Efficient Multipole Model and Linear Scaling of NDDO-Based Methods

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Fast growth of computational costs with that of the system's size is a bottleneck for the applications of traditional methods of quantum chemistry to polyatomic molecular systems. This problem is addressed by the development of linear (or almost linear) scaling methods. In the semiempirical domain, it is typically achieved by a series of approximations to the self-consistent field (SCF) solution. By contrast, we propose a route to linear scalability by modifying the trial wave function itself. Our approach is based on variationally determined strictly local one-electron states and a geminal representation of chemical bonds and lone pairs. A serious obstacle previously faced on this route were the numerous transformations of the two-center repulsion integrals characteristic for the neglect of diatomic differential overlap (NDDO) methods. We pass it by replacing the fictitious charge configurations usual for the NDDO scheme by atomic multipoles interacting through semiempirical potentials. It ensures invariance of these integrals and improves the computational efficiency of the whole method. We discuss possible schemes for evaluating the integrals as well as their numerical values. The method proposed is implemented for the most popular modified neglect of diatomic overlap (MNDO), Austin model 1 (AM1), and PM3 parametrization schemes of the NDDO family. Our calculations involving well-justified cutoff procedures for molecular interactions unequivocally show that the proposed scheme provides almost linear scaling of computational costs with the system's size. The numerical results on molecular properties certify that our method is superior with respect to its SCF-based ancestors.

1. Introduction

The perspectives of quantum chemistry as a valuable tool in chemical research are generally attributed to its ability to predict the electronic structures and properties of molecular systems with a high degree of accuracy for reasonable time intervals. Nowadays, modern ab initio methods allow us to obtain very accurate results for small molecules.[1] The price for this accuracy is very fast growth of the required computational resources with that of the system's size ($N^4 \div N^7$ where N is the dimension of the basis set). It limits the area of applicability of these methods to small- and medium-sized molecules. Although the development of computer technology pushes forward our computational abilities, the problem of large-scale calculations remains actual, especially taking into account the growing needs of biological chemistry and nanochemistry.

There are two solutions to this problem proposed in the literature. The first one is the construction of hybrid schemes where different parts of a molecule are treated using different methods:[2,3] Typically, a reaction center is described by some quantum chemical methods, while the environment is accounted by classical force fields. The second solution is based on the construction of schemes with linear or almost linear dependence of the required computational resources on the system's size ($O(N)$-methods).[4,5] The localization of electronic degrees of freedom due to the exponential decay of the one-electron density matrix elements in the coordinate space[6] and the "principle of nearsightedness" by Kohn[7] provide physical grounds for these schemes. It is important that most of the $O(N)$-methods are targeted to the tight-binding model, and the required scalability is achieved by a loss of accuracy.

In the semiempirical domain, the growth of computational costs with the system's size scales as N^3 because of the necessity to diagonalize the Fock matrix. A series of approaches has been proposed to avoid this step: the divide-and-conquer scheme,[8,9] the density matrix search method,[10] and methods based on the localized molecular orbitals in orthogonal[11] and nonorthogonal[12] formulations. The possibility to devise semiempirical $O(N)$-methods opens access to the development of the quantum mechanical (QM)/QM hybrid schemes, where the environmental region is treated by semiempirical methods of quantum chemistry.[13] It allows us to solve the problem of the intersubsystem junction in these methods by a sequential derivation based on the perturbation expansions.[3]

The main purpose of semiempirical methods is to provide a reliable quantum description for large and ultralarge molecular systems. The developmental perspectives for the semiempirical domain are usually considered[14] from the viewpoint of improving the existing parametrization schemes, adding classical terms responsible for the dispersion interactions and introducing sophisticated orthogonalization corrections[15] and effective core potentials.[15,16] These modifications are devised within the basic one-determinant approximation. An alternative route is based on the account of electron correlation given by several techniques employing perturbation expansions,[17] effective Hamiltonians,[18] valence bonds,[19] and multireference configuration interaction.[20] In the present paper, we pursue the goal of improving both the wave function's structure and the scalability properties in the framework of the NDDO parametrization.

In a series of papers,[21−23] we have proposed and developed a family of variational semiempirical methods based on the trial wave function in the form of the antisymmetrized product of strictly local geminals (SLG). It takes into account the intrabond ("left−right") electron correlation, while the interbond electron transfers are totally neglected because of the strictly local (atom-centered) character of one-electron states. These methods (quite surprisingly) required only a minor re-parametrization of the

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standard parameters' sets and provide the numerical estimates of heats of formation and eqilibrium geometries,[21,23] as well as vertical ionization potentials,[22] which are superior by accuracy with respect to the corresponding SCF procedures. It was also shown that the SLG methods have a great potential in the derivation of classical force fields[24] and the development of hybrid quantum/classical schemes.[3,25]

When the MINDO/3 semiempirical Hamiltonian[26] is used, the SLG scheme leads to almost linear scaling of computational costs with the system's size (the quadratic term becomes dominating only for very large molecular systems).[21] The NDDO-type Hamiltonian assumes a more detailed account of the two-center Coulomb interactions. In combination with the SLG wave function, it leads to the necessity of numerous integral transformations induced by basis set transformations. This step dominates the whole procedure and predetermines the quadratic scalability of the SLG-NDDO methods[23] with substantial coefficients at the quadratic terms. In the present paper, we consider long-range Coulomb interactions in the standard NDDO methods (MNDO,[27] AM1,[28] and PM3[29]) and demonstrate that the scheme previously adopted for estimates of the two-center repulsion integrals is not optimal for a local description of electronic structure. In the next section, we describe the SLG-NDDO approximation for the electronic structures of molecules and show that a modified form of molecular integrals leads to significant simplification of the whole procedure. Then, we compare different schemes for the estimates of the two-center repulsion integrals and present numerical results demonstrating the scalability properties and the quality of the calculated heats of formation for the modified SLG-NDDO procedure. Finally, we draw several conclusions on the perspectives of fast semiempirical methods with a local description of both electron correlation and one-electron states.

