

How good are molecular local-density methods? Case studies: The quadrupole moment of benzene, geometry and electrostatics of dimethyl sulfoxide, and the conformations of dimethoxy ethane

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The performance of different local density approaches for the calculation of various molecular properties is compared among the models themselves, with conventional wave function and perturbation-based schemes, and with experiment, where available. Three test cases are studied: The molecular quadrupole moment and the atomic charge distribution of the benzene molecule; the geometry, dipole moment and charge distribution of dimethyl sulfoxide; and the relative energetics of the all-trans, trans-gauche-trans and trans-gauche⁺-gauche⁻ conformers of dimethoxy ethane (glyme) and the solvent stabilisation of the trans-gauche-trans conformation.

I. Introduction

In spite of having been used for decades in condensed-matter theory, density-functional techniques have been a niche method in quantum chemistry until very recently. Since a few years, however, they have become popular for molecular systems, too. Many techniques of density-functional theory (DFT), especially in the local spin-density approximation (LSDA), have recently become widely available as part of major quantum-chemistry program packages.

From their first appearance in molecular electronic structure calculations, LSDA methods have been hailed as superior to traditional quantum-chemical methods in various ways: they provide molecular geometries with an accuracy better than Hartree-Fock (HF) and they are computationally cheaper than even the simplest correlated methods such as low-order many-body perturbation theory (MBPT). At times, they have been touted as being even faster than HF. However, this is probably an effect of features not inherent in DFT, but of methods used to implement it (basis sets, treatment of electrostatics, pseudopotentials, etc.). One must, however, not forget that DFT methods have disadvantages, too: Their use for electronically excited states is

problematic, and spin eigenstates are hard to obtain.

A practical disadvantage of DFT methods is, that while the equations are in principle exact, there is substantial variation in the approximations used in the description of electron exchange and correlation. Hence, there are always many functional forms to choose from, and it is not clear which functional is most suitable for which property. As an example: a recent Car-Parrinello calculation on liquid H₂O gave the wrong density and radial distribution function with a functional that accounted for both exchange and correlation, but yielded considerably better results with an exchange-only functional^[1]. The reasons for this are not understood.

A practical approach seems to be the only way to improve the situation. The performance of various density functional methods has to be benchmarked against each other and against the conventional methods of accounting for electron exchange and correlation. This has to be done for many different systems and molecular properties. In this contribution, we have picked three completely unrelated molecules, which for different reasons are currently of interest in our laboratory^[2-5]. We have studied them with several local-density methods

provided in the Gaussian92/DFT package^[6], keeping the other parameters (basis sets) the same for all calculations. We have also performed HF and MBPT calculations of various order using the same basis, for comparison.

II. Density-functional methods

Just like restricted Hartree-Fock (RHF) theory, the LSDA yields a single-determinant wave function if Kohn-Sham eigenfunctions are used as a representation. Instead of the RHF expression (closed shell) for the energy^[7]

$$E_{HF} = 2 \sum_i^{\text{occ}} \langle i|h|i \rangle + 2 \sum_i^{\text{occ}} \sum_j^{\text{occ}} (ii|jj) - \sum_i^{\text{occ}} \sum_j^{\text{occ}} (ij|ij), \quad (1)$$

we have the Kohn-Sham (KS)^[8] expression for the energy

$$E_{KS} = 2 \sum_i^{\text{occ}} \langle i|h|i \rangle + \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' - E_{XC}. \quad (2)$$

The summations extend over all molecular orbitals i (here, KS eigenfunctions). The one-electron part (first term) is identical in both approximations, and so is - in principle - the Coulomb part (second term). The different notation only indicates that HF theory universally evaluates this term exactly by means of the appropriate sums of two-electron integrals, whereas in some DFT schemes the Coulomb energy is calculated in approximate manner (mesh, extra charge fitting basis sets). The third term in the HF equation is an exact evaluation of the exchange interaction from two-electron integrals. It is this term, where the KS equation differs fundamentally from the HF equation. It has been shown that this term, the exchange-correlation energy, is a functional of the electron density, and further, that the KS equation is exact (in spite of yielding a single-determinant wave function) if this functional is evaluated exactly. Unfortunately, this functional is not known for molecular systems.

