Semiempirical implementation of APSLG approach

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Abstract

The method using the trial wave function in the form of the antisymmetrized product of strictly localized geminals (APSLG) is developed on the semiempirical level. The Hamiltonian is taken in the MINDO/3 form but with resonance parameters slightly reparameterized. The equilibrium geometries and heats of formation of a series of organic compounds are calculated in its framework and compared with the experimental data and results of the SCF-MINDO/3 approach. Two different schemes of calculation of the ionization potentials are developed and thoroughly tested. The $O(N)$-scalability and acceptable accuracy are proven for the proposed APSLG-MINDO/3 method.

1 Introduction

Nowadays, the problem of relative preference of either localized or delocalized description of the molecules remains unsolved [?]. The localized picture is closer to the usual chemists' concepts and operates if not the quantities of obvious chemical sense but at least with those experimentalists are used to. At the same time the delocalized picture based on the Hartree-Fock approximation became our days more elaborated and can be applied to a wide range of molecules. In this work we describe our efforts in developing an approach employing a localized wave function but possessing some obvious advantages as compared to the delocalized approach of a similar level of complexity and accuracy.

The localized description can be obtained for molecular electronic structure either *a posteriori* or *a priori*. The first approach usually uses the results of a previously performed delocalized Hartree-Fock calculation and achieves the localization by unitary transformations restricted to the space of the occupied molecular orbitals [?, ?, ?, ?, ?]. These methods are normally used either for interpretation of the results of the delocalized approaches in chemical terms or as a starting point for subsequent account of electron correlations. *A priori* approach provides more possibilities. The localization in these methods is usually achieved by the proper choice of the underlying basis functions and of the form of the N-electron trial wave function. For example, the method of strictly localized molecular orbitals (SLMO) [?] takes the trial wave function in the form of Slater determinant with the SLMO's assigned either to chemical bonds or lone pairs and expressed through the several basis hybrid orbitals (HO's) assigned to the same bond (lone pair). This form of the wave function significantly reduces the computational costs but the method of SLMO is proved to be poorer than the standard Hartree-Fock method because the so-called tails (non-local part) of the one-electron wave functions are totally neglected.

Another disadvantage of the SLMO approach is that the large intrabond correlations are not taken into account. The PCILO approach [?] takes them into account perturbationally, but the large value of the corrections does not allow for the perturbation treatment of intrabond correlations. However, the intrabond correlations can be covered variationally without significant complications by using the geminal form of the bond building blocks for the molecular electronic wave function. The concept of geminals (two-electron wave functions) was originally introduced by V.A. Fock [?, ?]. The wave function of the molecule with $2n$ electrons can be represented by the antisymmetrized product of spin geminals (APSG) [?]. The representation of the electronic wave function of organic molecules as constructed of bond two-electron building blocks was elaborated in the work [?] and implemented on the *ab initio* level by different authors [?, ?]. At the same time this method has been applied only to a very small set of molecules and the results obtained do not allow to estimate the quality of this approach.

Semiempirical implementation allows for some useful expansion of the local geminal-based method. It is well known how important large molecules (especially biological) are. *Ab initio* approaches (even on the Hartree-Fock level) can not be applied to these systems due to incredible computational costs, which grow proportionally to $N^4 \div N^7$ with the increasing of the system size (where N is the number of basis one-electron functions). The costs of semiempirical methods grow as the N^3 due to diagonalization of the Fock matrix. Even this growth is very rapid when the calculations on biomolecules are concerned. Therefore, an important development would be a construction of methods with linear dependence of the computational costs on the system size (the so-called $O(N)$ methods). Such dependence is achieved, for example, by ignoring some matrix elements of the Fock matrix that results in avoiding the diagonalization of $N \times N$ matrix [**?**, **?**] or by using pseudodiagonalization instead of diagonalization. In the case of the neglect of matrix elements it is not counterbalanced. Incidentally, avoiding the diagonalization of $N \times N$ matrix and, therefore, the approximately linear dependence of the computational costs on the system size for the semiempirical approaches can be reached by balanced local description of the molecular electronic structure. The typical examples of this statement are the SLMO and PCILO methods in their semiempirical implementation. The geminal method of the local description of the electronic structure provides the possibility to obtain the computationally fast variational method with proper account of intrabond correlations.

The general term "geminal approach" can be further specified as the antisymmetrized product of strictly localized geminals (APSLG) [?]. It is close to other pair theories, for example, to the GVB theories [**?**]. The comparison of the APSLG and GVB *ab initio* implementations exemplified by methane dissociation is given in Refs. [?, ?]. It is stressed in Ref. [?] that the geminal approach is particularly well adapted to the study of ion-molecule reactions and can be applied to an additive separation of the total electronic energy into components associated with the various bonds and lone pairs. At the same time it is essential that only a limited class of molecules can be fairly described by the electron pair picture. The structure of inorganic and many organic (for example, aromatic) compounds does not fit into the classical picture of definite chemical bonds and electron pairs dating back to Boutleroff [**?**] and Lewis [**?**].

The important aspect in the derivation of *a priori* local approaches is the method they employ to obtain the HO's. The latter are linear combinations of several AO's centered on the same atom. There are different approaches which are based either on the geometric consideration when one attempts to figure out the HO's directions towards the other end of the bond [?] or on the maximization of the overlap between the HO's, belonging to different ends of the bond [?]. These criteria give quite different results for strained cyclic hydrocarbons (for example, for cyclopropane). It results in an ambiguity of the electronic structure evaluation. At the same time it is obvious that the total electronic energy depends on the coefficients of the HO's expansion through the initial AO basis set. The expansion coefficients are the parameters of the wave function and, hence, must be obtained variationally.

Another aspect of chemical behavior of molecular systems is related to the relative ease of electron extraction, *i.e.* to their ionization potentials (IP's). Their numerical estimates are important not only for interpreting photoelectron spectra but also for predicting chemical reactivity. It is a common practice to estimate the IP's in the Hartree-Fock approximation with use of the Koopmans' theorem. The approaches based on the configuration interaction schemes are not widely used. The success of the molecular orbitals methods in the explanation of the form of photoelectron spectra (especially, of the degeneracy of the ionic states which coincide with the orbital degeneracies) have led to a widely spread belief that the form of the photoelectron spectra confirms the orbital (and thus ultimately the delocalized) concept of molecular electronic structure and also the one-electron character of the molecular wave functions. The ionic states are usually delocalized (it is clearly seen in the case of highly symmetric systems). Therefore, it would be interesting to see, whether the method based on the local description of the molecular electronic structure can reproduce the form of the photoelectron spectra.

