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The origin of the problems with the PM3 core repulsion function

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Abstract

We investigate the cause of failures of PM3 for H···H, O···H and N···H interactions. We show that the actual choice of parameters for the Gaussian correction functions leads to spurious oscillations in the interatomic core repulsion functions and in the potential energy surfaces. The positions of the minima of the Gaussian correction functions considerably influence the positions of the minima on the potential energy hypersurface of weak interactions. The PM3 potential energy curve of water dimer as a function of the O···H distance clearly illustrates the problem. The minimum at 1.8 Å and the wide shoulder at 2.1 Å correspond to a minimum and a maximum of the O···H Gaussian correction function, respectively. © 1997 Elsevier Science B.V.

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1. Introduction

Several spectacular failures [1–7] of the popular PM3 method inspired us to further investigate the origin of the problem. Our previous analysis of the core repulsion function (CRF) showed that the CRF works correctly in many cases [2]. However, it can be the source of a stabilization effect for H–H interactions between 1.8 and 2.0 Å, an artifact in the physical sense [1,2,4]. We shall present a similar behaviour of the CRF that influences the breakdown of PM3 for the calculation of intermolecular complexes.

MNDO [8], AM1 [9], and PM3 [10] semiempirical SCF methods are extensively used in theoretical studies of molecular structure [11]. These methods differ in the treatment of the CRF, which is extensively parametrized in the AM1 and PM3 methods. These methods neglect the repulsive orthogonalization corrections and the attractive penetration integrals of the one-centre core Hamiltonian matrix elements. These two terms are of comparable magnitude and show similar decay with increasing distance [12]. However, they do not compensate each other fully, and empirical corrections are therefore needed to remedy this error. Dewar et al. [8] observed that the neglected repulsive terms are larger than the attractive terms. They introduced an empirical exponential correction term into the CRF of MNDO [8] to adjust the balance between the attractive and repulsive terms more precisely. This approach was further refined in the AM1 [9] and PM3 [10] methods by adding several repulsive and attractive Gaussian functions. The amplitude, the steepness and the displacement of these functions have been extensively parametrized. Despite the considerable parametrization efforts, these methods frequently provide unrealistic results, and thus the results usually require careful control. This control is not always feasible

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owing to computational costs, as the most precise correlated methods are very expensive for large molecules. The more economical HF calculations suffer from a lack of correct accounting for electron correlation, and thus cannot be considered as unquestionable benchmarks. Even these calculations are 3 or 4 orders of magnitude more expensive than the semiempirical calculations. The recently developed generalized gradient approximation (GGA) DFT methods do provide correlated results; however, the present implementations [13] are slightly more expensive than the HF calculations with the same basis set. Thus, improvement in the reliability of semiempirical methods would fill an important gap.

The molecular mechanics (MM) methods, *if appropriately parametrized*, are capable of providing quite correct molecular geometries, relative conformational energies and energy barriers. These results are often superior to the corresponding semiempirical results. However, it should be noted that MM methods do not use the electron density or the molecular orbitals. Thus, frontier orbital interactions, ionization potentials, charge densities, spin densities and other quantum chemically important features are missing from MM calculations. To solve this problem the so-called hybrid methods were constructed [14–18]. In these methods the central part of the molecule is treated semiempirically or ab initio and the rest is treated by MM methods.

The precision of the semiempirical methods is limited by the accuracy of the experimental data used in obtaining parameters. It should be noted that it is frequently necessary to transform the experimental data before comparing to calculated results. For example, in order to make a correct comparison between experimental and calculated molecular geometries, the calculated r_e structure should be converted to measured thermal average structures [19]: e.g. r_g, r_z, r_a, r_α, or vice-versa. It is also known that for precise comparison of ab initio total energies and semiempirical heats of formation with the experimental values, entropy corrections should be considered. This type of transformation was not performed consistently during the parametrization procedure of the above-mentioned semiempirical methods. Parametrizing the semiempirical methods to reproduce the best available theoretical results would solve this problem. However, two serious problems remain: how to determine the best form of parametric functions and how to find the best minimum on the parameter hypersurface [20]. The development of the corrections to CRF illustrates the difficulties. It was found that the MNDO [8] parametrization is unable to correctly describe the core–core repulsion in crowded molecules. The reparametrized AM1 method [9] tried to remedy this problem by introducing Gaussian correction functions (GCF) to the CRF. These corrections are outside the quantum-mechanical framework, their role being to adjust the nuclear–nuclear repulsion terms. Utilizing the GCF, the AM1 method provided consistently superior results over the MNDO method. Later a fully optimized parameter set was produced by Stewart [10]. This parameter set is called PM3.