2. Method

2.1. Strictly Local Geminals. In this section, we consider a sequence of basic steps leading to semiempirical NDDO methods employing a trial wave function in the form of the antisymmetrized product of strictly local geminals.[23] The first step in the wave function construction consists of orthogonal 4×4 transformations of atomic orbitals (AOs) for each atom A with an {sp} basis set producing hybrid orbitals (HOs) t_m

$$t_{m\sigma}^+ = \sum_{i \in A} h_{mi}^A a_{i\sigma}^+ \qquad (1)$$

Each transformation matrix h^A is parametrized by six Jacobi angles. For hydrogen atoms, the only HO coincides with the 1s orbital.

The HOs are assigned to geminals representing chemical bonds and lone pairs: Each chemical bond is spanned by two orbitals r and l for the right and left ends of the bond; each lone pair is described by only one HO (r). The mth geminal representing a lone pair is given by one configuration

$$g_m^+ = r_{m\alpha}^+ r_{m\beta}^+ \qquad (2)$$

with both electrons residing on the same HO, while the same geminal representing a chemical bond is a linear combination of three singlet configurations

$$g_m^+ = u_m r_{m\alpha}^+ r_{m\beta}^+ + v_m l_{m\alpha}^+ l_{m\beta}^+ + w_m(r_{m\alpha}^+ l_{m\beta}^+ + l_{m\alpha}^+ r_{m\beta}^+) \quad (3)$$

where the first two configurations are ionic and the last one is covalent. The geminals are mutually orthogonal and satisfy the

normalization condition

$$\langle 0|g_m g_m^+|0\rangle = u_m^2 + v_m^2 + 2w_m^2 = 1 \qquad (4)$$

Thus constructed geminals are strictly local, because their carrier spaces are formed by strictly local (one-center) orbitals. The total wave function is constructed as their antisymmetrized product

$$|\Psi\rangle = \prod_m g_m^+|0\rangle \qquad (5)$$

The electronic structure of geminals can be characterized by the elements of one- and two-electron density matrices

$$P_m^{tt'} = \sum_\sigma \langle 0|g_m t_{m\sigma}^+ t'_{m\sigma} g_m^+|0\rangle$$

$$\Gamma_m^{tt'} = \langle 0|g_m t_{m\sigma}^+ t'^+_{m-\sigma} t'_{m-\sigma} t_{m\sigma} g_m^+|0\rangle$$

$$P_m^{rr} = 2(u_m^2 + w_m^2)$$

$$P_m^{ll} = 2(v_m^2 + w_m^2)$$

$$P_m^{rl} = P_m^{lr} = 2(u_m + v_m)w_m$$

$$\Gamma_m^{rr} = u_m^2$$

$$\Gamma_m^{ll} = v_m^2$$

$$\Gamma_m^{rl} = \Gamma_m^{lr} = w_m^2 \qquad (6)$$

(Notation here differs from that adopted in refs 21 and 23, namely, by coefficient 2 at $P_m^{tt'}$.)

The total energy is the sum of the electronic energy and the core—core repulsion. The form of the last term adopted in the MNDO, AM1, and PM3 methods is given in refs 27−29, respectively. The electronic energy can be expressed through the density matrices and molecular integrals. The transformation of the one-electron basis set induces the transformation of all molecular integrals (those of resonance, core attraction, and intraatomic and interatomic Coulomb repulsion). The electronic energy is a sum of five terms according to the types of interactions in the Hamiltonian

$$E = E_{\text{c−attr}} + E_{\text{oc−rep}} + E_{\text{res}} + E_{\text{tc−rep}} + E_{m-b} \qquad (7)$$

The contribution from the attraction of electrons to cores is

$$E_{\text{c−attr}} = \sum_A \sum_{t_m \in A} \left(U_{t_m t_m}^A + \sum_{B \neq A} V_{t_m t_m, B}^A\right) P_m^{tt} \qquad (8)$$

The intraatomic contribution due to the electron repulsion is a sum of contributions involving one and two HOs

$$E_{\text{oc−rep}} = \sum_A \left\{ \sum_{t_m \in A} (t_m t_m | t_m t_m)^A \Gamma_m^{tt} + \frac{1}{4} \sum_{\substack{t_m, t'_n \in A \\ m \neq n}} [2(t_m t_m | t'_n t'_n)^A - (t_m t'_n | t'_n t_m)^A] P_m^{tt} P_n^{t't'} \right\} \quad (9)$$

The resonance interaction (electron transfer) is a sum of intrabond contributions

$$E_{\text{res}} = -2 \sum_{A < B} \sum_{m \in AB} \beta_{r_m l_m}^{AB} P_m^{rl} \qquad (10)$$

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where the notation $m \in AB$ means that the mth bond is one between atoms A and B. The two-center electron repulsion can be written as

$$E_{\text{tc-rep}} = \sum_{A<B} \sum_{t_m \in A} \sum_{t'_n \in B} (t_m t_m | t'_n t'_n)^{AB}[(1 - \delta_{mn})P_m^{tt} P_n^{t't} +$$

$$2\delta_{mn}\Gamma_m^{rl}] \quad (11)$$

The last contribution describes NDDO-specific interactions of single bonds constituting one multiple bond

$$E_{m-b} = -\sum_{\substack{t_m t'_n \in A \\ m<n}} (t_m t'_n | \tilde{t}'_n \tilde{t}_m)^{AB} P_m^{rl} P_n^{rl} \quad (12)$$

where $\tilde{t} = l$ for $t = r$ and $\tilde{t} = r$ for $t = l$.

The total energy is a function of two classes of electronic structure parameters (transformation matrices h^A and geminal amplitudes u_m, v_m, and w_m) which are all determined variationally. It is important that the total number of these parameters is proportional to the system's size (for the traditional SCF scheme, the number of electronic structure parameters − MO LCAO coefficients or elements of one-electron density scales as N^2) and they describe local fragments of electronic structure. It is a necessary prerequisite for constructing a linearly scaling method. The limiting factor in calculations are summations over the two-center repulsion integrals (i.e., transformations of these integrals from the basis of AOs to the basis of HOs). Here, we consider a direct way to accelerate this step and to construct a linearly scaling procedure for NDDO calculations of molecular energies.

