
Semiempirical Implementation of Strictly Localized Geminals for Analysis of Molecular Electronic Structure

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ABSTRACT: Approximate electronic trial wave function taken as the antisymmetrized product of strictly localized geminals (APSLG) is implemented for semiempirical analysis of molecular electronic structure of "organic" compounds and for calculations of their heats of formation. This resulted in an $O(N)$ -scaling method. Using the MINDO/3 form of the semiempirical Hamiltonian with reparameterized β_{AB} values in combination with the APSLG form of the wave function yields the computational procedure BF'98. Calculations on the heats of formation and the equilibrium geometries for a wide range of molecules show that the APSLG-MINDO/3 approach is more favorable than its self-consistent field-based counterpart. Also, the APSLG formalism allows to interpret molecular electronic wave function in chemically sensible terms. © 2001 John Wiley & Sons, Inc. *J Comput Chem* 22: 752–764, 2001

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Introduction

Modern *ab initio* methods of quantum chemistry when applied to molecular objects of practical interest achieve acceptable results by extending the basis set of one-electron states, and by taking into account a great deal of electron correlation corrections of higher orders. These approaches

require considerable computational resources that increase like $N^5 \div N^7$ (where N is the dimension of the basis of one-electron states involved) when the system size grows. This reduces the applicability of *ab initio* methods to the systems of real interest (especially to their chemical transformations).¹ Semiempirical methods employing the self-consistent field (SCF or Hartree–Fock) approximation for the trial electronic wave function attain chemically reasonable results by using sophisticated parameterization schemes. Nevertheless, the required computational resources in this case also grow as N^3 . Therefore, even the application of semiempirical methods to large systems may as well become prob-

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lematic. That high requirements to the computational resources do not allow applying the quantum chemical methods to the massive calculations of potential energy surfaces (PES) of molecular systems of practical interest. These calculations may become necessary, for example, in the context of molecular dynamics studies on reactivity of large molecules. Thus, it is important to develop quantum chemical methods with a weaker dependence on the size of the system than the cubic one. Preferably it should be $O(N)$ -scaling methods, i.e., those with a linear dependence of the required computation resources on the system (basis) size. Several attempts to construct such methods are reported in the literature. In refs. 2 and 3 it was proposed to eliminate the diagonalization of the matrices of the size $N \times N$ by ignoring matrix elements of the Fock matrix between the basis functions centered on distant atoms. This leads to the $O(N)$ -scalability of the resulting procedure, but the elimination of the matrix elements of the Fockian was not counterbalanced. Another way to the methods with smaller computational costs has been proposed in ref. 4. It is constructed to get the local one-electron states directly from the SCF equations. The electron correlations can then be more effectively taken into account in the basis of the local one-electron states than it can in the basis of the delocalized canonical MO LCAOs. There are also other approaches aimed to accelerate the calculations based either on the pseudodiagonalization^{5,6} or on other assumptions.^{7,8}

The $O(N)$ -scalability can be also achieved by employing the basis of one-electron states that are obtained without performing the Hartree–Fock step at all. The latter can be avoided by making use of some different form of the trial electronic wave function. Semiempirical quantum chemical methods can be constructed for arbitrary form of the electronic trial wave function; the specific choice of its form is stipulated by the class of molecules the method is designed for, and by the class of physical properties or phenomena it has to describe. Thus, for description of chemical transformations the trial wave function has to assure a correct asymptotic behavior when chemical bonds are cleaved or formed. Meanwhile, the trial wave function of the SCF MO LCAO approximation is generally known to have a wrong asymptotic behavior at large interatomic separations, which is evident from the example of the hydrogen molecule: the electronic wave function in the SCF approximation (in the valence basis, of course) does not depend on the distance between the hydrogen atoms, and thus, the weights of ionic and covalent con-

figurations in the ground state remain equal (and constant) for all internuclear separations. It leads to the physically absurd description of the system at large interatomic distances. This problem obviously persists for all homolytic cleavages of σ -bonds.

With the above example in mind, we consider a theory of separate electron pairs with the trial wave function of the ground state of $2n$ -electron system taken as the antisymmetrized product of spin geminals⁹ as a starting point for constructing a semiempirical theory alternative to the SCF. The concept of two-electron bond wave functions (geminals) is due to Fock¹⁰ as the concept of single determinant wave function is. That construction takes into account different contributions to the bond wave functions—the covalent and ionic ones—with the amplitudes of these contributions determined by variation of the total energy. Such a wave function includes the intrabond correlations, and has correct asymptotic behavior for the homolytic cleavage of σ -bonds.

In the well-known PCILO approach¹¹ the strong intrabond electron correlations are taken into account with use of the perturbation theory. There is, however, no real reason to use the perturbational approach in this case, because the intrabond correlations can be alternatively taken into account variationally. For this end one must solve a set of quantum mechanical problems for each of two-electron bonds (electron pairs) in the subspace of one-electron functions ascribed to each bond. By this we arrive at a theory that gives the optimal local two-electron wave functions (geminals), representing chemical bonds. Such treatment of electron pairs in the molecules corresponds to the intuitive Lewis concept of two-electron bond.¹² In this framework the Lewis' picture appears as a result of optimization of the total energy in a specific class of electronic trial wave functions.

Variational methods using strictly local orbitals are also known in the literature. These orbitals are localized on the bonds or on the electron lone pairs, and do not contain tails on the other atoms of the molecule. Such MOs are called strictly localized (SLMO).¹³ For saturated organic molecules the canonical MOs can be localized satisfactorily by standard methods.^{14–18} The orbitals relevant to the SLMO approach turn out to be close to the LMOs obtained by localization of the canonical (delocalized) MO LCAO, which are solutions of the Hartree–Fock–Roothaan equations. These *a posteriori* transformations from the atomic basis to the hybrid one are ambiguous. There exist several criteria for it, based on the geometry factors, when one

either attempts to direct the hybrid orbitals (HOs) towards the other end of the bond¹⁹ or tries to maximize the overlap between the HOs, belonging to different ends of the bond.²⁰ However, it is more consistent to evaluate the HOs on the basis of the variational principle (i.e., from the energy minimum condition) together with other parameters of the trial wave function.

