represent the Fermi operator in a numerically stable way. Close to this scheme is the truncated-moment approach.[13] The energy renormalization group method allows one to effectively calculate extended systems with small gaps by relation of the density matrix to a "telescopic" sum of terms.[14] The Fermi operator expansion method is based on the use of orthogonal basis sets. It was shown that the condition of orthogonality is environment-dependent[15] and the use of nonorthogonal basis sets can be important for construction of effective molecular dynamics schemes. The $O(N)$ nonorthogonal tight-binding molecular dynamics scheme[16] solves this problem. It is based on the identification of the density matrix with the general Green's function in real space. Recursion method[17] based on estimation of diagonal elements of Green's function using Lanczos transformation can be used as an effective instrument for calculation of the local density of states. There are also a number of approaches[4,18−21] exploiting the variational principle in different formulations for obtaining an $O(N)$ scalability. They can be based, for example, on minimizing the grand canonical potential instead of energy.[22,23] An important possibility to make the calculations faster is provided by using localized orbitals[19,20,24,25] to avoid diagonalizations scaling as $O(N^3)$. Direct determination of localized Hartree−Fock orbitals can be a ground for construction of these schemes.[26] It should be mentioned that the methods based on the localized orbitals allow a direct way to take the electron correlation into account. For example, the MP2 scheme with linear scaling was proposed in ref 27. Acceleration of computation can be also achieved by pseudodiagonalization[28] or by special tricks with wave function.[29,30] The methods based on the density matrix renormalization group[31,32] seem quite promising for quantum chemistry because the results obtained using these methods can compete in quality with the most elaborated methods of conventional quantum chemistry.[33] However, most of the linear-scaling methods are oriented on the tight-binding model and within the total SCF approach special linear-scaling Hamiltonian-buildup techniques are necessary.[34] The methods with approximately

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linear N-scalability were applied to very large systems such as carbon nanotubes,[35] silicon defects,[36] or DNA.[37] It should be also mentioned that there are excellent reviews of the growing field of construction and application of $O(N)$ scaling techniques.[38,39]

The second type of solution is based on construction of so-called hybrid quantum mechanical/molecular mechanical (QM/MM) schemes in which different parts of the system are treated with different levels of accuracy and, therefore, with different computational costs. The motivation of these methods is that the chemical transformation usually occurs only in a small region (reactive center), while the environment only slightly modifies the PES. After the pioneering work by Warshell and Levitt,[40] hybrid techniques became very popular.[41−45] At the same time, the important question about junction between different subsystems is solved in these methods in an ad hoc manner and not by means of sequential separation of variables.

Recently, we proposed a special procedure of deriving the junction between subsystems described by quantum mechanical and molecular mechanical methods.[46] It is based on the trial wave function having a form of the antisymmetrized product of strictly localized geminals (APSLG). This form is taken in ref 46 as an underlying one for the molecular mechanical part of the molecule. At the same time, the APSLG wave function can itself be employed to construct the $O(N)$-scalable methods because the strictly local structure of the trial wave function allows one to eliminate the diagonalization of the matrices of the size $N \times N$. In this paper, we exploit this possibility.

The use of local orbitals is a direct way to good scalability properties.[10] These orbitals can be obtained, for example, by orthogonal transformations of canonical MOs.[47,48] At the same time, these orbitals are not centered on the pair of atoms and have electronic "tails" on other atoms. The localized orbitals without "tails" are called strictly localized molecular orbitals and can be obtained in special variational SCF procedure for electronic structure.[49] The well-known perturbative configuration interaction using localized orbitals (PCILO) scheme[50] also uses local orbitals but treats them by a sort of perturbation technique. In the framework of the present work, we use a special type of local orbitals, hybrid orbitals (HOs), obtained by transformations of minimal basis sets for each atom.[51]

The APSLG approximation is similar to other pair theories especially those based on various implementations of geminals.[52] The general antisymmetrized product of strongly orthogonal geminals (APSG) approach was introduced by Kutzelnigg,[53] who gave the natural expansion of geminals and proposed procedures for optimization of geminals. An important approach in the pair theories is the extended geminal model by Røeggen,[54,55] which tries to approach the exact solution in terms of geminals by taking into account the intergeminal correlation. The generalized method of valence bonds (GVB)[56] is another example of effective method for electronic structure calculations based on the pair wave functions. The difference between GVB and APSLG approaches lies in the way the one-electron states to be used for the bond function are chosen and, therefore, in the degree of the wave function localization. The ab initio version of the APSLG approach[57] uses nonvariational Pauling's HOs[51] for constructing the geminals. This approach was applied only to a small number of very simple molecules. The results do not allow one to make a conclusion about general applicability of the scheme to large molecules because, even in the case of the CH_3F molecule, the APSLG electronic energy is significantly higher than that of the SCF approach.[58] The calculations of the C−H bond dissociation show that the APSLG energy is lower than the GVB one for equilibrium bond distance but it is higher in the dissociation limit.[57]

The semiempirical implementation of the APSLG approach[59] is performed with a simple molecular Hamiltonian of the modified intermediate neglect of differential overlap (MINDO)/3 type.[60,61] The drawbacks of this approach are inherited from the MINDO/3 approximation: heats of formation for unsaturated organic compounds are too negative, and those for branched molecules are very positive; chemical bonds between atoms with lone electron pairs are too short, and bond angles are not well reproduced. There are different possible ways to cure these drawbacks: to further adjust parametrization, to take into account perturbation corrections to the wave function/energy, or to use more elaborated Hamiltonians having new interactions. In the present paper, we investigate the last option because in the case of the SCF approach it recommended itself as quite successful. Thus, we use in this paper the Hamiltonians of the neglect of diatomic differential overlap (NDDO) family taking in detail the two-center Coulomb interactions as implemented in the well-known modified neglect of diatomic overlap (MNDO),[62,63] first-Austin method (AM1),[64] and third-parametric method (PM3)[65] schemes. The principal difference between the MINDO and NDDO schemes and theoretical justification of the NDDO Hamiltonian are discusseqd in detail in ref 62. To summarize, we try to obtain a quantum chemical method with weak dependence of computational costs on the size of the system by replacing the SCF wave function by the APSLG one. We also try to reach reliable (not worse than in the SCF method) description of molecular properties such as heats of formation and molecular geometries. As an extra, the change of wave function should allow us to cure such an unpleasant property of the SCF wave function as its incorrect asymptotic behavior under the homolytic cleavage of chemical bonds.

