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An Improved Semiempirical MO PM3 Method for Hydrogen-Bonded Systems[†]

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[†] Dedicated to the memory of Prof. Dr. Davorin Dolar

Abstract

Semiempirical methods are known to show artifacts in predicting the interaction energies and structures of hydrogen-bonded systems. The origin of the artifacts is the correction function of the core-core interaction term, which was introduced to adjust the repulsion between the nuclei. Recently a new PM3 core-core correction function based on the atom-atom parameters has been proposed and the parameters for O-O, O-H, and H-H interactions have been reported. In this work the new core-core correction function has been implemented in the semiempirical molecular orbital package MOPAC97. The test calculations have been performed on the following simple systems: a protonated water dimer, a cyclic water trimer, a cyclic water tetramer, four conformers of a water dimer, a water monomer, an oxonium ion, hydrogen peroxide, and hydrogen trioxide. The results were compared to the values obtained with the standard PM3 method, ab initio methods, and to experimental data, where available. In all of the examples, except for the case of hydrogen peroxide, the modified semiempirical PM3 method provides a significant improvement of the description of the geometries and interaction energies of the test systems, indicating that the reparametrization of the core-core interaction term may play an important role in the future development of semiempirical methods.

Key words: core-core repulsion, hydrogen bonds, semiempirical methods, PM3, MOPAC, water

1. Introduction

Quantum mechanical methods allow detailed studies of the structure and reactivity of various systems. Since electrons are explicitly included in the calculations, electronic properties such as dipole moments and charge densities can be investigated. The disadvantage of quantum mechanical methods, however, is their computational cost. In spite of the rapid development of computer technology over the past decades high-level theoretical investigations of large macromolecular systems are still considerably limited and quantum mechanical calculations can yet only be performed on systems of lower complexity. For studies of larger systems, such as biomolecules, computationally less demanding methods have been developed. Computationally least expensive methods employed in molecular modeling are based on molecular mechanic potentials. In molecular mechanics calculations the electrons are neglected and the molecules are described as a collection of classical particles. The potential energy of the system and the forces acting on the particles are determined via a potential energy function or force field, which relates the coordinates of a system with its energy. However, the calculations based on molecular mechanic potentials can not be used for studies of processes involving the redistribution of electron density, such as bond breaking or forming. Such systems can either be studied with so-called hybrid QM/MM methods in which the electronically important part is treated on a quantum mechanical level and the rest of the system is treated using the molecular mechanic potential or with the semiempirical methods. An important application of the QM/MM methods is the investigation of the proton and hydride transfer reactions in enzymes, where the quantum effects describing the bond-breaking and -forming events in the active site as well as the dynamics and solvation of the entire enzyme need to be addressed in order to comprehend its catalytic activity.[1-4]

Semiempirical methods are based on the quantum mechanical framework but use an approximate Hamiltonian, avoiding the calculation of computationally expensive two-center integrals.[5-8] To compensate for the approximations, empirical parameters derived from high-level ab initio data, theoretical formulas, or from experimental data are introduced into the quantum-mechanical formalism. Semiempirical methods are thus less general than ab initio methods and their accuracy is limited by the accuracy of the data used to obtain the parameters as well as by the form of the parametric functions. Like high-level ab initio methods, semiempirical methods can be coupled with molecular mechanics methods in the QM/MM approaches, allowing the studies of large systems consisting of several hundreds or thousands of atoms.[9-13] The most often used semiempirical methods are MNDO[14], and AM1[15] and PM3.[16]

There are several cases in which semiempirical methods yield reliable results complementing the experimental observations.[9,12,17,18] However, when describing intermolecular and intramolecular interactions, particularly hydrogen bonds, results obtained using semiempirical calculations have to be treated with caution[19-29]. The main source of inaccuracy in semiempirical methods in describing intermolecular interactions lies in the treatment of the core-core repulsion. In the MNDO semiempirical method the core-core repulsion between atoms A and B is described as

$$E_{AB}^{core} = Z_A Z_B \langle S_A S_A | S_B S_B \rangle \left(1 + e^{-\alpha_A R_{AB}} + e^{-\alpha_B R_{AB}}\right) \quad (1)$$