This communication is devoted to the elaboration of the semiempirical variant of the APSLG approach and the systematical investigation of its properties. As a starting point of our considerations we have chosen the well known MINDO/3 form of the Hamiltonian and its set of parameters [?]. As it is noted in Ref. [?], the one-center parameters of the MINDO/3 method are close to those estimates derived from the spectra of free atoms and ions [?] and/or those made in the framework of the theory of the effective valence shell Hamiltonian [?]. This allows to conclude that the incorrect asymptotic behavior of the trial SCF wave function is compensated within the MINDO/3 approach by the two-center parameters of the MINDO/3 method whereas the one-center parameters are quite universal and are not strictly bound to the form of the trial electronic wave function.

2 Theory

2.1 Wave function and the Hamiltonian

We use the second quantization technique which is convenient for deriving the form of the electronic energy. The AO basis set is transformed into the HO one by unitary transformations of four (one of s-type and three of p-type) orbitals on each "heavy" (non hydrogen) atom. Each of the HO's thus obtained is uniquely assigned to a chemical bond or a lone pair. Therefore, the HO's can be labelled as $|r_m\rangle$ and $|l_m\rangle$ (right and left HO's of the m-th bond). We use the notation $|t_m\rangle$ for the both $|r_m\rangle$ and $|l_m\rangle$ when the type of the orbital is not specified. The operators annihilating electron with the spin projection σ on the HO's can be presented as

$$t_{m\sigma} = \sum_{i \in A} h_{mi}^{A} a_{i\sigma}, \tag{1}$$

where 4×4 matrices $h^A \in SO(4)$ mix the AO's of the heavy atom A. The geminal representing a single chemical bond is constructed from two HO's (or four spin-HO's) assigned to this bond. We consider only singlet two-electron configurations. Therefore, the geminal is a superposition of two ionic and one covalent (Heitler-London type) configurations with variable amplitudes:

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

In the case of an electron lone pair only one HO is assigned to it. Therefore, only the ionic (in the above sense) contribution to the geminal remains. Without the loss of generality we assume that this contribution is

$$g_m^+ = r_{m\alpha}^+ r_{m\beta}^+. \tag{3}$$

The geminals are normalized and orthogonal due to the previously assumed orthogonality of the HO's:

$$\langle 0| g_m g_{m'}^+ |0\rangle = u_m u_{m'} + v_m v_{m'} + 2 w_m w_{m'} = \delta_{mm'}. \tag{4}$$

The electronic wave function is the antisymmetrized product of these geminals:

$$|\Phi\rangle = \prod_m g_m^+ |0\rangle . \tag{5}$$

The wave function $|\Phi\rangle$ is normalized and hence the electronic energy in the APSLG approximation is

$$E = \langle\Phi| H |\Phi\rangle . \tag{6}$$

The MINDO/3 Hamiltonian in the atomic (or hybrid) basis is a sum of one- and two-center contributions:

$$H = \sum_A H_A + \frac{1}{2} \sum_{A \neq B} H_{AB}. \tag{7}$$

The construction of the APSLG method requires the transformation of the molecular integrals from AO basis to the HO one. The attraction of electrons to its own core transforms as:

$$U_m^t = \sum_{i \in A} \left(h_{mi}^A\right)^2 U_i(A), \tag{8}$$

where $i \in \{s, p_x, p_y, p_z\}$. The electron attraction to other cores and repulsion of electrons on the orbitals of different atoms are invariant under the basis transformation used. Only the Coulomb and exchange integrals of the electron repulsion on the same atom are known in the AO basis. The transformation to the HO basis generates other types of integrals. Nevertheless it must be stressed that the expression for the electronic energy requires only the Coulomb and exchange repulsion integrals also in the hybrid basis. The transformation reads

$$\begin{array}{c}
\left(\begin{smallmatrix} t_1 & t_2 \\ m_1 & m_2 \end{smallmatrix} \mid \begin{smallmatrix} t_3 & t_4 \\ m_3 & m_4 \end{smallmatrix} \right)^A = \sum_{i \in A} h_{m_1 i}^A h_{m_2 i}^A h_{m_3 i}^A h_{m_4 i}^A (ii \mid ii)^A + \\
+ \sum_{i<j \in A} (ii \mid jj)^A (h_{m_1 i}^A h_{m_2 i}^A h_{m_3 j}^A h_{m_4 j}^A + \\
+ h_{m_1 j}^A h_{m_2 j}^A h_{m_3 i}^A h_{m_4 i}^A) + \sum_{i<j \in A} (ij \mid ij)^A \times \\
\times (h_{m_1 i}^A h_{m_2 j}^A h_{m_3 i}^A h_{m_4 j}^A + h_{m_1 i}^A h_{m_2 j}^A h_{m_3 j}^A h_{m_4 i}^A + \\
+ h_{m_1 j}^A h_{m_2 i}^A h_{m_3 i}^A h_{m_4 j}^A + h_{m_1 j}^A h_{m_2 i}^A h_{m_3 j}^A h_{m_4 i}^A).
\end{array} \tag{9}$$

The resonance integral (corresponding to a one-electron transfer) between the HO t_{m_1} (centered on the atom A) and the HO t'_{m_2} (centered on the atom B) is expressed through the resonance integrals in the AO basis:

$$\beta^{AB}_{t_{m_1}t'_{m_2}} = \sum_{i\in A}\sum_{j\in B} h^{A}_{m_1 i} h^{B}_{m_2 j} \beta^{AB}_{ij}. \tag{10}$$

The MINDO/3 Hamiltonian in the hybrid basis has the form of Eq. (**??**) with the following contributions:

$$\begin{array}{c}
H_A = \sum\limits_{\substack{t_m\in A\\ \sigma}} \left(U^t_m - \sum\limits_{B\neq A} \gamma_{AB} Z_B \right) t^+_{m\sigma} t_{m\sigma} - \\
- \sum\limits_{\substack{t_{m_1},t'_{m_2}\in A\\ m_1<m_2}} \sum\limits_{\sigma} \beta^{AA}_{t_{m_1}t'_{m_2}} \left(t^+_{m_1\sigma} t'_{m_2\sigma} + h.c. \right) + \\
+\frac{1}{2} \sum\limits_{\substack{t_{m_1},t'_{m_2}\in A\\ t''_{m_3},t'''_{m_4}\in A}} \sum\limits_{\sigma\tau} \left(\begin{smallmatrix} t & t' \\ m_1 & m_2 \end{smallmatrix} \mid \begin{smallmatrix} t'' & t''' \\ m_3 & m_4 \end{smallmatrix} \right)^A t^+_{m_1\sigma} t''^+_{m_3\tau} t'''_{m_4\tau} t'_{m_2\sigma}, \\
H_{AB} = - \sum\limits_{\substack{t_{m_1}\in A\\ t'_{m_2}\in B}} \sum\limits_{\sigma} \beta^{AB}_{t_{m_1}t'_{m_2}} \left(t^+_{m_1\sigma} t'_{m_2\sigma} + h.c. \right) + \\
+\gamma_{AB} \sum\limits_{\substack{t_{m_1}\in A\\ t'_{m_2}\in B}} \sum\limits_{\sigma\tau} t^+_{m_1\sigma} t'^+_{m_2\tau} t'_{m_2\tau} t_{m_1\sigma},
\end{array} \tag{11}$$

where $h.c.$ denotes the hermitean. conjugation.