The paper is organized as follows: in the next section, we consider general theoretical principles underlying the APSLG approach and its NDDO implementation; then, we describe parametrization procedure and calculations of molecular properties using the APSLG−NDDO schemes; these results are discussed and, finally, the conclusions about general applicability and advantages and disadvantages of the procedure proposed are given.

2. Theory

The electronic wave function in the APSLG approximation has the form

$$|\Psi\rangle = \prod_m g_m^+ |0\rangle \tag{1}$$

where the mth geminal is presented by a linear combination of singlet two-electron configurations given by products of two operators creating electrons on HOs corresponding to "right" (r) and "left" (l) atoms of chemical bond with the spin projections σ (= α, β):

$$g_m^+ = u_m r_{m\alpha}^+ r_{m\beta}^+ + v_m l_{m\alpha}^+ l_{m\beta}^+ + w_m (r_{m\alpha}^+ l_{m\beta}^+ + l_{m\alpha}^+ r_{m\beta}^+) \tag{2}$$

These geminals are mutually orthogonal and satisfy a normalization condition:

$$\langle 0 | g_m g_m^+ | 0 \rangle = {u_m}^2 + {v_m}^2 + 2{w_m}^2 = 1 \tag{3}$$

The amplitudes u_m, v_m, and w_m correspond to two ionic configurations and a covalent one (of the Heitler−London type). This form of wave function was originally proposed by

Weinbaum.[66] In the case of electron lone pair, only one configuration survives (for the sake of definiteness, we assume it to be the right-end ionic contribution) and the geminal has the form

$$g_m^+ = r_{m\alpha}^+ r_{m\beta}^+ \tag{4}$$

with normalization condition automatically fulfilled.

The important question is about particular construction of HOs r_m and l_m. These one-electron functions form the carrier space for geminals (the so-called Arai subspaces[67]). Strictly local character of the geminals (and thus of the wave function itself) assumes that the HOs have no "tails", that is, they are expressed through the basis functions centered on one atom only. In the case of minimal basis set used, the orthogonality of geminals immediately leads to the mathematical structure of HOs as produced by orthogonal ($SO(4)$) transformations of the initial set of atomic orbitals (AOs) for each "heavy" (non-hydrogen) atom. These transformations, h^A, act in the four-dimensional spaces spanned by one s- and three p-AOs:

$$t_{m\sigma}^+ = \sum_{i\in A} h_{mi}^A a_{i\sigma}^+ \tag{5}$$

where t denotes a HO (right, r, or left, l) located on the atom A.

The transformation of the basis set produces transformation of molecular integrals entering the NDDO Hamiltonian. These integrals in the HO basis are linear combinations of the same type of integrals in the AO basis with coefficients taken as products of the elements of the transformation matrices. Here, we present only integrals that are actually necessary for estimation of the electronic energy. The attraction of an electron on the HO t_m to its own core is

$$U_{t_m t_m}^A = \sum_{i\in A} (h_{mi}^A)^2 U_{ii}^A \tag{6}$$

or, using properties of $SO(4)$ matrix h^A, we can express it as a function of the weight of the s-AO only:

$$U_{t_m t_m}^A = U_{\rm pp}^A + (U_{\rm ss}^A - U_{\rm pp}^A)(h_{m\rm s}^A)^2 \tag{7}$$

Two-electron one-center molecular integrals for the sp-shell can be as well expressed through the expansion coefficients for the s-function only:

$$\begin{gathered}(t_m t_m|t_m t_m)^A = C_1^A + C_2^A(h_{m\rm s}^A)^2 + C_3^A(h_{m\rm s}^A)^4,\\ g_{t_k t'_m}^A = 2(t_k t_k|t'_m t'_m)^A - (t_k t'_m|t'_m t_k)^A = C_4^A + C_5^A[(h_{m\rm s}^A)^2 + \\ (h_{k\rm s}^A)^2] + C_3^A(h_{m\rm s}^A h_{k\rm s}^A)^2\end{gathered} \tag{8}$$

where the combinations of the five Slater−Condon parameters[68] are introduced,

$$\begin{gathered}C_1^A = F_0^A({\rm pp}) + 4F_2^A({\rm pp}),\\ C_2^A = 2F_0^A({\rm sp}) + 4G_1^A({\rm sp}) - 2F_0^A({\rm pp}) - 8F_2^A({\rm pp}),\\ C_3^A = F_0^A({\rm ss}) - 2F_0^A({\rm sp}) - 4G_1^A({\rm sp}) + F_0^A({\rm pp}) + 4F_2^A({\rm pp}),\\ C_4^A = 2F_0^A({\rm pp}) - 7F_2^A({\rm pp}),\\ C_5^A = 2F_0^A({\rm sp}) - G_1^A({\rm sp}) - 2F_0^A({\rm pp}) + 7F_2^A({\rm pp})\end{gathered} \tag{9}$$