Z_A and Z_B are the core charges of atoms A and B, S_A and S_B are the s atomic orbitals, R_{AB} is the internuclear distance, and α_A and α_B are the atomic parameters. For the case when A is oxygen or nitrogen and B is hydrogen, the leading exponential term is multiplied by R_{AH}. It has been shown that expression (1) overestimates the repulsion between the atoms. However, the term E_{AB}^{core} is outside the quantum mechanical framework and it allows the testing of different empirical functions and parameters in order to obtain better agreement with experimental or high level ab initio data. In the semiempirical methods AM1 and PM3, which are based on the MNDO method, Gaussian correction functions are added to the core-core repulsion term:

$$\begin{aligned} E_{AB}^{core} &= Z_A Z_B \langle S_A S_A | S_B S_B \rangle \left(1 + e^{-\alpha_A R_{AB}} + e^{-\alpha_B R_{AB}}\right) \\ &\quad + g(A,B) \end{aligned} \quad (2)$$

where

$$g(A,B) = \frac{Z_A Z_B}{R_{AB}} \left(\sum_i K_{A,i} e^{-L_{A,i}\left(R_{AB} - M_{A,i}\right)^2} + \sum_j K_{B,j} e^{-L_{B,j}\left(R_{AB} - M_{B,j}\right)^2} \right) \quad (3)$$

K, L and M are adjustable parameters that modulate the amplitude, steepness, and the displacement of the Gaussian functions. The introduction of Gaussian correction functions in the AM1 and PM3 methods has improved many results, yet the Gaussian correction functions still proved to be inadequate for the description of the potential energy surface of the water dimer and some other systems.[30-33]

Recently the core-core interaction terms in the Hamiltonian of the semiempirical PM3 method have again been reparametrized, leading to a significant improvement in the description of structure and energetics of hydrogen bonded systems.[34-36] A scheme has been proposed in which the Gaussian correction functions *g(A,B)* have been replaced by a new function that uses the atom-atom parameters and not the pure atomic parameters as in the case of the AM1 and PM3 methods. The so-called parameterizable interaction function (PIF) is the sum of atom-pair contributions, each one having five adjustable parameters:

$$g^{PIF}(A,B) = \alpha_{AB} e^{-\beta_{AB} R_{AB}} + \frac{\chi_{AB}}{R_{AB}^6} + \frac{\delta_{AB}}{R_{AB}^8} + \frac{\varepsilon_{AB}}{R_{AB}^{10}} \quad (4)$$

Parameters α_{AB}, β_{AB}, χ_{AB}, δ_{AB}, and ε_{AB} depend the on atom types of A and B. The parameterizable interaction function was initially parameterized for O-O, O-H, and H-H atom pairs. Recently the parameterization has been extended to H-C, H-N, O-C, and O-N atom pairs, which allows the study not only of interactions between water molecules but also of the interactions of some organic molecules in aqueous solution.[36] The main limitation of the approach in which the parameterizable interaction functions are used is that the intermolecular and intramolecular terms have to be treated separately. The parameterizable interaction functions namely well describe the interactions of an atom pair AB provided that the interatomic separation is well beyond the AB bond length. To improve that, a new $g^{MAIS}(A,B)$ function has been derived that behaves like the original $g(A,B)$ function in the bonding region while it goes to the $g^{PIF}(A,B)$ function as the interatomic distance increases[35]:

$$g^{MAIS}(A,B) = \sum_{n=1}^{3} \alpha_{n_{AB}} e^{-\beta_{n_{AB}}\left(\gamma_{n_{AB}} - R_{AB}\right)^2} \quad (5)$$

The PM3-MAIS approach, where MAIS stands for *Method Adapted for Intermolecular Studies*, is again based on the atom-atom parameters (α_{nAB}, β_{nAB}, and γ_{nAB}), which have been optimized to reproduce the ab initio intermolecular potential energy surface of a water dimer.[35] To test the new PM3-MAIS parameters the H_3O^+-H_2O system was investigated and it has been shown that the interaction energies between the two molecules calculated with the new PM3-MAIS method are in better agreement with the ab initio results than the interaction energies calculated with the original PM3 method.[35] However, the PM3-MAIS parameters have so far only been derived for O-O, O-H, and H-H atom pairs. In order to extend the calculations to molecules consisting of atoms other than O and H the reparametrization will have to be done for other atom pairs as well.

In this work the PM3-MAIS method has been introduced in the semiempirical molecular orbital package MOPAC97.[37, 38] Afterwards, the new PM3-MAIS method has been used to optimize the geometries of the following test systems: a protonated water dimer, a cyclic water trimer, a cyclic water tetramer, four conformers of a water dimer, a water monomer, an oxonium ion, hydrogen peroxide, and hydrogen trioxide. The results of the calculations were compared to the results of ab initio methods and, when possible, to experimental data.