In the present paper we use a decomposed form of the CRF, and show that the optimized parameters used in the PM3 method can lead to physically incorrect results. We shall present the manifestation of the problem for water dimer.

2. Computational methods

We used the GAUSSIAN 94 program [13] for AM1, PM3, and CCSD calculations. The CCSD calculations were performed using a 6-311 G(d,p) [21] basis set. The calculations were performed on Silicon Graphics and IBM workstations.

3. Results and discussion

3.1. Atomic and diatomic GCF curves

The GCF are composed of Gaussians centred at a given distance from the nucleus (N), thus providing a repulsive or attractive sphere around the nucleus, depending on the sign of the pre-exponential constant. We use the GCF in the following form:

$$E_N(i,j) = \mathrm{CRF}_N^{\mathrm{MNDO}}(i,j) + \mathrm{GCF}(i,j,r_{ij}), \tag{1}$$

$$\mathrm{GCF}(i,j,r_{ij}) = Z_j \cdot \mathrm{GCF}(i,r_{ij}) + Z_i \cdot \mathrm{GCF}(j,r_{ij}), \tag{2}$$

$$\mathrm{GCF}(i,r_{ij}) = \frac{Z_i}{r_{ij}}\left(\sum_{k=1,2,3,4} a_{ki} \exp\left[-b_{ki}(r_{ij}-c_{ki})^2\right]\right), \tag{3}$$

where $E_N(i,j)$ is the nuclear–nuclear repulsion term between two atoms (i and j), $CRF_N^{MNDO}(i,j)$ is the MNDO CRF term, Z_i is the effective nuclear charge corresponding to the number of valence electrons on atom i, r_{ij} is the interatomic distance, a_{ki}, b_{ki}, and c_{ki} are atomic parameters of Gaussians corresponding to intensity, steepness and displacement, respectively. Eq. (3) is a convenient decomposition of the interatomic GCF(i,j) that makes it possible to analyze the GCF at atomic levels.

It was experienced that a simple, repulsive GCF provided too large interatomic core–core repulsion at large interatomic distances. Dewar et al. [9] proposed reducing this excessive interatomic repulsion by two methods: (1) by introducing one or more attractive Gaussians at large distance (c_{ki}) from the nucleus, or (2) by putting the Gaussian closer to the nucleus. For H, C and N one or two small-amplitude attractive (negative) Gaussians was positioned at above 2 Å (c.f. Table 1). For oxygen, two repulsive (positive) Gaussians were applied relatively close to the nucleus (at 0.848 and 1.445 Å). Dewar et al. [9] stated that attempts to use only repulsive Gaussians for the elements other than O led to poorer results. It should be noted that the positioning of the Gaussians was at best an educated guess and after each choice of the positions the method was fully reparametrized. 'This approach... needs infinite patience and enormous amounts of computer time.' [9] Initially, the b_{ki} atomic parameters were not optimized at all in AM1. Subsequently, Stewart introduced a powerful parameter optimization method [10]. Using that method he was able to fully optimize all semiempirical parameters in the PM3 method. He proposed to reduce the number of Gaussians in the GCF to two in order to reduce the complexity of the optimization process.

Comparing the AM1 and PM3 atomic GCF parameters for H, C, N and O, the following observations can be made: the PM3 GCFs for H, N and O atoms are composed from two almost equally large-amplitude Gaussians with opposite signs, and these Gaussians are centred very close to each other (Table 1). The AM1 method utilizes significantly smaller Gaussians and these Gaussians have a considerable distance between them. It is interesting to note that the PM3 parametrization contradicts Dewar's proposition that two positive Gaussians are necessary on the oxygen atom. Stewart puts two Gaussians of opposite sign on the oxygen, and he applies two positive Gaussians to the carbon atom (Table 1).

Fig. 1 shows the PM3 GCF. As was noticed earlier [1,2,4], the GCF of the H atom has an artificial minimum at 1.8 Å. Fig. 1(b) shows how this artifact is amplified further in the N–H and O–H interactions. This minimum is missing from the C–N and C–O PM3 GCFs (Fig. 1(c)) and they remain repulsive in the whole range shown in the figure. However, for the

Table 1
GCF parameters for PM3 and AM1 methods[a]