The formulas in eqs 7 and 8 show that one-center molecular integrals (and therefore one-center energy) are independent of the directions of HOs. The dependence of the energy on the whole structure of HOs is given by two-center molecular integrals. The diagonal element of attraction of an electron on the HO t_m to other cores is

$$V_{t_m t_m,B}^A = \sum_{i,j\in A} V_{ij,B}^A h_{mi}^A h_{mj}^A \tag{10}$$

Other matrix elements depend on the form of HOs for pairs of atoms. The resonance (electron-transfer) matrix elements between the "right" and "left" HOs of the mth bond have the form

$$\beta_{r_m l_m}^{AB} = \sum_{i\in A}\sum_{j\in B} h_{mi}^A h_{mj}^B \beta_{ij}^{AB} \tag{11}$$

The matrix elements of the Coulomb repulsion of electrons located on different atoms A and B are

$$(t_{m_1} t_{m_1}|t'_{m_2} t'_{m_2})^{AB} = \sum_{\substack{i,j\in A\\ k,l\in B}} (ij|kl)^{AB} h_{m_1 i}^A h_{m_1 j}^A h_{m_2 k}^B h_{m_2 l}^B \tag{12}$$

In the case of multiple bonds, additional two-center matrix elements become necessary:

$$(t_{m_1} t'_{m_2}|\tilde{t}'_{m_2} \tilde{t}_{m_1})^{AB} = \sum_{\substack{i,j\in A\\ k,l\in B}} (ij|kl)^{AB} h_{m_1 i}^A h_{m_2 j}^A h_{m_2 k}^B h_{m_1 l}^B \tag{13}$$

where $\tilde{t} = l$ if $t = r$ and $\tilde{t} = r$ if $t = l$. These matrix elements correspond to electron transfers within a pair of single bonds between the same pair of atoms. It should be noted that the molecular integrals in the AO basis entering the above expressions are taken to be the same as they are in the corresponding predecessor SCF-based procedures.[62−65]

The electronic Hamiltonian for a molecular system written in the HOs' basis is a sum of one- and two-center contributions:

$$H = \sum_A H_A + \frac{1}{2}\sum_{A\neq B} H_{AB} \tag{14}$$

In the second quantization notation, they are

$$\begin{aligned}H_A = {}& \sum_{t_m\in A}(U_{t_m t_m}^A + \sum_{B\neq A} V_{t_m t_m,B}^A)\sum_\sigma t_{m\sigma}^+ t_{m\sigma} + \\ & \sum_{\substack{t_k,t'_m\in A\\ k<m}}\sum_{B\neq A} V_{t_k t'_m,B}^A \sum_\sigma (t_{k\sigma}^+ t'_{m\sigma} + {\rm hc}) + \\ & \frac{1}{2}\sum_{\substack{t_{m_1},t'_{m_2}\in A\\ t''_{m_3},t'''_{m_4}\in A}} (t_{m_1} t'_{m_2}|t''_{m_3} t'''_{m_4})^A \sum_{\sigma\tau} t_{m_1\sigma}^+ t''^+_{m_3\tau} t'''_{m_4\tau} t'_{m_2\sigma}\end{aligned} \tag{15}$$

and

$$\begin{aligned}H_{AB} = {}& -\sum_{\substack{t_{m_1}\in A\\ t'_{m_2}\in B}} \beta_{t_{m_1} t'_{m_2}}^{AB} \sum_\sigma (t_{m_1\sigma}^+ t_{m_2\sigma} + {\rm hc}) + \\ & \sum_{\substack{t_{m_1},t'_{m_2}\in A\\ t''_{m_3},t'''_{m_4}\in B}} (t_{m_1} t'_{m_2}|t''_{m_3} t'''_{m_4})^{AB} \sum_{\sigma\tau} t_{m_1\sigma}^+ t''^+_{m_3\tau} t'''_{m_4\tau} t'_{m_2\sigma}\end{aligned} \tag{16}$$

where hc stands for hermitean conjugation.

The total energy of a molecule is a sum of the electronic energy and that of the core−core interaction. The specific forms of the last term are, respectively, taken without changes from refs 62, 64, and 65 for the MNDO, AM1, and PM3 versions of the semiempirical APSLG-based method. The electronic energy is obtained by averaging the Hamiltonian, eq 14, over the APSLG trial wave function, eq 1. The average in its turn depends only on the intrabond elements of one- and two-electron density matrices:

$$P_m^{tt'} = \langle 0|g_m t^+_{m\sigma} t'_{m\sigma} g^+_m|0\rangle, \quad \Gamma_m^{tt'} = \langle 0|g_m t^+_{m\beta} t'^+_{m\alpha} t'_{m\alpha} t_{m\beta} g^+_m|0\rangle,$$
$$P_m^{rr} = {u_m}^2 + {w_m}^2, \quad P_m^{ll} = {v_m}^2 + {w_m}^2,$$
$$P_m^{rl} = P_m^{lr} = (u_m + v_m)w_m, \quad \Gamma_m^{rr} = {u_m}^2,$$
$$\Gamma_m^{ll} = {v_m}^2, \Gamma_m^{rl} = \Gamma_m^{lr} = {w_m}^2 \quad (17)$$

These matrix elements are spin-independent. Taking into consideration different contributions to the Hamiltonian eqs 15 and 16, one can represent the electronic energy as a sum of five terms:

$$E = E_{\mathrm{c-attr}} + E_{\mathrm{oc-rep}} + E_{\mathrm{res}} + E_{\mathrm{tc-rep}} + E_{\mathrm{m-b}} \quad (18)$$