2. Experimental

2.1. Implementation of the PM3-MAIS method

We have implemented the semiempirical method PM3-MAIS in the MOPAC97 program as a new version of the standard PM3 semiempirical method. MOPAC is a semiempirical molecular orbital program for the theoretical study of chemical and physical properties and reactions involving molecules, ions, or polymers.[37,38] It incorporates over 200 subroutines, almost all of which are also powerful algorithms on their own. To incorporate the PM3-MAIS method in the MOPAC program, the following files in the source code had to be adapted: the data file BLOCK in which the parameters of the semiempirical calculations are stored (the atom-atom parameters α_{nAB}, β_{nAB}, and γ_{nAB} of the $g^{MAIS}(A,B)$ function have been added to the BLOCK data file by analogy to the atom-atom parameters of the MINDO/3 semiempirical method[39]); the subroutine COMPFG where the electronic and geometric parts of the program are joined and in which the total heat of formation of the system is evaluated; the subroutine ENPART in which the energy of a molecule is partitioned into its monatomic and diatomic components; the subroutine ROTATE in which the two-electron repulsion integrals, the electron-nuclear attraction integrals, and the nuclear-nuclear repulsion terms between two atoms are calculated; the subroutine ANALYT in which the analytical derivatives of the energy with respect to Cartesian coordinates for all atoms are calculated; and the subroutine ITER where the Fock and density matrices and the electronic energy are calculated. It has to be pointed out that the new parametrization of the core-core interaction term prevents the calculation of the correct heats of formation since the relationships which connect the heat of formation with the total energy have not yet been properly modified. Since the original source code of the MOPAC program is written to optimize the heat of formation of the system we have adapted the COMPFG and ITER subroutines so that instead of the heat of formation the total energy enters in the self consistent field (SCF) calculation.

2.2. Test calculations

Using the modified version of the MOPAC97 program the geometries of simple test systems consisting of hydrogen and oxygen atoms were fully optimized with the semiempirical PM3 and PM3-MAIS methods. All the calculations were performed in vacuo. The starting configurations of the monomers and the complexes were generated using the MOLDEN program.[40] The geometry optimizations were performed without symmetry constraints applying the geometry-optimizing routine EF (eigenvector following)[41] and were completed after reaching a gradient norm of 0.01 kcal/mol/Å.

3. Results and discussion

3.1. Water monomer and oxonium ion

First, the new PM3-MAIS method as implemented in the MOPAC97 program has been tested by performing a geometry optimization of a water monomer and an oxonium ion. In Table 1 we show the geometrical parameters that were calculated with the semiempirical PM3 and PM3-MAIS methods. For comparison ab initio[42, 43] and experimental[44, 45] results are also listed.

It can be seen from Table 1 that in the case of the water molecule the O-H bond distance calculated with the PM3-MAIS semiempirical method is in better agreement with the ab initio and experimental data than the O-H distance calculated with the standard PM3 method which predicts too short an O-H distance. It can also be seen from the Table 1 that in the case of

Table 1. Geometrical parameters of a water molecule and oxonium ion as determined by PM3 and PM3-MAIS semiempirical calculations, ab initio calculations, and by experiment. The distances are reported in Å and the angles are reported in degrees.

System	Parameter	Method			
		PM3-MAIS	PM3	MP2/aug-cc-pVTZ	Exp.
H_2O	R(O-H)	0.955	0.951	0.959[a]	0.958[c]
	φ(H-O-H)	106.8	107.7	104.3[a]	104.5[c]
H_3O^+	R(O-H)	0.982	0.978	0.980[b]	0.976[d]
	φ(H-O-H)	108.9	109.4	111.5[b]	111.3[d]

[a] Taken from ref. 42.
[b] Taken from ref. 43.
[c] Taken from ref. 44.
[d] Taken from ref. 45.

the water molecule both PM3 and PM3-MAIS method overestimate the H-O-H angle. However, we note that the H-O-H angle calculated with the new PM3-MAIS method is in better agreement with the ab initio and experimental results than the value calculated with the standard PM3 method. In the case of the oxonium ion the ab initio and experimental results are nearly identical. Both semiempirical methods, however, underestimate the H-O-H angle while the results for the O-H bond length obtained by the PM3 and PM3-MAIS methods agree reasonably well with ab initio and experimental data.

