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SO(4) group and deductive molecular mechanics

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Abstract

Analysis of electronic structure of organic molecules performed on the basis of the APSLG trial electronic wave function with use of the biquaternion parameterization of the SO(4) hybridization manifold of nonhydrogen atoms provided a logical framework for deductive transition from quantum mechanical (QM) description of molecular electronic structure to molecular mechanical (MM) description of molecular potential energy surface. This derivation resulted in an alternative form of MM in which atoms are not considered as interacting point masses ('balls'), but manifest more complex structure reflecting their valence state. The latter may be correlated with the atom 'types' introduced in standard MM on the basis of analysis of failed attempts to reproduce certain sets of experimental data in the respective model frameworks.

Keywords: Molecular mechanics-Derivation of QM/MM junctions; Quantum mechanics; One-electron states

1. Introduction

A problem of constructing a transition route from quantum mechanical (QM) description of molecular electronic structure to molecular mechanical (MM) [1,2] description of potential energy surface (PES) is well known. Only on this route one may expect to find a solution for the long lasting problems like sequential derivation of QM/MM junctions. Recently we performed some preparatory work for that. It consisted (i) in constructing an appropriate underlying QM description of molecular electronic structure to start the derivation from [3–5], (ii) in establishing (a degree of) transferability of relevant electronic structure parameters (ESPs) [6,7], and (iii) in constructing an adequate mathematical description of hybridization [7]. It turned out that the ESPs like one- and two-electron density matrix elements in the basis of the strictly localized hybrid orbitals (HOs) ascribed to each bond or lone pair are fairly transferable (see Ref. [6] and below). This allowed to derive the transferable energy contributions required for the MM additive form of the total energy (the force fields) in terms of these quantities. This all may serve as a starting point in sequential construction of theoretically substantiated additive systematics in a spirit of Ref. [8].

It is interestingly enough that such a realm not related directly to the additivity concept as stereochemistry can be also considered within the same setting. Stereochemistry can be regarded as

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a qualitative tool to rationale the shapes the atoms and groups form when attached to some other atom. For a century, two fundamental facts shaped this area: the tetrahedral carbon introduced by van t'Hoff and Le Bel [9,10] and the pyramidal nitrogen. Despite that long development history no common viewpoint upon the source of the energy dependence on valence angles has not been developed within the stereochemistry itself. By contrast, even very simple quantum chemical methods reproduce the observed geometry features. In quite general terms it is known that the form of the coordination polyhedron is ultimately controlled by relation between the bonding (two-center) interactions which favor population of excited and ionized states of an atom under consideration and the excitation energies of this atom itself, which tend to keep it in its ground (nonhybridized) state [11]. (Recently these notions again have been brought to discussion in Ref. [12]). However, no sequential derivation has been proposed to bridge two banks of the river: general theoretical understanding on one hand and specific force fields of MM or empirical rules in stereochemistry.

In fact the Nyholm–Gillespie explanatory scheme [13–15] well established in stereochemistry proposes a point of view alternative to that by Coulson [11]. According to the former the angular dependence of energy is a result of (Coulomb) repulsion between electron pairs residing in the valence shell (valence shell electron pair repulsion—VSEPR). In the literature there exist quite a number of attempts to reconcile the qualitative and intellectually very attractive picture by Nyholm and Gillespie with the results of the quantum chemical calculations, which are reviewed in Ref. [8]. These attempts, turned out to be discouraging, however. It has been found that the intraatomic energy terms responsible for the molecular shape cannot be identified with the interpair Coulomb interactions. This finding applies both to the carbon and to the nitrogen stereochemistry. Neither of them is based (according to Ref. [8]) upon interpair Coulomb repulsion. On the other hand one cannot ignore the enormous heuristical strength of the Nyholm–Gillespie concept and also the fact that some correlation (but not *equivalence*) between the pair interaction energies and the forms of coordination polyhedra nevertheless do exist [16]. In any case the quantum chemical calculations do not provide any explanation *why* molecules have that or another stereochemistry: they simply fix the same fact by means of yet another—now numerical—experiment.

It the present paper we propose a derivation of a mechanistic model of molecular PES departing from certain underlying QM description of molecular electronic structure. A general sketch of the derivation is the following. First we describe briefly the semiempirical APSLG-MINDO/3 method being a QM basis for this undetaking [17]. Particular attention will be paid to analysis of the SO(4) manifold—the mathematical tool to describe hybridization—and employing this tool to derive a mechanistic picture of atoms in molecules, which is an alternative to that used in the standard MM schemes, and ultimately leads to an alternative form of MM itself. Next we describe approximate procedures for estimating the ESPs of the underlying QM method (APSLG-MINDO/3). Finally we describe several forms of the alternative MM originating from different recipies of fixing the ESPs.

2. QM method underlying MM description

The basic idea underlying the whole derivation undertaken in the present paper is that the *experimental fact* that the MM description of molecular PES is that successful as it is reported in the literature must have certain *theoretical explanation* [18]. The only way to get such an explanation is to start a derivation from certain form of the trial wave function of electrons in a molecule which belongs to a rather wide class. Any QM method employing the trial wave function of the self-consistent field (SCF or Hartree–Fock) approximation hardly can be used to perform such a derivation since it results in inherently delocalized description of the molecular electronic structure. Subsequent a posteriori localization procedures prescribed in the literature as a remedy allowing to obtain localized one-electron states to be used as building blocks of a localized description in fact create more problems than provide solutions. First, the localization procedures are numerous and the fact that they give close (but any way not identical) results simply makes the choice of a unique one more difficult since there is no clear selection criterion. Second, the local *representation* of the Slater determinant does not provide real local description since the electron number fluctuations [19] after the localization remain the same as they were before since the transition from the canonical MOs to the localized ones does not change the many-electron state represented by this determinant. Third, irrespective to the localization procedure used the a posteriori localized one-electron states always have some residual amplitudes on other atoms of the molecules known as ‘tails’. The subsequent ‘tail cutting’ can be hardly formalized nor reconciled with the general requirement for transferability of the one-electron states. All these obstacles made us to undertake a search for an alternative to the existing QM methods to be used as a starting point for deriving a mechanistic description. The requirements for such method had been formulated in Ref. [18]. According to the latter the key feature of the underlying QM method must be that it (i) describes electronic structure in terms relevant for the MM picture, i.e. in those of bonds and lone pairs; (ii) the variational character of the method is desirable; (iii) semi-empirical implementation of the method.

A method satisfying the formulated criteria has been designed recently [3]. It uses the geminal form of the electronic wave function [20] and strictly local HOs [21] as one-electron basis set to construct it. It was checked numerically that the bond and lone pair geminals (see below) are fairly transferable from one molecule to another and that the electronic energy may naturally be rewritten in this approximation with use of really local quantities—such that their local nature is established by the variational procedure for the total energy. In next several subsections we describe basic features of the method.

2.1. Trial wave function underlying the MM description

The wave function of electrons in the molecule is taken in Ref. [3] as the antisymmetrized product of the geminals:

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

The specific form of the geminals used in Eq. (1) goes back to Weinbaum [22]. With use of the second quantization notation they are written as:

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

for (two-center) chemical bonds and:

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

for lone pairs. The amplitudes of the configurations (u_m, v_m, and w_m) in Eq. (2) are determined with use of the variational principle. The normalization condition is imposed on the amplitudes:

$$u_m^2 + v_m^2 + 2w_m^2 = 1. \tag{4}$$

This results in a series of diagonalizations of 3 × 3 matrices of effective Hamiltonians formed separately for each two-center bond but weakly dependent on each other. It the present setting three states of the geminal are allowed for each bond, and one used in the expansion Eq. (1) corresponds to the lowest eigenvalue of the effective bond Hamiltonian.

2.2. Semiempirical QM energy expression underlying the MM description

Treating the molecular Hamiltonian of the MINDO/3 form [23] with the APSLG trial wave function Eqs. (1) and (2) in Ref. [3] resulted in a semiempirical APSLG-MINDO/3 QM method. In it the total energy acquires a form close to the MM potential energy function [2,8]:

$$E_{\text{total}} = \sum_A E_A + \sum_{A<B} E_{AB},$$

where

$$E_A = \sum_{m\in A}\left\{\sum_{t\in\{r,l\}\cap A}[2U_m^t P_m^{tt} + (t_m t_m|t_m t_m)^{T_k}\Gamma_m^{tt}] + \sum_{k<m}\sum_{tt'\in\{r,l\}\cap A} 2g_{t_k t'_m}^{T_k} P_k^{tt} P_m^{t't'}\right\}. \tag{5}$$

$$E^{\text{bond}}_{R_mL_m} = 2\gamma_{R_mL_m}[\Gamma^{rl}_m - 2P^{rr}_m P^{ll}_m] - 4\beta^{R_mL_m}_{r_ml_m} P^{rl}_m,$$

$$E^{\text{nonbond}}_{AB} = \frac{1}{2}(Z_AZ_BD_{AB} + Q_AQ_B\gamma_{AB}),$$

in that sense that the bonded and nonbonded atoms are treated differently. In the above expression U^t_m is the HO core attraction; $(t_mt_m|t_mt_m)$ is the intra-HO Coulomb interaction; $g^{T_k}_{t_kt'_m}$ is the inter-HO Coulomb interaction; γ_{AB} is the two-center Coulomb interaction parameter; $\beta^{R_mL_m}_{r_ml_m}$ is the resonance (one-electron hopping) integral for the r_m- and l_m-th HOs ascribed to the m-th bond; R_m and L_m refer, respectively, to the right- and left-end atoms of this bond; D_{AB} is the MINDO/3 core-core repulsion function for cores A and B describing its deviation from the simple Coulomb repulsion.

This expression is written in terms of the intrabond matrix elements of one- and two-electron densities:

$$\begin{aligned}
P^{tt'}_m &= \langle 0|g_m t^+_{m\sigma} t'_{m\sigma} g^+_m|0\rangle,\\
\Gamma^{tt'}_m &= \langle 0|g_m t^+_{m\beta} t'^+_{m\alpha} t'_{m\alpha} t_{m\beta} g^+_m|0\rangle,\\
P^{rr}_m &= u^2_m + w^2_m,\ \ P^{ll}_m = v^2_m + w^2_m,\\
P^{rl}_m &= P^{lr}_m = (u_m + v_m)w_m,\\
\Gamma^{rr}_m &= u^2_m,\ \ \Gamma^{ll}_m = v^2_m,\ \ \Gamma^{rl}_m = \Gamma^{lr}_m = w^2_m,
\end{aligned} \tag{6}$$

where t and $t'(=\pm 1)$ correspond to r or l, respectively. They comprise the subset of the QM ESP's related to geminal amplitudes. The effective atomic charges can be also represented through the diagonal ESP's:

$$Q_A = 2\sum_{t_m\in A} P^{tt}_m - Z_A, \tag{7}$$

where Z_A stand for the core charges.