2.2 Electronic energy

To obtain an expression for the electronic energy in the APSLG approximation we evaluate the elements of the density matrix for the APSLG N-electron trial wave function. The required one-geminal matrix elements of one- and two-electron density matrices are spin independent and can be denoted as

$$\begin{array}{c}
P^{tt'}_m = \langle 0 |\, g_m t^+_{m\sigma} t'_{m\sigma} g^+_m \,| 0 \rangle\,, \\
\Gamma^{tt'}_m = \langle 0 |\, g_m t^+_{m\sigma} t'^+_{m-\sigma} t'_{m-\sigma} t_{m\sigma} g^+_m \,| 0 \rangle\,.
\end{array} \tag{12}$$

These matrix elements can be directly evaluated

$$\begin{array}{c}
P^{rr}_m = u^2_m + w^2_m,\ P^{ll}_m = v^2_m + w^2_m, \\
P^{rl}_m = P^{lr}_m = (u_m + v_m) w_m, \\
\Gamma^{rr}_m = u^2_m,\ \Gamma^{ll}_m = v^2_m,\ \Gamma^{rl}_m = \Gamma^{lr}_m = w^2_m.
\end{array} \tag{13}$$

The contribution to the energy from the interaction of electrons with the cores in its turn is expressed in terms of diagonal elements of the one-electron density matrix:

$$E_1 = 2 \sum_A \sum_{t_m \in A} \left(U_m^t - \sum_{B \neq A} \gamma_{AB} Z_B \right) P_m^{tt}. \tag{14}$$

The one-center Coulomb repulsion of electrons contributes to the energy:

$$\begin{gathered} E_{coul}^{(1)} = \sum_A \sum_{t_m \in A} \left({t \atop m} {t \atop m} \mid {t \atop m} {t \atop m} \right)^A \Gamma_m^{tt} + \\ +2 \sum_A \sum_{\substack{t_{m_1}, t'_{m_2} \in A \\ m_1 < m_2}} \left[2 \left({t \atop m_1} {t \atop m_1} \mid {t' \atop m_2} {t' \atop m_2} \right)^A - \left({t \atop m_1} {t' \atop m_2} \mid {t' \atop m_2} {t \atop m_1} \right)^A \right] P_{m_1}^{tt} P_{m_2}^{t't'} \end{gathered} \tag{15}$$

through both the one- and two-electron density matrices. The contribution to the energy from the resonance interaction (one-electron interatomic transfers) is:

$$E_{res} = -4 \sum_m \beta_{r_m l_m}^{R_m L_m} P_m^{rl}, \tag{16}$$

where we use notation R_m for the right- and L_m for the left-end atom of the m-th bond. The contribution from the Coulomb interaction of electrons located on different atoms (two-center) to the total energy can be written as:

$$E_{coul}^{(2)} = 4 \sum_{A<B} \gamma_{AB} \sum_{\substack{t_{m_1} \in A \\ t'_{m_2} \in B \\ m_1 \neq m_2}} P_{m_1}^{tt} P_{m_2}^{t't'} + \sum_m \gamma_{R_m L_m} \Gamma_m^{rl} \tag{17}$$

and also involves the matrix elements of both one- and two-electron density matrices.

Finally, the electronic energy is a sum of the above four terms:

$$E = E_1 + E_{coul}^{(1)} + E_{res} + E_{coul}^{(2)}. \tag{18}$$

The molecular integrals entering the above expressions Eqs. (**??**)-(**??**) depend on the elements of the $SO(4)$ matrices h^A. The $SO(4)$ group transformations depend in their turn on six parameters each [**?**], which define six sequential rotations in two-dimensional subspaces of each four-dimensional space spanned by the AO's of each heavy atom A. Thus the total number of parameters of the wave function to be varied is $6L+2M$, where L is the number of heavy atoms and M is the number of geminals, representing chemical bonds (not the lone electron pairs). Each iteration step includes optimization of the HO parameters (six angles per heavy atom) 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 HO's the amplitudes of the geminals are determined. The alternating optimizations are consistent and the convergence is rapidly achieved in all variables. To obtain the optimal parameters of the matrices h^A we use the direct gradient minimization of the energy. At the same time the optimal geminal amplitudes are obtained by diagonalizing the effective bond Hamiltonians. The effective Hamiltonian for the k-th bond can be written as

$$\begin{aligned} H_k^{eff} = W_{1k}^r \sum_\sigma r_{k\sigma}^+ r_{k\sigma} + W_{1k}^l \sum_\sigma l_{k\sigma}^+ l_{k\sigma} + W_{1k}^{rl} \sum_\sigma \left(r_{k\sigma}^+ l_{k\sigma} + l_{k\sigma}^+ r_{k\sigma} \right) + \\ + W_{2k}^r r_{k\alpha}^+ r_{k\beta}^+ r_{k\beta} r_{k\alpha} + W_{2k}^l l_{k\alpha}^+ l_{k\beta}^+ l_{k\beta} l_{k\alpha} + W_{2k}^{rl} \sum_\sigma r_{k\sigma}^+ l_{k-\sigma}^+ l_{k-\sigma} r_{k\sigma}, \end{aligned} \tag{19}$$