3.2. Water dimers

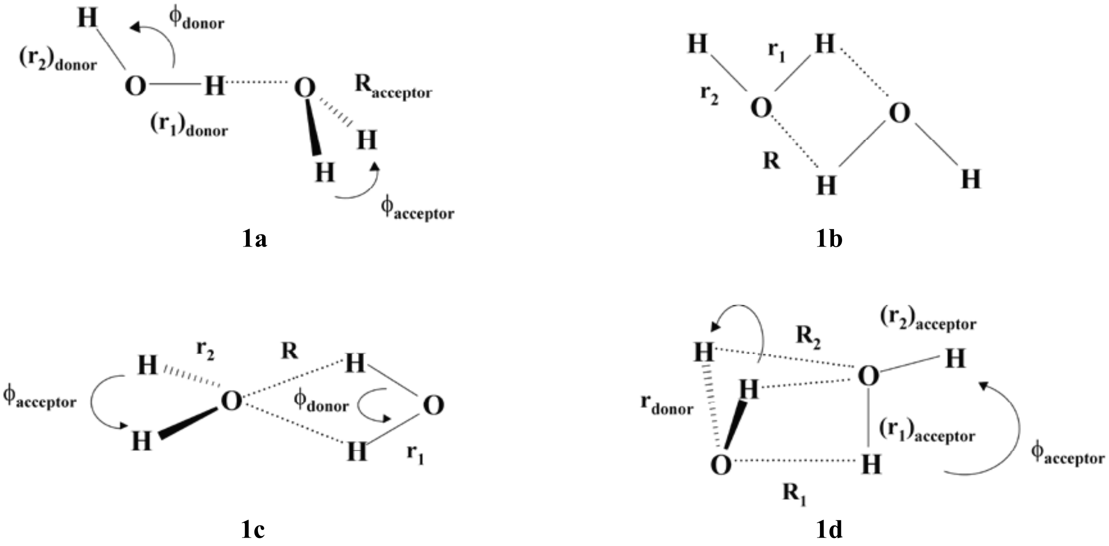
The water dimer is one of the most important and best understood hydrogen-bonded systems. Using ab initio methods and microwave spectroscopy the structure of the water dimer with a linear hydrogen bond and C_s equilibrium geometry (Fig. 1a) has been established as a global minimum on the potential energy surface. However, several other stable structures of the water dimer also exist. In the present work geometry optimizations have been performed on the following structures: a water dimer with a linear hydrogen bond (Fig. 1a), a planar cyclic water dimer (Fig. 1b), a bifurcated water dimer (Fig.1c) and a triply-hydrogen-bonded water dimer (Fig. 1d). The calculated geometrical parameters are collected in Table 2.

In the case of all of the studied water dimers the geometrical parameters calculated with the PM3-MAIS method are in better agreement with ab initio results than the geometrical parameters calculated with the standard PM3 method (see Table 2). This is of course not surprising considering that the parametrization of the PM3-MAIS method has been performed on the

Table 2. Geometrical parameters of water dimers calculated using the PM3 and PM3-MAIS semiempirical methods and ab initio methods[46]. The distances are reported in Å and the angles in degrees. The parameters are defined in Fig. 1.

System	Parameter	Method		
		PM3-MAIS	PM3	MP2/6-31 +G(d,p)[a]
1a	$R(O\cdots H)$	1.857	1.809	1.941
	$\phi(O\cdots H\text{-}O)$	175.7	178.9	175.6
	ϕ_{donor}	106.3	107.8	105.6
	$\phi_{acceptor}$	106.9	107.9	105.7
	$R_{acceptor}(O\text{-}H)$	0.957	0.952	0.964
	$(r_1)_{donor}(O\text{-}H)$	0.968	0.960	0.969
	$(r_2)_{donor}(O\text{-}H)$	0.954	0.950	0.962
1b	$\phi(H\text{-}O\text{-}H)$	106.6	107.8	106.5
	$\phi(O\text{-}H\cdots O)$	107.8	117.5	108.5
	$R(O\cdots H)$	2.258	2.685	2.276
	$r_1(O\text{-}H)$	0.958	0.952	0.965
	$r_2(O\text{-}H)$	0.955	0.951	0.962
1c	ϕ_{donor}	105.1	107.2	101.7
	$\phi_{acceptor}$	107.0	108.0	105.6
	$R(O\cdots H)$	2.545	3.221	2.452
	$r_1(O\text{-}H)$	0.958	0.952	0.964
	$r_2(O\text{-}H)$	0.956	0.951	0.963
1d	ϕ_{donor}	106.0	106.8	103.1
	$\phi_{acceptor}$	106.9	111.0	106.2
	$R_1(O\cdots H)$	2.720	1.870	2.620
	$R_2(O\cdots H)$	2.920	1.871	2.571
	$(r_1)_{acceptor}(O\text{-}H)$	0.957	0.958	0.964
	$(r_2)_{acceptor}(O\text{-}H)$	0.955	0.950	0.963
	$r_{donor}(O\text{-}H)$	0.956	0.957	0.964

[a] Ab initio values are taken from ref. 46.