An approach using geminals representing chemical bonds has been used in the work.²¹ It has been implemented with use of the *ab initio* Hamiltonian. This approach uses Pauling's HOs to construct the geminals. It restricts the flexibility of the wave function, and does not allow obtaining the hybridization on the ground of variational principle. This approximation is called according to the type of the trial wave function employed, i.e., that of antisymmetrized product of strictly localized geminals (APSLG). The APSLG approximation is similar to other pair theories like the generalized method of valence bonds (GVB)²² and its descendants—those making use of perfect pairing²² and complete active space.²³ The difference between these methods lays in the way of determination of the one-electron states to be used for the bond function and, therefore, in the degree of localization of the wave function.

The *ab initio* APSLG approach²¹ was tested only for a limited series of simple molecules. Results obtained there do not allow to derive unambiguous conclusion about the validity of this approximation for larger molecules, because, even in the case of the CH₃F molecule, the electronic energy of the APSLG approximation is significantly higher than that for the SCF method (in the same basis).²⁴ The calculation of the potential curve for dissociation of one C—H bond in methane molecule shows that for the C—H separations close to those at the equilibrium the APSLG approximation results in a lower energy value than the GVB but for the dissociation limit the reverse is true.²¹ In this context we considered the possibility of semiempirical implementation of a quantum chemical method using the trial wave function of the APSLG approximation.²⁵

Semiempirical implementation requires assessing a set of parameters to be used in calculations. We have used the well-known MINDO/3 parameterization²⁶ as a starting point for parameters evaluation. This set of parameters, when used with the trial wave function of the HFR approximation for the valence electrons, gives an adequate set of the energy characteristics and the equilibrium geometries for organic molecules. Furthermore, as it was noticed in ref. 27, the one-center parameters

of the MINDO/3 method are close to their estimates derived from the spectra of free atoms and ions²⁸ and/or those made in the framework of the theory of the effective valence shell Hamiltonian.²⁹ This allows conclusion that the one-center parameters are quite universal, and do not depend on the type of the trial electronic wave function. In this article we construct the energy functional with use of the trial wave function of the APSLG type and with the MINDO/3 type of parameterization for atomic and two-center integrals. The variation of this functional gives the estimate of parameters of the wave function and the electronic (and total) energy of the system in question.

Theory

WAVE FUNCTION AND THE HAMILTONIAN

The wave function of electrons in the APSLG approximation has the form:

$$|\Phi\rangle = \prod_m g_m^+ |0\rangle, \quad (1)$$

where the *m*th geminal (i.e., the two-electron function of the *m*th bond) is expanded through the operators creating electrons with the spin projections σ on the "right" and the "left" HO of the appropriate bond, respectively:

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

The normalization and orthogonality conditions for the geminals read:

$$\langle 0 | g_m g_{m'}^+ | 0 \rangle = u_m u_{m'} + v_m v_{m'} + 2\tau w_m \tau w_{m'} = \delta_{mm'}. \quad (3)$$

Such functions describe singlet states of electron pairs. The quantities u_m and v_m are the amplitudes of the ionic contributions to the geminal of the *m*th bond, and w_m is proportional to the amplitude of the covalent contribution. If the HOs $|r_m\rangle$ and $|l_m\rangle$ are symmetrical, the latter is the Heitler–London wave function. If all the amplitudes are accidentally equal then the function obtained is the spin restricted SCF wave function built on the HOs $|r_m\rangle$ and $|l_m\rangle$. Electron lone pairs represent special case of geminals. For them, only one ionic contribution to the geminal does not vanish: for the sake of definiteness we assume that the lone pair geminals have the u_m amplitudes equal to unity.

The electronic energy in the APSLG approximation is

$$E = \langle \Phi | H | \Phi \rangle, \quad (4)$$

where $|\Phi\rangle$ is defined by eqs. (1) and (2).

The HOs $|r_m\rangle$ and $|l_m\rangle$ result from orthogonal transformations applied to the initial set of AOs for each "heavy" (nonhydrogen) atom. Unlike most modern methods that use the HOs, satisfying some external localization criteria we determine the HOs variationally, i.e., by applying the minimum condition to the energy functional. For each heavy atom (A) it is necessary to determine six independent angles which define the matrix $h^A \in SO(4)$ of the orthogonal transformation in four-dimensional space spanned by one s - and three p -orbitals per heavy atom.³⁰ The annihilation operators for the HOs are:

$$t_{m\sigma} = \sum_{i \in A} h_{mi}^A a_{i\sigma}; \quad t = r, l. \quad (5)$$

The Hamiltonian for a molecular system in the MINDO/3 approximation can be presented as a sum of one- and two-center contributions:

$$H = \sum_A H_A + \frac{1}{2} \sum_{A \neq B} H_{AB}. \quad (6)$$

Molecular integrals for the MINDO/3 approximation are originally known in the basis of the valence s - and p -AO. As the geminals are expressed through the HOs, all the integrals have to be transformed to the HO basis, as well.

Suppose that $|t_m\rangle$ is any of the HOs ($|r_m\rangle$ or $|l_m\rangle$) belonging to the m th geminal. At the same time the HO $|t_m\rangle$ belongs to the subspace spanned by the valence (s - and p -) orbitals centered on the atom A (this is denoted as $t_m \in A$). The parameter U_m^t representing the attraction of an electron on the HO $|t_m\rangle$ to the core of the atom A has the form:

$$U_m^t = \sum_{i \in A} (h_{mi}^A)^2 U_i(A), \quad (7)$$

where the index i enumerates the s - and p -AOs belonging to the heavy atom A and $U_i(A)$ is the attraction of an electron on the i th AO to its own core. The attraction of electron to other cores and repulsion of electrons on the orbitals of different atoms do not depend on the angular momentum (azimuthal) quantum number l . Thus, the energy shifts of the one-electron states on the atom A due to the Coulomb interactions with the atomic cores are equal for the s - and p -AOs, and therefore, for all their linear combinations. Thus, they can be expressed through the Coulomb two-center integrals γ_{AB} and the core charges Z_B as in the standard MINDO/3 method.