If one approximates E_{XC} as an integral over a local functional of the density $\epsilon_{XC} = \epsilon_{XC}[\rho(\mathbf{r})]$, one obtains the LSDA. (As an aside: even if the exchange-correlation functional depends on the gradient of the density as well as on the density, it still is a local

functional in a mathematical sense.) Many exchange-correlation functionals of different parentage have been devised. We have listed some of the ones available in the latest distribution of the Gaussian program package (Gaussian92/DFT) in Table 1. They can be roughly grouped into four classes. Firstly, there are the traditional approximations to the exchange-correlation energy (Hartree-Fock-Slater and Xa). The more modern methods usually employ separate functionals for exchange and correlation and use functional forms that contain the electron density as well as its gradient for either one or both parts. (Note that in an inhomogeneous system one cannot strictly separate exchange and correlation, and that this labelling reflects more the parentage of the functional.) The second class uses a gradient-corrected exchange functional (Becke) either with no correlation functional or a non-gradient-corrected correlation functional (BVWN, BPL). The third and most sophisticated class uses gradient-corrected functionals for both exchange and correlation (BVWN5, BLYP, BP86). Finally, there are linear combinations of exchange and correlation functionals with the Hartree-Fock exchange term. Here, the coefficients of the different functionals have been adjusted to reproduce experimental properties of a larger group of molecules. Examples of this fourth type of method are the "Becke-3" exchange functionals which can be combined with the non-local Perdew (B3P86) or LYP functionals (B3LYP).

III. The quadrupole moment and charge distribution of benzene

Static electric moments are a sensitive test of the charge distribution in a molecule. In addition, from a wave function, atomic partial charges can be generated. Atomic charges are not observables and, hence, there is no quantum-mechanical operator which generates them. However, they are often needed as force field parameters in molecular simulation, and a number of recipes for their calculation has been devised. If one charges-fitting method and one basis set are used consistently, one can - within limits - compare molecular charge distributions of different wave functions, in spite of the arbitrariness of the whole procedure of obtaining molecular charges.

Table 1: Level of approximation used for describing electron exchange and correlation in the methods of this work.

| method | exchange ^{a)} | correlation ^{a)} | reference |
|---|------------------------|--------------------------------|------------|
| Hartree-Fock (HF) | exact | none | 7 |
| HF + many-body perturbation theory (MBPT) | exact | depending on the order of MBPT | 7 |
| Hartree-Fock-Slater (HFS) | local ^{b)} | none | 9 |
| X-alpha ($X\alpha$) $\alpha=0.7$ | local ^{b)} | | 9 |
| Becke (HFB) | gradient-corrected | none | 10 |
| Becke+VWN (BVWN) | gradient-corrected | local ^{b)} | 10, 11 |
| Becke+Perdew 1980 (BPL) | gradient-corrected | local ^{b)} | 10, 12 |
| Becke+VWN5 (BVWN5) | gradient-corrected | gradient-corrected | 10, 11 |
| Becke + Lee-Yang-Parr (BLYP) | gradient-corrected | gradient-corrected | 10, 13 |
| Becke + Perdew 1986 (BP86) | gradient-corrected | gradient-corrected | 10, 14 |
| Becke + HF + Perdew 1986 (B3P86) | gradient-corrected | gradient-corrected | 10, 14 |
| Becke + HF + LYP - VWN (B3LYP) | gradient-corrected | gradient-corrected | 10, 11, 13 |

a) Note: In the LSDA treatment of inhomogeneous systems, it is not possible to separate strictly the exchange and correlation contributions. Nonetheless, these terms are being commonly used to label the concepts behind the derivation of the functional.

b) The attribute "local" is often employed to denote a functional without gradient corrections, a practice followed here. In a mathematical sense, all of the functional listed here are local.

We have performed calculations of the benzene molecule (D_{6h} symmetry, the sixfold axis is in z direction, $R_{CC} = 1.4 \text{ \AA}$, $R_{CH} = 1.08 \text{ \AA}$) using the 6-311G** basis set. The “tight” convergence criterion was used throughout. A dense numerical grid in the DFT calculations was used by specifying the INT=FINEGRID option. Cartesian components of the quadrupole moment ($Q_{xx} = Q_{yy}$ and Q_{zz}) have been obtained analytically from the wave function (HF, DFT, MBPT2) or by centred differences (higher-order MBPT) using static external electric quadrupole fields of 0.0001 and 0.0005 atomic units (a.u.). For MBPT2 the finite-difference and analytical quadrupole moments agreed to all figures reported here. Because of the symmetry of the benzene molecule, only one independent spherical component of the quadrupole moment can be measured: $O = O_{zz} = -2Q_{xx} = Q_{zz} - Q_{zz}^{[17]}$.