with

$$\begin{aligned} W_{1k}^r &= U_k^{R_k} - \sum_{B \neq R_k} \gamma_{R_k B} Z_B + 2 \sum_{B \neq R_k} \gamma_{R_k B} \sum_{\substack{t_n \in B \\ n \neq k}} P_n^{tt} + \\ &+ \sum_{\substack{t_n \in R_k \\ n \neq k}} \left[2 \left(\begin{smallmatrix} r & r \\ k & k \end{smallmatrix} \mid \begin{smallmatrix} t & t \\ n & n \end{smallmatrix} \right)^{R_k} - \left(\begin{smallmatrix} r & t \\ k & n \end{smallmatrix} \mid \begin{smallmatrix} t & r \\ n & k \end{smallmatrix} \right)^{R_k} \right] P_n^{tt}, \\ W_{1k}^l &= U_k^{L_k} - \sum_{B \neq L_k} \gamma_{L_k B} Z_B + 2 \sum_{B \neq L_k} \gamma_{L_k B} \sum_{\substack{t_n \in B \\ n \neq k}} P_n^{tt} + \\ &+ \sum_{\substack{t_n \in L_k \\ n \neq k}} \left[2 \left(\begin{smallmatrix} l & l \\ k & k \end{smallmatrix} \mid \begin{smallmatrix} t & t \\ n & n \end{smallmatrix} \right)^{L_k} - \left(\begin{smallmatrix} l & t \\ k & n \end{smallmatrix} \mid \begin{smallmatrix} t & l \\ n & k \end{smallmatrix} \right)^{L_k} \right] P_n^{tt}, \\ W_{1k}^{rl} &= -\beta_{r_k l_k}^{R_k L_k}, \ W_{2k}^{rl} = \gamma_{R_k L_k}, \\ W_{2k}^r &= \left(\begin{smallmatrix} r & r \\ k & k \end{smallmatrix} \mid \begin{smallmatrix} r & r \\ k & k \end{smallmatrix} \right)^{R_k}, \ W_{2k}^l = \left(\begin{smallmatrix} l & l \\ k & k \end{smallmatrix} \mid \begin{smallmatrix} l & l \\ k & k \end{smallmatrix} \right)^{L_k}. \end{aligned} \tag{20}$$

In the basis of the two-electron states contributing to the k-th geminal it becomes a 3×3 matrix, whose lowest eigenvalue and the amplitudes characterizing this eigenstate can be easily found.

2.3 Ionization potentials

Now we consider the configuration interaction scheme for obtaining the vertical ionization potentials. The construction of configurations is conveniently done in the basis of bond orbitals (BO's). These orbitals (bonding b_m and antibonding a_m) are defined in terms of the HO's by:

$$\left\{ \begin{array}{l} b_{m\sigma} = x_m l_{m\sigma} + y_m r_{m\sigma} \\ a_{m\sigma} = -y_m l_{m\sigma} + x_m r_{m\sigma} \end{array} \right. . \tag{21}$$

The normalization condition requires $x_m^2 + y_m^2 = 1$. The BO's obey the usual and L-orthogonality conditions ($c, d \in \{a, b\}$):

$$\langle 0| c_{m\sigma} d^+_{m\sigma} |0\rangle = \langle 0| g_m c_{m\sigma} d^+_{m\sigma} g^+_m |0\rangle = \delta_{cd}. \tag{22}$$

In the basis of BO's the geminals have a simple form

$$g^+_m = U_m b^+_{m\alpha} b^+_{m\beta} + V_m a^+_{m\alpha} a^+_{m\beta}, \tag{23}$$

where $U_m^2 + V_m^2 = 1$.

Two approaches to constructing the ionized configurations are thinkable. The first way is that one electron is extracted from a geminal and the remaining electron occupy either bonding or antibonding orbital. All other bonds are represented by their ground state geminals. The many-electron ($(N-1)$-electron) configurations in this case are:

$$\left(\prod_{k \neq m} g^+_k \right) c^+_{m\sigma} |0\rangle . \tag{24}$$

The second approach to construct the basis configurations is to extract an electron from a geminal, but then to readjust the remaining geminals to the extra potential induced by a hole. It takes into account the polarization of remaining geminals by a hole. The polarized geminals are obtained by solving the eigenvalue problem

$$H^{eff}_{kc_{m\tau}} \tilde{g}_{kc_{m\tau}} = \tilde{\epsilon}_{kc_{m\tau}} \tilde{g}_{kc_{m\tau}} \tag{25}$$

(where $\tilde{g}_{kc_{m\tau}}$ is the k-th geminal polarized by a hole on the m-th geminal with remaining electron on the bond spin orbital $|c_{m\tau}\rangle$ ($|c_m\rangle$=$|a_m\rangle$ or $|b_m\rangle$)) and by taking the lowest eigenstate. The effective Hamiltonian for a geminal interacting with an extra attracting potential induced by the hole in some other geminal differs from that of Eq. (**??**) and (**??**) and can be presented as:

$$H^{eff}_{kc_{m\tau}} = H^{core}_{kc_{m\tau}} + H^{1,intra}_{kc_{m\tau}} + H^{1,inter}_{kc_{m\tau}} + H^{res}_{kc_{m\tau}} + H^{2,intra}_{kc_{m\tau}} + H^{2,inter}_{kc_{m\tau}}, \tag{26}$$

where the attraction of electrons to the core gives:

$$H^{core}_{kc_m\tau} = \sum_{t\in\{r,l\}} \left(U_k^{T_k} - \sum_{B\neq T_k} \gamma_{T_k B} Z_B \right) \sum_\sigma t^+_{k\sigma} t_{k\sigma}. \tag{27}$$

The intrabond repulsion of electrons on the same atom contributes:

$$H^{1,intra}_{kc_m\tau} = \sum_{t\in\{r,l\}} \begin{pmatrix} t\ t & | & t\ t \\ k\ k & | & k\ k \end{pmatrix}^{T_k} t^+_{k\alpha} t^+_{k\beta} t_{k\beta} t_{k\alpha}, \tag{28}$$

while the interbond one-center repulsion of electrons can be written as:

$$\begin{aligned} H^{1,inter}_{kc_m\tau} &= \sum_{t\in\{r,l\}} \sum_{\substack{t'_q\in T_k \\ q\neq k,m}} \left[2 \begin{pmatrix} t\ t & | & t'\ t' \\ k\ k & | & q\ \ q \end{pmatrix}^{T_k} - \begin{pmatrix} t\ t' & | & t'\ t \\ k\ q & | & q\ k \end{pmatrix}^{T_k} \right] P^{t't'}_q \sum_\sigma t^+_{k\sigma} t_{k\sigma} + \\ &+ \sum_{tt'\in\{r,l\}} \delta_{T_k T'_m} (\eta^{t'c}_m)^2 \left[\begin{pmatrix} t\ t & | & t'\ t' \\ k\ k & | & m\ m \end{pmatrix}^{T_k} \sum_\sigma t^+_{k\sigma} t_{k\sigma} - \begin{pmatrix} t\ t' & | & t'\ t \\ k\ m & | & m\ k \end{pmatrix}^{T_k} t^+_{k\tau} t_{k\tau} \right], \end{aligned} \tag{29}$$

where

$$\eta^{tc}_m(t\in\{r,l\}\,; c\in\{a,b\}) = \left\langle 0 \left| t_{m\sigma} c^+_{m\sigma} \right| 0 \right\rangle \tag{30}$$

and it is simply the coefficient of the HO $|t_m\rangle$ in the expansion for the BO $|c_m\rangle$ Eq. (**??**). The resonance contribution is:

$$H^{res}_{kc_m\tau} = -\beta^{R_k L_k}_{r_k l_k} \sum_\sigma \left(r^+_{k\sigma} l_{k\sigma} + l^+_{k\sigma} r_{k\sigma} \right). \tag{31}$$