1a **1b**

1c **1d**

Figure 1. Schematic structures and parameters of the water dimers investigated in this work.

potential energy surface of a water dimer.[35] In the case of the water dimer with a linear hydrogen bond (Fig. 1a), for example, the H-O-H angle, which was overestimated by the standard PM3 method, is now closer to the ab initio values. The same holds for the lengths of the O-H bonds, which were underestimated by the standard PM3 method. Moreover, the O···H hydrogen bond length, which was too small when calculated with the PM3 method, and the O···H-O angle, which was too large, have also been improved. Similar improvements can be seen in the case of the planar cyclic water dimer (Fig. 1b) and in the case of the bifurcated water dimer (Fig. 1c). However, in the latter case the H-O-H angle in the donor and acceptor molecules remains too wide and the O-H bonds remain too short. On the other hand, the result for the O···H hydrogen bond length, which was considerably overestimated by the standard PM3 method, is now in very good agreement with the ab initio data. A remarkable improvement in the description of the structure of the water dimers is also evident in the case of a triply-hydrogen-bonded water dimer (Fig. 1d) in which particularly the O···H hydrogen bond lengths, which were underestimated by the PM3 method, have been improved with respect to the ab initio data.

3.3. Protonated water dimer

The protonated water dimer $H_5O_2^+$ plays an important role in the kinetics of aqueous solutions as well as in atmospheric chemistry. Because the potential energy surface of the protonated water dimer is relatively flat the results of the ab initio methods are strongly dependent on the level of theory employed in the calculations. The global minimum of the protonated water dimer obtained with high-level ab initio calculations is shown on Fig. 2a.[47] The structure has C_2 symmetry. The midpoint hydrogen atom, which bridges the two water molecules, is centered approximately 1.2 Å from each of the oxygen atoms. Another stationary point on the potential energy surface, the energy of which is only 0.4 kcal/mol higher than the global minimum, is shown on Fig. 2b. It is a structure with C_s symmetry in which the midpoint hydrogen bond is no longer centered between the oxygen atoms but is closer to one of them. The structural parameters of the protonated water dimer calculated with the PM3 and PM3–MAIS semiempirical methods are listed in Table 3. While the standard PM3 method predicts an unsymmetrical structure with a nonlinear hydrogen bond (see Fig. 3), the structure calculated with the PM3-MAIS method agrees with the geometry of the global minimum structure calculated with ab initio methods.

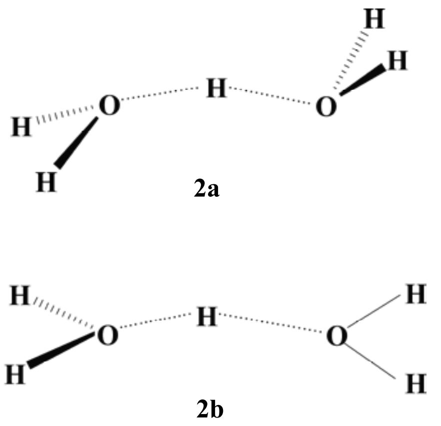


Figure 2. Stationary points on the potential energy surface of the protonated water dimer.

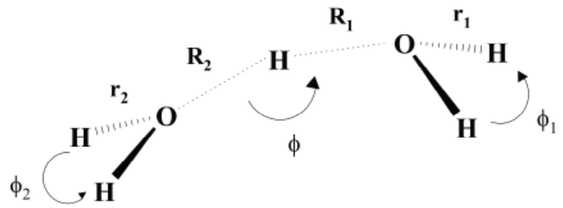


Figure 3. Optimal configuration of the protonated water dimer as predicted by the semiempirical PM3 method and the definition of its internal coordinates.

Table 3. Geometrical parameters of a protonated water dimer calculated using the PM3 and PM3-MAIS semiempirical methods and ab initio methods[47]. The distances are reported in Å and the angles in degrees. The parameters are defined in Fig. 3.

System	Parameter	Method		
		PM3-MAIS	PM3	TZ2P*f* CCSD[a]
$H_5O_2^+$	ϕ_1(H-O-H)	108.3	108.9	109.1
	ϕ_2(H-O-H)	108.3	108.3	109.1
	ϕ(O···H-O)	179.9	145.1	174.0
	R_1(O-H)	1.192	1.663	1.193
	R_2(O···H)	1.192	1.007	1.193
	r_1(O-H)	0.967	0.973	0.964
	r_2(O-H)	0.967	0.955	0.964

[a] Ab initio values are taken from ref. 47.