Atomic charges were generated by Mulliken population analysis and by the Merz-Singh-Kollman electrostatic potential fitting procedure^[15,16]: Here, the atomic charges are adjusted to reproduce the electrostatic potential on a numerical grid which covers the surface of the molecule. All Merz-Singh-Kollman charges are averaged over all atoms, since the numerical grid introduces small deviations from a fully symmetric charge distribution. For the traditional ab initio methods, Mulliken charges have the correct symmetry. However, for DFT methods, they, too, have to be averaged because the numerical meshes used in solving for the exchange and correlation potentials cause a minor distortion of the charge distribution.

The results for benzene are listed in Table 2. We leave it to the reader to judge for him/herself the quality of the various methods. We confine our analysis to one feature: How well does a given method reproduce the value obtained using the best available correlated calculation using the same basis set? The most sensible parameters to use for comparison are probably the cartesian components of the quadrupole moment Q_{xx} and Q_{zz} : they are well-defined quantities, and are less susceptible to fortuitous cancellations of errors than the spherical quadrupole moment O (the fact, that of all methods, HF reproduces best the experimental O must be attributed to factors unaccounted for in all of the present calculations like effects of molecular vibration). As reference values, we take the MBPT4 quadrupole

moments and the MBPT2 atomic charges: the software in its current state does not allow the determination of atomic charges at the MBPT4 level. The only method which brings both the xx and the zz component of the quadrupole tensor within 0.2 a.u. of the reference value is MBPT2 with MBPT3 following suit. The best density-functional method is BLYP with a Q_{zz} deviation of 0.465 a.u. In the range of methods that are closer than 0.7 a.u., we find methods as different as $X\alpha$, HFS, HFB, BP86 and B3LYP. We note, that four DFT methods (BPL, BVWN, BVWN5 and B3P86) perform even worse than Hartree-Fock.

For the experimentally measurable quadrupole moment O , only four methods could reproduce the MBPT4 value to within 0.3 a.u.: MBPT2, MBPT3, BP86 and B3LYP, the latter two benefiting from cancellation of errors in the cartesian quadrupole components. The other DFT methods follow, their relative performance being uncorrelated to their degree of sophistication.

MBPT2 atomic charges are reproduced by all methods to within 0.02 e (Mulliken) and 0.03 e (MSK), and again there is no particular order among the methods. It is interesting to note that HF is both among the worst performers (Mulliken) and among the best (MSK). A method that gives close agreement with MBPT2 charges for both charge-fitting techniques is B3LYP. En passant, we note that an effective charge of 0.14 e (for a rigid benzene molecule at the present geometry) would be consistent with the experimental value of O .

IV. Structure and properties of dimethyl sulfoxide

Structural parameters of DMSO calculated in various approximations are listed in Table 3 along with experimental data for the different phases^[18]. After trying a few basis sets at the Hartree-Fock level, we opted for a 6-311(2d,p) basis set: adding f functions on the heavy atoms led to no significant structural changes. The largest changes were a shortening of the SO bond by 0.0057 Å and the SC bonds by 0.0048 Å, changes in CH bond length being of the order of 0.0003 Å and bond angles being virtually identical. Most demanding computationally, is the SO bond distance which has been subject to detailed investigations previously^[19,20].

Table 2: Electrostatic properties of the benzene molecule (6-311G** basis, $R_{CC} = 1.4 \text{ \AA}$, $R_{CH} = 1.08 \text{ \AA}$). Quadrupole moments in D \AA , hydrogen charges in e ($q_C = -q_H$), CPU times in seconds on a Silicon Graphics 380 (parallelised version) unless indicated otherwise.