The Coulomb repulsion between electrons on the different atoms is divided into the intrabond

$$H^{2,intra}_{kc_m\tau} = \gamma_{R_k L_k} \sum_\sigma r^+_{k\sigma} l^+_{k-\sigma} l_{k-\sigma} r_{k\sigma} \tag{32}$$

and the interbond

$$\begin{aligned} H^{2,inter}_{kc_m\tau} &= \sum_{t\in\{r,l\}} \sum_{B\neq T_k} \gamma_{T_k B} \times \\ \times \sum_{\substack{t'_q\in B \\ q\neq k}} &\left[\delta_{qm} (\eta^{t'c}_m)^2 + 2(1-\delta_{qm}) P^{t't'}_q \right] \sum_\sigma t^+_{k\sigma} t_{k\sigma}. \end{aligned} \tag{33}$$

contributions. After the adjusted (polarized) geminals are calculated according to Eqs. (**??**)-(**??**) they can be used for constructing many-electron basis states:

$$\left(\prod_{k \neq m} \tilde{g}^{+}_{k b_{m\sigma}} \right) c^{+}_{m\sigma} \left| 0 \right\rangle . \tag{34}$$

The vertical ionization potentials and the eigenstates of the ion are obtained by the diagonalization of the operator $\mathbf{H} - E_0 \mathbf{I}$ (E_0 is the APSLG energy of the ground state) in one of configuration basis sets ((**??**) or (**??**)). For the case of non-polarized geminals (**??**) the matrix elements of the operator $\mathbf{H} - E_0 \mathbf{I}$ can be relatively easily written. The MINDO/3 Hamiltonian does not contain the matrix elements of interaction of many-electron states (**??**) with different spin projections. Therefore, the matrix of the Hamiltonian is block-diagonal with two equal blocks on the diagonal. The total dimension of the matrix to be diagonalized is $2M + N$, where M is the number of chemical bonds and N is the number of electron lone pairs in the molecules. The diagonal matrix elements of the operator $\mathbf{H} - E_0 \mathbf{I}$ are

$$\begin{gathered}
H_{c_m c_m} = \left\langle 0 \middle| \left(\prod_{k' \neq m} g_{k'} \right) c_{m\sigma} \left(\mathbf{H} - E_0 \mathbf{I} \right) c^{+}_{m\sigma} \left(\prod_{k \neq m} g^{+}_{k} \right) \middle| 0 \right\rangle = \\
= \sum_{t \in \{r,l\}} \{ \left(U^{t}_{m} - \sum_{B \neq T_m} \gamma_{T_m B} Z_B \right) [(\eta^{tc}_{m})^2 - 2 P^{tt}_{m}] - \left(\begin{smallmatrix} t & t \\ m & m \end{smallmatrix} \middle| \begin{smallmatrix} t & t \\ m & m \end{smallmatrix} \right)^{T_m} \Gamma^{tt}_{m} \} - \\
-2 \beta^{R_m L_m}_{r_m l_m} (\eta^{rc}_{m} \eta^{lc}_{m} - 2 P^{rl}_{m}) - 2 \gamma_{R_m L_m} \Gamma^{rl}_{m} + \\
+ \sum_{t \in \{r,l\}} \sum_{\substack{t'_q \in T_m \\ q \neq m}} \left[2 \left(\begin{smallmatrix} t & t \\ m & m \end{smallmatrix} \middle| \begin{smallmatrix} t' & t' \\ q & q \end{smallmatrix} \right)^{T_m} - \left(\begin{smallmatrix} t & t' \\ m & q \end{smallmatrix} \middle| \begin{smallmatrix} t' & t \\ q & m \end{smallmatrix} \right)^{T_m} \right] P^{t't'}_{q} [(\eta^{tc}_{m})^2 - 2 P^{tt}_{m}] + \\
+2 \sum_{t \in \{r,l\}} [(\eta^{tc}_{m})^2 - 2 P^{tt}_{m}] \sum_{B \neq T_m} \gamma_{B T_m} \sum_{\substack{t'_q \in B \\ q \neq m}} P^{t't'}_{q} .
\end{gathered} \tag{35}$$

We introduce the notation:

$$\begin{gathered}
\overline{c} = \left\{ \begin{array}{l} a, \ if \ c = b \\ b, \ if \ c = a \end{array} \right. , \\
C_{mc} = \left\{ \begin{array}{l} U_m, \ if \ c = b \\ V_m, \ if \ c = a \end{array} \right. .
\end{gathered} \tag{36}$$

The off-diagonal matrix elements of the operator $\mathbf{H} - E_0 \mathbf{I}$ can be divided in two classes: those between ionized states with electron extracted from the same geminal (these states differ by the BO, the remaining electron occupies):

$$
\begin{aligned}
H_{c_m\bar{c}_m} &= \left\langle 0 \left| \left(\prod_{k'\neq m} g_{k'} \right) c_{m\sigma} \left(\mathbf{H} - E_0\mathbf{I} \right) \bar{c}^{+}_{m\sigma} \left(\prod_{k\neq m} g^{+}_{k} \right) \right| 0 \right\rangle = \\
&= \sum_{t\in\{r,l\}} \left(U^t_m - \sum_{B\neq T_m} \gamma_{T_m B} Z_B \right) \eta^{tc}_m \eta^{t\bar{c}}_m - \beta^{R_m L_m}_{r_m l_m} \left(\eta^{rc}_m \eta^{l\bar{c}}_m + \eta^{r\bar{c}}_m \eta^{lc}_m \right) + \\
&+ \sum_{t\in\{r,l\}} \eta^{tc}_m \eta^{t\bar{c}}_m \sum_{\substack{t'_q\in T_m \\ q\neq m}} \left[2 \left(\begin{smallmatrix} t & t \\ m & m \end{smallmatrix} \middle| \begin{smallmatrix} t' & t' \\ q & q \end{smallmatrix} \right)^{T_m} - \left(\begin{smallmatrix} t & t' \\ m & q \end{smallmatrix} \middle| \begin{smallmatrix} t' & t \\ q & m \end{smallmatrix} \right)^{T_m} \right] P^{t't'}_q + \\
&\qquad +2 \sum_{t\in\{r,l\}} \eta^{tc}_m \eta^{t\bar{c}}_m \sum_{B\neq T_m} \gamma_{B T_m} \sum_{\substack{t'_q\in B \\ q\neq m}} P^{t't'}_q
\end{aligned}
\tag{37}
$$