2.2. Multipole Expansions. The energy of the Coulomb interaction for two nonbonded atoms A and B can be extracted from the total SLG energy and rewritten in a simple form

$$E_{\text{coul}}^{AB} = Z^A Z^B (ss|ss)^{AB} + \sum_{m \in A} \sum_{n \in B} P_m^A P_n^B (mm|nn)^{AB} -$$

$$Z^A \sum_{n \in B} P_n^B (ss|nn)^{AB} - Z^B \sum_{m \in A} P_m^A (mm|ss)^{AB} \quad (13)$$

where we use the simplified notation m for t_m and P_m^A is the total electron density on this HO. It is important that E_{coul} includes only the standard Coulomb part of the core−core repulsion. The two-center repulsion integrals entering eq 13 can be readily rewritten in the basis of AOs

$$(ss|nn)^{AB} = \sum_{kl \in B} h_{kn}^B h_{ln}^B (ss|kl)^{AB}$$

$$(mm|ss)^{AB} = \sum_{ij \in A} h_{im}^A h_{jm}^A (ij|ss)^{AB}$$

$$(mm|nn)^{AB} = \sum_{ij \in A} \sum_{kl \in B} h_{im}^A h_{jm}^A h_{kn}^B h_{ln}^B (ij|kl)^{AB} \quad (14)$$

These integrals have the tensor properties of corresponding multipole−multipole interactions. It can be used to construct effective schemes for their approximate evaluation.[30] The standard NDDO schemes (MNDO, AM1, and PM3) replace the multipoles by charge configurations.[30] A point dipole is replaced by two point charges of opposite sign, while the diagonal and nondiagonal components of a quadrupole moment are modeled by three and four point charges, respectively. It is assumed that these point charges interact through semiempirical potentials, producing necessary expressions for two-center molecular integrals. This formulation does not allow one to get simple expressions for the energy of the Coulomb interaction between

nonbonded atoms, and numerous summations in eqs 13 and 14 must be explicitly performed, making the whole procedure very time-consuming.

The Coulomb interaction between nonbonded atoms given by eq 13 can be formally rewritten in the form

$$E_{\text{coul}}^{AB} = [-Z_A(ss|^A + \sum_{m \in A} P_m^A(mm|^A] \bullet [-Z_B|ss)^B + \sum_{n \in B} P_n^B|nn)^B] \quad (15)$$

where $\bullet$ denotes interaction between two charge distributions. The strictly local character of one-electron basis functions forming carrier spaces for geminals allows us to introduce point multipoles describing charge distributions for atoms (given by the expressions in square brackets in eq 15) with definite densities on the HOs. For convenience, we write them in the units $-e$. The atomic charge (monopole) is then

$$q^A = \sum_{m \in A} P_m^A - Z^A \quad (16)$$

The characteristic lengths defining the dipole moment for an (sp)-distribution and the quadrupole moment for a (pp)-distribution depend on the principal quantum number n for the sp shell and the orbital (Slater) exponents

$$D_1 = \frac{2n + 1}{\sqrt{3}} \frac{(4\zeta_{ns}\zeta_{np})^{n+1/2}}{(\zeta_{ns} + \zeta_{np})^{2n+2}}$$

$$D_2 = \sqrt{\frac{(2n + 1)(2n + 2)}{20}} \zeta_{np}^{-1} \quad (17)$$

By using these parameters and the representation of a hybrid orbital in the quaternion form $(s_m, \vec{v}_m)$,[24] where s_m and three components of $\vec{v}_m$ are, respectively, the coefficients of the s and p_x, p_y, p_z AOs in the expansion of HOs explicitly referring to their tensor properties (i.e., to the fact that the coefficients s_m are invariant under rotations of either the molecule itself or the laboratory coordinate frame, whereas the coefficents forming $\vec{v}_m$ transform as components of a 3-vector under similar rotations), we obtain the dipole moment of the charge distribution on atom A to be

$$\vec{\mu}^A = 2D_1^A \sum_{m \in A} P_m^A s_m \vec{v}_m^A \quad (18)$$

The standard theory of multipole moments defines the quadrupole moment for a system of charges as

$$Q_{\alpha\beta} = \sum q(3x_\alpha x_\beta - r^2 \delta_{\alpha\beta}) \quad (19)$$

This tensor is defined as a traceless one, because the trace enters only the energy contributions proportional to Δf (where f is a potential, and Δ is a sum of second derivatives with respect to Cartesian coordinates, i.e., the Laplacian), which vanishes exactly for the Coulomb potential $1/R$.

The Poisson equation $\Delta f = 0$ is, however, not valid for semiempirical potentials f. Therefore, in the semiempirical context, it is more convenient to introduce a second-order tensor with a nonvanishing trace instead of the usual quadrupole moment

$$\hat{S}^A = \frac{1}{2} \sum q x_\alpha x_\beta = (D_2^A) \sum_{m \in A} P_m^A \vec{v}_m^A \otimes \vec{v}_m^A \quad (20)$$

It describes the distribution of charges but does not imply any

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assumptions about the properties of their interaction potential. To get back to the usual quadrupole moment, we introduce the total density on the p orbitals of atom A as $P_p^A = \sum_{m \in A} P_m^A[1 - (s_m)^2]$. It leads to a compact expression for the true quadrupole moment on atom A

$$\hat{Q}^A = 6\hat{S}^A - 2(D_2^A)^2 P_p^A \hat{I} \tag{21}$$

The potentials acting between the multipoles are not those known from electrostatics, since they are based not on the Coulomb interaction of the form of $^1/_R$ but rather on a semiempirical interaction potential approximating the effective values of integrals in the region of intermediate interatomic distances. The most popular semiempirical potential adopted in the NDDO methods is that proposed by Dewar, Sabelli, and Klopman[31,32]