| Method | Q_{xx} (D \AA) | Q_{yy} (D \AA) | Q_{zz} (D \AA) | Θ (D \AA) | Mulliken charge (average) | MK charge (average) | cpu time (s) |
|-----------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|---------------------------------|------------------------|---------------------|
| HF | -31.664 | -31.665 | -40.543 | -8.878 | 0.0999 | 0.1455 | 820 |
| MBPT2 | -32.257 | -32.257 | -39.904 | -7.647 | 0.0955 | 0.1255 | 18635 |
| MBPT3 | -32.187 | -32.187 | -39.886 | -7.699 | | | |
| MBPT4 | -32.407 | -32.407 | -39.821 | -7.414 | | | 26740 ^{a)} |
| HF 6-311(2df,p) | -31.593 | -31.593 | -40.334 | -8.760 | 0.1065 | 0.1430 | 259 ^{a)} |
| MBPT2 6-311(2df,p) | -31.910 | -31.910 | -39.755 | -7.845 | 0.1107 | 0.1284 | 8999 ^{a)} |
| experiment [17] | | | | -8.69 0.51 | | | |
| | | | | | | | |
| HFS | -32.6498 | -32.6502 | -40.4956 | -7.846 | 0.1159 | 0.1290 | 642 |
| X α | -31.8603 | -31.8608 | -39.9797 | -8.119 | 0.1197 | 0.1334 | 715 |
| Becke | -33.0737 | -33.0744 | -39.5967 | -6.523 | 0.0663 | 0.1076 | 648 |
| BPL | -32.0408 | -32.0416 | -38.9462 | -6.905 | 0.0754 | 0.1136 | 569 |
| BVWN | -31.8807 | -31.8815 | -38.8452 | -6.964 | 0.0769 | 0.1145 | 632 |
| BVWN5 | -32.0068 | -32.0075 | -38.9200 | -6.913 | 0.0752 | 0.1137 | 634 |
| BLYP | -32.2885 | -32.2891 | -39.3612 | -7.072 | 0.0831 | 0.1164 | 644 |
| BP86 | -31.7551 | -31.7558 | -39.4459 | -7.690 | 0.1027 | 0.1262 | 703 |
| B3LYP | -31.8617 | -31.8622 | -39.5351 | -7.673 | 0.0939 | 0.1260 | 1028 |
| B3P86 | -31.3228 | -31.3233 | -39.5226 | -8.200 | 0.1105 | 0.1344 | 1186 |

a) IBM RS6000/590.

The MBPT2 method finds a value close to experiment (gas and liquid). Of all DFT methods, only $X\alpha$, B3P86 and B3LYP are within 0.006 Å of this value. Most DFT methods overestimate this particular bond distance. As an extreme case, the Becke functional misses wider than HF, although in different direction.

The experimental SC bond distance, surprisingly is best reproduced by HF and HFS. Of all DFT methods, only $X\alpha$ and B3P86 can compete with MBPT2 in reliability.

The CH bond distances seem to be non-critical. They are, in general, well reproduced by all methods except HF, HFS, $X\alpha$ and Becke.

Given the scatter of experimental values for the bond angles, all theoretical methods appear to perform satisfactorily. HF seems to give the largest CSC bond angle (97.9 degrees) while the smallest values are produced by $X\alpha$ and HFS (94.9 and 94.7 degrees, respectively), with the other methods falling in between. The scatter among the theoretical OSC bond angles is even smaller.

V. Conformational equilibria of dimethoxy ethane

Dimethoxy ethane (ethylene glycol dimethyl ether, glyme, $\text{CH}_3\text{-O-CH}_2\text{-CH}_2\text{-O-CH}_3$) has 9 possible unique conformations which can be classified by combinations of trans ($\sim 180^\circ$), gauche⁺ ($\sim +60^\circ$) and gauche⁻ ($\sim -60^\circ$) orientations of the three dihedral angles COCC, OCCO, and CCOC. Equilibria among these conformers have been subject of intense theoretical and experimental study (see Ref. 3 and references therein). Of all conformers, the all-trans (ttt), trans-gauche-trans (tgt) and the trans-gauche⁺-gauche⁻ (tg^+g^-) are lowest in energy. We studied the relative energetics of these conformers, as well as that of the trans-to-gauche barrier (central dihedral OCCO fixed at 120°). In addition, we have used the self-consistent reaction-field method^[21,22] in order to estimate solvent effects on the stability of the tgt conformer (for details, see Ref. 3).