There are only a few integrals characterizing the repulsion of two electrons on one atom, essential for

the energy estimates with use of the APSLG wave function. These are:

$$\begin{aligned} \left(\begin{smallmatrix} t & t \\ m & m \end{smallmatrix} \middle| \begin{smallmatrix} t & t \\ m & m \end{smallmatrix} \right)^A &= \sum_{i \in A} (h_{mi}^A)^4 (ii|ii)^A + 2 \sum_{i < j \in A} (h_{mi}^A h_{mj}^A)^2 \\ &\quad \times [(ij|jj)^A + 2(ij|ij)^A]; \end{aligned} \quad (8)$$

$$\begin{aligned} \left(\begin{smallmatrix} t & t & t' & t' \\ m_1 & m_1 & m_2 & m_2 \end{smallmatrix} \middle| \begin{smallmatrix} t' & t' \\ m_2 & m_2 \end{smallmatrix} \right)^A &= \sum_{i \in A} (h_{m_1 i}^A h_{m_2 i}^A)^2 (ii|ii)^A \\ &\quad + \sum_{i < j \in A} [(h_{m_1 i}^A h_{m_2 j}^A)^2 \\ &\quad \quad + (h_{m_1 j}^A h_{m_2 i}^A)] (ij|ij)^A \\ &\quad + 4 \sum_{i < j \in A} h_{m_1 i}^A h_{m_1 j}^A h_{m_2 i}^A h_{m_2 j}^A (ij|ij)^A; \end{aligned} \quad (9)$$

$$\begin{aligned} \left(\begin{smallmatrix} t & t' \\ m_1 & m_2 \end{smallmatrix} \middle| \begin{smallmatrix} t' & t \\ m_2 & m_1 \end{smallmatrix} \right)^A &= \sum_{i \in A} (h_{m_1 i}^A h_{m_2 i}^A)^2 (ii|ii)^A \\ &\quad + 2 \sum_{i < j \in A} h_{m_1 i}^A h_{m_1 j}^A h_{m_2 i}^A h_{m_2 j}^A (ii|jj)^A \\ &\quad + \sum_{i < j \in A} [2h_{m_1 i}^A h_{m_1 j}^A h_{m_2 i}^A h_{m_2 j}^A \\ &\quad \quad + (h_{m_1 i}^A h_{m_2 j}^A)^2 \\ &\quad \quad + (h_{m_1 j}^A h_{m_2 i}^A)^2] (ij|ij)^A. \end{aligned} \quad (10)$$

The summation indices i and j in these sums refer to the s - and p -AOs of the heavy atom A .

The resonance integral between the right (centered on the atom A) and the left (centered on the atom B) HOs is expressed through the resonance integrals in the AO basis:

$$\beta_m = \sum_{i \in A} \sum_{j \in B} h_{mi}^A h_{mj}^B \beta_{ij}^{AB}. \quad (11)$$

To evaluate the electronic energy we use the second quantization technique. The fermion operators related to the HOs obey usual anticommutation relations. The contributions to the molecular Hamiltonian eq. (6) in terms of these operators have the form:

$$\begin{aligned} H_A &= \sum_{\substack{t_m \in A \\ \sigma}} \left(U_m^t - \sum_{B \neq A} \gamma_{AB} Z_B \right) t_{m\sigma}^+ t_{m\sigma} \\ &\quad - \sum_{\substack{t_{m_1}, t_{m_2} \in A \\ m_1 < m_2}} \sum_{\sigma} \beta_{m_1 m_2}^{AA} (t_{m_1 \sigma}^+ t_{m_2 \sigma} + h.c.) \\ &\quad + \frac{1}{2} \sum_{\substack{t_{m_1}, t_{m_2} \in A \\ t_{m_3}, t_{m_4} \in A}} \sum_{\sigma \tau} \left(\begin{smallmatrix} t & t' \\ m_1 & m_2 \end{smallmatrix} \middle| \begin{smallmatrix} t'' & t''' \\ m_3 & m_4 \end{smallmatrix} \right)^A \\ &\quad \times t_{m_1 \sigma}^+ t_{m_3 \tau}^{t''+} t_{m_4 \tau}^{t'''} t_{m_2 \sigma}, \end{aligned} \quad (12)$$

where $\beta_{m_1 m_2}^{AA}$ is the resonance integral corresponding to electron transfer from the HO of the geminal m_1 to the HO of the geminal m_2 in the case if these HOs belong to the same (heavy) atom. Next

$$H_{AB} = - \sum_{\substack{t_{m_1} \in A \\ t_{m_2} \in B}} \sum_{\sigma} \beta_{m_1 m_2}^{AB} (t_{m_1 \sigma}^+ t_{m_2 \sigma}' + h.c.) + \gamma_{AB} \sum_{\substack{t_{m_1} \in A \\ t_{m_2} \in B}} \sum_{\sigma \tau} t_{m_1 \sigma}^+ t_{m_2 \tau}' t_{m_2 \tau} t_{m_1 \sigma}, \quad (13)$$

where $\beta_{m_1 m_2}^{AB}$ is the resonance integral corresponding to electron transfer between the HOs centered on different atoms. (Here and above *h.c.* stands for hermitian conjugation.) If $m_1 = m_2$, the previous resonance integral transforms to the β_m integral for the m th geminal [(bond) eq. (11)].

ELECTRONIC ENERGY IN THE APSLG-MINDO/3 APPROXIMATION

Now let us consider the contributions to the energy from the one-center terms $\langle \Phi | H_A | \Phi \rangle$. To do so we evaluate the averages of the operators with the APSLG wave function. The one-center part of the Hamiltonian contains the operators proportional to the number of electrons operator. The contribution from it to the energy can be presented as:

$$E_1 = \sum_A \sum_m \left(U_m^t - \sum_{B \neq A} \gamma_{AB} Z_B \right) \sum_{\sigma} P_m^{t\sigma}, \quad (14)$$

where

$$P_m^{t\sigma} = \langle 0 | g_m t_{m\sigma}^+ t_{m\sigma} g_m^+ | 0 \rangle \quad (15)$$

and $P_m^{t\sigma}$ are expressed through the amplitudes of the m th geminal:²⁵

$$P_m^{r\sigma} = u_m^2 + w_m^2, \quad P_m^{l\sigma} = v_m^2 + w_m^2 \quad (16)$$

and does not depend on σ . (Hereinafter we drop the σ superscript in one-electron densities.) Thus:

$$E_1 = 2 \sum_A \sum_{t_m \in A} \left(U_m^t - \sum_{B \neq A} \gamma_{AB} Z_B \right) P_m^t. \quad (17)$$