2.3. Invariance of the ESP's related to geminal amplitudes

The energy expression Eq. (5) is written in terms of the one- and two-electron density matrix elements Eq. (6) expressed through the amplitudes of the geminals Eq. (1). In the APSLG-MINDO/3 framework it implies constructing effective 3×3 Hamiltonians for each of the geminals with subsequent diagonalization in search for the amplitudes. However, the required ESPs can be directly expressed in terms of the matrix elements of the effective Hamiltonians and even more, their dependence on the matrix elements is in certain sense weak thus allowing to fix the required ESPs at reasonable transferable values. Indeed, there exist two parameters characterizing two aspects of any two-center bond: the correlation parameter ζ_m and the polarity parameter μ_m, respectively.

$$\begin{aligned}
\zeta_m &= 4\beta^{R_mL_m}_{r_ml_m}/\Delta\gamma_m,\\
\mu_m &= \frac{\epsilon^L_m - \epsilon^R_m}{\Delta\gamma_m \Gamma(\zeta_m)},\\
\Gamma(\zeta_m) &= \sqrt{1+\zeta^2_m}.
\end{aligned} \tag{8}$$

where ϵ^L_m and ϵ^R_m are the diagonal matrix element of the effective Hamiltonian for the m-th (bond) geminal [7], corresponding to the ionic states with two electrons residing on the left- and right-end HOs, respectively; and

$$\Delta\gamma_m = \frac{1}{2}\sum_{t\in\{r,l\}} (t_mt_m|t_mt_m)^{T_m} - \gamma_{R_mL_m}. \tag{9}$$

The QM parameters characteristic for the real bonds correspond to the limit $\zeta_m \to \infty$. In this limit we obtain the transferable values of the geminal related ESPs:

$$\Gamma^{tt'}_{0m} = \frac{1}{4}, \qquad P^{tt'}_{0m} = \frac{1}{2}. \tag{10}$$

which depend neither on molecular geometry nor on the nature nor on hybridization of the atoms bonded. For the lone pair geminals these quantities are chosen correspondingly ($\Gamma^{rr}_{0m} = P^{rr}_{0m} = 1$) and all other are vanishing. The bond- and atom-specific corrections [7]:

$$\Gamma^{tt'}_m = \frac{1}{4} + \delta\Gamma^{tt'}_m, \qquad P^{tt'}_m = \frac{1}{2} + \delta P^{tt}_m,$$

$$\begin{aligned}
\delta P^{tt}_m &= \frac{t_m\mu_m}{2}; &\qquad \delta P^{rl}_m &= -\frac{\mu^2_m}{4} - \frac{1}{4\zeta^2_m};\\
\delta\Gamma^{tt}_m &= \frac{t_m\mu_m}{2} - \frac{1}{4\zeta_m}; &\qquad \delta\Gamma^{rl}_m &= -\frac{\mu^2_m}{2} + \frac{1}{4\zeta_m}.
\end{aligned} \tag{11}$$

are of the first and second order in ζ^{-1}_m and μ_m. However, the ESP P^{rl}_m which is the spin bond order [3] of the m-th bond is affected by the small bond- and atom-specific parameters ζ^{-1}_m and μ_m only in the second order.

The bond polarity parameter μ_m affects remarkably (in the first order) only the diagonal density matrix elements; the off-diagonal ones acquire the corrections of the second order in μ_m. Taking into account the corrections to the geminal related ESPs of different orders results in a hierarchy of approximate mechanistic procedures to treat the molecular energy (see below).

2.4. One-electron states underlying the MM description

The expression for the energy Eq. (5) is written in the one-electron basis of HOs given by the formula (see Ref. [3] and reference therein):

$$t_{m\sigma} = \sum_{i=\mathrm{s,p}\in A} h^t_{mi}(A) a_{i\sigma}; \quad t = r, l, \tag{12}$$

for each 'heavy' (nonhydrogen) atom. The $h(A)$ matrices are SO(4) matrices due to obvious orthonormality conditions. They produce another subset of the ESPs of the APSLG-MINDO/3 method, which can be characterized as a hybridization related ones. Within the APSLG-MINDO/3 method the matrices h^A transforming the AO basis to the HO one are determined variationally. They affect the energy through the molecular integrals in the HO's basis. The molecular integrals U^t_m, $(t_m t_m | t_m t_m)^A$, and $g^A_{t_k t'_m}$ depend on hybridization only; $\gamma_{R_m L_m}$—on geometry only; and $\beta^{AB}_{t_m t'_m}$ depend on the both.

In order to evaluate the hybridization dependence of the energy it is necessary to have a handy description of the whole hybridization manifold. The SO(4) group (i.e. the group of 4 × 4 orthonormal matrices with unit determinant) is a so-called 'dynamical' group producing the whole possible variety of hybridizations at each heavy atom [24] while acting on the AOs set residing on the latter. The matrix generating the HO's is a matrix product:

$$h(A) = h(\vec{\omega}^A) = R(\vec{\omega}^A_l) H(\vec{\omega}^A_b), \tag{13}$$

where the matrix multipliers responsible for the orientation (R) of the whole set of the HOs at a given atom and for the hybridization (H), i.e. for the relative weights of the s- and p-orbitals in the HOs are themselves the products of the corresponding Jacobi matrices:

$$\begin{aligned} &R(\vec{\omega}_l) = J_{yz}(\omega_{yz}) J_{xz}(\omega_{xz}) J_{xy}(\omega_{xy}), \\ &H(\vec{\omega}_b) = J_{sz}(\omega_{sz}) J_{sy}(\omega_{sy}) J_{sx}(\omega_{sx}), \\ &\vec{\omega}_l = (\omega_{yz}, \omega_{xz}, \omega_{xy}), \\ &\vec{\omega}_b = (\omega_{sz}, \omega_{sy}, \omega_{sx}). \end{aligned} \tag{14}$$

The SO(4) group is thus a six-parametric group with a coordinates $\omega_{\mu\nu}$.

The set of six infinitesimal operators of the SO(4) group defined according to:

$$B_\gamma = \left. \frac{\partial H(\vec{\omega}_b)}{\partial \omega_{s\gamma}} \right|_{\vec{\omega}_b = 0} \text{ and } \epsilon_{\alpha\gamma\beta} L_\gamma = \left. \frac{\partial R(\vec{\omega}_l)}{\partial \omega_{\alpha\beta}} \right|_{\vec{\omega}_l = 0}, \tag{15}$$

where $\epsilon_{\alpha\beta\gamma}$ is the complete antisymmetric (Levi-Cività) tensor, has inconvenient commutation properties. The subset of infinitesimal operators L_γ obeys the usual commutation relations for the angular momentum components. However, the set of pseudomomentum components B_γ (in fact these infinitesimal operators differ from the true momentum operators by themultiplier i) is not close with respect to commutation relations and does not commute with the angular momentum components [24]:

$$\begin{aligned} &[L_\alpha, L_\beta] = \epsilon_{\alpha\beta\gamma} L_\gamma, \quad [B_\alpha, B_\beta] = \epsilon_{\alpha\beta\gamma} L_\gamma, \\ &[B_\alpha, L_\beta] = [L_\alpha, B_\beta] = \epsilon_{\alpha\beta\gamma} B_\gamma. \end{aligned} \tag{16}$$

This suggests that the map Eq. (14) is not a very good one, since it masks the fundamental fact that the SO(4) group is a direct product of two SO(3) subgroups (SO(4) = SO(3) × SO(3)). The latter is recovered by a coordinate transform:

$$\omega_{\gamma\pm} = \epsilon_{\alpha\beta\gamma} \omega_{\alpha\beta} \pm \omega_{s\gamma}, \tag{17}$$

giving a new set of infinitesimal operators:

$$F_\gamma = \frac{1}{2}(L_\gamma + B_\gamma), \quad G_\gamma = \frac{1}{2}(L_\gamma - B_\gamma). \tag{18}$$

Their commutation relations perfectly reflect the direct product structure of the SO(4) group, since as one can check:

$$[F_{\alpha}, G_{\beta}] = 0, \quad [F_{\alpha}, F_{\beta}] = \epsilon_{\alpha\beta\gamma} F_{\gamma}, \qquad (19)$$
$$[G_{\alpha}, G_{\beta}] = \epsilon_{\alpha\beta\gamma} G_{\gamma}, \ \forall \alpha, \beta, \gamma,$$

so that the vector operator $\vec{F}$ commutes with the $\vec{G}$ and each of them forms a basis in the tangent space to the corresponding SO(3) subgroup of the SO(4) group of interest. The new set of parameters (angles $\vec{\omega}_{\pm}$), however, lacks any clear physical meaning since they represent neither pure rotation nor pure deformation of the system of HOs. These conceptually important transformations can be recovered either by setting $\vec{\omega}_{+} = \vec{\omega}_{-}$, which results in a pure rotation, or $\vec{\omega}_{+} = -\vec{\omega}_{-}$, which corresponds to a pure deformation.

The mapping given just above is a significant improvement as compared to Eq. (14). Nevertheless, it is still a clumsy combination of trigonometrical functions of two triples of parameterizing angles $\vec{\omega}_{\pm}$. So, as in the case of the SO(3) group [24] a quaternion [25] parameterization may be useful also for the SO(4) group. The preference of such a parameterization is that, for example, matrix elements of any SO(3) rotation matrix when expressed in terms of the corresponding normalized quaternion are quadratic functions of the quaternion components obeying one normalization condition.

A similar parameterization for the SO(4) group is constructed as follows. First we notice that the (para)rotations by the triples of angles $\vec{\omega}_{\pm}$ can be represented as (para)rotations by angles

$$\omega_{\pm} = \sqrt{\sum_{\gamma} \omega_{\pm}^{2}\gamma}, \qquad (20)$$

around axes with the directing cosines $\omega_{\pm\gamma}/\omega_{\pm}$, respectively. The normalized quaternions **q** and **p** corresponding to these pararotations have the following components:

$$q_0 = \cos\frac{\omega_+}{2}, \ q_1 = \frac{\omega_{+x}}{\omega_+}\sin\frac{\omega_+}{2}, \ q_2 = \frac{\omega_{+y}}{\omega_+}\sin\frac{\omega_+}{2}, q_3 = \frac{\omega_{+z}}{\omega_+} + \sin\frac{\omega_+}{2}, \qquad (21)$$

$$p_0 = \cos\frac{\omega_-}{2}, \ p_1 = \frac{\omega_{-x}}{\omega_-}\sin\frac{\omega_-}{2},$$
$$p_2 = \frac{\omega_{-y}}{\omega_-}\sin\frac{\omega_-}{2}, \ p_3 = \frac{\omega_{-z}}{\omega_-}\sin\frac{\omega_-}{2}.$$