3.4. Cyclic water trimer and tetramer

Water clusters are important in the investigations of the hydration phenomena. The higher the number of water molecules in the cluster, the better the cluster resembles the structure and properties of liquid water. However, predicting the structure of a water cluster is a difficult task since each of the clusters exists in several stable conformations. Moreover, water clusters are followed with difficulty in an experiment because they are rapidly converted from one form to another. Water trimer is the smallest of all of the water clusters.

The optimal structure is cyclic with an almost planar six-membered ring that possesses three exocyclic -OH groups[42, 48, 49] (Fig. 4a). The water molecules forming the cluster are at the same time hydrogen bond donors and acceptors. Also in the case of the water tetramer a cyclic structure can be found as a global minima on the potential energy surface (Fig. 4b).[42,50] However, the cluster of the water tetramer is larger and the O···H-O hydrogen bond angles deviate less from linearity. The results of a geometry optimization of the cyclic water trimer and tetramers using the PM3 and PM3-MAIS methods are listed in Table 4. It can be seen that according to ab initio data, both semiempirical methods describe the investigated water clusters very well. Moreover, the geometries of the investigated water clusters calculated with the PM3-MAIS method resemble the ab initio structures even more than the geometries calculated with the standard PM3 method.

Table 4. Geometrical parameters of the cyclic water trimer and tetramer calculated using the PM3 and PM3-MAIS semiempirical methods and ab initio methods.[42] The distances are reported in Å and the angles in degrees. The parameters are defined in Fig. 4.

System	Parameter	Method		
		PM3-MAIS	PM3	MP2/aug-cc-pVDZ[a]
$(H_2O)_3$	R(O-O)	2.788	2.668	2.800
	$R(O-H)_f$	0.955	0.951	0.964
	$R(O-H)_b$	0.973	0.966	0.978
	r(O···H)	1.890	1.796	1.901
	ϕ(H-O-H)	106.8	108.3	105.3
	δ(O···H-O)	152.0	148.3	151.1
$(H_2O)_4$	R(O-O)	2.707	2.723	2.743
	$R(O-H)_f$	0.956	0.951	0.965
	$R(O-H)_b$	0.981	0.965	0.985
	r(O···H)	1.740	1.780	
	ϕ(H-O-H)	106.6	108.0	105.0
	δ(O···H-O)	168.1	165.5	167.7

[a] Ab initio values are taken from ref. 42.

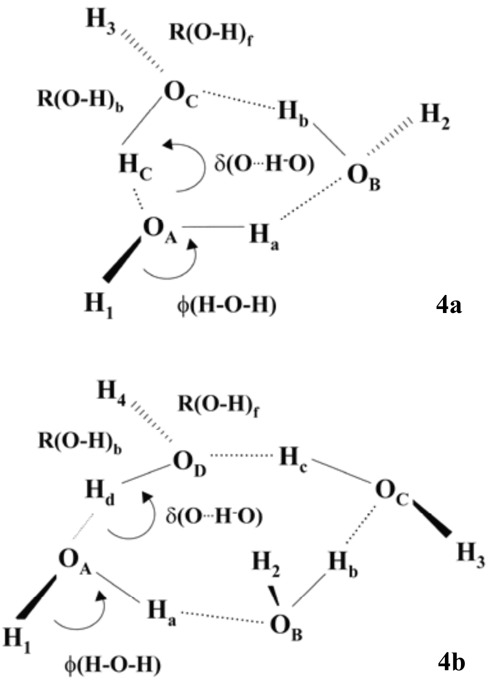


Figure 4. Schematic structures and geometric parameters of the water trimer (4a) and the water tetramer (4b).

3.5. Hydrogen peroxide and hydrogen trioxide

Hydrogen peroxide and hydrogen trioxide are systems that do not consist of water molecules. The transferability of the PM3-MAIS atom-atom parameters has therefore been tested in these two systems.