The contribution from the Coulomb repulsion of electrons located on the same atom is:

$$E_{coul}^{(1)} = \sum_A \left[\sum_{t_m \in A} \left(\begin{matrix} t & t \\ m & m \end{matrix} \middle| \begin{matrix} t & t \\ m & m \end{matrix} \right)^A R_m^t \right.$$

$$\left. + 2 \sum_{\substack{t_{m_1}, t_{m_2} \in A \\ m_1 < m_2}} \left(2 \left(\begin{matrix} t & t \\ m_1 & m_1 \end{matrix} \middle| \begin{matrix} t' & t' \\ m_2 & m_2 \end{matrix} \right)^A - \left(\begin{matrix} t & t' \\ m_1 & m_2 \end{matrix} \middle| \begin{matrix} t' & t \\ m_2 & m_1 \end{matrix} \right)^A \right) P_{m_1}^t P_{m_2}^{t'} \right]. \quad (18)$$

It is proportional to the averages of the form [see eq. (12)]:

$$\begin{aligned} & \langle \Phi | t_{m_1 \sigma}^+ t_{m_2 \tau}' t_{m_3 \tau}'' t_{m_4 \sigma}''' | \Phi \rangle \\ &= \delta_{m_1 m_2} \delta_{m_3 m_4} \delta_{m_1 m_3} (1 - \delta_{\sigma \tau}) R_{m_1}^t \\ &+ [\delta_{m_1 m_4} \delta_{m_2 m_3} (1 - \delta_{m_1 m_2}) \\ &- \delta_{m_1 m_3} \delta_{m_2 m_4} (1 - \delta_{m_1 m_2}) \delta_{\sigma \tau}] P_{m_1}^t P_{m_2}^{t'}, \quad (19) \end{aligned}$$

where the relevant elements of two-electron density matrix are:

$$R_m^r = \langle 0 | g_m r_{m\beta}^+ r_{m\alpha}^+ r_{m\alpha} r_{m\beta} g_m^+ | 0 \rangle = u_m^2 \quad (20)$$

for the right HO and

$$R_m^l = \langle 0 | g_m l_{m\beta}^+ l_{m\alpha}^+ l_{m\alpha} l_{m\beta} g_m^+ | 0 \rangle = v_m^2 \quad (21)$$

for the left HO of the m th geminal.

The contribution to the energy from the resonance term of the Hamiltonian is proportional to the spin bond order between the HOs of the m th geminal:

$$Q_m^{\sigma} = \langle 0 | g_m r_{m\sigma}^+ l_{m\sigma} g_m^+ | 0 \rangle = (u_m + v_m) w_m. \quad (22)$$

The bond order is also σ -independent for the singlet geminal. The overall contribution to the energy from the resonance interaction is:

$$E_{res} = -4 \sum_{A < B} \sum_{m \in A, B} \beta_m Q_m. \quad (23)$$

The contribution from the Coulomb interaction of electrons located on different atoms (two-center) to the total energy is proportional to the following element of the two-electron density matrix:

$$\langle \Phi | \hat{n}_{m_1}^t \hat{n}_{m_2}^{t'} | \Phi \rangle = \sum_{\sigma \tau} \langle \Phi | t_{m_1 \sigma}^+ t_{m_2 \tau}' t_{m_2 \tau} t_{m_1 \sigma} | \Phi \rangle. \quad (24)$$

So, the last (Coulomb two-center) contribution to the energy can be written as:

$$E_{coul}^{(2)} = 2 \sum_{A < B} \gamma_{AB} \left[2 \sum_{\substack{t_{m_1} \in A, t_{m_2} \in B \\ m_1 \neq m_2}} P_{m_1}^t P_{m_2}^{t'} + \sum_{m \in A, B} w_m^2 \right]. \quad (25)$$

Total electronic energy is a sum of the above four terms:

$$E = E_1 + E_{coul}^{(1)} + E_{res} + E_{coul}^{(2)}. \quad (26)$$

As we have mentioned above, the quantities entering the operators H_A [eq. (12)] and H_{AB} [eq. (13)] depend on the $SO(4)$ matrices h^A , where A refers to a "heavy" atom. According to ref. 30, the elements of the group $SO(4)$ 4×4 matrix are functions of six angular parameters. The electronic energy of the system is thus a function of $6L$ angles (L is the number of heavy atoms in the molecule), determining the matrices h^A of transformation from the AO basis to the HO basis on each of the heavy atoms A and of $2M$ parameters defining the amplitudes of different contributions to the geminals (M is the number of bonds). Each sextuple of angles defines an $SO(4)$ matrix for one atom. This matrix can be presented as a product of six sequential rotation matrices in different two-dimensional subspaces of the whole four-dimensional space of atomic one-electron states (the Jacobi matrices). Each rotation is defined by one angle. The optimal wave function of the system is obtained by varying these angles $\bar{\alpha}^A$ for the matrices h^A defining the HOs expansion coefficients for the heavy atom A and those for the amplitudes u_m , v_m , and w_m for the bond geminals. The optimal amplitudes u_m , v_m , and w_m are obtained by diagonalizing the effective bond Hamiltonians for each bond geminal. Each iteration step includes optimization of the HO parameters and of the geminal amplitudes. For the set of the amplitudes u_m , v_m , and w_m the angles determining the matrices h^A are obtained. After that, for the fixed coefficients of the HOs the expansion coefficients of the geminals are determined. The alternating optimizations and diagonalizations are consistent, and the convergence is rapidly achieved in all variables. The number of iterations remains approximately constant and, therefore, the number of elementary steps (diagonalizations of 3×3 matrices and minimizations of the functions of six angular parameters) in the procedure of the optimization of the energy functional for a molecule grows linearly while its size increases.

Results

The scheme of determination of the optimal parameters of the variational APSLG wave function described in the previous section has been implemented as a program suite BF'98³¹ designed for calculation of the electronic structure of organic molecules. To estimate the validity of the APSLG approach we, first, performed calculations with use of the BF'98 package that uses both the form of the MINDO/3 Hamiltonian and the precise numerical

values of its parameters.²⁶ Some preliminary results obtained for the fixed experimental geometries were published in ref. 25. The calculated electronic energies can be compared with the same quantities obtained by the standard MINDO/3 calculations for the structures optimized with use of the standard SCF-MINDO/3 method.²⁵ Comparison of the electronic energies allows evaluation of the relative importance of delocalization and correlation of electrons. For the dihydrogen molecule, the APSLG wave function is that of the full configuration interaction in the basis of two s -AO. That is why the energy of dihydrogen molecule is lower for the APSLG function than for the SCF function for the same bond length with the same parameterization.