With use of these quaternions one can easily recover two SU(2) matrices acting each in a separate spinor space [26,27]. The corresponding SU(2) matrix defined by the quaternion $\mathbf{q} = \mathbf{q}(\vec{\omega}_+)$ is:

$$\begin{pmatrix} q_0 - \mathrm{i}q_3 & -\mathrm{i}q_1 - q_2 \\ -\mathrm{i}q_1 + q_2 & q_0 + \mathrm{i}q_3 \end{pmatrix} \begin{pmatrix} |+\frac{1}{2}\rangle \\ |-\frac{1}{2}\rangle \end{pmatrix}, \qquad (22)$$

and analogous one for the quaternion $\mathbf{p} = \mathbf{p}(\vec{\omega}_-)$. Now the problem reduces to that of constructing of an SO(4) matrix in terms of two SU(2) matrices parameterized by **q** and **p**. Each of the SU(2) matrices acts in a separate space of two-component spinors [26,27] which corresponds to the two-dimensional representation of the SU(2) group (or of that of the SO(3) group locally isomorphous to SU(2)) with the rank 1/2. The latter is the configuration space of a particle with spin 1/2 (like an electron). Since the SO(4) group is a direct product of two SO(3) (SU(2)) groups the space in which it acts is a direct product of two spinor spaces. Then following the analogy with the theory of electron spin coupling we consider a pair of spins. The configuration space for this pair is spanned by four product functions:

$$\left|\pm\frac{1}{2}; \pm\frac{1}{2}\right\rangle, \qquad (23)$$

(all four possible combinations of plus and minus signs are used). The matrix acting in this space is a direct (Kronecker) product of the SU(2) matrices representing the **q**- and **p** -pararotations with that notion that the **q**-dependent matrix Eq. (22) acts on the first spinor and the **p**-dependent one on the second spinor in the product state. Then we form linear combinations of the above states which correspond to specific values of the total momentum and desired spatial symmetry. Namely, the combination which corresponds to the zero total momentum transforms as a scalar, i.e. (singlet) s-function. Those which correspond to the total momentum equal to unity form the basis in the three-dimensional (triplet) space of p-functions. The coordinate (x-, y-, and z-) functions are obtained by the following transforms:

$$\begin{aligned}
|s\rangle &= \frac{1}{\sqrt{2}}\left(|+\tfrac{1}{2};-\tfrac{1}{2}\rangle - |-\tfrac{1}{2};+\tfrac{1}{2}\rangle\right),\\
|x\rangle &= \frac{\mathrm{i}}{\sqrt{2}}\left(|+\tfrac{1}{2};+\tfrac{1}{2}\rangle - |-\tfrac{1}{2};-\tfrac{1}{2}\rangle\right),\\
|y\rangle &= \frac{1}{\sqrt{2}}\left(|+\tfrac{1}{2};+\tfrac{1}{2}\rangle + |-\tfrac{1}{2};-\tfrac{1}{2}\rangle\right),\\
|z\rangle &= -\frac{\mathrm{i}}{\sqrt{2}}\left(|+\tfrac{1}{2};-\tfrac{1}{2}\rangle + |-\tfrac{1}{2};+\tfrac{1}{2}\rangle\right).
\end{aligned} \tag{24}$$

The Kronecker product matrix in this basis gives an SO(4) matrix:

$$h = \begin{pmatrix}
q_0p_0+q_1p_1+q_2p_2+q_3p_3 & q_0p_1-q_1p_0-q_2p_3+q_3p_2 & q_0p_2+q_1p_3-q_2p_0-q_3p_1 & q_0p_3-q_1p_2+q_2p_1-q_3p_0\\
-q_0p_1+q_1p_0-q_2p_3+q_3p_2 & q_0p_0+q_1p_1-q_2p_2-q_3p_3 & -q_0p_3+q_1p_2+q_2p_1-q_3p_0 & q_0p_2+q_1p_3+q_2p_0+q_3p_1\\
-q_0p_2+q_1p_3+q_2p_0-q_3p_1 & q_0p_3+q_1p_2+q_2p_1+q_3p_0 & q_0p_0-q_1p_1+q_2p_2-q_3p_3 & -q_0p_1-q_1p_0+q_2p_3+q_3p_2\\
-q_0p_3-q_1p_2+q_2p_1+q_3p_0 & -q_0p_2+q_1p_3-q_2p_0+q_3p_1 & q_0p_1+q_1p_0+q_2p_3+q_3p_2 & q_0p_0-q_1p_1-q_2p_2+q_3p_3
\end{pmatrix}. \tag{25}$$

This comprises the parameterization of the SO(4) group by a pair of normalized quaternions.

Further we shall need also the small variations of the system of HOs residing at a given atom. Due to the algebraic group structure of the HOs manifold any small variation of HOs in a vicinity of any given set of HOs h can be obtained with use of the SO(4) matrix H close to the unity matrix I :

$$\begin{aligned}
&H = I + \delta^{(1)}H + \delta^{(2)}H,\\
&h' = Hh \approx h + \delta^{(1)}h + \delta^{(2)}h, \qquad (26)\\
&\delta^{(1)}h = \delta^{(1)}Hh, \quad \delta^{(2)}h = \delta^{(2)}Hh,
\end{aligned}$$

where the general form of matrix is given by singling out the contributions Eq. (25) up to the second order with respect to the (small) components of the vector parts of the quaternions **q** and **p** [7].

2.5. *Quaternion form of the hybrids and hybridization tetrahedron*

In Section 2.4 we used quaternions to construct the parameterization of the (SO(4) group) hybridization manifold. However, the strictly local HOs allow for the quaternion representation for themselves. Indeed, the quaternion may be characterized as an entity comprising a scalar and a 3-vector part: $\mathbf{q} = (s, \vec{v})$. The coefficient of the s-orbital does not change under the spatial rotation of the molecule, whereas the coefficients at the p-functions transform as if they were the components of the three-dimensional vector. Thus each of the HOs located at a heavy atom can be presented as a quaternion:

$$\mathbf{q}_m = (s_m, \vec{v}_m), \quad s_m^2 + |\vec{v}_m|^2 = 1. \tag{27}$$

For an arbitrary HO in the quaternion representation the first order correction obtained under variations $\delta\vec{\omega}_l$ and $\delta\vec{\omega}_b$ of the triples of the Jacobi angles acquire a particularly simple form:

$$\begin{aligned}
\delta^{(1)}s &= -(\delta\vec{\omega}_b, \vec{v}),\\
\delta^{(1)}\vec{v} &= s\delta\vec{\omega}_b + \delta\vec{\omega}_l \times \vec{v}.
\end{aligned} \tag{28}$$

The HOs and thus the quaternions representing the latter are subject to the normalization condition. This allows to construct a visual picture of hybridization by using four vector parts $\vec{v}_m$ at a given atom. The formal operation is the the projection by:

$$I - |s\rangle\langle s|, \tag{29}$$

which cuts out the scalar part of each HO $(s_m, \vec{v}_m)$ in the quaternion representation. It can be easily recovered from the normalization condition. The rest forms a *hybridization tetrahedron*. Directions of the vectors forming the latter coincide with those of the HOs themselves, the angles between the vectors coincide with the interhybrid angles, the lengths of the vectors are square roots of the weights of the p-states. These vectors can be assumed to have a common origin coincident with the position of the atom.

Despite they seem to be very flexible objects (the lengths of the vectors, intervector angles are likely to be variable) the hybridization tetrahedra are in fact subject to very strict conditions due to the orthonormality of the HOs at a given atom. Only a three-dimensional manifold of the possible forms of the hybridization tetrahedra spanned by the triple $\vec{\omega}_b^A$ of the Jacobi angles is available. This considerably reduces the freedom in allowed shapes of the hybridization tetrahedra. As one can easily check the standard sp^3-hybridization is naturally represented by a perfect tetrahedron with$|\vec{v}_m| = \sqrt{3}/2$; the sp^2-hybridization is represented by a trigonal pyramid with one of the vectors (aligned to its height) having a unit length, and three others representing the sp^2-hybrids laying in the plane with $|\vec{v}_m| = \sqrt{2/3}$; finally, the nonhybridized atom is represented by a tetrahedron formed by three perpendicular unit vectors while the fourth one representing the pure s HO is a zero vector. Three Jacobi angles defining the forms of hybridization tetrahedra cover all the intermediate situations. In fact this parameterization may serve as a basis of establishing correspondence between different MM atom types and different hybridization states controlled (flexibly enough) by the $\vec{\omega}_b^A$ triples and represented by hybridization tetrahedra of different shape (see below).

3. Constructing alternative forms of molecular mechanics

The representation of the molecular electronic energy in the APSLG approximation present above allows for a mechanistic representation which can be in some sense considered as a ‘generic’ or ‘deductive’ form of MM. Although the simplistic ‘balls-and-springs’ model hardly can be justified from a general point of view, it does not mean that some other mechanistic model can not be justified either. More sophisticated approaches which are constructed with an additional (artificial) condition that the interactions between the ‘atoms’ are required to have ‘classical’ form [28] also seem to be too much restrictive: the classic (in fact—electrostatic) form of the interatomic interaction cannot be substantiated in the ultimately quantum realm of molecular electronic structure.

The related history dates back to the beginning of the last century. As Prof. Kozelka cites in his excellent review Ref. [29] as early as in the year 1901 certain company advertised a model set of wooden (i.e. rigid) tetrahedra which were designed to represent the forms (spatial arrangement) of atoms in organic molecules. An MM description (if someone had had pursued this direction) could then naturally arise in terms of parameters of such tetrahedra, rather than balls’ sizes and the springs’ elasticities known now. Such a description in principle should not be worse than a conventional ‘balls-and-springs’ MM at least for that reason that atoms with bonds are to the same extent similar to balls with springs (or sticks) as they are to the wooden tetrahedra. The model QM expression for molecular energy Eq. (5) allows, however, to substantiate namely the ‘tetrahedral’ form of the MM. Indeed, a mathematical object called the ‘hybridization tetrahedron’ introduced above to visualize the shape of the HO system residing at a given atom can be modeled by some tetrahedral shapes assigned to ‘heavy’ atoms. Of course, tetrahedral shapes have been previously used in the literature to *visualize* atoms. It is enough to mention the textbook [30]. However, as far as we know, nobody tried to proceed further and to ascribe any definite energy significance to the form and relative orientation of these tetrahedra, though the qualitative considerations due to Pauling himself, leading to the maximal hybrid strength or the maximal overlap [31] principles, are well known. We are going, however, to deduce a mechanistic model for molecular energy from the QM method described above. It will be seen that performing necessary moves, following the line mentioned in the Introduction results naturally in such a tetrahedral representation of heavy atoms which is consistent with facts known from stetreochemistry.

The derivation reduces to the following: certain classes of the ESPs introduced in Section 2 are fixed according to some rules. The idea to fix at least a part of the ESPs immediately rises a question at what values they must be fixed and what governs the choice. In the semiempirical APSLG-MINDO/3 approach two classes of the ESP’s appear: the geminal amplitudes and the HOs related ones, respectively. This is of course a specific case of the two types of variables which appear in the MC SCF realm [32] to which the APSLG-MINDO/3 method belongs by construction. In the MC SCF two sets of variables are considered—the configurations’ expansion coefficients which relate to our geminal amplitudes and the MO expansion coefficients which correspond to our HOs’ parameters. The procedures of fixing these ESPs can be classified according to the specific subset which is kept fixed (this respectively results in the FA or the *fixed* geminal *amplitudes* and the FO or the fixed hybrid *orbitals* approaches) or is *tuned* to reproduce the effect of geometry variations or substitutions (this results in the TA and TO approaches). In what follows we shall construct a variety of approximate treatments of the expression Eq. (5) each leading to a specific mechanistic description.