and those between the states where an electron is extracted from different geminals

$$
\begin{aligned}
H_{c_m c'_n} &= \left\langle 0 \left| \left(\prod_{k'\neq m} g_{k'} \right) c_{m\sigma} \left(\mathbf{H} - E_0\mathbf{I} \right) c'^{+}_{n\sigma} \left(\prod_{k\neq n} g^{+}_{k} \right) \right| 0 \right\rangle = \\
&= \sum_{tt'\in\{r,l\}} C_{mc} C_{nc'} \eta^{tc}_m \eta^{t'c'}_n \times \\
&\times \left\{ \beta^{T_m T'_n}_{t_m t'_n} - \delta_{T_m T'_n} \sum_{\substack{t''_q\in T_m \\ q\neq m,n}} P^{t''t''}_q \left[2 \left(\begin{smallmatrix} t'' & t'' \\ q & q \end{smallmatrix} \middle| \begin{smallmatrix} t & t' \\ m & n \end{smallmatrix} \right)^{T_m} - \left(\begin{smallmatrix} t'' & t \\ q & m \end{smallmatrix} \middle| \begin{smallmatrix} t'' & t' \\ q & n \end{smallmatrix} \right)^{T_m} \right] \right\} - \\
&- \sum_{tt'\in\{r,l\}} \delta_{T_m T'_n} \eta^{tc}_m \eta^{t'c'}_n \left(\begin{smallmatrix} t & t \\ m & m \end{smallmatrix} \middle| \begin{smallmatrix} t & t' \\ m & n \end{smallmatrix} \right)^{T_m} C_{nc'} \left[(\eta^{ta}_m)^2 C_{ma} + (\eta^{tb}_m)^2 C_{mb} \right] - \\
&- \sum_{tt'\in\{r,l\}} \delta_{T_m T'_n} \eta^{tc}_m \eta^{t'c'}_n \left(\begin{smallmatrix} t' & t' \\ n & n \end{smallmatrix} \middle| \begin{smallmatrix} t' & t \\ n & m \end{smallmatrix} \right)^{T_m} C_{mc} \left[(\eta^{t'a}_n)^2 C_{na} + (\eta^{t'b}_n)^2 C_{nb} \right].
\end{aligned}
\tag{38}
$$

The expressions for the matrix elements of the operator $\mathbf{H} - E_0\mathbf{I}$ in the basis of ionic states with the polarized geminals Eq. (**??**) are not presented here due to their complexity. The main difference in the off-diagonal matrix elements corresponds to multiplying them by the respective overlap factors. Meanwhile, the diagonal matrix elements are shifted due to changes in the contributions to the Hamiltonian coming from the non-ionized geminals due to their polarization.

3 Results

The formulae given above developed recently in Refs. [?, ?] were implemented as a computational tool called BF [?]. The search of the equilibrium molecular geometric structure was implemented using the gradient minimization. The important problem in the context of constructing a semiempirical approach is the choice of the Hamiltonian parameters. The parameters of the semiempirical SCF approaches implicitly include the correlation of electrons. In Ref. [?] we adjusted the resonance parameters β_{AB} of the MINDO/3 Hamiltonian to cure the discrepancies due to neglect of the electron correlations. These parameters were readjusted on the ground of the results on the heats of formation and the modified values can be found in the Ref. [?], also containing the discussion of criteria for adjusting the parameters. Table 1 contains the results of the calculations of the heats of formation for the set of organic molecules obtained by the APSLG-MINDO/3 and SCF-MINDO/3 methods with the optimized geometric structures in comparison with experimental data taken from Ref. [?] devoted to the parameterization of the MNDO method.The results obtained demonstrate that the APSLG-MINDO/3 and SCF-MINDO/3 methods have the similar precision when applied to the description of the heats of formation (the mean deviation from the experiment is 6.6 kcal/mol for the APSLG-MINDO/3 method and 7.6 kcal/mol for the SCF-MINDO/3 method). At the same time the results for the branched compounds are rather poor for both computational methods, *i.e.* the account of the intrabond correlation does not improve this disadvantage of the MINDO/3 approach. It was shown in our previous works [?, ?] that the total energies obtained by the APSLG-MINDO/3 method are approximately additive in the homologic series in agreement with experiment [?, ?]. The differences between the homologues are correctly reproduced by the present method in contrast with the SCF-MINDO/3 approach. Therefore, when the molecular size increases the estimates of the heats of formation within the APSLG-MINDO/3 method significantly improve as compared to those of the SCF-MINDO/3 method.

Consistent reproducing the heats of formation does not suffice to demonstrate the consistence of a quantum chemical method. It is also important that the estimates of acceptable precision for the heats of formation would be obtained together with the geometry structure, *i.e.* positions of the minima on the potential energy surfaces. We have compared the equilibrium geometry structures obtained by the APSLG-MINDO/3 method with the experimental ones. The APSLG-MINDO/3 method predicts the length of the H-H bond in the dihydrogen molecule longer than the experimental value by 0.01 Å. At the same time the calculated length of the C-H bond in the methane (1.092 Å) fairly coincides with the experimental one (1.094 Å). The situation for the C-C bond in the hydrocarbons is more complex: the value of the length of the C-C bond in the ethane calculated by the SCF-MINDO/3 method is 1.474 Å, which is significantly smaller than the experimental value of 1.536 Å. The APSLG-MINDO/3 method gives the value 1.484 Å for this length. This result is better than that of the SCF-MINDO/3 but the difference with the experiment is still too large. This situation is slightly better for the higher hydrocarbons. At the same time the difference between the calculated and experimental length of the C=C bond in the ethylene is not very great (1.335 Å *vs.* 1.339 Å). The SCF-MINDO/3 method gives the value 1.313 Å for this quantity which is significantly lower than the experiment. Fascinating example is the optimization of the geometric structure of the norbornadiene and quadricyclane molecules. Starting from the same geometry but with different positions of the chemical bonds (connectivity scheme) we obtain different results. If all the bonds are admitted to be single the optimization procedure results in the geometric structure very close to that of the quadricyclane. If two bonds are set to be double the geometry obtained is close to that of the norbornadiene.