The first contribution is attributed to electron attraction to cores:

$$E_{\mathrm{c-attr}} = 2\sum_{A}\sum_{t_m \in A}(U^A_{t_m t_m} + \sum_{B \neq A} V^A_{t_m t_m, B})P^{tt}_m \quad (19)$$

The one-center electron−electron repulsion is a sum of contributions from repulsion of electrons on one or two different HOs:

$$E_{\mathrm{oc-rep}} = \sum_{A}\sum_{t_m \in A}(t_m t_m|t_m t_m)^A \Gamma^{tt}_m + 2\sum_{\substack{t_{m_1}, t'_{m_2} \in A \\ m_1 < m_2}} g^A_{t_{m_1} t'_{m_2}} P^{tt}_{m_1} P^{t't'}_{m_2} \quad (20)$$

The overall contribution to the energy from the resonance interaction is

$$E_{\mathrm{res}} = -4\sum_{A<B}\sum_{m \in AB}\beta^{AB}_{r_m l_m} P^{rl}_m \quad (21)$$

where notation $m \in AB$ means that the mth bond is one between atoms A and B. The interatomic contribution from repulsion of electrons also depends on the type of interaction, between different bonds (or lone pairs) or inside one chemical bond:

$$E_{\mathrm{tc-rep}} = 2\sum_{A<B}\sum_{t_{m_1} \in A}\sum_{t'_{m_2} \in B}(t_{m_1} t_{m_1}|t'_{m_2} t'_{m_2})^{AB}[2(1 -$$
$$\delta_{m_1 m_2})P^{tt}_{m_1} P^{t't'}_{m_2} + \delta_{m_1 m_2}\Gamma^{rl}_{m_1}] \quad (22)$$

All the above contributions have their analogues in the APSLG construction[59] based on the MINDO[60,61] implementation. The NDDO Hamiltonian is believed to be superior to the MINDO one. It contains a specific contribution corresponding to interaction of single bonds constituting one multiple bond:

$$E_{\mathrm{m-b}} = -4\sum_{\substack{t_{m_1} t'_{m_2} \in A \\ m_1 < m_2}}(t_{m_1} t'_{m_2}|\tilde{t}'_{m_2} \tilde{t}_{m_1})^{AB} P^{rl}_{m_1} P^{rl}_{m_2} \quad (23)$$

The electronic (and total) energy thus depends on two classes of electronic structure parameters (ESPs): (i) amplitudes u_m, v_m, and w_m of eq 2 through the elements of density matrices, eq 17, and (ii) elements of the $SO(4)$ matrices h^A through the molecular integrals. The total number of independent amplitudes is $2M$ (M is a number of chemical bonds) due to normalization condition, eq 3. The total number of hybridization-defining parameters is $6L$ (L is a number of heavy atoms) because the $SO(4)$ group is a six-parametric one. We use parametric representation of the $SO(4)$ group based on six subsequent Jacobi rotations in two-dimensional subspaces of a four-dimensional space spanned by valence AOs at each heavy atom. Therefore, six parameters are the corresponding angles of the Jacobi rotations. The determination of the ESPs is performed by using a variational principle by a series of iterations. The first step is a calculation of geminal amplitudes by diagonalizing of 3 × 3 effective bond Hamiltonians for each geminal representing a chemical bond. The next step is a series of energy minimizations with respect to sextuples of parameters defining $SO(4)$ transformations for each heavy atom. These minimizations are performed with use of analytical gradients of the energy with respect to the Jacobi angles. The alternating diagonalizations and minimizations are performed until convergence. The number of iterations (i.e., of the runs through the whole set of geminals/atoms) remains approximately constant with increasing of the molecular system size. The procedure of equilibrium geometry determination based on the analytical gradients of the total energy with respect to geometric parameters is also implemented.

3. Results and Discussion

In the previous section, we have constructed a scheme of determination of the ESPs for APSLG−NDDO method. Clearly, this scheme avoids diagonalization of $N \times N$ matrices. The number of elementary steps (construction and diagonalization of effective bond Hamiltonians and minimizations of energy with respect to sextuples of hybridization angles) is proportional to the size of the system. Each step, however, has a contribution requiring computational resources proportional to the size of the system with a small coefficient. Therefore, the scaling of computational costs is almost linear. The scaling can be further improved by substituting the explicit calculation of molecular integrals between the basis functions centered on distant atoms with multipole expansions for interactions between well-separated parts of molecule.[28,69,70] We do not give here any benchmark calculations because they are platform-dependent. At the same time, we note that the comparisons of SCF and APSLG calculation times are given for MINDO/3 implementation in ref 59. It was shown that for a system with 122 basis functions the APSLG procedure is 30 times faster than the SCF one.

The change of the trial wave function leads to changes in the calculated quantities. It should be noted that the difference in the total energy for the SCF and APSLG wave functions (with same form of the Hamiltonian and parametrization) can be understood as a sum of two effects: better account of static intrabond electron correlation and neglect of interbond delocalization (electron transfer) in the APSLG scheme. The former lowers the energy, while the latter increases it. In the case of the H_2 molecule, the interbond delocalization is absent and we always obtain lowering of the energy. We should state that the method after change of trial wave function even without change of parametrization remains to give sane results. It allowed us not to perform the total reparametrization but to restrict ourselves by only slight tuning of parameters. We have studied three mostly known NDDO schemes—MNDO, AM1, and PM3—and restricted ourselves to molecules containing H, C, N, O, and F atoms. The SCF results on these compounds are given in refs 62, 63, 64, 65, 71, and 72. We assume that the change of the wave function mostly affects the two-center contributions to the energy. So, we attempted to reach reliable results by tuning only a very small subset of parameters related to the resonance. The new resonance parameters are given in Table 1 and are compared with the SCF values. For all atomic orbital parameters, the corrections are small. It should be noted that using the MINDO/3-type scheme for the resonance integrals, which is more simple for parametrization, is not possible here because