3.1. Fixed amplitudes fixed orbitals (FAFO) model

This is a simplest possible mechanistic model of the PES following from an approximate treatment of the energy Eq. (5). The FA type of treatment implies that the geminal amplitude related ESPs Eq. (6) are fixed at their invariant values Eq. (10). This corresponds clearly to a simplified situation where all bonds are literally the single bonds. Within such a picture the dependence of the energy on the interatomic distance reduces to that of the matrix elements of the underlying QM (MINDO/3) Hamiltonian.

The FO type of treatment for the HOs implies that the weights of the s- and p-components in the HOs at each heavy atom are fixed. This also means that the shapes of the hybridization tetrahedra remain fixed. This can be done by a variety of ways, each producing a specific implementation of the FAFO model. The simplest way is to fix them at the standard sp^n hybridizations with integer $n = 1 \div 3$. Alternatively one may produce a series of hybridization tetrahedra by fitting the experimental data. Other methods may also be invented. In any case the tetrahedral shapes once found are fixed and interact with each other (and with the ‘spheres’ representing the hydrogen atoms). The number of bonding interactions each tetrahedron is allowed to take part in equals to four minus the number of lone pairs residing on it, i.e. is determined by the usual valence rules.

Analysis of the general energy expression Eq. (5) proves that the only HO orientation dependent contribution to the energy is the resonance energy of the two center bonds. It can be recast in the form of interaction between the hybridization tetrahedra which in its turn depends on the distance between the centers of the tetrahedra, on their mutual orientation, and on their orientation with respect to the straight line connecting the centers of the tetrahedra involved (the atoms). The latter can be proven by the following construction: consider the m-th two-center bond and the 4×4 matrix of the resonance integrals between the AOs in the diatomic coordinate frame (DCF) which is defined by setting its z-axis to coincide with the unit vector directed along the R_mL_m two center bond:

$$B^{R_mL_m} = \begin{pmatrix} \beta_{\sigma\sigma}^{R_mL_m} & 0 & 0 & \beta_{\sigma\zeta}^{R_mL_m} \\ 0 & \beta_{\pi\pi}^{R_mL_m} & 0 & 0 \\ 0 & 0 & \beta_{\pi\pi}^{R_mL_m} & 0 \\ \beta_{\zeta\sigma}^{R_mL_m} & 0 & 0 & \beta_{\zeta\zeta}^{R_mL_m} \end{pmatrix}, \tag{30}$$

Its elements depend on the R_mL_m-interatomic separation only. The resonance integral $\beta_{r_ml_m}^{R_mL_m}$ for the m-th bond (geminal) can be written in a concise form:

$$\beta_{r_ml_m}^{R_mL_m} = h_m^{R_m\dagger} B^{R_mL_m} h_m^{L_m},$$

where the HOs centered on nonhydrogen atoms are taken in the DCF as well. To get rid of the tight connection to the DCF we notice that the only necessary components of the vector parts of the HO quaternions i.e. their ζ-components have the CF invariant representation according to:

$$v_{m\zeta}^{T_m} = (v_m^{-T_m}, \vec{e}_{R_mL_m}). \tag{31}$$

With use of the latter the resonance integral can be rewritten in the form

$$\begin{aligned} \beta_{r_ml_m}^{R_mL_m} = {} & \beta_{\sigma\sigma}^{R_mL_m} s_m^{R_m} s_m^{L_m} + \beta_{\sigma\zeta}^{R_mL_m} s_m^{R_m} (\vec{v}_m^{L_m}, \vec{e}_{R_mL_m}) \\ & + \beta_{\zeta\sigma}^{R_mL_m} (\vec{v}_m^{R_m}, \vec{e}_{R_mL_m}) s_m^{L_m} \\ & + \beta_{\pi\pi}^{R_mL_m} (\vec{v}_m^{R_m}, \vec{v}_m^{L_m}) + (\beta_{\zeta\zeta}^{R_mL_m} - \beta_{\pi\pi}^{R_mL_m}) \\ & \times (\vec{v}_m^{R_m}, \vec{e}_{R_mL_m})(\vec{v}_m^{L_m}, \vec{e}_{R_mL_m}), \end{aligned} \tag{32}$$

which is coordinate frame independent. The shorthand form of the resonance integral is:

$$\beta_{r_ml_m}^{R_mL_m} = (s_m^{R_m}, \vec{v}_m^{R_m}) B^{R_mL_m} \begin{pmatrix} s_m^{L_m} \\ \vec{v}_m^{L_m} \end{pmatrix}, \tag{33}$$

with the resonance matrix following the quaternion structure of HOs with the scalar and vector parts:

$$B^{R_mL_m} = \begin{pmatrix} \beta_{\sigma\sigma}^{R_mL_m} & \beta_{\sigma\zeta}^{R_mL_m}\vec{e}_{R_mL_m} \\ \beta_{\zeta\sigma}^{R_mL_m}(\vec{e}_{R_mL_m})^{\dagger} & \beta_{\pi\pi}^{R_mL_m}\mathscr{I} + (\beta_{\zeta\zeta}^{R_mL_m} - \beta_{\pi\pi}^{R_mL_m})\vec{e}_{R_mL_m}\otimes\vec{e}_{R_mL_m} \end{pmatrix}, \qquad (34)$$

where $\mathscr{I}$ stands for the 3×3 unit matrix acting (as does the 3×3 diadic product $\vec{e}_{R_mL_m}\otimes\vec{e}_{R_mL_m}$) on the vector parts of HOs in the quaternion form.

The hybridization tetrahedra then interact according to Eq. (5) and the interaction energy depends on the mutual orientation of the tetrahedra and on that with respect to the bond axis. Multiplying the resonance integral by the quadrupled transferable spin bond order $P_{0m}^{rl} = 1/2$ Eq. (10) results in the resonance energy which is the only nontrivial contribution to the molecular energy at this (FAFO) level of approximation.

3.1.1. Local equilibrium conditions for hybridization tetrahedra and quasitorques

In the FAFO picture when the form of the hybridization tetrahedron is fixed the equilibrium condition for the HOs reduces to that for the orientation of the latter. Due to angular character of the variables involved the corresponding set of the energy derivatives with respect to the $\vec{\omega}_l^A$ components can be considered as a (quasi)torque (here the prefix *quasi* refers to the fact that no rotation of any physical body is involved in its definition rather that of a fictitious hybridization tetrahedron). As one can check, each bond incident to the given atom contributes to the quasitorque the following:

$$\vec{K}_m^{R_mL_m} = -4P_{0m}^{rl}\Big\{[\beta_{\zeta\sigma}^{R_mL_m}s_m^{L_m} + (\beta_{\zeta\zeta}^{R_mL_m} - \beta_{\pi\pi}^{R_mL_m}) \times(\vec{v}_m^{L_m},\vec{e}_{R_mL_m})]\vec{e}_{R_mL_m}\times\vec{v}_m^{R_m} + \beta_{\pi\pi}^{R_mL_m}\vec{v}_m^{L_m}\times\vec{v}_m^{R_m}\Big\}. \qquad (35)$$

Assuming to simplify the notations that for all the incident bonds the atom A is the right-end atom ($A = R_m$) we obtain the overall quasitorque acting upon the hybridization tetrahedron centered on the atom A and the corresponding energy minimum conditions with respect to orientations of all hybridization tetrahedra in the molecule:

$$\vec{K}_A = \sum_m \vec{K}_m^{R_mL_m}, \qquad (36)$$
$$\forall A,\ \vec{K}_A = 0.$$

Clearly enough, these are the equilibrium conditions analogous to those which appear in the problem of equilibrium of a system of rigid bodies [33].

Though the equilibrium conditions Eq. (36) require that a sum of the contributions Eq. (35) vanishes, it is of interest to consider archetypical situations when each of these contributions vanish. These situations are twofold since two vector terms in Eq. (35) sum up to give a quasitorque contribution. The first one, proportional to $\vec{e}_{R_mL_m}\times\vec{v}_m^{R_m}$, vanishes if the HO on the right-end atom and the bond vector are collinear. If the same holds also for the left-end atom one can see that the vector parts of both HOs ascribed to the bond under consideration are collinear so that the second vector term proportional to $\vec{v}_m^{L_m}\times\vec{v}_m^{R_m}$ also vanishes. This clearly corresponds to the equilibrium condition for two singly σ-bonded hybridization tetrahedra. A quasitorque appears if an HO is not collinear with the bond axis it is ascribed to and tends to align them.

For a pair of HOs not containing any s-contribution an alternative equilibrium condition is possible. For two pure p-orbitals residing on the right- and left-end atoms of the bond the numerical coefficients at the first vector terms vanish if the HOs are perpendicular to the bond axis. In this case the second vector term vanishes if two vectors representing the pure p-orbitals are parallel. This clearly corresponds to the π-bonding between the hybridization tetrahedra. A quasitorque then appears tending to orient two hybridization tetrahedra in such away that the two heights of unit length of two tetrahera are parallel.

3.1.2. Global equilibrium conditions for hybridization tetrahedron

In Section 3.1.1 we formulated the equilibrium conditions for the hybridization tetrahedra which follow from the FAFO approximation for the molecular energy Eq. (5). They do not seem to be practical for performing calculations since require tedious recalculations on the scalar and vector parts of the HOs after a step along the energy gradient Eq. (36)

is performed. An alternative would be to use the formulae Eqs. (13) and (14) with fixed pseudorotation angles $\vec{\omega}_b^A$ which produce the matrix $H(\vec{\omega}_b^A)$ with the columns corresponding to the system of HOs at a given atom. If these HOs are treated as quaternions, their vector parts $\vec{v}_m^{A(0)}$ form the hybridization tetrahedron at the atom A. The actual orientations of these tetrahedra are defined by interactions of each hybridization tetrahedron with their neighbors: either other tetrahedra or spheres, representing hydrogen atoms. For each atom the orientation of its system of HOs is given by a rotation matrix $R(\vec{\omega}_l^A)$ Eqs. (13) and (14) according to:

$$\begin{pmatrix} s_m^A \\ \vec{v}_m^A \end{pmatrix} = R^A \begin{pmatrix} s_m^A \\ \vec{v}_m^{A(0)} \end{pmatrix}. \tag{37}$$

The rotation matrices $R^A = R(\vec{\omega}_l^A)$ have the following structure:

$$R = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & & & \\ 0 & & \mathscr{R} & \\ 0 & & & \end{pmatrix}, \tag{38}$$

ensuring the invariance of the scalar parts of the HOs. The vector parts of all HOs residing at a given atom transform according to:

$$\vec{v}_m^A = \mathscr{R}^A \vec{v}_m^{A(0)}, \tag{39}$$

which ultimately gives the actual orientation of the hybridization tetrahedra in the molecule. The rotation matrix R^A can be written in the form [24,25]:

$$\mathscr{R} = \begin{pmatrix} r_0^2 + r_1^2 - r_2^2 - r_3^2 & 2(r_1 r_2 - r_0 r_3) & 2(r_1 r_3 + r_0 r_2) \\ 2(r_1 r_2 + r_0 r_3) & r_0^2 - r_1^2 + r_2^2 - r_3^2 & 2(r_2 r_3 - r_0 r_1) \\ 2(r_1 r_3 - r_0 r_2) & 2(r_2 r_3 + r_0 r_1) & r_0^2 - r_1^2 - r_2^2 + r_3^2 \end{pmatrix}, \tag{40}$$

where r_0, r_1, r_2, and r_3 are the components of a normalized quaternion $\mathbf{r}$ defining the required (quasi)rotation of the hybridization tetrahedron residing at the atom in question. The resonance energy thus becomes a quadratic function of the components of the normalized quaternions $\mathbf{r}^A$. The orientation of these tetrahedra satisfies the energy minimum condition. Taking derivatives with respect to the components of $\mathbf{r}^A$ and including the normalization conditions $\| \mathbf{r}^A \| = 1$ by using the Lagrange multipliers ξ^A results in a set of four-dimensional linear eigenvalue problems:

$$\Xi^A \mathbf{r}^A = \xi^A \mathbf{r}^A, \tag{41}$$

which must be solved self-consistently for all nonhydrogen atoms, since matrices Ξ^A depend on orientation of the hybridization tetrahedra on atoms bonded to A. The eigenvector $\mathbf{r}^A$ corresponding to the lowest eigenvalue ξ^A must be taken throughout the iteration process.