$$f_{l_1 l_2}(R) = [R^2 + (\rho_{l_1} + \rho_{l_2})^2]^{-1/2} \tag{22}$$

It depends on the type of interaction (indices l_1 and l_2 correspond to the 2^{l_1} and 2^{l_2} poles located on atoms A and B, respectively). The semiempirical approach to molecular integrals prompts two types of formulas for interactions including quadrupoles: those based on the tensor $\hat{S}$ and those based on an additional *assumption* of validity of the Poisson equation and, thus, expressible through the usual quadrupole moment tensors $\hat{Q}$. In the latter case, semiempirical potential is treated as if it satisfied the condition $\Delta f = 0$, simplifying the formulas but mathematically incorrect. The general expression for the interaction energy can be rewritten in a general form with the components transforming as tensors

$$E_{coul}^{AB} = q^A G^{00} q^B + q^A G_\alpha^{01} \vec{\mu}_\alpha^B - \vec{\mu}_\alpha^A G_\alpha^{10} q^B - \vec{\mu}_\alpha^A G_{\alpha\beta}^{11} \vec{\mu}_\beta^B + q^A G_{\alpha\beta}^{02} \hat{S}_{\alpha\beta}^B + \hat{S}_{\alpha\beta}^A G_{\alpha\beta}^{20} q^B - \vec{\mu}_\alpha^A G_{\alpha\beta\gamma}^{12} \hat{S}_{\beta\gamma}^B + \hat{S}_{\alpha\beta}^A G_{\alpha\beta\gamma}^{21} \vec{\mu}_\gamma^B + \hat{S}_{\alpha\beta}^A G_{\alpha\beta\gamma\delta}^{22} \hat{S}_{\gamma\delta}^B \tag{23}$$

where

$$G_{\alpha\beta...\mu}^{l_1 l_2} = \nabla_\alpha \nabla_\beta ... \nabla_\mu f_{l_1 l_2}(R) \tag{24}$$

and ∇_α, ∇_β, ... denote the Cartesian components of the gradient operator. The Coulomb interactions between two nonbonded atoms A and B are classified according to the quantum numbers l_1 and l_2 of the AOs involved in the potential eq 22. The following cases can be specified (we assume that the values of all functions are estimated at R_{AB} and write R instead of R_{AB} for brevity).

The charge−charge, $\{l_1 l_2\} = \{00\}$, contribution reads

$$E_{00}^{AB} = q^A q^B f_{00} \tag{25}$$

The charge−dipole, $\{l_1 l_2\} = \{01\}$ or $\{10\}$, interaction gives two contributions

$$E_{01}^{AB} = q^A f'_{01}(\vec{n}_{AB}, \vec{\mu}^B)$$

$$E_{10}^{AB} = q^B f'_{10}(\vec{n}_{BA}, \vec{\mu}^A) \tag{26}$$

where $\vec{n}_{AB}$ is the unit vector directed from atom A to atom B.

The dipole−dipole, $\{l_1 l_2\} = \{11\}$, interaction can be written as a sum of contributions proportional to the scalar product of

dipole moments and the product of their projections on the line connecting atoms A and B

$$E_{11}^{AB} = -\frac{f'_{11}}{R}(\vec{\mu}_A, \vec{\mu}_B) - \left(f''_{11} - \frac{f'_{11}}{R}\right)(\vec{\mu}_A, \vec{n}_{AB})(\vec{\mu}_B, \vec{n}_{AB}) \tag{27}$$

The charge−quadrupole, $\{l_1 l_2\} = \{02\}$ or $\{20\}$, interactions for semiempirical potentials are the following

$$E_{02}^{AB} = q^A\left[\frac{f'_{02}}{R}tr\hat{S}^B + \left(f''_{02} - \frac{f'_{02}}{R}\right)(\vec{n}_{AB}, \hat{S}^B, \vec{n}_{AB})\right]$$

$$E_{20}^{AB} = q^B\left[\frac{f'_{20}}{R}tr\hat{S}^A + \left(f''_{20} - \frac{f'_{20}}{R}\right)(\vec{n}_{AB}, \hat{S}^A, \vec{n}_{AB})\right] \tag{28}$$

Under the additional assumption $\Delta f = 0$, one obtains

$$E_{02}^{AB} = \frac{q^A}{6}\left(f''_{02} - \frac{f'_{02}}{R}\right)(\vec{n}_{AB}, \hat{Q}^B, \vec{n}_{AB})$$

$$E_{20}^{AB} = \frac{q^B}{6}\left(f''_{20} - \frac{f'_{20}}{R}\right)(\vec{n}_{AB}, \hat{Q}^A, \vec{n}_{AB}) \tag{29}$$

The dipole−quadrupole, $\{l_1 l_2\} = \{12\}$ or $\{21\}$, interaction in general formulation can be written as

$$E_{12}^{AB} = \frac{f''_{12}R - f'_{12}}{R^2}[(\vec{\mu}^A, \vec{n}_{BA})tr\hat{S}^B + 2(\vec{\mu}^A, \hat{S}^B, \vec{n}_{BA})] + \frac{f'''_{12}R^2 - 3f''_{12}R + 3f'_{12}}{R^2}(\vec{\mu}^A, \vec{n}_{BA})(\vec{n}_{AB}, \hat{S}^B, \vec{n}_{AB})$$

$$E_{21}^{AB} = \frac{f''_{21}R - f'_{21}}{R^2}[(\vec{\mu}^B, \vec{n}_{AB})tr\hat{S}^A + 2(\vec{\mu}^B, \hat{S}^A, \vec{n}_{AB})] + \frac{f'''_{21}R^2 - 3f''_{21}R + 3f'_{21}}{R^2}(\vec{\mu}^B, \vec{n}_{AB})(\vec{n}_{AB}, \hat{S}^A, \vec{n}_{AB}) \tag{30}$$

while in the case of the additional assumption $\Delta f = 0$, one gets

$$E_{12}^{AB} = \frac{f''_{12}R - f'_{12}}{3R^2}(\vec{\mu}^A, \hat{Q}^B, \vec{n}_{BA}) + \frac{f'''_{12}R^2 - 3f''_{12}R + 3f'_{12}}{6R^2}(\vec{\mu}^A, \vec{n}_{BA})(\vec{n}_{AB}, \hat{Q}^B, \vec{n}_{AB})$$

$$E_{21}^{AB} = \frac{f''_{21}R - f'_{21}}{3R^2}(\vec{\mu}^B, \hat{Q}^A, \vec{n}_{AB}) + \frac{f'''_{21}R^2 - 3f'''_{21}R + 3f'_{21}}{6R^2}(\vec{\mu}^B, \vec{n}_{AB})(\vec{n}_{AB}, \hat{Q}^A, \vec{n}_{AB}) \tag{31}$$