TABLE 1: Resonance Parameters, β_{ij}^{AB} (eV)

orbital	MNDO SCF	MNDO APSLG	AM1 SCF	AM1 APSLG	PM3 SCF	PM3 APSLG
1s(H)	6.989 064	7.083	6.173 787	6.077	5.626 512	5.454
2s(C)	18.985 044	17.136	15.715 783	15.799	11.910 015	11.499
2p(C)	7.934 122	9.345	7.719 283	8.034	9.802 755	10.467
2s(N)	20.495 758	20.594	20.299 110	21.420	14.062 521	14.890
2p(N)	20.495 758	20.594	18.238 666	18.102	20.043 848	19.958
2s(O)	32.688 082	32.784	29.272 773	29.382	45.202 651	45.302
2p(O)	32.688 082	32.784	29.272 773	29.382	24.752 515	25.329
2s(F)	48.290 466	49.591	69.590 277	69.587	48.405 939	50.124
2p(F)	36.508 540	36.594	27.922 360	27.922	27.744 660	27.361

TABLE 2: Experimental and Calculated by the SCF and APSLG Methods Heats of Formation (kcal/mol)

molecule	expt	MNDO SCF	MNDO APSLG	AM1 SCF	AM1 APSLG	PM3 SCF	PM3 APSLG
H_2	0.0	0.7	−3.2	−5.2	−3.2	−13.4	−9.9
CH_4	−17.9	−11.9	−16.3	−8.8	−13.1	−13.0	−15.5
C_2H_6	−20.2	−19.7	−23.4	−17.4	−20.3	−18.1	−20.7
C_2H_4	12.5	15.3	15.8	16.5	12.4	16.6	12.6
C_2H_2	54.3	57.3	53.1	54.8	44.9	50.7	38.7
C_3H_8	−24.8	−24.9	−26.7	−24.3	−25.6	−23.6	−25.5
CH_2CHCH_3	4.8	5.0	8.4	6.6	6.9	6.4	6.4
$HCCCH_3$	44.2	41.4	43.4	43.4	42.3	40.2	35.7
n-C_4H_{10}	−30.4	−29.7	−30.2	−31.1	−31.0	−29.1	−30.1
iso-C_4H_{10}	−32.4	−26.8	−27.1	−29.4	−27.9	−29.5	−29.6
CH_3CCCH_3	34.8	24.9	34.5	32.0	40.2	29.8	33.7
n-C_5H_{12}	−35.1	−34.4	−33.5	−37.9	−36.1	−34.5	−34.6
neo-C_5H_{12}	−40.3	−24.6	−23.3	−32.8	−30.2	−35.8	−33.7
cyclopropane	12.7	11.2	13.7	17.8	17.7	16.3	14.9
cyclobutane	6.8	−11.9	−4.9	0.2	6.0	−3.8	−1.9
cyclopentane	−18.4	−30.5	−29.0	−28.8	−24.8	−23.9	−25.7
cyclohexane	−29.5	−34.8	−28.0	−38.5	−28.8	−31.0	−28.8
spiropentane	44.3	33.7	47.1	50.5	59.1	43.1	50.6
cubane	148.7	99.1	98.6	151.2	150.5	113.8	97.7
N_2	0.0	8.0	−8.6	11.2	−6.1	17.6	2.2
NH_3	−11.0	−6.3	−14.1	−7.3	−13.9	−3.1	−10.1
CH_3NH_2	−5.5	−7.5	−5.3	−7.4	−4.9	−5.2	−6.1
$C_2H_5NH_2$	−11.4	−12.9	−10.8	−15.1	−9.0	−11.1	−11.5
n-$C_3H_7NH_2$	−16.8	−17.9	−14.6	−22.1	−13.2	−16.5	−15.7
iso-$C_3H_7NH_2$	−20.0	−16.0	−12.2	−19.2	−11.1	−18.7	−15.3
$(CH_3)_2NH$	−4.4	−6.6	8.2	−5.6	7.7	−7.9	−2.2
N_2H_4	22.8	14.3	13.9	13.7	14.7	22.9	18.3
cis-N_2H_2	50.9	33.7	33.4	32.4	34.2	42.9	38.6
CH_3NHNH_2	22.6	16.6	18.6	17.0	22.9	17.9	18.0
HCN	32.3	34.9	26.2	31.0	20.0	33.0	20.7
CH_3CN	20.9	19.2	17.0	19.3	17.9	23.3	20.0
H_2O	−57.8	−60.9	−65.9	−59.2	−62.4	−53.4	−60.3
CH_3OH	−48.1	−57.4	−49.4	−57.0	−50.8	−51.9	−51.5
C_2H_5OH	−56.2	−63.0	−54.2	−62.7	−53.5	−56.9	−55.2
1-C_3H_7OH	−61.2	−67.7	−57.5	−70.6	−58.5	−62.2	−59.7
2-C_3H_7OH	−65.1	−65.4	−55.1	−67.7	−54.8	−63.9	−58.4
H_2O_2	−32.5	−38.2	−42.6	−35.3	−37.1	−40.8	−50.1
$(CH_3)_2O$	−44.0	−51.2	−27.7	−53.2	−34.6	−48.3	−39.7
CH_2O	−26.0	−33.0	−18.5	−31.5	−22.1	−34.1	−31.6
F_2	0.0	7.3	−0.9	−22.5	−34.1	−21.7	−28.7
HF	−65.1	−59.8	−67.3	−74.3	−74.6	−62.7	−68.3
CH_3F	−56.8	−60.9	−56.0	−61.0	−53.7	−53.8	−52.8
C_2H_5F	−62.9	−65.1	−59.5	−66.3	−57.3	−60.2	−56.5
HOF	−23.5	−18.7	−24.7	−22.6	−28.5	−29.2	−37.4
F_2O	5.9	18.2	18.2	10.5	5.8	−4.8	−12.0
FCN	8.6	−2.7	14.0	−4.4	21.7	6.5	16.2

the relation between different types of resonance integrals (β_{ss} and β_{sp}) is fixed by the AO ionization potentials, which led to absurd molecular geometries—planar ammonia, linear water molecule, etc.