The matrix elements of Ξ^A can be evaluated with use of two fundamental facts concerning quaternions. First, the rotation of the vector part of an HO according to Eqs. (37)–(40) in a quaternion representation can be written as:

$$\mathbf{h}_m^A = \mathbf{r}^A \diamond \mathbf{h}_m^{A(0)} \diamond \vec{\mathbf{r}}^A, \tag{42}$$

where $\diamond$ stands for the quaternion multiplication. Second, for a pair of quaternions **a** and **b** written in the form Eq. (27):

$$\mathbf{a} = (a_0, \vec{a}); \qquad \mathbf{b} = (b_0, \vec{b}),$$

but not necessarily normalized, the following holds:

$$\mathbf{a} \diamond \mathbf{b} = (a_0 b_0 - (\vec{a}, \vec{b}), a_0 \vec{b} + b_0 \vec{a} + \vec{a} \times \vec{b}). \tag{43}$$

Then taking into account that by definition $\tilde{\mathrm{a}} = (a_0, -\vec{a})$ and performing the necessary algebra we arrive to a pair of 4×4 matrices

$$\begin{pmatrix} 0 & \frac{1}{2} \vec{v}_m^{R_m(0)} \times \vec{e}_{R_m L_m} \\ \frac{1}{2} (\vec{v}_m^{R_m(0)} \times \vec{e}_{R_m L_m})^\dagger & (\vec{v}_m^{R_m(0)}, \vec{e}_{R_m L_m}) \mathscr{I} + \frac{1}{2} (\vec{v}_m^{R_m(0)} \otimes \vec{e}_{R_m L_m} + \vec{e}_{R_m L_m} \otimes \vec{v}_m^{R_m(0)}) \end{pmatrix}$$

$$\begin{pmatrix} 0 & \frac{1}{2} \vec{v}_m^{R_m(0)} \times \vec{v}_m^{L_m} \\ \frac{1}{2} (\vec{v}_m^{R_m(0)} \vec{v}_m^{L_m})^\dagger & (\vec{v}_m^{R_m(0)}, \vec{v}_m^{L_m}) \mathscr{I} + \frac{1}{2} (\vec{v}_m^{R_m(0)} \otimes \vec{v}_m^{L_m} + \vec{v}_m^{L_m} \otimes \vec{v}_m^{R_m(0)}) \end{pmatrix},$$

which must be respectively multiplied by

$$(\beta_{\zeta\sigma}^{R_mL_m} s_m^{L_m} + (\beta_{\zeta\zeta}^{R_mL_m} - \beta_{\pi\pi}^{R_mL_m})(\vec{v}_m^{L_m}, \vec{e}_{R_mL_m})) \text{ and } \beta_{\pi\pi}^{R_mL_m},$$

and then summed and multiplied by the quadrupled bond orders for all bonds incident to the given atom which we habitually take to be the right-end one for them all for the sake of simplicity of notation. Summing up these contributions for all bonds incident to the given atom results in the required symmetric matrix Ξ^A. This comprises the global equilibrium condition for hybridization tetrahedra in the FAFO model. Their direct relation with the molecular shape which enters in an invariant manner through the bond vectors $\vec{e}_{R_mL_m}$ is remarkable enough.

3.1.3. Libration energy of hybridization tetrahedra

In the previous subsections we considered the equilibrium conditions for the hybridization tetrahedra in molecule, which represent the orientation of the systems of HOs at each heavy atom with fixed weights of the s- and p- functions in each HO. In order to have a description of the energy in the vicinity of the equilibrium the second order corrections to it are necessary. The terms of interest are of two types. First, these are the terms of the second order with respect to quasirotation angles $\delta\vec{\omega}_l^A$ at a given atom which describe the energy variation when the hybridization tetrahedron of the atom at hand slightly rotates (librates) while all surrounding hybridization tetrahedra for heavy atoms and spheres representing hydrogens remain in their equilibrium positions. Second, these are the terms of the overall second order bilinear with respect to $\delta\vec{\omega}_l^{R_m}$ and $\delta\vec{\omega}_l^{L_m}$. These terms describe the correction to the energy which appears when hybridization tetrahedra residing on two bonded atoms simultaneously librate.

Due to the FAFO approximations only the resonance energy is affected by the librations of the hybridization tetrahedra. The terms of the first type may be obtained by inserting the second order correction $(\delta^{(2)}s_m^{R_m}, \delta^{(2)}\vec{v}_m^{R_m})$ to the right-end HOs into the expression for the resonance integral Eq. (33). In the FO approximation $\delta^{(2)}s_m^{R_m}$ naturally vanishes. Inserting the second order corrections for the HOs in Eq. (32) results in the second order correction to the resonance integrals. The latter must be habitually multiplied by the quadrupled spin bond orders and summed. This procedure has been performed in Refs. [7,17] for the sp^3 hybridized atom with four symmetric substituents. In this case the energy correction is a diagonal quadratic form in $\delta\vec{\omega}_l^{R_m}$ with three degenerate eigenvalues:

$$\delta_{\omega l\omega l}^{(2)}E = 4P_0^{rl}\mathcal{G}_{ll}^{R_mR_m}(\delta\vec{\omega}_l^{R_m})^2,$$

$$\mathcal{G}_{ll}^{R_mR_m} = \frac{4}{\sqrt{3}}\left(\beta_{\zeta\sigma}^{R_mL_m} s_m^{L_m} - \beta_{\zeta\zeta}^{R_mL_m}\sqrt{1-(s_m^{L_m})^2}\right). \tag{44}$$

The corrections of the second type can be easily obtained if one inserts the first order corrections $(\delta^{(1)}s_m^{R_m}, \delta^{(1)}\vec{v}_m^{R_m})$ and $(\delta^{(1)}s_m^{L_m}, \delta^{(1)}\vec{v}_m^{L_m})$ to Eq. (33). As previously $\delta^{(1)}s_m^{R_m} = \delta^{(1)}s_m^{L_m} = 0$ due to the FO approximation. After some algebra we get:

$$\delta_{\omega l\omega l}^{(2)}E = 4P_{0m}^{rl}(\delta\vec{\omega}_l^{R_m}|\mathcal{G}_{ll}^{R_mL_m}|\delta\vec{\omega}_l^{L_m}),$$

where

$$\begin{aligned}\mathcal{G}_{ll}^{R_mL_m} &= \beta_{\pi\pi}^{R_mL_m}((\vec{v}_m^{R_m}\otimes\vec{v}_m^{L_m}) - (\vec{v}_m^{R_m}, \vec{v}_m^{L_m})\mathcal{I}) \\ &\quad + (\beta_{\zeta\zeta}^{R_mL_m} - \beta_{\pi\pi}^{R_mL_m})(\vec{v}_m^{R_m} \times \vec{e}_{R_mL_m})\otimes \\ &\qquad (\vec{v}_m^{L_m} \times \vec{e}_{R_mL_m}).\end{aligned} \tag{45}$$

The terms of this type must be summed over all bonds between the heavy atoms. The formulae Eqs. (44) and (45) represent the potential energy of the molecular system as a quadratic function in small variations of the variables $\delta\vec{\omega}_l^A$. This may be used either in a frame of linear response analysis of reaction of the system of hybridization tetrahedra to various perturbations or (if the tetrahedra are supplied by fictitious inertia momenta) as potential energy of the system of the tetrahedra in a frame of the Car-Parinello [35] procedure. The interaction of the neighbor hybridization tetrahedra is particularly simple if the tetrahedra involved correspond to the sp^3 hybridized atom with equivalent bonds. In this case the HOs are collinear with the bond vectors so that the formula Eq. (45) becomes:

$$\mathcal{G}_{ll}^{R_mL_m} = \frac{3}{4}\beta_{\pi\pi}^{R_mL_m}((\vec{e}_{R_mL_m}\otimes\vec{e}_{R_mL_m}) - \mathcal{I}).$$

Numerical estimates for the libration force constant can be easily done. For the methane molecule only the term of Eq. (44) appears. With the MINDO/3 parameterization at the equilibrium geometry of methane it amounts to 17.19 eV/rad^2 For neopentane at the same conditions the diagonal libration force constant is 21.15 eV/rad^2, whereas the coefficient at the off-diagonal 3×3 matrix block responsible for coupling of librations of two neighbor carbon hybridization tetrahedra is only 2.02 eV/rad^2.

3.2. Fixed amplitudes tuned orbitals (FATO) model

The deductive mechanistic model for molecular PES proposed in Section 3.1 corresponds to the picture of the rigid (‘wooden’) hybridization tetrahedra. Within such a picture whatever perturbations taking place to a molecule may result in variations of the orientation of the hybridization tetrahedra representing the systems of HOs residing at each heavy atom. Meanwhile, the proposed treatment of the SO(4) hybridization manifold may be used to construct another, wider (but also deductive) mechanistic representation of molecular energy where heavy atoms are depicted as flexible (rubber) tetrahedra. Analysis of results of semiempirical calculations by the APSLG-MINDO/3 method underlying our derivation, performed in Ref. [6], shows that the hybridization related ESPs are much more sensitive to various perturbations affecting the molecule than the geminal amplitudes related ones. This puts to agenda developing an approximation which allows first of all the adjustment of the shape of the HOs at each heavy atom to various perturbations. The geminal related ESPs may be still considered to be fixed at their transferable values.

In the FA approximation the one-center energies E_A Eq. (5) related to the carbon atom remains hybridization independent (see below and Refs. [7, 17]). This result which ultimately comes from the fact that in carbon the valence shell (with the principal quantum number 2) is half filled distinguishes carbon among other elements. For that reason (in the FA approximation) only the resonance contribution to the total energy depends both on orientation (as in the FAFO model) and on the form of the hybridization tetrahedra. This considerably simplifies the derivation in the case of carbon atoms. For that reason we consider it separately.