For more complex molecules the APSLG electronic energy with the standard MINDO/3 parameters can be either higher or lower than that of the SCF approximation. Similar picture was also obtained in the nonempirical calculations²¹ using the APSLG trial wave function. As for calculations on the energy of molecules with electron lone pairs, the effects of the intrabond correlation outweigh those of delocalization. Thus, the energy loss owing to the restriction in the flexibility of one-electron states in the APSLG-MINDO/3 compared to the SCF-MINDO/3 method (HOs vs. MO LCAO) is smaller than the energy gain due to better description of intrabond electron correlations. At the same time, the delocalization contribution is more important for the molecules with bonds between heavy atoms.

The calculated and experimentally observed heats of formation are shown in Table I. Comparison of the results of the APSLG-MINDO/3 method with the standard MINDO/3 parameterization (column 3) with the experimental ones (column 2) shows that its accuracy is not sufficient even for description of the simplest organic compounds. It is thus necessary to modify the parameters for the APSLG method. Indeed, the forms of the variational wave functions underlying, respectively, the SCF-MINDO/3 and the APSLG-MINDO/3 method are quite different. The SCF-based semiempirical theories, on the other hand, usually assume that all electron correlations can be absorbed by their parameters. However, the parameterization cannot reproduce the qualitative features of the electronic structure that depend on correlation. For example, when the parameters are fixed, the dissociation energy (the valley depth) of, say, the H_2 molecule obtained by the SCF method, is always larger than that obtained with use of variational function allowing for correlation. In the MINDO/3 method this

TABLE I. Heats of Formation (kcal/mol) of Test Molecules Obtained Experimentally and Calculated with the Use of the SCF-MINDO/3 and APSLG-MINDO/3 Methods.

Molecule	ΔH_f (Expt.)	ΔH_f MINDO/3 (APSLG)	ΔH_f Modified (APSLG)	ΔH_f MINDO/3 (SCF)
H ₂	0.0	-1.475	-0.101	0.131
CH ₄	-17.8	-5.655	-8.430	-6.275
C ₂ H ₆	-20.04	-8.254	-19.514	-19.849
C ₃ H ₈	-25.00	-5.500	-25.185	-26.527
<i>n</i> -C ₄ H ₁₀	-30.00	-2.226	-29.993	-32.655
<i>iso</i> -C ₄ H ₁₀	-32.00	5.351	-22.379	-24.710
<i>n</i> -C ₅ H ₁₂	-35.09	1.027	-35.225	-38.973
<i>neo</i> -C ₅ H ₁₂	-40.15	22.811	-12.126	-14.632
Cyclopropane	12.7	41.000	18.472	8.524
Cyclobutane	6.8	33.459	-8.867	-8.088
Cyclopentane	-18.3	12.694	-28.193	-27.795
Cyclohexane	-29.49	19.855	-29.166	-32.505
NH ₃	-11.0	-21.245	-4.529	-9.125
CH ₃ NH ₂	-5.5	4.583	-1.034	-4.615
C ₂ H ₅ NH ₂	-11.3	2.007	-11.777	-15.708
<i>n</i> -C ₃ H ₇ NH ₂	-16.8	5.270	-16.776	-21.874
<i>iso</i> -C ₃ H ₇ NH ₂	-20.0	6.940	-14.718	-18.341
<i>tert</i> -BuNH ₂	-28.9	22.597	-6.757	-13.215
(CH ₃) ₂ NH	-4.4	33.488	5.535	4.310
(CH ₃) ₃ N	-5.7	68.316	19.136	21.027
N ₂ H ₄	22.8	1.792	21.307	3.166
CH ₃ NHNH ₂	22.6	24.637	23.102	8.366
(CH ₃) ₂ NNH ₂	20.1	56.978	33.039	22.242
CH ₃ NHNHCH ₃	22.0	50.517	27.588	15.019
H ₂ O	-57.8	-60.451	-55.677	-53.611
CH ₃ OH	-48.16	-33.099	-48.549	-50.573
C ₂ H ₅ OH	-56.21	-36.503	-60.167	-64.292
1-C ₃ H ₇ OH	-60.98	-33.325	-65.113	-70.417
2-C ₃ H ₇ OH	-65.19	-34.383	-66.008	-69.117
<i>tert</i> -BuOH	-74.7	-24.387	-63.509	-65.614
(CH ₃) ₂ O	-60.3	1.337	-33.905	-51.191
H ₂ O ₂	-32.5	-38.670	-32.720	-29.265

discrepancy with the experiment is partially cured by adjusting the corresponding β_{AB} parameter. Additionally, a special functional form for the core repulsion is introduced and parameterized in the MINDO/3 method for heavier atoms as well. The APSLG-MINDO/3 method by construction explicitly takes some fraction of correlation into account. Thus, the β_{AB} parameters must be readjusted.

To find the resonance parameters conforming to the APSLG form of the trial wave function we performed calculations on electronic structure for the test set of molecules containing hydrogen, carbon, nitrogen, and oxygen atoms. This set was taken from previous works devoted to the para-

meterization of semiempirical methods MNDO,³² AM1,³³ and PM3.³⁴ These articles also contain a set of experimental data on the heats of formation of the molecules involved. The parameters β_{AB} were adjusted to reproduce the experimental values of the heats of formation for the test set of molecules taken at their optimized structures by the APSLG-MINDO/3 method. The optimization criterion was based on the reproducing the energy increments for the homologic series rather than the heats of formation for each member of a series. The resulting set of the β_{AB} parameters of the APSLG-MINDO/3 method compared to those of the SCF-MINDO/3 method is given in Table II.

TABLE II.
Parameters β_{AB} of the APSLG-MINDO/3 and SCF-MINDO/3 Methods (eV).