The quadrupole−quadrupole, $\{l_1 l_2\} = \{22\}$, interaction includes derivatives of a semiempirical potential up to the fourth order

$$E_{22}^{AB} = \frac{f''_{22}R - f'_{22}}{R^3}[tr\hat{S}^A tr\hat{S}^B + 2tr(\hat{S}^A\hat{S}^B)] + \frac{f'''_{22}R^2 - 3f''_{22}R + 3f'_{22}}{R^3}(\vec{n}_{AB}, \{\hat{S}^A tr\hat{S}^B + \hat{S}^B tr\hat{S}^A + 4\hat{S}^A\hat{S}^B\}, \vec{n}_{AB}) + \frac{f_{22}^{IV}R^3 - 6f'''_{22}R^2 + 15f''_{22}R - 15f'_{22}}{R^3} \times (\vec{n}_{AB}, \hat{S}^A, \vec{n}_{AB})(\vec{n}_{AB}, \hat{S}^B, \vec{n}_{AB}) \tag{32}$$

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Under the additional assumption $\Delta f = 0$, it yields

$$E_{22}^{AB} = \frac{f_{22}''R - f_{22}'}{18R^3} tr(\hat{Q}^A \hat{Q}^B) +$$

$$\frac{f_{22}'''R^2 - 3f_{22}''R + 3f_{22}'}{9R^3}(\vec{n}_{AB}, \hat{Q}^A \hat{Q}^B, \vec{n}_{AB}) +$$

$$\frac{f_{22}^{IV}R^3 - 6f_{22}'''R^2 + 15f_{22}''R - 15f_{22}'}{36R^3} \times$$

$$(\vec{n}_{AB}, \hat{Q}^A, \vec{n}_{AB})(\vec{n}_{AB}, \hat{Q}^B, \vec{n}_{AB}) \quad (33)$$

The formulas given above allow for relatively fast estimates of the two-center contribution to the total energy. Moreover, derivatives of the total energy with respect to molecular geometry parameters can be easily calculated and used for an efficient optimization. We implemented the SLG-NDDO method employing the true multipole scheme for the two-center repulsion integrals. In the next section, we give some numerical results illustrating its potential in semiempirical electronic structure calculations.

3. Results and Discussion

In the present paper, we develop a semiempirical method based on the SLG wave function. Special attention is paid to the two-center repulsion integrals and interactions between nonbonded atoms. These integrals are the most important part of the NDDO scheme. It has been shown more than 50 years ago[33,34] that multipole expansions can adequately reproduce analytical electron repulsion integrals for a wide range of interatomic distances. These ideas are used in the standard NDDO methods where point multipoles are modeled by appropriate charge configurations. The last approximation makes the integrals non-invariant with respect to rotations of the coordinate frame, because the charge configurations have nonvanishing higher multipole moments. In actual calculations, this non-invariance is masked by performing them in the diatomic coordinate frame (rotations of the coordinate axes induce rotation of the diatomic coordinate frame, and the integrals are calculated identically). The formulas given in the previous section restore the invariance, because they are written in a tensor form. The change of the computation scheme leads to changes in numerical estimates, although both schemes have the same asymptotic behavior at $R \rightarrow \infty$. We analyze the consequences of these modifications for the molecular integrals and the total energy.

First, we consider the two-center repulsion integrals on the example of two carbon atoms. Equation 22 shows that the Dewar−Sabelli−Klopman semiempirical potential depends on three parameters (ρ_0, ρ_1, and ρ_2). In the standard formulation,[30] these parameters are determined from the condition that at the limit $R \rightarrow 0$ the one-center integrals describing the interaction between two monopoles (g_{ss}), two dipoles (h_{sp}), and two quadrupoles (h_{pp}) must be reproduced. This condition is of course arbitrary, and for example, the one-center limit for the integral $(ss|zz)$ is not reproduced by this scheme. The reason is simple: In the sp basis, there are five independent one-center integrals (Slater−Condon parameters F^0, F^2, G^1), which in the general case cannot be reproduced by only three parameters ρ. Moreover, these formulas are designed for interatomic distances not approaching zero. In the case of small interatomic distances, the difference between integrals evaluated using the formulas based on the charge configurations and based on the true multipoles becomes significant. Therefore, when we change the
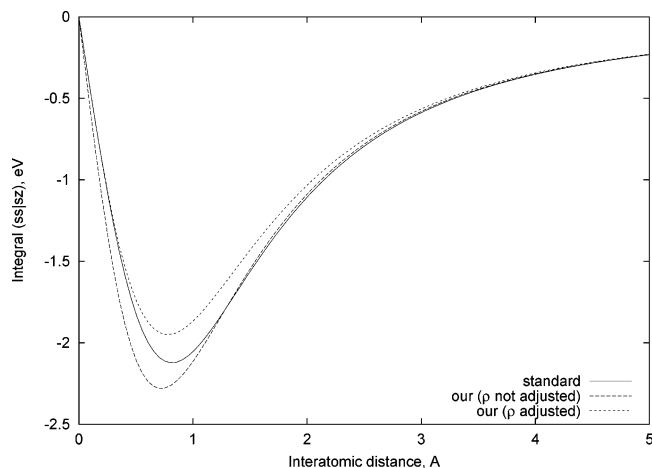