3.2.1. FATO molecular mechanics of sp^3 carbons

Local equilibrium conditions for sp^3 *carbons and pseudotorques*. As it is mentioned previously the only hybridization dependent contribution to the total energy in the case of carbon atom is the resonance energy. Thus the equilibrium conditions with respect to the shape and orientation of the hybridization tetrahedra representing the system of HOs residing at a carbon atom A reduce to a requirement of evanescence of the first derivatives of the resonance energy with respect to pseudo- and quasirotation angles Eq. (14). Using the expansion for the resonance energy up to linear terms [17] in small pseudo- and quasirotations ($\delta\vec{\omega}_b^A$ and $\delta\vec{\omega}_l^A$) results in the equilibrium conditions:

$$\vec{N}^A = \nabla_{\vec{\omega}_b^A} E = \vec{K}^A = \nabla_{\vec{\omega}_l^A} E = 0; \;\; \forall A,$$

where the quasitorque $\vec{K}^A$ is defined by Eq. (35), whereas the pseudotorque $\vec{N}^A$ is:

$$\begin{aligned} \vec{N}^A = -4 \sum_{m \in A} P_{0m}^{rl} \{ & \beta_{\sigma\sigma}^{R_m L_m} \vec{v}_m^{R_m} s_m^{L_m} \\ & + \beta_{\sigma\zeta}^{R_m L_m} \vec{v}_m^{R_m} (\vec{v}_m^{L_m}, \vec{e}_{R_m L_m}) - \beta_{\zeta\sigma}^{R_m L_m} s_m^{R_m} s_m^{L_m} \vec{e}_{R_m L_m} \\ & - \beta_{\pi\pi}^{R_m L_m} s_m^{R_m} \vec{v}_m^{L_m} - (\beta_{\zeta\zeta}^{R_m L_m} - \beta_{\pi\pi}^{R_m L_m}) \\ & \times s_m^{R_m} (\vec{v}_m^{L_m}, \vec{e}_{R_m L_m}) \vec{e}_{R_m L_m} \}. \end{aligned} \tag{46}$$

As previously we assumed here for the sake of simplicity of notation that for all bonds incident to the atom A this atom is a ‘right-end’ atom of the bond. Though the equilibrium conditions are rather cumbersome, for symmetric cases they can be solved leading to obvious answers: the carbon atom in symmetric tetrahedral environment acquires the sp^3 hybridization with the HOs collinear to the bonds, etc.

The analog of the global equilibrium conditions Eq. (41) for the FAFO model can be obtained in the FATO setting as well. In order to do so we notice that inserting the SO(4) matrix parameterized by a pair of quaternions Eq. (25) yields the resonance energy as a function bilinear in each of the normalized quaternions $\mathbf{q}^A$ and $\mathbf{p}^A$ describing together the shape and orientation of the hybridization tetrahedron. Combining this bilinear form with the normalization conditions for the quaternions: $\|\mathbf{q}^A\| = \|\mathbf{p}^A\| = 1$ taken into account with use of the Lagrange multipliers θ^A and ν^A results in a system of pairs of coupled linear equations:

$$\Theta^A \mathbf{q}^A = \theta^A \mathbf{p}^A; \, Y^A \mathbf{p}^A = \nu^A \mathbf{q}^A,$$

which must be solved consistently for all A. We do not give the explicit form of matrices Θ^A and Y^A here both because they are too cumbersome and also for the reason that the given treatment of the global equilibrium can not be generalized to atoms other than carbon since their one-center energies involve higher powers of the HO coefficients (see below).

Second order corrections to energy of sp^3 *carbon.* In order to construct the required mechanistic picture the estimate of the restoring force which opposes both the quasi- and pseudorotation (deformation) of the hybridization tetrahedra is necessary. That can be obtained by a linear response procedure. For the sp^3 carbon atom in the symmetric tetrahedral environment the related resonance energy is a diagonal quadratic form with respect to small quasi- and pseudorotations together with triply degenerate eigenvalues [7,17]:

$$\delta^{(2)}_{\omega\omega}E = 4P^{rl}_{0m}(\mathscr{G}^{R_mR_m}_{bb}(\delta\omega^{R_m}_b)^2 + \mathscr{G}^{R_mR_m}_{ll}(\delta\omega^{R_m}_l)^2),$$

where

$$\mathscr{G}^{R_mR_m}_{bb} = 2\Bigg[\left(\beta^{R_mL_m}_{\sigma\sigma} + \frac{1}{\sqrt{3}}\beta^{R_mL_m}_{\zeta\sigma}\right)s^{L_m}_m - \left(\beta^{R_mL_m}_{\sigma\zeta} + \frac{1}{\sqrt{3}}\beta^{R_mL_m}_{\zeta\zeta}\right)\sqrt{1-(s^{L_m}_m)^2}\Bigg]. \quad (47)$$

This is used to obtain the response of the shape and orientation of the hybrids ($\delta\vec{\omega}_b$ and $\delta\vec{\omega}_l$) to various perturbations (see below). Analogous expressions can be obtained with use of formula Eq. (25) for arbitrary hybridization and this will be done elsewhere [7].

Further terms are necessary to describe the interaction between the two bonded tetrahedra which appears when either of them is quasi- or pseudorotated in the vicinity of the equilibrium. These formulae can be obtained by considering those cross terms in the resonance integral expansion which are bilinear in $\delta\vec{\omega}^{R_m}$ and $\delta\vec{\omega}^{L_m}$, respectively. This results in the following 6×6 off-diagonal $\mathscr{G}^{R_mL_m}$ blocks

$$\delta^{(2)}_{\omega\omega}E = 4P^{rl}\begin{pmatrix} \mathscr{G}^{R_mL_m}_{bb} & \mathscr{G}^{R_mL_m}_{bl} \\ \mathscr{G}^{R_mL_m}_{lb} & \mathscr{G}^{R_mL_m}_{ll} \end{pmatrix},$$

where the 3×3 subblocks $\mathscr{G}^{R_mL_m}_{bb}$, $\mathscr{G}^{R_mL_m}_{bl}$, $\mathscr{G}^{R_mL_m}_{lb}$ are:

$$\begin{aligned}\mathscr{G}^{R_mL_m}_{bb} &= \beta^{R_mL_m}_{\sigma\sigma}\vec{v}^{R_m}_m\otimes\vec{v}^{L_m}_m - \beta^{R_mL_m}_{\sigma\zeta}s^{R_m}_m\vec{v}^{R_m}_m\otimes\vec{e}_{R_mL_m} \\ &\quad - \beta^{R_mL_m}_{\zeta\sigma}s^{R_m}_m\vec{e}_{R_mL_m}\otimes\vec{v}^{L_m}_m + \beta^{R_mL_m}_{\pi\pi}s^{R_m}_m s^{L_m}_m\mathscr{I} \\ &\quad + (\beta^{R_mL_m}_{\zeta\zeta} - \beta^{R_mL_m}_{\pi\pi})s^{R_m}_m s^{L_m}_m\vec{e}_{R_mL_m}\otimes\vec{e}_{R_mL_m}, \\ \mathscr{G}^{R_mL_m}_{bl} &= -\beta^{R_mL_m}_{\sigma\zeta}\vec{v}^{R_m}_m\otimes(\vec{v}^{L_m}_m\times\vec{e}_{R_mL_m}) - \beta^{R_mL_m}_{\pi\pi}s^{R_m}_m\mathscr{V}^{L_m}_m \\ &\quad + (\beta^{R_mL_m}_{\zeta\zeta} - \beta^{R_mL_m}_{\pi\pi})s^{R_m}_m\vec{e}_{R_mL_m}\otimes(\vec{v}^{L_m}_m\times\vec{e}_{R_mL_m}), \\ \mathscr{G}^{R_mL_m}_{lb} &= -\beta^{R_mL_m}_{\zeta\sigma}(\vec{v}^{R_m}_m\times\vec{e}_{R_mL_m})\otimes\vec{v}^{L_m}_m + \beta^{R_mL_m}_{\pi\pi}s^{L_m}_m\mathscr{V}^{R_m}_m \\ &\quad + (\beta^{R_mL_m}_{\zeta\zeta} - \beta^{R_mL_m}_{\pi\pi})s^{L_m}_m(\vec{v}^{R_m}_m\times\vec{e}_{R_mL_m})\otimes\vec{e}_{R_mL_m},\end{aligned}$$

$\mathscr{V}^{R_m}_m$ stands for the 3×3 matrix representing the vector multiplication by $\vec{v}^{R_m}_m$; and the $\mathscr{G}^{R_mL_m}_{ll}$ subblock is defined by Eq. (45). These subblocks couple in a bilinear fashion small pseudo- and quasirotations of the hybridization tetrahedra corresponding to the right- and left-end atoms of the bond (in the specified order). Their form particularly simplifies for the sp^3 carbon atom in a symmetric environment for which we have:

$$\begin{aligned}\mathscr{G}^{R_mL_m}_{bb} &= \tfrac{1}{4}\beta^{R_mL_m}_{\pi\pi}\mathscr{I} - \tfrac{1}{4}\Big[3\beta^{R_mL_m}_{\sigma\sigma} + \sqrt{3}\beta^{R_mL_m}_{\sigma\zeta} \\ &\quad - \sqrt{3}\beta^{R_mL_m}_{\zeta\sigma} - (\beta^{R_mL_m}_{\zeta\zeta} - \beta^{R_mL_m}_{\pi\pi})\Big]\vec{e}_{R_mL_m}\otimes\vec{e}_{R_mL_m},\end{aligned}$$

$$\mathscr{G}^{R_mL_m}_{bl} = \mathscr{G}^{R_mL_m}_{lb} = \tfrac{1}{2}\beta^{R_mL_m}_{\pi\pi}\mathscr{E}_{R_mL_m}.$$

where $\mathscr{E}_{R_mL_m}$ stands for the 3×3 matrix representing the vector multiplication by $\vec{e}_{R_mL_m}$.

For the diagonal restoring force constants related to the deformations of the hybridization tetrahedra the following estimates can be obtained: 30.58 eV/rad^2 in CH$_4$; 34.49 eV/rad^2 in neopentane.