A	B	β_{AB} (APSLG)	β_{AB} (MINDO/3)
H	H	0.243007	0.244770
H	C	0.315839	0.315011
H	N	0.353716	0.360776
H	O	0.414559	0.417759
C	C	0.427797	0.419907
C	N	0.429386	0.410886
C	O	0.486514	0.464514
N	N	0.379342	0.377342
O	O	0.657007	0.659407

This set slightly differs from that obtained in our previous work.²⁵ The similarity of the parameters of two methods using fundamentally different trial wave functions indicates some internal consistency of the MINDO/3 parameterization (see above). All subsequent calculations are made with use of the adjusted parameters β_{AB} (Table II). Table I contains, besides the experimental data, the heats of formation calculated by the APSLG-MINDO/3 method (column 4) and those calculated by the standard MINDO/3 method (column 5) at the respectively optimized molecular geometries. In the previous work²⁵ we have found that the total energies are approximately additive in the homologous series in agreement with experiment.^{35,36} The analysis of the analogous data for optimized geometries shows that the additivity is well fulfilled and, moreover, the difference between them tends to the same value ($-3613 \text{ kcal} \cdot \text{mol}^{-1}$) as in the case of the experimental molecular geometries. Data of Table I show that the difference between the heats of formation calculated by the APSLG-MINDO/3 method for the closest homologues—saturated hydrocarbons (excluding the methane–ethane pair) is about $5 \text{ kcal} \cdot \text{mol}^{-1}$ that is in a good agreement with the experimental data.³² The analogous increment calculated by the SCF-MINDO/3 method is larger than $6 \text{ kcal} \cdot \text{mol}^{-1}$. The deviation from the experiment by more than $1 \text{ kcal} \cdot \text{mol}^{-1}$ causes significant divergence between the experimental data on the heats of formation and the estimates by the SCF-MINDO/3 method increasing with the number of carbon atoms in the hydrocarbon molecule. Cyclic hydrocarbon, in their turn, do not manifest the additivity, and should not, because the strain energies for different cycles differ.

The total energy increment in the APSLG-MINDO/3 method for homologous normal amines rapidly converges to the above value characteristic for the normal alkanes. This additivity, i.e., the linear dependence of the system properties on its size allows to hope that the present semiempirical method based on the APSLG approximation can serve as a natural starting point for sequential derivation of numerous additive schemes known in the literature. The comparison with experiment for two computational methods (see Table I) shows that the APSLG-MINDO/3 and the SCF-MINDO/3 methods reach similar accuracy when address the heats of formation of organic compounds. At the same time we can note that the mean deviation in the heats of formation given by the formulae

$$\sigma = \frac{1}{N} \sum_{i=1}^N |\Delta H_f^{\text{theor}} - \Delta H_f^{\text{exp}}| \quad (27)$$

is 6.9 kcal/mol for the APSLG-MINDO/3 method and 7.6 kcal/mol for the SCF-MINDO/3 method for the test set of molecules. The choice of the criterion [eq. (27)] is stipulated by the special character of the data under consideration. The heats of formation of branched compounds are systematically overestimated in both the APSLG and SCF approaches. The intrabond correlations in the APSLG-MINDO/3 method does not cure this defect, which is common for both the MINDO/3 methods (and may be inherent for the MINDO/3 parameterization itself). The standard mean square deviation essentially overestimates the contribution from the data with systematic error. Moreover, these data give prevailing contribution. There are different possibilities to reduce the contribution from the data with systematic error. The choice of the mean deviation in the form eq. (27) is the simplest one.

The closeness of the calculated and experimental heats of formation cannot be the ultimate criterion for the quality of calculation. It is also essential to reach some consistency of the calculated minima positions on the potential energy surfaces with the experimental molecular geometries. Therefore, we do not restrict ourselves by the calculations at the selected points of the nuclear configuration space, and have implemented the procedure of the gradient search for the local minima of the total energy. The expressions for the energy gradients with respect to the nuclear displacements were obtained analytically. Using the adjusted values of the parameters β_{AB} , given in Table II, we have calculated the optimal geometry structures for a series of simple molecules. In the case of the hydrogen mole-

cule the length of the H—H bond is longer than the experimental value by 0.01 Å. The internuclear C—H separation in the methane molecule calculated by the APSLG-MINDO/3 method coincides with the experimental one with the accuracy of 0.002 Å (our theoretical value 1.092 Å, experiment—1.094 Å³²). At the same time, the calculated length of the C—C in ethane equals to 1.484 Å. This is smaller than the experimental value of 1.536 Å. However, for propane and other higher alkanes the discrepancy between the calculated and experimental bond lengths is slightly smaller (the improvement is by the 0.01 Å for propane and then the optimized lengths of the C—C bonds steadily tend to the experimental ones with the growth of the chain length). Notice that the standard SCF-MINDO/3 method gives for the length of the C—C bond in ethane the value of 1.474 Å and, therefore, the transition to the APSLG-MINDO/3 approach slightly improves it. The optimized length of the C=C bond in the unsaturated ethylene molecule equals to 1.335 Å, which is very close to the experimental value of 1.339 Å. The SCF-MINDO/3 method gives the value 1.313 Å, which is not as good agreement with the cited experimental value. A more interesting example is the optimization of geometry of quadricyclane and norbornadiene molecules, which are isomers and differ by the bond distribution. Starting from the same geometry but different connectivity schemes (distributions of chemical bonds) we obtain after the geometry optimization two significantly different geometrical structures—one close to the experimentally observed structure of quadricyclane [lengths of four single bonds in the cyclobutane ring of the quadricyclane molecule equal to 1.539 Å each (the experimental value for clathrate of quadricyclane with deoxycholic acid is 1.530 Å)] and norbornadiene, respectively [lengths of two double bonds equal to 1.342 Å (the experimental value for clathrate of norbornadiene with deoxycholic acid is 1.350 Å) but the distance between the adjacent carbon atoms of two different double bonds equals to 2.460 Å (the experimental value is 2.395 Å)]. Large discrepancy (0.065 Å) between experimental and calculated estimates for the distance between nonbonded C atoms is the consequence of bad description of branched compounds. The problems in the description of branched compounds results in the both overestimated heat of formation and incorrect valence angles for tertiary C atoms.

Reproducing the geometrical structure of the cyclobutane molecule is a complex problem for molecular mechanics and quantum chemistry. For

example, ref. 37 states that the proper description of cyclobutane requires large basis sets with polarization functions. The experimentally observed structure is nonplanar with the out-of-plane bending angle of 27 degrees. At the same time, most of the computational procedures (e.g., SCF-MINDO/3) lead to the planar structure. The analysis of the PES for the cyclobutane molecule by the APSLG-MINDO/3 method shows that the global minimum on the PES corresponds to the planar configuration as well. At the same time, the calculated PES has the local minimum for the nonplanar configuration with the bending angle of 22 degrees. It is possibly due to overestimation of valence angle bending energies.