Both schemes of the calculation of vertical ionization potentials and wave functions of the ionized states described in Section 2.3 were implemented in the computational package BF [?]. The results of both methods can be discussed with use of the concept of Dyson orbitals [**?**]. These orbitals are defined by the expression:

$$g_n(x) = \left\langle \Psi_n^+ \left| \psi(x) \right| \Psi_0 \right\rangle, \tag{39}$$

where $\psi(x)$ is the operator annihilating an electron in the point $x = (\mathbf{r}, \sigma)$. In the case of the SCF-MINDO/3 method using the Koopmans' theorem for description of the ionic states, the Dyson orbitals coincide with the molecular orbitals and are, therefore, normalized. In the case of the geminal trial wave function for the ground state of the neutral molecule the Dyson orbitals are not normalized. We applied both procedures to the calculation of the ionization potentials in a series of normal hydrocarbons from CH_4 to

$C_{20}H_{42}$. The results obtained by the both APSLG-type computational procedures are presented in Fig. 1 in comparison with relevant experimental data and the results obtained by the SCF-MINDO/3 method. Also we computed the first vertical ionization potentials for some other hydrocarbons and organic molecules containing oxygen and nitrogen. These values are calculated within the scheme with fixed geminals. The results accompanied by the corresponding experimental data are present in Table 2.

4 Discussion

The essential feature of the APSLG-MINDO/3 approach is the partial account of electron correlations in contrast with the SCF-MINDO/3 approach. This may be thought to be unimportant from the refined theoretical point of view since the method itself anyway belongs to the family of other semiempirical methods where the correlations are all the same at least to some extent taken into account by parameterization. However, the correlated and local form of the trial wave function of the APSLG-based approach allows for correct asymptotic behavior for the bond cleavage. To this extent one may expect that the APSLG method is capable to reproduce qualitative features of molecular electronic structure for reactive species. At the same time APSLG-MINDO/3 method neglects the interbond one-electron transfers which are covered by the parent SCF-MINDO/3 approach. It is interesting to find out which factor (the intrabond electron correlations or interbond electron transfers) is more important for description of the electronic structure. The data of the Table 1 on the heats of formation and equilibrium geometries show that both factors are of similar importance. The transition to the APSLG structure of the wave function has advantages for the equilibrium geometries. The wave function of the SCF method has wrong limit under bond cleavage.

The local character of the APSLG approach provides a possibility of linear dependence of the computational costs on the size of a molecule. To demonstrate it we carried out calculations of the electronic structure for a series of normal saturated hydrocarbons from CH_4 to $C_{20}H_{42}$ without geometry optimization by the APSLG-MINDO/3 and SCF-MINDO/3 methods. The dependencies of the computation time (in seconds) on the number of carbon atoms in the chain are presented in the Fig. 2. It is clearly seen that the method APSLG-MINDO/3 possesses a linear dependence of the computational costs on the length of the chain in contrast with the SCF-MINDO/3 method. In the case of normal hydrocarbon $C_{20}H_{42}$ the computation time for two methods differs 30 times in favor of the APSLG approach.

The HO's for double bonds are normally ambiguously defined. Does this bond consist of two equivalent (bent or "banana") or non-equivalent (σ- and π-) bonds? The variational determination of the HO's in the proposed approach allows to discriminate between the two models on the ground of the energy criterion. Our calculations have revealed that the σ-/π-separated model is only less than 1 kcal mol^{-1} energetically more favorable than the model with the bent bonds. The question about the preferability of one or another representation of the double bond was also studied in Ref. [**?**] with use of the full GVB approach. In the case of the ethylene molecule the conclusion about closeness of the energies for the two ways of bonding has been drawn as well. The calculations with the frozen core have shown that the σ-/π-separation is slightly more preferable in agreement with our results.

Another question is about the form of the HO's in strained cyclocarbons (especially, cyclopropane). Our calculations predict that the optimal HO's are not directed along the C-C bonds. In the framework of the APSLG approach certain concepts specific for chemistry became natural. For example, the hybridization can be considered as a parameter of the wave function and is determined on the basis of the variational principle. The bond ionicity, covalency and polarity become clearly defined if the geminal is rewritten in the form

$$g_m^+ = \frac{I_m}{\sqrt{2}} \left[\sqrt{1+\lambda_m} r_{m\alpha}^+ r_{m\beta}^+ + \sqrt{1-\lambda_m} l_{m\alpha}^+ l_{m\beta}^+ \right] + \frac{C_m}{\sqrt{2}} \left[r_{m\alpha}^+ l_{m\beta}^+ + l_{m\alpha}^+ r_{m\beta}^+ \right], \tag{40}$$

where I_m and C_m are the total amplitudes of the ionic and covalent contributions respectively, and λ_m is the bond polarity (*i.e.* asymmetry of the charge distribution in the m-th bond). Table 3 represents the data on bond covalency, ionicity and polarity as well as the atomic charges obtained with use of the Mulliken's scheme. Table 3 shows that the covalent contribution exceeds the ionic contribution for all considered molecules and these contributions are only weakly sensitive to the chemical structure of the bond and its surrounding. At the same time the numerical values of the parameter λ_m vary significantly and corresponds to the chemists' intuitive ideas concerning the bond polarity. Taking into account the weak dependence of the covalency and ionicity on the type of bond, the bond polarities ultimately control the charges on the atoms. The interesting result is obtained for the methane molecule: the SCF-MINDO/3 method predicts positive charge for the carbon atom. At the same time the APSLG-MINDO/3 method gives the reverse charge distribution (bond polarity) in accordance with the results of *ab initio* calculations and with the intuitive belief of organic chemists.

It is also interesting to consider the hybridization as determined variationally. In the case of methane the sp^3-hybridization is obtained. The transition to ethane essentially changes the hybridization: the HO's of the C-C bond have the $sp^{2.26}$-hybridization and the HO's of the C-H bonds have the $sp^{3.33}$-hybridization. It can be noted that in the molecule with lone electron pairs the latter have substantially the s-character and, therefore, the HO's assigned to the chemical bonds have mainly the p-character. For example, the HO of the F-H bond in the HF molecule has $sp^{39.0}$-hybridization. It is necessary to mention that the mixing the HO's of different lone electron pairs which are centered on the same atom does not change the electronic energy and degree of this mixing is controlled by initial conditions of the optimization.