Figure 1. Dependence of the $(ss|sz)^{CC}$ integral on the interatomic distance.
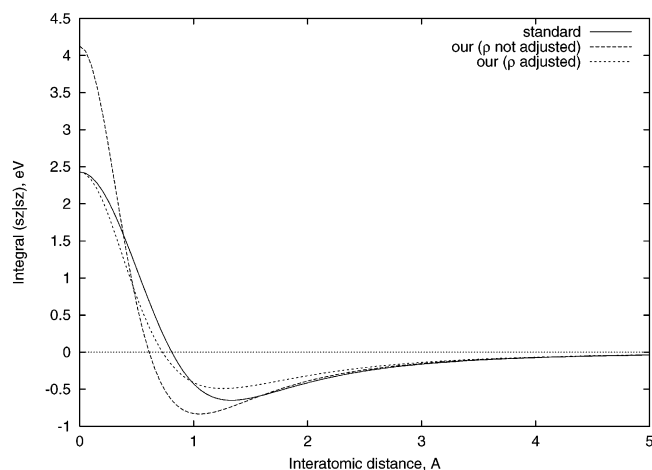

Figure 2. Dependence of the $(sz|sz)^{CC}$ integral on the interatomic distance.

computation scheme, the one-center limit values also change. Taking this into account, we can propose two different recipes: The first one is based on the standard values of ρ, while the second one uses modified values of ρ reproducing the one-center limits (g_{ss}, h_{sp}, and h_{pp}). In the latter case, the value of ρ_0 is not modified ($=2g_{ss}^{-1}$). The parameters ρ_1 and ρ_2 in the standard scheme are determined numerically. When we use the point multipoles and their interactions, we can obtain analytical expressions for these parameters. For example

$$\rho_1 = \frac{1}{2}\left(\frac{h_{sp}}{D_1^2}\right)^{1/3} \quad (34)$$

It leads to the estimate $\rho_1 = 0.969\,982\,7$ au for carbon, which can be compared with the standard value of $0.813\,098\,3$ au.[27]

Figures 1−3 illustrate the dependence of the integrals $(ss|sz)$, $(sz|sz)$, and $(sx|sx)$ (z axis connects two atoms in the diatomic coordinate frame) for the scheme based on the charge configurations and for that based on the true multipoles with the standard and modified parameters ρ_1. These figures show that the curves differ significantly in the region of small interatomic distances. By contrast, in the case of $R > 2$ Å, all the curves are quite close, so that only the closest neighbors are touched by the modification of the procedure. The convergence rate strongly depends on the integral type. In general, the curves with the adjusted value of ρ_1 seem to be a better approximation to the standard ones than those based on the point multipoles
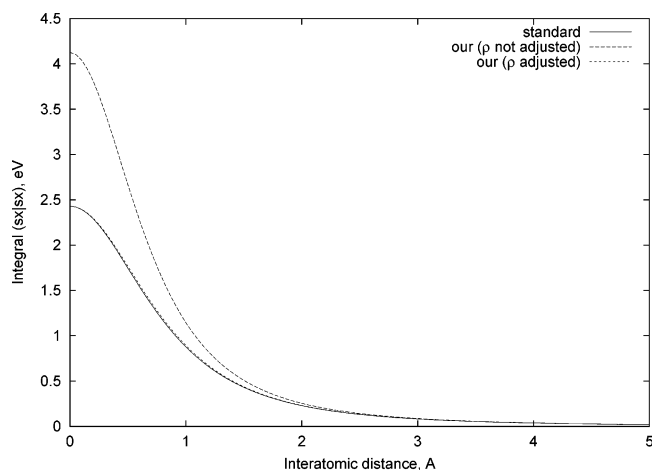
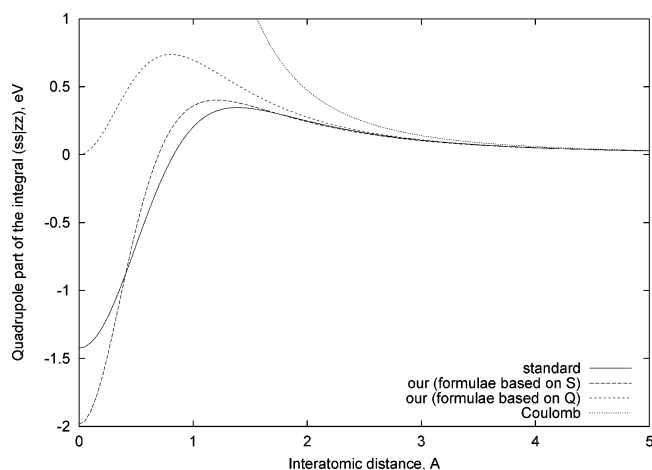**Figure 3.** Dependence of the $(sx|sx)^{CC}$ integral on the interatomic distance.

Figure 4. Dependence of the difference $(ss|zz)^{CC} - (ss|ss)^{CC}$ on the interatomic distance.

Figure 5. Dependence of the difference $(ss|xx)^{CC} - (ss|ss)^{CC}$ on the interatomic distance.

Figure 6. Ratio of computation times for the SLG-MNDO method with different schemes for the two-center repulsion integrals.

with ρ_1 unchanged. At the same time, in the case of the integral $(sz|sz)$, the better coincidence of the curve based on modified ρ_1 with the standard curve in the region of small R leads to a worse agreement for larger values of R.