Atom (i)	k	PM3[b]			AM1[c]		
		a_{ik}	b_{ik}	c_{ik}	a_{ik}	b_{ik}	c_{ik}
H	1	1.1288	5.10	1.5375	0.1228	5.00	1.20
	2	− 1.0603	6.00	1.5702	0.0050	5.00	1.80
	3				− 0.0183	2.00	2.10
C	1	0.0507	6.00	0.8925	0.0114	5.00	1.60
	2	0.0501	6.00	1.6422	0.0459	5.00	1.85
	3				− 0.0200	5.00	2.05
	4				− 0.0013	5.00	2.65
N	1	1.5017	5.90	1.7107	0.0253	5.00	1.50
	2	− 1.5058	6.00	1.7161	0.0290	5.00	2.10
	3				− 0.0058	2.00	2.40
O	1	− 1.1379	5.95	1.5984	0.2810	5.00	0.848
	2	1.1311	6.00	1.6073	0.0814	7.00	1.445

[a] Rounded values.
[b] Ref. [10].
[c] Ref. [9].

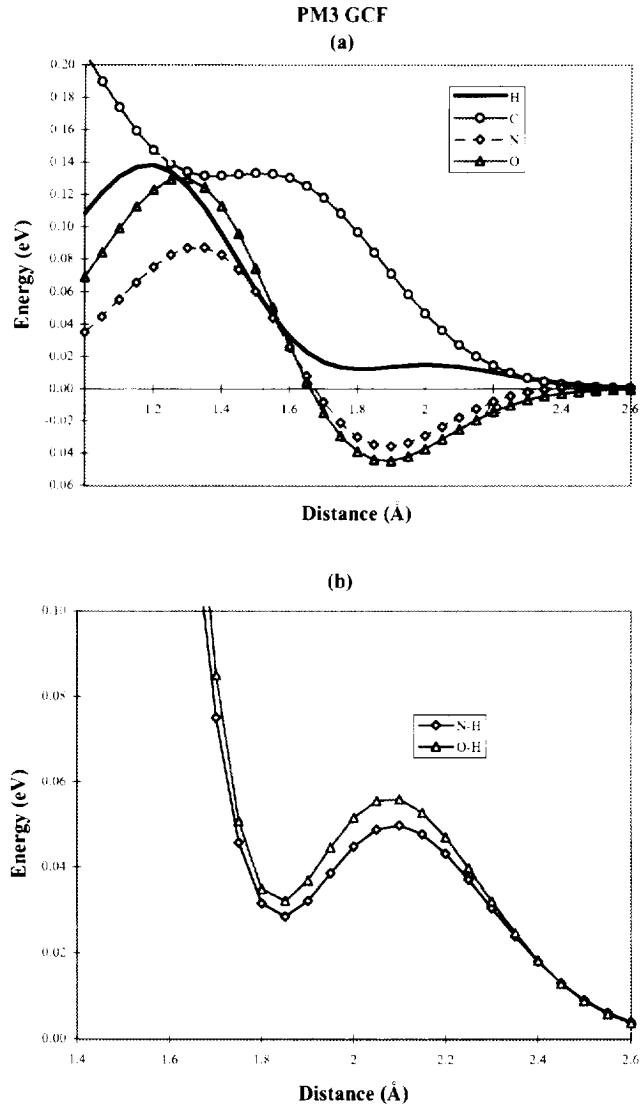

Fig. 1. The PM3 GCFs for H, C, N, O and for several atom pairs. The distance is the distance from a selected (a) nucleus or the interatomic distance (b and c).

N–O atom pair a spurious, relatively large stabilization occurs at about 1.9 Å.

For comparison we show several AM1 GCFs in Fig. 2. The AM1 GCFs are free of the oscillations. The gradients of these curves are small and the curves are smooth at large distances.

3.2. Water dimer

Fig. 3 shows the calculated potential energy curves for the water dimer with C_s symmetry. The two water molecules were positioned in such a way that one of the hydrogen atoms of the water molecule on the left points towards the lone pair of the water molecule on the right. The water dimer has been extensively studied in the literature, both experimentally [22] and theoretically [23–25]. The MP2/6-31+G(d) [24], 6-311++G(2d,2p) [23], and aug cc-pVTZ [24] results provide similar C_s structures (see Fig. 3) for the water dimer in agreement with microwave spectroscopy

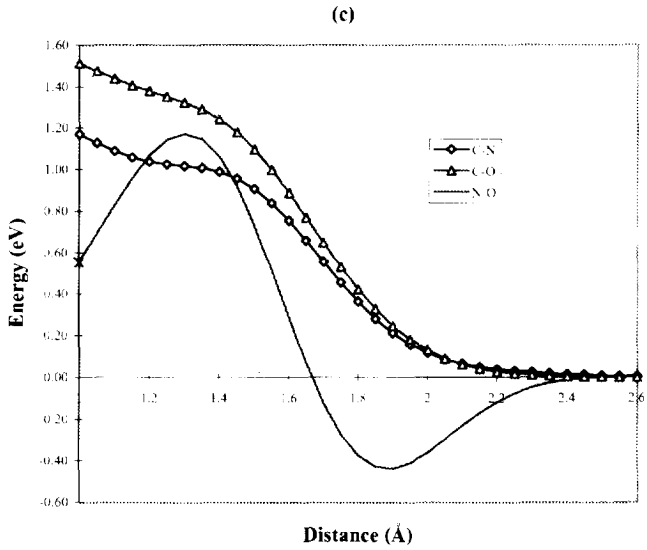

Fig. 1. Continued.