The correct geometry of the hydrogen peroxide molecule is, despite its simplicity, very difficult to calculate and so far only ab initio methods have been successful in predicting the structure of hydrogen peroxide.[51] As is evident from Table 5 the new PM3-MAIS semiempirical method also does not correctly describe the geometry of hydrogen peroxide. Similarly to the PM3 method, it predicts a planar structure with the H-O-O-H dihedral angle being approximately 180° while the experimental value is 111.8° [52] (see Fig. 5a). On the other hand, both semeimpirical methods, particularly the new PM3-MAIS method, describe the structure of hydrogen trioxide very well (see Table 6). Hydrogen trioxide (Fig. 5b) is the third homolog in a series of hydrogen oxides, following water and hydrogen peroxide. According to ab initio calculations hydrogen trioxide is a non-planar molecule similar to hydrogen peroxide.[53] Recently, the structure of hydrogen trioxide has also been determined experimentally.[54]

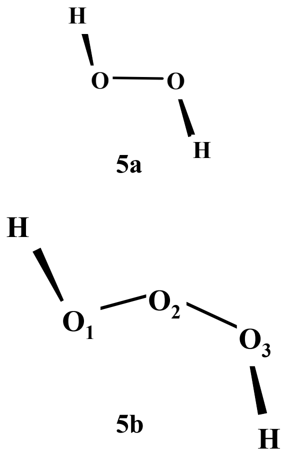


Figure 5. Schematic structures of hydrogen peroxide (5a) and hydrogen trioxide (5b).

Table 5. Geometrical parameters of hydrogen peroxide as determined by PM3 and PM3-MAIS semiempirical calculations, ab initio calculations, and by experiment. The distances are reported in Å and the angles are reported in degrees.

System	Parameter	Method			
		PM3-MAIS	PM3	RS-MP/ [4s3p1d/2s1p][a]	Exp.[b]
H_2O_2	ϕ(O-O-H)	97.0	96.5	99.3	99.4
	θ(H-O-O-H)	179.5	180.0	119.3	111.8
	R(O-O)	1.411	1.482	1.451	1.464
	R(O-H)	0.951	0.945	0.967	0.965

[a] Taken from ref. 51.

[b] Taken from ref. 52.

Table 6. Geometrical parameters of hydrogen trioxide as determined by PM3 and PM3-MAIS semiempirical calculations and ab initio calculations. The distances are reported in Å and the angles are reported in degrees. The parameters are defined in Fig. 5.

System	Parameter	Method			
		PM3-MAIS	PM3	CCSD(T)/ cc-pVQZ[a]	Exp.[a]
H_2O_3	$R(O_1\text{-}O_2)$	1.426	1.426	1.427	1.428
	$R(O_2\text{-}O_3)$	1.426	1.426	1.427	1.428
	$R(H\text{-}O_1)$	0.948	0.946	0.966	0.963
	$R(O_3\text{-}H)$	0.948	0.946	0.966	0.963
	$\phi(O_2\text{-}O_3\text{-}H)$	98.7	100.5	101.1	101.1
	$\phi(H\text{-}O_1\text{-}O_2)$	98.7	100.5	101.1	101.1
	$\phi(O_1\text{-}O_2\text{-}O_3)$	113.7	99.2	107.0	107.0
	$\theta(H\text{-}O_1\text{-}O_2\text{-}O_3)$	80.5	101.1	81.1	81.8
	$\theta(O_1\text{-}O_2\text{-}O_3\text{-}H)$	80.5	101.1	81.1	81.8

[a] Taken from ref. 54.

3.6. Interaction energies

The interaction energies for the set of investigated hydrogen-bonded systems are collected in Table 7. The comparison between the interaction energies calculated with PM3 and PM3-MAIS method shows that the stability of the complexes predicted with PM3-MAIS method is considerably higher, and the calculated values agree reasonably well with the ab initio results. On the other hand, the stabilities of hydrogen-bonded complexes predicted by PM3 method are systematically too low. Both semiempirical methods, PM3 and PM3-MAIS, recognize the linear water dimer as the most stable form of the water dimers although the differences between the interaction energies of different forms are relatively small (See Table 7). If we divide the interaction energies of the water trimer and water tetramer with the number of hydrogen bonds in each of the clusters then the energy of a hydrogen bond in the two clusters can be estimated. The results of both semiempirical methods show that the energy of a hydrogen bond in a cyclic water tetramer is lower than in a cyclic water trimer, which is in agreement with the results obtained by Rzepa and Yi.[55] The results for the energy of a hydrogen bond calculated with the PM3 and PM3-MAIS are -3.4 (-3.8) kcal/mol for a cyclic water trimer and -4.6 (-5.4) kcal/mol for a cyclic water tetramer (the values calculated with the PM3-MAIS method are given in brackets). Experimental values for the energy of a hydrogen bond in water clusters range between -4.4 and -5.4 kcal/mol, respectively.[42, 56]

Table 7. Interaction energies for the investigated hydrogen-bonded systems. Comparison of semiempirical, ab initio, and experimental values.