We tested the performance of two types of procedures tentatively possible for evaluating interactions involving quadrupoles. We considered the $(ss|zz)$ and $(ss|xx)$ integrals. The interaction of charges gives the main contribution to these integrals. It is not affected by our modifications of the computation scheme. Therefore, we analyze only the contribution having the form of the charge−quadrupole interactions (or, equivalently, the differences $(ss|zz) - (ss|ss)$ and $(ss|xx) - (ss|ss)$). These interactions constitute about 5% of the integrals at the region of characteristic interatomic distances between bonded atoms, and their contribution decreases as R^{-2} for larger R. Figures 4 and 5 represent the dependence of these differences on the interatomic distance calculated using the standard formulas and also formulas based on eqs 28 and 29. For comparison, we also plot these contributions for the usual Coulomb law $1/R$. As expected, the expressions which do not use the assumption of validity of the Poisson equation for the potential give a better approximation to the standard values (especially for small R). The difference between two approximations based on the multipole−multipole interactions converges to zero in both cases as R^{-2}. In the case of the charge−quadrupole interactions given by eq 29, the one-center limit is exactly zero ($(ss|pp)$ and $(ss|ss)$ are equal). It illustrates
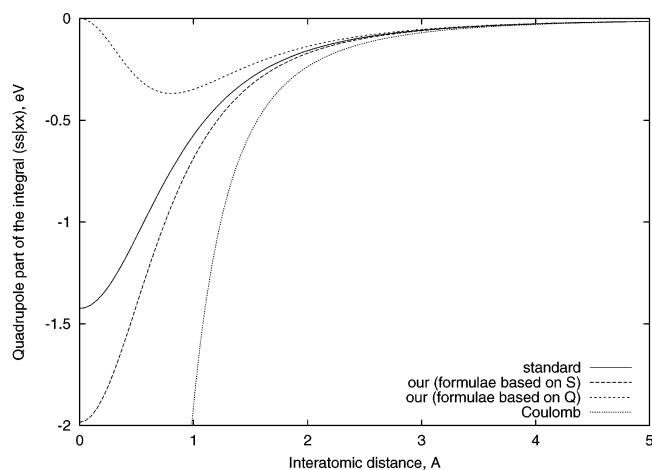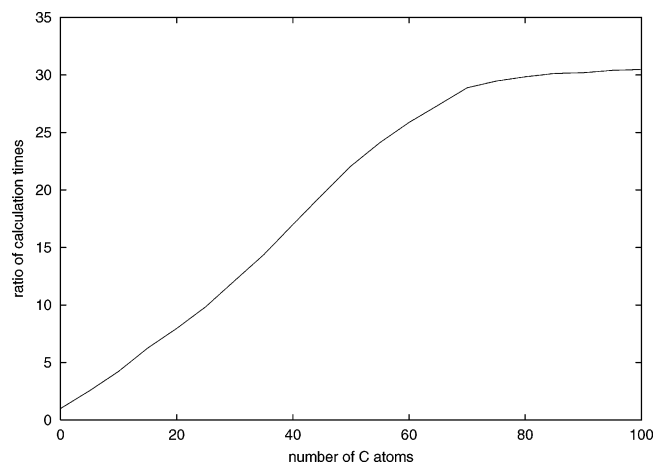
the fact that all one-center integrals cannot be reproduced as limiting cases of the corresponding two-center ones. In other cases (standard scheme and that based on $\hat{S}$), the one-center limit for the difference between these integrals (which is equal to −0.76 eV for the one-center integrals used in the MNDO scheme) is significantly overestimated.

It is important to test how the proposed modification of the computation scheme affects the performance of the SLG-NDDO approach. The first step in this direction is to analyze the computation time as a function of the scheme and the system's size. As test objects, we consider regular hydrocarbon chains C_nH_{2n+2}. Figures 1−5 demonstrate that at larger R the change of the scheme can only slightly affect the values of the integrals. Therefore, if the scheme based on the atomic multipoles is applied only to well-separated pairs of atoms, the modified SLG-NDDO method can be used even with the parameters given in ref 23 (i.e., without any additional re-parametrization). In subsequent calculations, we adopt the atomic multipole scheme for $R > 3$ Å, while the short-range repulsion integrals are calculated using the charge configurations scheme. To further specify the computation scheme, we use the MNDO semiempirical Hamiltonian with the standard values of the ρ parameters and the formulas based on the $\hat{S}$ tensor for the interactions involving quadrupoles.

Figure 6 demonstrates the ratio of computation times for two SLG-MNDO schemes (based on the charge configurations and multipoles, respectively) as a function of the number of carbon
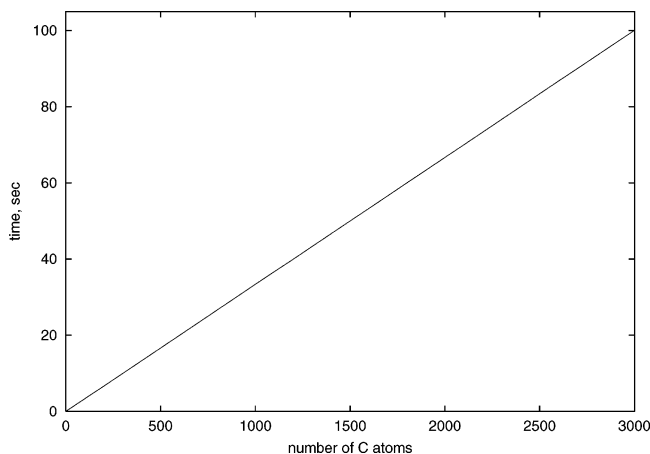
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Figure 7. Dependence of computation times on the system's size.

Figure 8. Empirical distribution of errors for heats of formation as obtained by the SLG-MNDO method.

Figure 9. Empirical distribution of errors for heats of formation as obtained by the SCF-MNDO method.

atoms n in C_nH_{2n+2}. It can be seen that the dependence has two regions: It is almost linear for smaller n, and it is close to a constant for larger n. It can be readily understood by taking into account that in the case of the charge configurations scheme a qudratic contribution to the dependence of computation costs on the system's size dominates over linear contribution even for small molecules. At the same time, the scheme proposed above significantly reduces namely the quadratic component of this dependence, and for relatively small molecules, a linear contribution dominates. It is important that in the limit of large n, where a quadratic contribution is again dominant, the true multipole scheme leads to more than 30 ple acceleration of SLG-NDDO calculations.