As is shown, the APSLG-MINDO/3 method works not well enough when applied to branched compounds or to description of the geometric structure of cyclobutane. The possible way to improve the description of these substances is to take into account the interactions between bonds that are not regarded in the standard APSLG approach. The attempt to cover dispersion and delocalization corrections to the SLG wave function was made on the *ab initio* level in the framework of the coupled cluster method.^{21, 38, 39} It was found that the correlation energy accounted for by these corrections was significantly smaller than those accounted for by the APSLG approach itself. In the framework of the semiempirical APSLG-MINDO/3 method we also have made an attempt to improve it by taking into account perturbationally different types of interaction between bonds. The result of this work will be published elsewhere.⁴⁰

Discussion

As it is mentioned in the Introduction, quantum chemistry of large molecules faces an important problem of constructing calculation procedures with the growth of computational costs linear in N (N characterizes the size of the system). Solution of this problem requires applying that or another approach to separation of electronic variables. The standard way of doing this assumed in quantum chemistry is the SCF (one-electron, Hartree-Fock) approximation for the wave function of the ground state of electrons. The requirements for computational resources of the SCF procedure grow as N^3 and, hence, the latter cannot be considered as a basis for constructing methods linear in N . Moreover, the SCF approximation requires additional account

of correlation to become useful for description of bond cleavage. Of course, it is not clear *a priori* what is preferable: to take into account one-electron transfers (resonance) between different AOs with maximal completeness, and by this to get to a delocalized form of the one-electron states and to an incorrect description of the homolytic cleavage of the σ -bond, or to take into account pair electron correlations in the bonds, to get by this the correct behavior of the trial wave function under homolytic cleavage of bonds, and to be forced to consider the interbond one-electron transfers as corrections. At any rate, the second way preserves the prospects for the linear dependence of the computational costs on the system size and allows to recover traditional (and efficient) chemical concepts of bonds and lone pairs on the basis of direct variational calculation.

To demonstrate the computational capacities of the APSLG-MINDO/3 method we carried out calculations (for the fixed geometry) for a series of normal saturated hydrocarbons ranging from CH_4 to $\text{C}_{20}\text{H}_{42}$ by the APSLG-MINDO/3 and SCF-MINDO/3 methods. Figure 1 shows the dependence of the computation time (in seconds) on the number of carbon atoms in the homologue for the both methods. It can be easily seen that the dependence of computation time on the system size

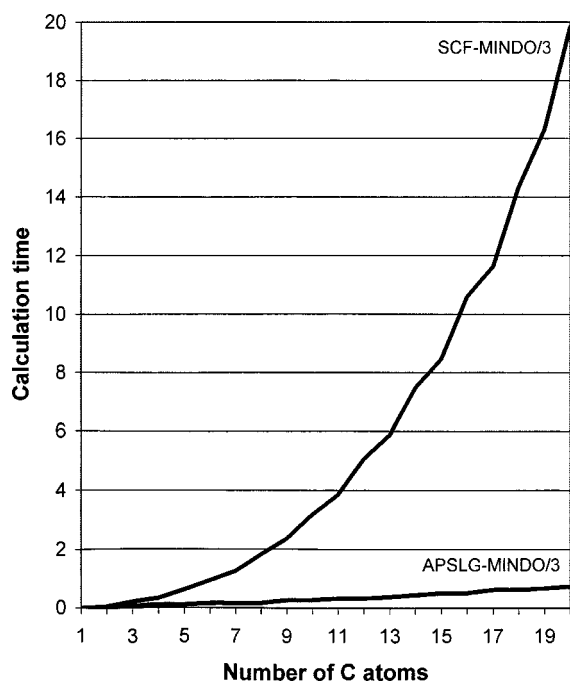


FIGURE 1. Comparison of calculation times for SCF-MINDO/3 and APSLG-MINDO/3 methods.

is essentially nonlinear in the case of the SCF approximation and is practically linear for the geminal approach. The APSLG-MINDO/3 procedure is faster than the SCF-MINDO/3 one already for the simplest hydrocarbons. In the case of the normal hydrocarbon $\text{C}_{20}\text{H}_{42}$ (its semiempirical calculation uses 122 basis functions), the computation time for two methods differs 30 times in favor of the APSLG approach.

The APSLG-MINDO/3 approach can be also applied to unsaturated organic molecules (but not to aromatic ones). In this case, two different geminals are assigned to each of the double bonds. In this context an old question about the character of each of two C—C bonds in ethylene⁴¹ (and other unsaturated hydrocarbons) can be readdressed. The APSLG-MINDO/3 method allows to construct two different APSLG wave functions for the ethylene molecule: one with two equivalent geminals for the double C=C bond, which corresponds to equivalent (bent-type or “banana”) bonds between the carbon atoms, and another one with two nonequivalent geminals which correspond to σ - and π -bonds. The initial conditions of the energy minimization turn out to be very important. The type of double C=C bond (bent or σ - π -separated) remains unchanged in the course of optimization. In the case of the bent-type bonds, the optimal value of energy is higher than that for the σ - π -separated bond, i.e., the energy calculation with use of the APSLG-MINDO/3 approach and optimized molecular geometry shows that the electronic structure with the nonequivalent σ - and π -bonds is energetically favorable. However, the difference is very small, because the local minimum on the energy surface corresponding to the σ - π double bond is merely by less than $1 \text{ kcal}\cdot\text{mol}^{-1}$ deeper than that of the bent-type bond. The optimized bond length for the bent-type double bond is also only slightly (by 0.0003 \AA) larger than that for the σ - π -double bond. The question about the preferability of one or another type of double bond was also studied in ref. 42 by the full GVB method. In the case of the ethylene molecule, the conclusion about closeness of the energies for the two ways of bonding was drawn. The calculations with the frozen core⁴² have shown that the σ - π -separation is slightly more preferable in agreement with our results.