The correct description of the ionization potentials requires the same level of the calculation of the ion and neutral molecule. It can be only approximately achieved in the case when the molecule is described by the local method, because the ion must be described as essentially delocalized. The data of the Fig. 1 demonstrate that the APSLG-based method with fixed geminals gives the vertical ionization potentials which are slightly larger than the experimental adiabatic ones. At the same time, the scheme with the polarization of the geminals by a hole predicts the vertical ionization potentials which are significantly lower even than the experimental adiabatic ones. It is due to different degree of correlation accounted in the ion and neutral molecule. It is necessary to mention that different explorers obtain experimentally very divergent values for the ionization potentials (for example, authors of Refs. [**?**, **?**, **?**] report very different results for the methane molecule).

It is interesting to consider the structure of a hole in the polyethylene. The one-electron approximation predicts the delocalized character of the hole (the corresponding Dyson orbital is a plane wave). At the same time the variation of the lengths of the chemical bonds in the ion can localize the hole [**?**]. In the case of the APSLG-based method the Dyson orbital of the hole is slightly more localized than that in the case of the SCF approach but it also has the sinus-like form with the maximum at the middle of the chain. In the case of the APSLG-MINDO/3 method with the fixed geminals the charges on the hydrogen atoms are very close to those in the neutral molecule while in the case of the APSLG-MINDO/3 method with the polarized geminals the charges on the hydrogen atoms became essentially more positive than in the neutral molecule, due to electron redistribution in the C-H bonds, though they are not affected by the ionization directly.

In the case of highly symmetric molecules the ionization experiments manifest the degeneracy of the ionic states. The molecular orbital theories correlate it with the degeneracy of the molecular orbitals the electron is extracted from. The localized method like APSLG can describe the degeneracy only if the interaction between the local configurations is turned on. The degeneracies of the states are due to the symmetry of the Hamiltonian matrix. Our calculations demonstrate that the APSLG-MINDO/3 approach reproduces the degeneracies and the order of the ionized states (in the case of methane we obtained the triply degenerated, in the case of ethane and ammonia the doubly degenerated first ionization states).

The analysis of the data of the Table 2 shows that the APSLG-MINDO/3 based method with fixed geminals gives the value of the first vertical ionization potential for all classes of molecules close to the experimental ones. The ionization potentials of the methylamine and ethylamine are very close because the lone pare mainly contributing to the ionized state is only slightly affected by the changing in the remote surrounding. In contrast the addition of alkyl-groups to the atom with lone electron pair significantly decreases the first vertical ionization potential due to electron-donating character of alkyl-groups in the closest surrounding of the lone electron pair.

5 Conclusions

A semiempirical method using the trial wave function in the form of the antisymmetrized product of strictly localized geminals is constructed and implemented as a computational tool. The quality (accuracy) of the results related to the heats of formation and equilibrium geometries obtained by the APSLG-MINDO/3 method is comparable and somewhat better than that of the SCF-MINDO/3 method. At the same time the method APSLG-

MINDO/3 possesses three important features: (1) it guarantees the correct behavior of the wave function under the homolytic cleavage of chemical bonds; (2) the computational costs of the method increase linearly with the growth of the system size and (3) some chemical concepts such as the hybridization, covalency, ionicity, polarity of chemical bonds are naturally defined in the framework of the APSLG approach. The APSLG-based configuration interaction schemes for the calculation of the vertical ionization potentials correctly reproduce the degeneracies of the ionic states. At the same time only the APSLG-based method with fixed geminals gives the values of the first vertical ionization potential, which are close to the experimental ones. Analogous approach with polarization of geminals systematically lowers the values of the first ionization potential.

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Table 1: Heats of formation (kcal/mol) of test molecules obtained experimentally and calculated with use of the APSLG-MINDO/3 and SCF-MINDO/3 methods.

Molecule	ΔH_f (expt.)	ΔH_f APSLG	ΔH_f SCF
H_2	0.0	-0.101	0.131
CH_4	-17.8	-8.430	-6.275
C_2H_6	-20.04	-19.514	-19.849
C_3H_8	-25.00	-25.185	-26.527
n-C_4H_{10}	-30.00	-29.993	-32.655
iso-C_4H_{10}	-32.00	-22.379	-24.710
n-C_5H_{12}	-35.09	-35.225	-38.973
neo-C_5H_{12}	-40.15	-12.126	-14.632
cyclopropane	12.7	18.472	8.524
cyclobuthane	6.8	2.360	-8.088
cyclopenthane	-18.3	-28.193	-27.795
cyclohexane	-29.49	-29.166	-32.505
NH_3	-11.0	-4.529	-9.125
CH_3NH_2	-5.5	-1.034	-4.615
$C_2H_5NH_2$	-11.3	-11.777	-15.708
n-$C_3H_7NH_2$	-16.8	-16.776	-21.874
iso-$C_3H_7NH_2$	-20.0	-14.718	-18.341
tert-$BuNH_2$	-28.9	-6.757	-13.215
$(CH_3)_2NH$	-4.4	5.535	4.310
$(CH_3)_3N$	-5.7	19.136	21.027
N_2H_4	22.8	21.307	3.166
CH_3NHNH_2	22.6	23.102	8.366
$(CH_3)_2NNH_2$	20.1	33.039	22.242
$CH_3NHNHCH_3$	22.0	27.588	15.019
H_2O	-57.8	-55.677	-53.611
CH_3OH	-48.16	-48.549	-50.573
C_2H_5OH	-56.21	-60.167	-64.292
1-C_3H_7OH	-60.98	-65.113	-70.417
2-C_3H_7OH	-65.19	-66.008	-69.117
tert-BuOH	-74.7	-63.509	-65.614
$(CH_3)_2O$	-60.3	-33.905	-51.191
H_2O_2	-32.5	-32.720	-29.265

Table 2: The first vertical ionization potentials (eV) for some simple molecules obtained by the APSLG method with fixed geminals and some experimental results.

Molecule	**Calculated value, eV**	**Experimental value, eV**
H_2	15.614	15.43 [?]
cyclopropane	10.058	11.0 [?]
C_2H_4	10.418	10.51 [?]
NH_3	10.117	10.15 [?]
N_2H_4	8.856	8.74 [?]
CH_3NH_2	8.741	8.97 [?]
$C_2H_5NH_2$	8.789	8.66 [?]
H_2O	12.794	12.62 [?]
CH_3OH	10.781	10.84 [?]
C_2H_5OH	10.470	10.47 [?]

Table 3: 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