The calculated and experimentally observed heats of formation are given in Table 2 for all three parametrizations and both (SCF and APSLG) trial wave functions for a set of typical molecules taken from refs 63 and 71. The numerical results show that the APSLG parametrization is internally consistent. The estimates of the heats of formation obtained in the framework of the SCF and APSLG methods are of the same quality. It is seen that the use of the NDDO Hamiltonian in combination with the APSLG trial wave function cures the main problems of the APSLG−MINDO/3 approach, poor description of branched and unsaturated molecules. At the same time, we note that problems of SCF−NDDO schemes are mirrored in the APSLG implementation. It is well seen on the example of the cubane molecule in which both the SCF−MNDO and APSLG−MNDO methods give very large error while both the SCF−AM1 and APSLG−AM1 methods predict the experimental value of the heat of formation relatively well. It should be noted that in the case of molecules with triple bonds (especially N_2) the APSLG method leads to heats of formation significantly smaller than the SCF method. This is due to the small importance of interbond electron transfer as compared to the intrabond correlation due to symmetry of the problem.

As an essential problem of the approach proposed, we can mention the strong underestimation of rotation barriers. We exemplify it by calculations of rotation barriers for ethane, methylamine, and methanol. In the case of C−C bond in ethane, the values obtained by APSLG−MNDO, −AM1, and −PM3 methods (0.38, 0.33, and 0.58 kcal/mol, respectively) are significantly smaller than the experimental one (2.9 kcal/mol). Analogously, calculated rotation barriers for C−N bond in methylamine (0.32, 0.32, and 0.43 kcal/mol) and C−O bond in methanol (0.23, 0.25, and 0.14 kcal/mol) are far from the experiment (2.0 and 1.1 kcal/mol, respectively). These results are not surprising because the APSLG wave function does not account for contributions to the energy significant for rotation barrier formation: those of delocalization and overlap. The importance of these contributions is known in the literature. The effects of nonorthogonality were considered in refs 73 and 74, in which the transferability of nonorthogonalized bond orbitals and rotation barriers were studied. Effects of wave function localization were thoroughly studied in refs 75 and 76 in which a special perturbation formalism based on the local Brillouin theorem was used to investigate the delocalization of bond orbitals. At the same time, we note that the effects of intergeminal overlap and delocalization can be taken into account for the APSLG wave function used. This work is now in progress, and we hope that such modification of energy expression will allow us to improve the rotation barriers description.

Another important characteristic of the quality of the quantum chemical method is its ability to reproduce correctly the parameters of molecular structure. The calculated and experimental geometric parameters are given in Table 3 for typical, most characteristic, and most difficult cases. The numerical results show that the APSLG-based method suits somewhat better to reproduce the molecular geometries than the SCF one. Using the APSLG scheme allows us to cure significant problems of the SCF approach—incorrect description of torsion angles in cyclobutane and hydrogen peroxide molecules. In the case of the ab initio SCF approach, the acceptable result for cyclobutane can be achieved only by using large basis sets with polarization functions.[77] Moreover, the description of bond lengths in many cases is significantly improved by taking into account the intrabond correlation (for example, the N−N bond in hydrazine, the F−O bond in F_2O). At the same time, we find that use of the correlated APSLG wave function typically leads to increasing of bond length for atoms with electron lone pairs and to diminishing of valence angles (see NH_3 and H_2O molecules) in comparison with the SCF scheme. In some cases, such one-directional change of geometry parameters can lead to a worse agreement with experiment than that in the SCF-based semi-

TABLE 3: Experimental and Calculated Characteristic Geometry Parameters (Bond Lengths in Å, Angles in deg)