3.2.2. FATO molecular mechanics of nitrogen atom

As it has been shown above within the FA approximation the form of the HO on four-coordinated carbon atom is ultimately defined by the two-center resonance interactions. It is the SO(4) group structure of the hybrid manifold that restricts the capacity of the HOs residing on the atom to adjust themselves to the arrangements of the surrounding atoms (groups). In this subsection we apply linear response method to estimate the shape of the hybridization tetrahedron and to analyze stereochemistry and molecular mechanics of nitrogen atom. Even in the FA picture presence of the lone pairs on the nitrogen atom results in a significant hybridization dependence of the one-center energies Eq. (5) which cannot be considered as a small perturbation. For that reason we consider the hybridization dependent parts of molecular energy in order to extract information on equilibrium shapes of the corresponding hybridization tetrahedra. For the sake of simplicity we restrict ourselves with one in the ammonia molecule since this model problem retains all the characteristic features of the general case. In order to study it we consider the C_{3v} ammonia molecule with the third order axis directed along the z-axis of the coordinate frame. Its geometry is characterized by the pyramidalization angle δ equal to zero for the planar geometry. For the symmetry reasons the overall resonance energy of three N–H bonds is a function of only one pseudorotation angle ω_{sz} and of δ :

$$-\sqrt{3}P^{rl}\Big[\beta_{\sigma\sigma}^{R_mL_m}\cos\omega_{sz}+\beta_{\zeta\sigma}^{R_mL_m}\sin\delta\sin\omega_{sz}+\sqrt{2}\beta_{\zeta\sigma}^{R_mL_m}\cos\delta\Big]. \tag{48}$$

It is easy to see that the minimum of the above expression with respect to both its arguments is reached precisely for the planar configuration and the sp^2 hybridization ($\delta=0$, $\omega_{sz}=0$). The hybridization dependent part of the one-center energy of the nitrogen atom is:

$$\Big[(U_s-U_p)+\tfrac{1}{4}(3C_2+2C_3+4C_5)\Big]\sin^2\omega_{sz}+\tfrac{1}{4}C_3\sin^4\omega_{sz}, \tag{49}$$

with obvious extrema: a minimum at $\omega_{sz}=\pi/2$ (no hybridization) and a maximum at $\omega^{sz}=0$ (sp^2 hybridization). (The combinations C_n, ($n=1\div5$, see below) of the Slater–Condon parameters [36] have been introduced in Refs. [7,17]). Characteristic values of the atomic parameters [23] show that the contributions depending on Coulomb integrals can provide the total variation in energy less than 0.8 eV whereas the difference of the core attractions results in a huge amount of about 10 eV. Thus the nontrivial equilibrium in such a system is only possible if the strong deforming potential exerted by the first term and tending to no hybridization is counterpoised by other contributions. Within the FA approximation the only counterpoise is the resonance energy. By this we arrive to a very simple (but internally consistent) picture for hybridization/stereochemistry of the nitrogen atom. Two contributions to the energy exist. One (Eq. (49)) tends to keep the valence angles at 90°, another one (Eq. (48)) tends to place all substituents at the nitrogen atom to one plane with the latter. The observed pyramidal form is a result of the interplay between these two contributions. This results in a pyramidalization (inversion) potential in which no kind of interbond interactions is involved, by the way (see below).

In the present setting the equilibrium shape of the nitrogen hybridization tetrahedron is given by the value of the pseudorotation angle ω_{sz} only. In the vicinity of the equilibrium it is reasonable to assume that the latter value arises as a result of an action of a deforming force exerted due to the resonance interaction with hydrogens on the otherwise nonhybridized nitrogen atom. The nonplanar form is maintained by the reaction of the one-center energy proportional to the second derivative of Eq. (49) at the nonhybridized minimum. The total pseudotorque exerted by three symmetrical bonds equals to the derivative of Eq. (48) with respect to ω_{sz} at the point corresponding to the minimum of Eq. (49). Finally he correction to the pseudorotation angle is:

$$\delta\omega_{sz}=\frac{\sqrt{3}P_0^{rl}\beta_{\sigma\sigma}^{R_mL_m}}{2\Big[(U_s-U_p)+\tfrac{1}{4}(3C_2+2C_3+4C_5)\Big]},$$

which defines to a first approximation the shape of the hybridization tetrahedron of the nitrogen atom. That raw estimate results in the numerical value of $\delta\omega_{sz}$ of only ca. 0.38 rad. The equilibrium values of this pseudorotation angle is ca. 0.95 rad. That large discrepancy is clearly due to the pseudotorque and thus the tetrahedron shape are determined by the resonance interactions of the nitrogen's s-orbital only and for that reason do not depend on actual pyramidalization angle δ. The equilibrium pseudorotation angle in its turn is esimated at the equilibrium geometry where additional deforming force is exerted upon the system of the nitrogen HOs.

The above analysis of molecular energy unequivocally results in certain pyramidalization potential of rather nontrivial form which is reported elsewhere [7, 17]. Its existence is proven by sequential derivation from a QM expression for the energy Eq. (5) rather then decided on a 'school-wise basis' [34]. Formally, the source of this potential is a purely QM requirement of mutual orthogonality of HOs centered on an atom. Its physical nature may be characterized as the energy of excited configurations of the nitrogen atom admixed to its ground state by the perturbation induced by the resonance interaction with surrounding bonded atoms. The admixture coefficients (weights) of the excited atomic configurations appear as functions of hybridization parameters, which can be even explicitly written according to Ref. [11]. Neither of these sources has anything to do with interpair Coulomb interaction.

3.3. Tuned amplitudes fixed orbitals (TAFO) model

Further analysis of different possible approximation procedures for treating the energy Eq. (5) would be one which allows to tune the ESPs related to the geminal amplitudes (TA) but keeps intact the shapes of hybridization tetrahedra (FO). This results in a TAFO approach which a priori looks as an acceptable option for constructing an MM-like scheme for the molecular PES. However, a simple analysis of the above expansions allows one to conclude that in fact the sensitivity of two subsets of the ESPs characteristic for the underlying APSLG-MINDO/3 QM method opposes this approximation scheme. In fact whatever perturbation affects the HO-related ESPs much stronger than the geminal related ones. Thus in any case when the geminal amplitudes are expected to be affected by the environment the HOs are affected much stronger. The opposite situation may happen only if some very rare special perturbation (like completely symmetric deformation of the carbon tetrahedron) takes place. For that reason we do not discuss this approximation further in this paper.

3.4. Tuned amplitudes tuned orbitals (TATO) model

The mechanistic model of the PES closest to the underlying QM procedure (and eventually coincident with the latter [6]) is of course that where both classes of ESP's are adjusted to each other and to the geometry variations. Nevertheless, it can be shown that the corrections to the invariant (transferable values) of the geminal related ESPs are small, though not negligible. As for the HO related ESPs they remain as much sensitive to whatever perturbation as in the FATO class of approximations.

In the present subsection we consider the effects of small variations of the geminal related ESPs upon the shapes of the hybridization tetrahedra. Doing that we take into account only the corrections to the ESPs of the first order with respect to ζ^{-1} and μ. In this assumption the bond orders remain invariant which considerably simplifies the whole picture.

Since, the bond orders in the TATO model are kept at their invariant values, the energy modification occurs due to the one-center terms. The one-center energy Eq. (5) can be rewritten [7]:

$$E_A = E^{(0)} + E' = E_1 + E_2 + E_3,$$

where

$$E_i = E_i^{(0)} + E_i',$$

and

$$E_1^{(0)} = \sum_{t_m \in A} U_m^t, \quad E_1' = 2 \sum_{t_m \in A} U_m^t \delta P_m^{tt}, \tag{50}$$

$$E_2^{(0)} = \frac{1}{4} \sum_{t_m \in A} (t_m t_m | t_m t_m)^{T_m},$$

$$E_2' = \sum_{t_m \in A} (t_m t_m | t_m t_m)^{T_m} \delta \Gamma_m^{tt},$$

$$E_3^{(0)} = \frac{1}{4} \sum_{k \neq m} \sum_{tt'} g_{t_k t_m'}^{T_k}, \; E_3' = \sum_{k \neq m} \sum_{tt'} g_{t_k t_m'}^{T_k} (\delta P_k^{tt} + \delta P_m^{t't'}).$$

where we dropped the second order term $\delta P_k^{tt} \delta P_m^{t't'}$ from E_3'.

The following matrix elements are responsible for the hybridization dependence of the above expressions:

$$U_m^t = s_m^2 (U_s - U_p) + U_p, \tag{51}$$

$$(t_m t_m | t_m t_m) = C_1 + C_2 s_m^2 + C_3 s_m^4,$$

$$g_{t_k t'_m} = C_4 + C_5 [s_m^2 + s_k^2] + C_3 s_m^2 s_k^2.$$

The one-center energy components have no clear counterpart in the standard MM setting. In our approach the one-center contributions E'_i which arise due to deviations of the geminal related ESPs (δP_m^{tt} and $\delta \Gamma_m^{tt}$) from their transferable values are hybridization dependent. The derivatives of E'_i's with respect to the angles $\vec{\omega}_b$, $\vec{\omega}_l$ taken at the values characteristic for the stable hybridization tetrahedra shapes which appear in the FATO model yield quasi- and pseudotorques acting upon the hybridization tetrahedron. In order to evaluate these quantities we notice first of all that all the dependence on hybridization resides in the one center terms in that of the matrix elements Eq. (51). In the latter the only source of the hybridization dependence is that of the second and fourth powers of the coefficients of the s-orbital in the HOs. Since they do not depend on the orientation of the hybridization tetrahedra we immediately arrive to a conclusion that no quasitorques appear in the TATO setting:

$$\vec{K}'_i = 0.$$

For the pseudotorques we get:

$$\vec{N}'_1 = -4(U_s - U_p) \sum_{t_m \in A} \delta P_m^{tt} s_m \vec{v}_m,$$

$$\vec{N}'_2 = -2 \sum_{t_m \in A} \delta \Gamma_m^{tt} (C_2 + 2C_3 s_m^2) s_m \vec{v}_m,$$

$$\vec{N}'_3 = -2 \sum_{k \neq m} \sum_{tt'} (C_5 (s_m \vec{v}_m + s_k \vec{v}_k) + C_3 s_m s_k (s_k \vec{v}_m + s_m \vec{v}_k))(\delta P_k^{tt} + \delta P_m^{t't'}).$$

This general expression must be evaluated at characteristic points. If we want to evaluate say effect of single substitution at the sp^3 carbon atom the choice of symmetric hybrids is appropriate. At this point we have $\forall m\ s_m = 1/2$; $\vec{v}_m = \sqrt{3}/2 \vec{e}_{R_m L_m}$ which results in the following:

$$\vec{N}'_1 = -\sqrt{3}(U_s - U_p) \sum_{t_m \in A} \delta P_m^{tt} \vec{e}_{R_m L_m},$$

$$\vec{N}'_2 = -\frac{\sqrt{3}}{2}\left(C_2 + \frac{1}{2} C_3\right) \sum_{t_m \in A} \delta \Gamma_m^{tt} \vec{e}_{R_m L_m},$$

$$\vec{N}'_3 = -\frac{\sqrt{3}}{2}\left(C_5 + \frac{1}{4} C_3\right) \sum_{k \neq m} \sum_{tt'} (\vec{e}_{R_m L_m} + \vec{e}_{R_k L_k}) \times (\delta P_k^{tt} + \delta P_m^{t't'}).$$

The above pseudotorques give in the linear response approximation the following pseudorotations of the hybridization tetrahedron on the atom under consideration:

$$\delta \vec{\omega}_{bi} = \frac{N'_i}{8 P_{0m}^{rl} \mathcal{G}_{bb}^{R_m R_m}}; \qquad \delta \vec{\omega}_b = \sum_i \delta \vec{\omega}_{bi}. \tag{52}$$

These quantities ultimately define that which can be related to the atom types of the standard MM setting. Indeed, the atom types in the MM differ among other features by their preferable valence angles. In the deductive MM setting the counterpart for the preferred valence angles are the interhybrid angles or in other words the shapes of the hybridization tetrahedra. The latter may be characterized by interhybrid angles $\theta_{mm'}$ related to the coefficients of the s-functions in the corresponding HOs at a given atom:

$$\cos \theta_{mm'} = -\frac{s_m}{\sqrt{1 - s_m^2}} \frac{s_{m'}}{\sqrt{1 - s_{m'}^2}}. \tag{53}$$