System	E_{int} [kcal/mol]			
	PM3-MAIS	PM3	*Ab initio*	Experimental
$(H_2O)_2$				
1a	-4.64	-3.50	-4.97[a]	-5.4[c]
1b	-2.33	-1.52	-3.90[a]	
1c	-3.39	-1.99	-2.99[a]	
1d	-2.17	0.86	-2.98[a]	
$H_5O_2^+$	-35.0	-23.6	-34.5[e]	-31.8[d]
$(H_2O)_3$	-11.5	-10.1	-15.9[b]	
$(H_2O)_4$	-21.8	-18.3	-27.9[c]	

[a] Taken from ref. 34.

[b] Taken from ref. 46.

[c] Taken from ref. 42.

[d] Taken from ref. 56.

[e] Taken from ref. 47.

4. Conclusions

A new PM3 core-core correction function $g^{MAIS}(A,B)$ has been introduced in the MOPAC97 program for semiempirical molecular orbital calculations. The implementation of the new function has been tested by performing geometry optimizations of several simple systems consisting of hydrogen and oxygen atoms. From the comparison of the calculated results to the results obtained with the standard PM3 method, ab initio methods and to experimental data the following observations can be made: (1) the geometrical parameters of the complexes consisting of the water molecules or protonated water molecules are generally in better agreement with the ab initio and experimental data than the geometrical parameters calculated using the standard PM3 method; (2) we have noticed that despite the fact that both semiempirical methods mainly underestimate the interaction energy of the investigated hydrogen-bonded complexes, the new PM3-MAIS method stabilizes the hydrogen-bonded complexes more than the standard PM3 method. The energy of a hydrogen bond, which was systematically underestimated with the PM3 method, is now closer to the ab initio and experimental data; (3) both semiempirical methods, PM3 and PM3-MAIS, fail to reproduce the geometry of the hydrogen peroxide molecule. This is not a surprising result since the correct geometry of the hydrogen peroxide molecule is very difficult to calculate. Moreover, the geometry of hydrogen trioxide predicted by the semiempirical PM3 and PM3-MAIS methods is in good agreement with ab initio values, pointing to the possibility of transferring the parameters of the new PM3 core-core correction function to systems other than water clusters or protonated water clusters. We conclude that the new semiempirical PM3-MAIS method allowed for an improved description of the geometrical parameters and interaction energies of the testing systems. Despite the fact that the structural parameters calculated with the PM3 and PM3-MAIS methods can still deviate from the ab initio and experimental data, the reparametrization of the correction function in the core-core interaction term has been a successful step in the development of semiempirical methods. An extension of the reparametrization of the new PM3-MAIS method to atom pairs also containing C, N, and O atoms may improve the predictive power of semiempirical methods in enzyme reactions and particularly the modeling of proton transfer processes between hydrogen bonded molecules, which is a crucial event in many enzymes and signal transduction proteins.

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Povzetek

Znano je, da semiempirične metode slabo napovedujejo energije vodikovo vezanih sistemov in njihovo geometrijo. Vzrok temu je korekcijska funkcija pri členu, ki predstavlja interakcijo med sredicama atomov. Funkcija naj bi modelirala odboj med pari jeder atomov. Nedavno so v semiempirični model PM3 vpeljali novo korekcijsko funkcijo, ki je osnovana na parametrih po parih atomov. Objavili so tudi parametre za interakcijo parov O-O, O-H in H-H. V naši študiji smo omenjeno funkcijo vgradili v programski paket za semiempirične molekulsko orbitalne račune MOPAC97. Testne račune smo naredili na naslednjih enostavnih sistemih: molekuli vode, protoniranem dimeru vode, cikličnem trimeru in tetrameru vode, štirih različnih dimerih vode, oksonijevem ionu, vodikovem peroksidu in vodikovem trioksidu. Rezultate računov smo primerjali s tistimi, ki smo jih dobili s standardno PM3 metodo, ab initio metodami ter z eksperimentalnimi podatki, če obstajajo. V vseh primerih z izjemo vodikovega peroksida se je modificirana PM3 metoda pokazala kot bistveno boljša tako za opis geometrij kot tudi za velikosti interakcijskih energij testnih sistemov. Naše raziskave torej nakazujejo, da bo reparametrizacija člena za interakcijo sredic atomov igrala pomembno vlogo pri nadaljnjem razvoju semiempiričnih metod.