[22]. The calculated O···O distance shows a minor basis set dependence, and it varied between 2.901 and 2.911 Å as the basis set quality increased from 6-31+G(d) to 6-311++G(2d,2p) using the MP2 method [23,25]. The recent GGA DFT calculations, using a variety of basis sets, provide 2.890–2.938 Å for the O···O distance [24,26,27]. These calculated O···O distances are slightly smaller than the corrected experimental r_e(O···O) = 2.946 Å [22].

Comparing the PM3 GCF curve for the O–H interaction (Fig. 1(b)) and the PM3 water dimer potential energy curve (PEC) shows that the oscillating nature of the O–H GCF considerably distorts the PEC. Two features deserve to be noted: (1) the minimum is shifted to 1.8 Å, and (2) a wide shoulder occurs at 2.1 Å. We performed a series of single point energy calculations with the same dimer geometries using AM1 and CCSD/6-311G(d,p) methods. We present in Fig. 3 the difference of the CCSD and PM3 curves (Diff = ΔE(CCSD) − ΔE(PM3)). This error curve clearly shows the above-mentioned oscillations. It is worth noting that the position of the minimum on the GCF curve considerably influences the position of the minimum on the intermolecular PEC. Thus the PM3 and AM1 methods provide minima at 1.8 and 2.1 Å, respectively, for the water dimer PEC, very close to the minima of the corresponding GCF (cf. Fig. 1(b) and 2(b)). The CCSD method provides 2.957 Å for the O···O distance, which is in agreement with the corrected experimental result [22] (this calculation lasts about 10,000 times longer than a semiempirical calculation).

Comparison of the CCSD and AM1 curves on Fig. 3 proves that the AM1 seriously overestimates the repulsion between two water molecules closer than 2 Å. The PM3 curve is much less repulsive than the AM1 curve. The PM3 curve runs much closer to the CCSD curve at 1.7 Å, but this advantage is clearly lost at larger distances because of the large oscillations. These distortions of the potential energy surface lead to serious failures of the PM3 method when applied, for example, to carbohydrate chemistry [3,6,7] or for proton transfer reactions [28]. We also noticed that the H···H stabilization effect in the PM3 method leads to distorted ring structures in permethylated cyclopentasilanes [29]. The PM3 method stabilizes the equilibrium structures with methyl hydrogens at 1.8 Å distance.

The great success of the AM1 and PM3 methods proves that the introduction of GCF was successful in a practical sense; however the actual GCFs are subject to parametrization errors, mainly in PM3. The GCF terms act as van der Waals attraction and dispersion operators, and mimic long-range correlation effects, thus playing a decisive role in the long-range interactions. It should be noted that the successful MNDO/