Its variation under a small pseudorotation $\delta \vec{\omega}_b$ is:

$$\delta \theta_{mm'} = -\frac{1}{\sqrt{1 - s_m^2 - s_{m'}^2}} \times \left(s_{m'} (\delta \vec{\omega}_b, \vec{v}_m) \sqrt{\frac{1 - s_{m'}^2}{1 - s_m^2}} + s_m (\delta \vec{\omega}_b, \vec{v}_{m'}) \sqrt{\frac{1 - s_m^2}{1 - s_{m'}^2}} \right). \tag{54}$$

For the symmetric sp^3 tetrahedron the above expression simplifies to:

$$\delta \theta_{mm'} = -\sqrt{\frac{3}{8}} (\delta \vec{\omega}_b, \vec{e}_{R_m L_m} + \vec{e}_{R_{m'} L_{m'}}).$$

For the atoms with valence shell having the principal quantum number 2 the pseudotorque $\vec{N}'_1$ dominates the whole picture. Then assuming that only one HO acquires a density correction δP_1^{rr} we get as a first approximation:

$$\delta\theta_{1m} = -\frac{1}{4\sqrt{2}}\frac{U_s - U_p}{\mathcal{G}_{bb}^{RR}}\delta P_1^{rr} \;\; \forall m \neq 1.$$

$$\delta\theta_{mm'} = -\delta\theta_{1m} \;\; \forall mm' \neq 1.$$

Since $U_s - U_p < 0$ the density increase ($\delta P_1^{rr} > 0$) at the first HO results in an increase of the incident interhybrid angles and in equal decrease of the angles between otherwise nonperturbed HOs. This all, of course, relates to analysis performed in Ref. [34] with that difference that HOs here are not arbitrarily assumed to be collinear with the bonds. Numerical estimates are the following. The calculation on the CH_3F molecule results in the value of δP_1^{rr} for the C–F bond geminal of -0.13. With use of the above estimate of $\mathcal{G}_{bb}^{RR}$ performed for methane we get $\delta\theta_{1m} \approx -4°$ which is in a perfect agreement with the complete APSLG-MINDO/3 calculation.

This result allows to readdress the Nyholm–Gillespie [13–15] idea of electron pair Coulomb repulsion in the valence shell as a source of the observed stereochemistry. According to these authors (supported by the calculation Ref. [16]) the interpair repulsion energies conform to the rule that more populated bond repels the bonds incident to it stronger, which in the limit results in a rule that lone pair repels other bonds and the corresponding valence angles are smaller than the ideal tetrahedral ones. We have already shown that this result appears without any relation to the Coulomb repulsion while analyzing the source of the pyramidalization potential of nitrogen. Here as well, we see that an infinitesimal increase of electron population at one of the HOs makes others to increase the interhybrid angles with that, more populated, HO. Though this is in perfect agreement with the Nyholm–Gillespie rules the real source of the effective interhybrid interaction has nothing to do with Coulomb repulsion of electron pairs.

The above consideration is in agreement also with the well known qualitative Bent's rules [37] which states that the weight of the s-AO increases in the HO which is involved in bonding with a more electropositive substituents. Indeed, electropositive substituents would lead to the positive values of δP_1^{rr} and after using the formulae Eqs. (52) and (28) the variation for the s-coefficient becomes:

$$\delta s_1 = -\frac{3}{8}\frac{U_s - U_p}{\mathcal{G}_{bb}^{RR}}\delta P_1^{rr},$$

which is positive for the second row atoms. The latter formula shows that the Bent's rule validity crucially depends on the sign of the $U_s - U_p$ difference. If for any reasons the opposite sign of the above factor occurs or the effect of the $\vec{N}_1'$ pseudotorque is superceded by that of $\vec{N}_2'$ (it has an opposite sign and according to our estimate is much smaller for the atoms of the first period which is likely to change for heavier elements) the inversion of the Bent's rule takes place, and its modification proposed by Frenking [40] on the base of analysis of numerical experiments acquires theoretical explanation.

4. Discussion

In the context of a construct presented in this paper the relation with previous theories must explain on one hand the common points and on the other hand the differences and thus the reasons why previously developed approaches did not reach certain results we believe are acquired here. Here we performed a sequence of moves intended to bridge the gap between an approximate QM description of molecular electronic structure and a classical representation of the PES of organic molecules suitable for further parameterization and simplifications in order to reach a scheme similar to molecular mechanics. This construct may be qualified as a deductive molecular mechanics since each of its components has a transparent counterpart in the underlying QM description and the approximations and simplifications used can be uniquely characterized and formulated. From our point of view this gives a possible explanation to the enormous success both of MM in describing with considerable precision even tiny details of molecular geometry of organic compounds and of VSEPR in explaining and predicting characteristic features of molecular shapes. These two success stories made us consider them as experimental facts which require certain theoretical explanation. We felt that a demand for such an explanation is rather strong since according to Ref. [38] “the situation is scandalous:

… the method [MM] used in thousands of laboratories throughout the world does not have any reliable QM derivation". At the same time the kind of explanation we were looking for fits to a remark by Coulson [39] that"… any explanation *why* must be given in terms of concepts which are regarded as adequate or suitable. So the explanation must not be that the electronic computer shows that $D(H-F) \gg D(H-H)$, since this is not an explanation at all, but merely a confirmation of experiment" by some other means and the measure of consistency (or inconsistency) between results of different types of experiments (including numerical ones performed on an ab initio or semiempirical level) is a subject of separate theoretical consideration. We also feel that a sequential derivation based on well defined grounds might be as much useful for verification or falsification of whatever pragmatic model as accurate numerical experiments are [40].

Previous attempts to sequentially construct additive systematics for molecular energies (which a fortiori include the MM paradigm) reviewed in Ref. [8] had the following common points: the transferability hypothesis, one-determinant approximation for the underlying QM wave function, and a posteriori localization of the orbitals. These features together prevented authors of Ref. [8] from constructing a sequential route from the QM description of the molecular electronic structure to any additive systematics. The reason is that the real derivation of any additive systematics must include both a proof of transferability and a procedure of defining the relevant local states (whether transferable or not). Also one has to admit that it may well happen that 'a one-span bridge' between that much different paradigms as the QM and MM is not possible and bridging the gap may require a pier somewhere in between. For these reasons we have chosen an alternative approach to the problem technically based on the APSLG form of trial wave function [5] and the variational principle for molecular electronic energy. The key feature of the underlying QM approach is its local character recovering the common notion of chemical bonds and lone pairs on the basis of a non-Hartree–Fock electronic trial wave function treated variationally. The non single-determinant form of the trial wave function allowed to obtain a natural representation of molecular energy in terms of local quantities. Also the proof of transferability of key quantities entering the theory strongly relies upon the APSLG form of the trial wave function. The local character of the one-electron states is inherent within the approach suggested and the specific form of the one-electron states of interest appears as a result of energy minimization procedure which allowed to avoid poorly defined 'tail cutting'. All these features of the present approach allow as it is shown above to construct a sequential procedure of deriving a mechanistic description of molecular PES departing from a local QM description of molecular electronic structure.

The mechanistic picture obtained takes an intermediate position between QM methods and standard MM schemes. Though it can be used as a standalone mechanistic model of molecular PES the standard MM picture is still to be derived from it by eliminating the auxiliary (from this point of view) angular variables for quasi- and pseudorotation of the hybridization tetrahedra. In the present paper we did not address in detail the dependence of molecular energy on interatomic separations and the coupling of the bond stretching and valence angle bending with the variables describing the shape and orientation of the hybridization tetrahedra. It will be published elsewhere [7].

In the present paper we also gave a comparison of results of our derivations with predictions based on the VSEPR model of stereochemistry [13–15]. The latter ascribes a great significance to Coulomb bond–bond interactions in order to explain the observed molecular shapes. It has to be noticed that in the setting present in this paper molecular shapes themselves do not appear. The conjecture is that they follow somehow the shapes of the hybridization tetrahedra but there is shurely some difference due to other contributions to the energy. In the TATO model that would be interactions between the effective atomic charges. However, even in the TATO model where one could expect nontrivial effect of electron–electron interactions upon the shape of the hybridization tetrahedra only the topology of the hybridization manifold assures the latter in carbon atoms. The situation with other organogenic atoms at a first glance significantly differs from this picture. In the case of nitrogen and oxygen atoms even in the FA approximation the one-center energy is strongly hybridization dependent due to the one-electron terms describing the core attraction of electrons in the lone pair and sensitive to the relative weights of the s- and p-AOs in the corresponding HO. The source of this is of course the strong difference between the core attractions (also Coulomb by nature) in the s- and p-subshells with large preference towards purely s-lone pair for atoms with the valence shell with principal quantum number 2. In free atoms this immediately resulted in no hybridization at all for nitrogen and oxygen and in 90° valence angles predicted by older theories [11] for water and ammonia with subsequent need to explain the observed form of these molecules with the valence angles only slightly smaller than the tetrahedral ones and both exceeding 100°. Curiously enough, the authors of the VSEPR model seem to overlook this result well known for years (if not for decades) and did not consider it as a starting point and incidentally the limiting case of the electron pair repulsion and started their theory from a scratch. If we reside in the FA domain we have to admit that the only source of the observed stereochemistry can be found in the interplay between one-center hybridization dependent terms and the resonance energy. This was clear yet to Coulson [11], but seems to acquire a formal proof only here.

5. Conclusion

In the present paper we analyzed the semiempirical QM method which uses the APSLG form for the electronic trial wave function and strictly local HOs as a basis of one-electron states. Two elements of this analysis are crucial: (i) the variational character of treating molecular energy, which allowed for the linear response procedures; (ii) the adequate parameterization of the hybridization manifold for non-hydrogen atoms. This analysis resulted in a family of mechanistic models for molecular PES. This makes a step towards a QM substantiation of MM. Several alternative forms of molecular mechanics appear. The simplest one based on the fixed amplitudes fixed orbitals (FAFO) approximation for the APSLG ESPs results in a picture representing all nonhydrogen (heavy) atoms as rigid tetrahedra. The molecular energy then becomes a function of molecular geometry (internuclear separations), of mutual orientation of these tetrahedra, and of their orientation with respect to interatomic axes. More elaborated schemes inherit both the visual representation of heavy atoms by tetrahedral shapes and the form of the energy as a function of the distances between the tetrahedra centers and of their orientations. The FATO class of approximations leads to a model with flexible hybridization tetrahedra and allows to pose questions concerning the equilibrium shapes of these tetrahedra. Finally, the TATO class of approximations may be qualified as one closest to the underlying QM method: it allows for adjustment of both the electron density matrix elements and the shapes of the hybridization tetrahedra. At this level of consideration it becomes possible to analyse in a linear response the effect of population variations at HOs upon the shapes of hybridization tetrahedra. It was found that these effects are in agreement with the empirical rules known within the VSEPR theory, but the source is completely different.

When this paper has been already accepted a paper Ref. [41] came to the author's view. It deals to a large extent with the problem of parameterizing the hybridization manifold of a main group atom with the sp-valence shell. The coordinate map used in Ref. [41] differs from both Eqs. (14) and (25), but the general interrelations within the system of HOs at a given atom are the same since they are controlled by the dimensionality of this manifold.

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