It is clear that simple replacement of the charge configurations by the atomic multipoles cannot affect the scalability of the method. Indeed, even very fast estimation of the two-center Coulomb interactions leads to a quadratic dependence of computation costs on the system's size for larger molecules. To make the scheme truly linearly scaling, it is necessary to neglect interactions between very distant atoms. Cutoff procedures of that sort are well-justified only for local states. In the case of the SLG method, it is particularly simple, because one-electron states forming carrier spaces are atom-centered. Figure 7 shows the dependence of the required computation time on the system's size n for the modified SLG-NDDO method where all interactions between atoms separated by more than 20 Å are totally neglected. This figure unequivocally demonstrates that the method belongs to the family of $O(N)$-methods. It is important that the cutoff procedure leads to a very small modification of the calculated heats of formation (less than 0.03 kcal/mol per CH_2 fragment). Of course, in the case of more polarized molecules with significant effective atomic charges, the charge−charge interactions beyond 20 Å should be explicitly considered to obtain the same accuracy. We can try to compare our results (9000 atoms for about 100 s on a 0.7 GHz pentium III computer) with those obtained in the framework of the LocalSCF method (120 000 atoms for about 16 000 s on a 2.4 GHz pentium IV computer).[12] Direct comparison of these data shows that the modified SLG-NDDO method is about 2 orders of magnitude faster than the LocalSCF one. At the same time, such a comparison is not quite correct, because the protein calculated in ref 12 is not one-dimensional like the hydrocarbon chain and, therefore, requires more interactions to be taken into account. Moreover, the protein contains polar atoms whose long-range Coulomb interactions can affect the values of cutoff parameters necessary to obtain accurate results.
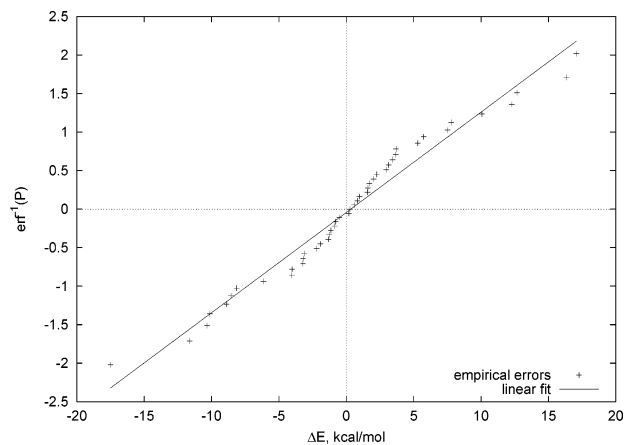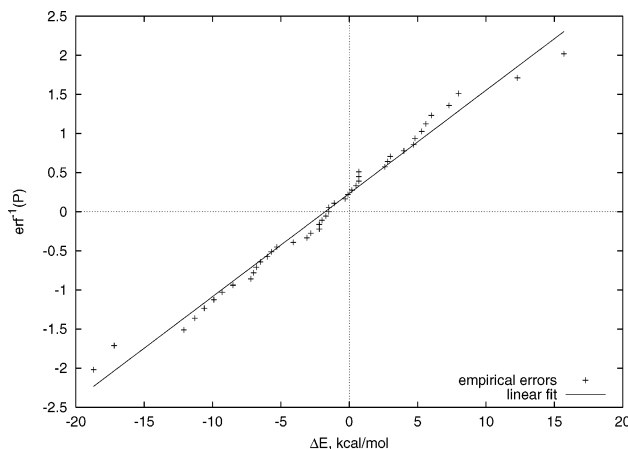
A detailed discussion of the quality of the SLG-NDDO numerical estimates as compared with the SCF−NDDO ones is given in ref 23. In the present paper, we consider only the heats of formation on the same set of molecules as given in ref 23. The difference between calculated and experimental values can be found for each of the molecules and for the calculation methods. This error can be considered as a random variable, and empirical distribution functions of errors for both methods can be readily constructed. Figures 8 and 9 represent these functions in the coordinates linearizing the normal distribution plotted for the SLG-MNDO and SCF-MNDO methods, respectively, as well as linear fits for both distributions. The assumption of a normal distribution law for the errors seems to be valid for both methods, because the sets of points are close to the corresponding linear fits (values of R^2 are 0.967 and 0.983, respectively). The abscissa for the crossing of a linear fit and the x axis gives the value of the a parameter (average of the error's distribution), while the slope of a linear fit is σ^{-1}. Our analysis shows that the methods have equal values of σ (about 7.6 kcal/mol), but the values of the a parameter differ significantly. In the case of the SCF-MNDO method, this value is −2.3 kcal/mol and certifies that heats of formation are significantly underestimated in this method, while in the case of the SLG-MNDO method, the average is positive and its magnitude is more than 5 times smaller, demonstrating the practical absence of the systematic error in the SLG-MNDO calculations. According to the Student's criterion, the average errors for these methods are statistically different with a probability larger than 90%.

4. Conclusions

In the present paper, we further develop semiempirical methods based on the strictly local geminals form of the trial wave function contrasting with the traditional SCF-based semiempirical quantum chemistry. The main result is that using invariant multipolar forms of the two-center repulsion integrals leads to a significant (more than 30 times) acceleration of the computation procedure. As a consequence, we propose the modified SLG-NDDO methods for electronic structure calculations of large molecular systems. These methods can be easily transformed into a linear scaling form by the applying a cutoff procedure for the two-center Coulomb interactions. It is particularly important that such a modification of the calculation procedure does not imply any re-parametrization. The SLG-NDDO methods provide high-quality estimates for the heats of formation of molecules, which are well-described by two-electron, two-center chemical bonds and by lone pairs.

An important component of the scheme proposed is the possibility to sequentially define and use in calculation the atomic multipoles. They can be further used to calculate electrostatic potentials inside and outside molecules.[35] The tentative prospects of this scheme can be considered from somewhat different points of view. The SLG-MINDO/3 method allowed us to construct a route from semiempirical quantum chemistry to classical force fields.[36] A multipole scheme for two-center interactions opens an access to the construction of an NDDO-based deductive molecular mechanics (DMM). The construction of a DMM procedure is only one of many ways to further develop the computation schemes of the SLG-NDDO method. It is possible to construct a method where all two-center repulsion interactions (including those between bonded atoms) are calculated using the multipole scheme. At the same time, this modification will require some re-parametrization of the Hamiltonian. An important way to generalize this treatment is to implement a scheme with local electron groups of arbitrary form (numbers of electrons and orbitals). A step in this direction has been made in ref 37, where the trial wave function in the form of the antisymmetrized product of strictly local geminals and molecular orbitals has been proposed and analyzed. On the other hand, it is clear that the SLG wave function totally neglects interbond electron transfers and dispersion interactions. They can be taken into consideration using perturbation expansions developed for the geminal-type wave functions.[38,39] These interactions are short-range, and therefore, their account will not destroy the linear scalability of the SLG-NDDO methods.

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