The proposed approach makes it possible to determine naturally such bond characteristics as ionic and covalent contributions and polarity of bond. We can rewrite the expression for each

geminal as:²¹

$$g_m^+ = \frac{I_m}{\sqrt{2}} \left[\sqrt{1 + \lambda_m} r_{m\alpha}^+ r_{m\beta}^+ + \sqrt{1 - \lambda_m} I_{m\alpha}^+ I_{m\beta}^+ \right] + \frac{C_m}{\sqrt{2}} [r_{m\alpha}^+ I_{m\beta}^+ + I_{m\alpha}^+ r_{m\beta}^+], \quad (28)$$

where I_m is the amplitude of the ionic contribution to the geminal, C_m and λ_m measure, respectively, the bond covalency and polarity and the normalization condition obviously leads $I_m^2 + C_m^2 = 1$. Obtained bond characteristics allow determination of charges on the atoms. Then for each electron pair (bond) we can determine the electron density on the right and left atoms of the m th bond, respectively:

$$\frac{C_m^2 + I_m^2(1 + \lambda_m)}{2}, \quad \frac{C_m^2 + I_m^2(1 - \lambda_m)}{2}. \quad (29)$$

For each atom the sum of the contributions eq. (29) over all its geminals including electron lone pairs gives the electron density on the atom, and consequently, the effective atomic charge. Table III contains ionic and covalent contributions and polarities of the bonds and atomic charges for some simple organic compounds calculated for the optimized geometries. The covalent contribution always prevails over the ionic one for all considered molecules. The ratio of the covalent and ionic contributions only slightly depends on the molecule type. For example, the weights of covalent con-

figuration differ for highly polar HF and unpolar H_2 molecules only by 0.03. The bond polarities themselves qualitatively correspond to relative electronegativities of different atoms accepted in the literature. The effective atomic charges can be compared with the charge distributions obtained by other methods. The APSLG-MINDO/3 method predicts a shift of electron density in methane from hydrogen atom to carbon atom, while the SCF-MINDO/3 gives the reverse picture in contradiction with concepts accepted in organic chemistry.⁴³ It should be noted that the C—N bond proves to be almost nonpolar (in the above sense). The parameters of the C—H bond in methane and the N—H bond in ammonia are very similar (see Table III).

Determination of hybridization for the HOs on the basis of variational principle is an important feature of the proposed approach. As it can be expected in methane, the sp^3 -hybridization is recovered under the variational determination. The HO of the F—H bond in the HF molecule is almost pure p -orbital (more precisely, the hybridization of this orbital can be represented as $sp^{39.0}$, which demonstrates an extreme unevenness of the hybridization scale). The HOs of electron lone pairs form two pure p -functions, and one almost pure s -function. There is an interesting question about the form (hybridization) of lone pairs in the molecules that have more than one lone pair. The answer on this question is

TABLE III. Charges, Ionic and Covalent Contributions, and Polarities of Chemical Bonds Calculated by the APSLG-MINDO/3 Method.

Molecule	Bond A—B	Ionic Contribution I^2	Covalent Contribution C^2	Bond Polarity λ	Charge A	Charge B
H_2	H—H	0.434	0.566	0	0	0
CH_4	C—H	0.415	0.585	-0.157	-0.260	0.065
C_2H_6	C—C	0.411	0.589	0	-0.126	-0.126
	C—H	0.411	0.589	-0.102	-0.126	0.043
N_2H_4	N—N	0.363	0.637	0	-0.114	-0.114
	N—H	0.415	0.585	-0.137	-0.114	0.057
NH_3	N—H	0.408	0.592	-0.111	-0.135	0.045
CH_3NH_2	C—N	0.398	0.602	0.051	-0.145	-0.142
	C—H	0.411	0.589	-0.133	-0.145	0.055
	N—H	0.415	0.585	-0.148	-0.142	0.061
HF	F—H	0.470	0.530	-0.699	-0.329	0.329
CH_3F	C—H	0.416	0.584	-0.147	0.032	0.061
	C—F	0.386	0.614	0.556	0.032	-0.215
H_2O	O—H	0.463	0.537	-0.523	-0.484	0.242

that for the method under consideration the mixing (quantum mechanical interference) of the HOs of different electron lone pairs (not bonds) that are centered on the same atom does not change the electronic energy. For example, in the case of water molecule, the degree of mixing between lone pairs depends on the initial conditions of optimization because this mixing does not affect the energy.

Despite the fact that the amplitudes of different two-electron states in the bond geminal expansions in methane and ammonia molecules are similar (see below), the HOs in ammonia differ significantly from the sp^3 ones characteristic for methane. The analysis of the AO to HO transformation matrix reveals the $sp^{7.14}$ -hybridization for the N—H bonds and the $sp^{0.58}$ -hybridization for the lone pair.

The HOs of the carbon atoms in ethane slightly deviate from the sp^3 -form. The p -character is slightly more pronounced for the C—H bonds. The HOs of the C—C bond are the $sp^{2.26}$ hybrids but the C—H bonds are the $sp^{3.33}$ ones. Directions of maximal density for the HOs of the C—C bonds in the cyclopropane molecule do not coincide with those of the bonds themselves. As for the HF molecule, the p -character of the HO participating in the chemical bond increases, but the electron lone pair has essentially the s -character. The C—F bond in CH_3F has essentially covalent character, and it is less polar than the H—F bond in HF. The amplitudes of the geminal expansion of the C—H bond are not very sensitive to its environment, and are the same for CH_4 , C_2H_6 , and CH_3F . The C—H bonds in C_2H_6 and CH_3F differ mainly due to hybridization of the orbitals involved. It is interesting that the HOs of fluorine in CH_3F are pretty close to those in HF ($sp^{37.9}$ vs. $sp^{39.0}$).

Conclusions

A semiempirical method of calculations on molecular electronic structure is developed in this work. The method uses the trial wave function of the antisymmetrized product of strictly localized geminals approximation. The calculations with the standard MINDO/3 parameterization have revealed that the APSLG wave function has quality comparable with that of the SCF version of the MINDO/3 approximation for the range of characteristic intramolecular interatomic distances and, moreover, have correct asymptotical behavior in the limit of cleaved bonds. It has been demonstrated that the slight modification of the pair resonance parameters β_{AB} makes it possible to obtain somewhat better agreement of the heats of formation

and the equilibrium geometries calculated by the APSLG-MINDO/3 method with the experimental data than the SCF-MINDO/3 procedure permits. The APSLG-MINDO/3 method satisfies the $O(N)$ -scalability condition and permits calculating the electronic properties of very large organic molecules. In the framework of the present approach based on the variational wave function of the APSLG approximation, it is possible to recover the intuitive chemical concepts like bonds, their ionic and covalent components, polarities, hybrid orbitals, and lone pairs, which are not so transparent in the SCF-type approaches. Also, the form of the electron lone pairs and bond hybrid orbitals is determined unequivocally on the basis of the variational principle.

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