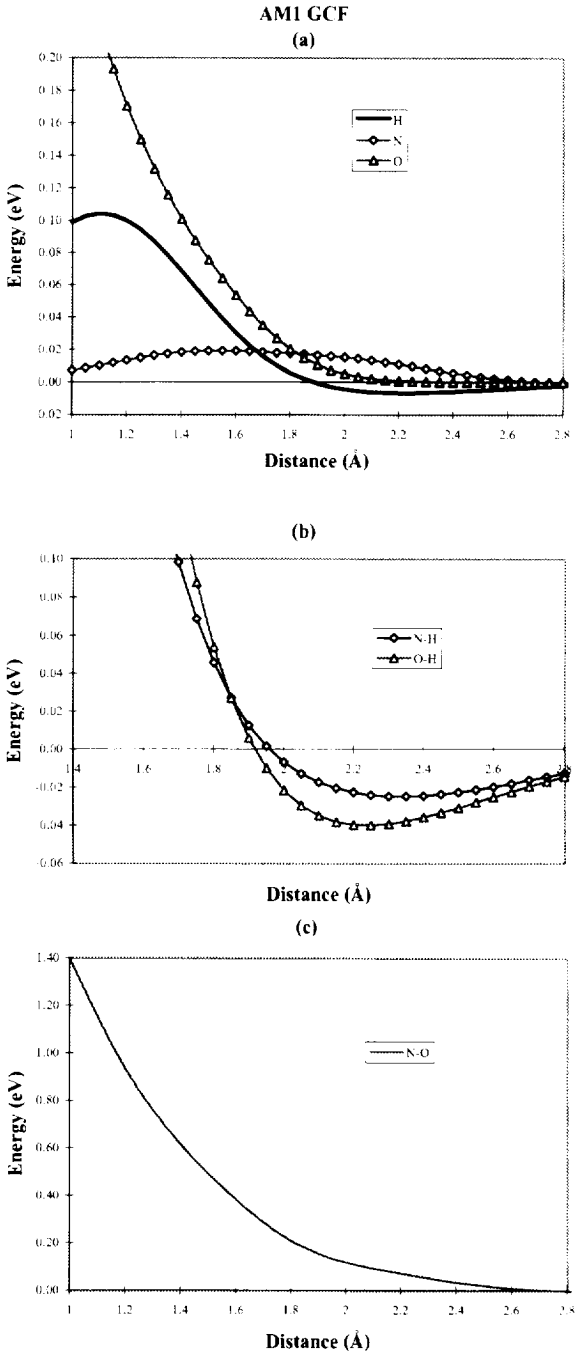

Fig. 2. The AM1 GCFs for H, C, N, O and for several atom pairs. The distance is the distance from a selected (a) nucleus or the interatomic distance (b and c).

d method [30] does not use GCF; however, introduction of the GCF (AM1/d or PM3/d methods) may provide further gains in performance [31]. More reliable semiempirical methods would play an important role in molecular dynamics research, because the trajectory studies require the fastest method possible [32].

4. Conclusions

The PM3 GCFs for the H, N, and O atoms are composed of two almost equally large, closely centred Gaussians. The actual choice of the parameters of these Gaussians leads to spurious oscillations in the corresponding interatomic CRFs and distortions of the energy hypersurface. The positions of the minima of the GCF considerably influence the positions of the minima on the potential energy hypersurface of weak interactions (e.g. hydrogen bonding). The example of the PEC of water dimer clearly illustrates the problem.

The introduction and parametrization of the GCF considerably improved the MNDO method and both the AM1 and PM3 methods provide clearly superior results. However, for inter- or intramolecular O···H, N···H or N···O interactions the PM3 method should be used with care. Before interpreting the semiempirical results, the potential energy surface of the GCF should be presented and checked against the above-mentioned spurious oscillations. The examples of the PM3 C–O and C–N GCFs and all of the AM1 GCFs show that it is possible to construct a smooth, oscillation-free GCF. The future development of semiempirical methods relying on the use of GCFs should provide oscillation-free GCFs. The position and the magnitude of the attractive Gaussians should be handled very carefully, as these Gaussians may play a decisive role in the weak interactions.

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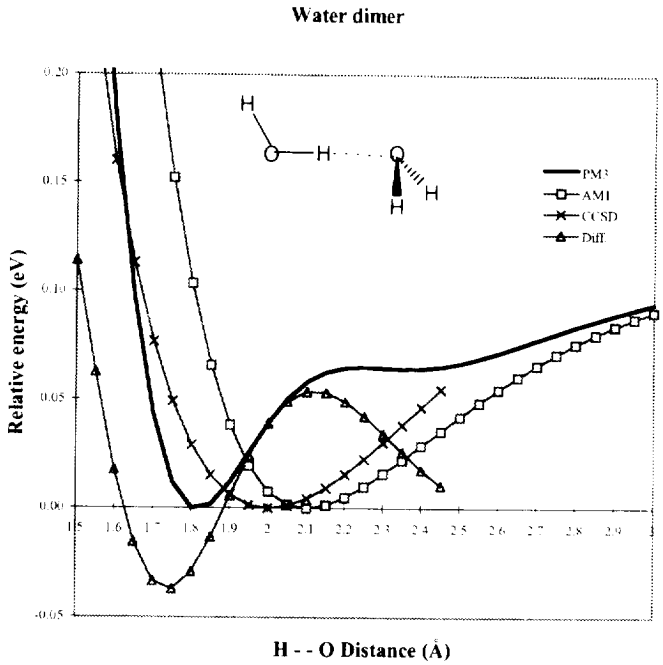

Fig. 3. PM3, AM1 and CCSD/6-311G(d,p) relative potential energy curves for water dimer as a function of the H···O distance. The relative energy difference between the PM3 and CCSD curve is also shown (Diff.).

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