molecule	param	expt	MNDO SCF	MNDO APSLG	AM1 SCF	AM1 APSLG	PM3 SCF	PM3 APSLG
H_2	HH	0.742	0.663	0.667	0.667	0.688	0.699	0.720
CH_4	CH	1.094	1.104	1.093	1.112	1.104	1.087	1.089
C_2H_6	CC	1.536	1.521	1.511	1.501	1.503	1.505	1.509
	CH	1.091	1.109	1.099	1.117	1.104	1.098	1.099
	HCC	110.9	111.2	110.2	110.7	110.3	111.6	110.2
C_2H_4	CC	1.339	1.335	1.326	1.325	1.331	1.322	1.330
	CH	1.086	1.089	1.088	1.098	1.090	1.086	1.090
	HCC	121.2	123.2	123.3	122.7	123.3	123.1	123.3
C_2H_2	CC	1.203	1.194	1.184	1.195	1.192	1.190	1.178
	CH	1.060	1.051	1.068	1.061	1.065	1.065	1.072
cyclobutane	CCCC	153.0	180.0	157.0	180.0	157.6	180.0	157.3
N_2	NN	1.094	1.103	1.114	1.106	1.112	1.098	1.103
NH_3	NH	1.012	1.007	1.015	0.998	0.995	0.999	1.000
	HNH	106.7	105.3	102.3	109.0	105.0	108.1	107.3
CH_3NH_2	NC	1.474	1.460	1.496	1.432	1.470	1.468	1.508
N_2H_4	NN	1.449	1.397	1.448	1.379	1.407	1.433	1.486
HCN	NC	1.154	1.160	1.159	1.160	1.162	1.156	1.152
	CH	1.063	1.055	1.063	1.069	1.062	1.070	1.064
H_2O	OH	0.957	0.943	0.948	0.962	0.969	0.951	0.951
	HOH	104.5	106.8	104.5	103.4	103.4	107.7	106.5
CH_3OH	OC	1.425	1.391	1.431	1.410	1.460	1.395	1.435
	OH	0.945	0.946	0.956	0.964	0.973	0.949	0.958
H_2O_2	OO	1.475	1.295	1.322	1.300	1.332	1.482	1.547
	OH	0.950	0.961	0.956	0.983	0.977	0.945	0.951
	HOO	94.8	107.3	105.6	105.9	103.7	96.5	96.8
	HOOH	119.8	180.0	117.7	128.3	117.7	179.3	118.7
F_2	FF	1.418	1.266	1.272	1.427	1.462	1.350	1.373
HF	FH	0.917	0.956	0.952	0.826	0.830	0.938	0.937
CH_3F	FC	1.382	1.347	1.367	1.375	1.411	1.351	1.363
HOF	OH	0.966	0.964	0.959	0.971	0.987	0.946	0.943
	FO	1.442	1.277	1.291	1.366	1.417	1.396	1.417
	HOF	96.8	107.9	107.7	103.9	104.1	98.4	101.3
F_2O	FO	1.412	1.281	1.301	1.355	1.404	1.378	1.444
	FOF	103.2	109.1	105.9	102.5	96.7	101.0	99.2

empirical procedure. These changes should be considered as characteristic effect of the trial wave function not depending on the parametrization.

The APSLG trial wave functional operates with quantities widely used in chemistry but not in quantum chemistry—bond characteristics and hybridization parameters. Here, we demonstrate how these characteristics determined on the ground of variational principle correspond to chemical intuition. We can rewrite the geminal expression eq 2 in the form[57]

$$g_m^+ = \frac{I_m}{\sqrt{2}}[\sqrt{1+\lambda_m}r_{m\alpha}^+ r_{m\beta}^+ + \sqrt{1-\lambda_m}l_{m\alpha}^+ l_{m\beta}^+] + \frac{C_m}{\sqrt{2}}[r_{m\alpha}^+ l_{m\beta}^+ + l_{m\alpha}^+ r_{m\beta}^+] \quad (24)$$

where $I_m{}^2$ can be considered as bond ionicity, $C_m{}^2$ ($=1 - I_m^2$) as bond covalency, and λ_m as bond polarity. In Table 4, we show the bond order ($2P_m^{rl}$), bond covalency, and bond polarity for some typical chemical bonds. It can be seen that the bond order is very close to unity for a very large number of σ-bonds. The results show, however, that different parametrizations lead to quite different descriptions of chemical bond structure. For example, the AM1 scheme is prone to polarize bonds significantly; the PM3 scheme leads to electronegativity of the carbon atom exceeding that of the nitrogen atom and also predicts the fluorine and oxygen atoms to have very close electronegativities.

TABLE 4: APSLG Characteristics of Typical Bonds

molecule	bond	method	bond order	covalency	polarity
H_2	HH	MNDO	0.996	0.547	0.000
		AM1	0.994	0.555	0.000
		PM3	0.986	0.584	0.000
CH_4	CH	MNDO	0.995	0.537	0.135
		AM1	0.990	0.535	0.247
		PM3	0.994	0.545	0.128
C_2H_6	CC	MNDO	0.998	0.533	0.000
		AM1	0.998	0.534	0.000
		PM3	0.998	0.529	0.000
C_2H_4	σCC	MNDO	0.999	0.517	0.000
		AM1	0.999	0.519	0.000
		PM3	1.000	0.514	0.000
C_2H_4	πCC	MNDO	0.935	0.677	0.000
		AM1	0.932	0.682	0.000
		PM3	0.938	0.673	0.000
C_2H_2	σCC	MNDO	1.000	0.510	0.000
		AM1	1.000	0.511	0.000
		PM3	1.000	0.507	0.000
C_2H_2	πCC	MNDO	0.969	0.624	0.000
		AM1	0.965	0.631	0.000
		PM3	0.972	0.618	0.000
NH_3	NH	MNDO	0.994	0.540	0.140
		AM1	0.989	0.533	0.261
		PM3	0.998	0.533	0.004
N_2H_4	NN	MNDO	0.993	0.560	0.000
		AM1	0.995	0.551	0.000
		PM3	0.997	0.536	0.000
CH_3NH_2	NC	MNDO	0.995	0.546	0.072
		AM1	0.996	0.543	0.077
		PM3	0.998	0.529	−0.057
N_2	σNN	MNDO	0.999	0.515	0.000
		AM1	0.999	0.516	0.000
		PM3	1.000	0.497	0.000
N_2	πNN	MNDO	0.969	0.624	0.000
		AM1	0.968	0.625	0.000
		PM3	0.975	0.611	0.000
HCN	σNC	MNDO	0.998	0.511	−0.126
		AM1	0.998	0.513	−0.104
		PM3	1.000	0.500	−0.061
HCN	πNC	MNDO	0.967	0.621	0.147
		AM1	0.966	0.627	0.091
		PM3	0.972	0.616	0.084
H_2O	OH	MNDO	0.985	0.525	0.330
		AM1	0.978	0.527	0.396
		PM3	0.983	0.520	0.357
CH_3OH	OC	MNDO	0.986	0.535	0.298
		AM1	0.985	0.544	0.290
		PM3	0.990	0.527	0.259
CH_2O	σOC	MNDO	0.997	0.521	0.131
		AM1	0.997	0.527	0.092
		PM3	0.997	0.509	0.162
CH_2O	πOC	MNDO	0.928	0.634	0.514
		AM1	0.928	0.625	0.549
		PM3	0.940	0.613	0.505
HF	FH	MNDO	0.954	0.499	0.569
		AM1	0.956	0.491	0.560
		PM3	0.979	0.550	0.356
F_2	FF	MNDO	0.989	0.576	0.000
		AM1	0.955	0.649	0.000
		PM3	0.970	0.622	0.000
F_2O	FO	MNDO	0.988	0.568	0.159
		AM1	0.977	0.606	0.009
		PM3	0.973	0.614	0.083

It is seen that π-bonds are significantly more covalent and more polarizable than σ-bonds in accordance with usual chemical intuition.

TABLE 5: Indices, *x*, in the sp^x Representation for a Series of HOs

molecule	HO	MNDO	AM1	PM3
CH_4	C−H	3.00	3.00	3.00
C_2H_6	C−H	2.98	2.91	2.84
	C−C	3.07	3.29	3.59
C_2H_4	C−H	2.18	2.09	1.99
	σC−C	1.69	1.83	2.02
C_2H_2	C−H	1.06	0.99	0.92
	σC−C	0.94	1.01	1.09
NH_3	N−H	7.76	5.56	4.14
	N-lp	0.52	0.84	1.40
	C−H	3.97	4.10	4.28
CH_3NH_2	C−N	2.76	2.73	2.70
	N−C	8.29	6.80	5.51
	N−H	7.31	5.37	3.71
N_2	σN−N	5.62	5.15	3.31
	N-lp	0.18	0.19	0.30
	C−H	0.85	0.81	0.69
HCN	σC−N	1.17	1.23	1.45
	σN−C	4.72	4.38	2.66
H_2O	O−H	8.49	11.14	6.19
	O-lp	1.53	1.39	1.77
	C−H	2.58	2.49	2.55
CH_3OH	C−O	5.20	6.08	5.43
	O−C	10.37	15.33	11.90
	O−H	8.61	11.23	6.07
HF	F−H	4.96	4.32	1.23
	F-lp	2.60	2.69	4.44
F_2	F−F	19.26	95.39	15.23
	F-lp	2.16	2.03	2.20

Another important parameter of electronic structure of the APSLG method is hybridization matrices. Here, they are determined variationally. This approach allows us to consider a question about the structure of multiple chemical bonds. Our calculations show that the σ/π separated chemical bonds are more preferable than those of the bent-type ("banana") in accordance with predictions of ref 78 based on the full GVB consideration. Analogously, we can confirm an old observation[79] that in the case of cyclopropane molecule the HOs are not directed along the C−C bonds (the deviation is 22° in remarkable agreement with ref 79).

It is typical to represent the ratio of s- and p-AOs in the HO as sp^x. We use this form of representation in Table 5 for some typical HOs. It can be seen that this type of representation is not very suitable for large and small weights of s-function because of its significantly nonlinear and nonuniform character. The data of Table 5 demonstrate that the most characteristic hybridization patterns (sp^3, sp^2, and sp) are reproduced in the calculation with small deviations due to nonequivalence of the bonds involved.

The form of HOs can be used for semiquantitative prediction of a series of properties. As it was shown in ref 80, the value of p*K* for hydrocarbon dissociation is approximately a linear function of the weight of s-function in the HO representing the C−H bond. Here, we construct these linear relations:

$$\begin{aligned} &\text{MNDO} && \mathrm{p}K = 74.13 - 1.01h_{ms}^{2} \\ &\text{AM1} && \mathrm{p}K = 73.91 - 0.98h_{ms}^{2} \\ &\text{PM3} && \mathrm{p}K = 73.64 - 0.94h_{ms}^{2} \end{aligned} \tag{25}$$

The data calculated by these relations, given in Table 6, are in good correspondence with the experimental ones.

TABLE 6: Estimates of p*K* for CH Bond Dissociation

molecule	expt	MNDO	AM1	PM3
C_2H_2	25	24.9	24.8	24.8
C_2H_4	42	42.3	42.3	42.3
cyclopropane	44	44.1	44.6	44.5
cyclopentane	48	48.1	47.9	48.1
cyclohexane	49	48.6	48.3	48.3

It should be noted that the proposed APSLG approach has significant limitations. It applies in its current form only to systems with well-defined chemical bonds without large delocalization. At the same time, generalization to the molecules with groups with high levels of electron delocalization is straightforward. The work in this direction is in progress now. Another problem is calculation of properties corresponding to significantly delocalized states such as ionization potentials. At the same time, in this case some types of configuration interaction procedures can be applied as it was demonstrated in ref 81.

4. Conclusions

A semiempirical method for molecular electronic structure calculations is developed in this work. It is based on the trial APSLG wave function with three NDDO-type Hamiltonians—MNDO, AM1, and PM3. It can be considered as different from the SCF point on the plane with axes Hamiltonian-wave function. Using local one-electron states allows us to achieve approximately linear dependence of computational costs on the size of the molecule. The APSLG method by construction has correct asymptotic behavior under cleavage of chemical bonds. It is shown that the quality of results on the heats of formation and molecular geometries obtained by the SCF and APSLG approaches is comparable. In the framework of the approach proposed, many chemically sensible concepts such as hybridization and bond characteristics found their theoretical substantiation by determination on the ground of variational principle.

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