For the comparative calculations, we used the 6-31G** basis set in all calculations. Full geometry optimisations were carried out for all conformers and all methods with the following exceptions: (i) for the trans-gauche barrier the OCCO dihedral was kept at 120° , (ii) for tgt in the reaction-field treatment at

the MBPT2 level, the geometry was not reoptimised, but the MBPT2 geometry obtained without the reaction field was used, (iii) calculations at MBPT orders higher than 2 and CISD calculations were performed at the respective MBPT2 geometries. In self-consistent reaction-field calculations we used a cavity radius of 4.0 Å and a dielectric constant ϵ of 80 for the continuum.

If we take the MBPT4 relative energies (Table 5), where available, as the reference, we find universally that the method to come closest is MBPT2. Only the more sophisticated DFT schemes come anywhere near in all cases. However, most DFT schemes seem to perform better than HF (and in fact CISD). In general, the tgt energy is underestimated by all DFT schemes, the simplest (HFS, $X\alpha$) even giving a negative value (that means tgt is lower in energy than ttt), while the more sophisticated (B3LYP, B3P86) approach the correct value from below. The energy of the tg^+g^- conformer is predicted most reliably by BP86 and BLYP, while HFS and $X\alpha$ have errors almost as bad as HF, although with a different sign. The trans-gauche barrier is substantially underestimated by all DFT methods: Here, B3LYP and B3P86 perform best among the DFT methods (although they are still far from the MBPT results), whereas HFS and $X\alpha$ - again - are unreliable. From an energetics point of view, one would prefer methods like BP86, BLYP, B3LYP and B3P86 whereas HFS and $X\alpha$ should definitely be shunned along with HF.

An interesting point is also the stabilisation of the tgt conformer by a reaction field treatment: None of the DFT methods comes close to the MBPT2 result, most are worse than HF. Inspection of Table 6 reveals the reason: all DFT methods produce dipole moments for the tgt conformer which are too low. The magnitude of the gas-phase dipole moment, on the other hand, is the most important single quantity to determine the reaction-field stabilisation.

A further detail worth noting in Table 5 is the fact that some of the DFT geometries fail to converge, particularly for the tg^+g^- conformation and for the tgt conformer in a reaction field. In these cases, the geometry optimisation proceeds smoothly until close to the minimum and then starts to orbit around the minimum usually jumping between 2-3 geometries. While the en-

Table 3: Optimised geometries of dimethyl sulfoxide (DMSO) calculated with a 6-311(2d,p) basis sets, all distances in Å, all angles in degrees.

| | R_{SO} | R_{SC} | R_{CH1} | R_{CH2} | R_{CH3} | ϕ_{CSC} | ϕ_{CSC} |
|-----------------|----------|----------|-----------|-----------|-----------|--------------|--------------|
| Experiment [18] | | | | | | | |
| gas | 1.485 | 1.799 | | | | 96.57 | 106.65 |
| solid | 1.531 | 1.8 | | | | 97.4 | 106.7 |
| liquid | 1.496 | 1.8 | | | | 99.2 | 107.2 |
| | | | | | | | |
| MBPT2 | 1.4947 | 1.8139 | 1.0910 | 1.091 | 1.0894 | 95.27 | 106.53 |
| HF | 1.4665 | 1.7967 | 1.0819 | 1.0826 | 1.0811 | 97.93 | 106.31 |
| HFS | 1.5084 | 1.8402 | 1.1196 | 1.1187 | 1.1169 | 94.73 | 106.50 |
| X α | 1.4905 | 1.8128 | 1.1054 | 1.1044 | 1.1028 | 94.91 | 106.47 |
| Becke | 1.5353 | 1.9281 | 1.1083 | 1.1095 | 1.1077 | 95.99 | 107.27 |
| BPL | 1.5157 | 1.8844 | 1.0924 | 1.0932 | 1.0917 | 95.99 | 107.15 |
| BVWN | 1.5126 | 1.8782 | 1.0899 | 1.0907 | 1.0892 | 95.95 | 107.15 |
| BVWN5 | 1.5146 | 1.8827 | 1.0916 | 1.0925 | 1.0909 | 95.99 | 107.14 |
| BLYP | 1.5132 | 1.8694 | 1.0964 | 1.0970 | 1.0952 | 95.47 | 106.98 |
| BP86 | 1.5080 | 1.8485 | 1.0991 | 1.0993 | 1.0977 | 95.28 | 106.93 |
| B3LYP | 1.4949 | 1.8335 | 1.0903 | 1.0905 | 1.0889 | 96.03 | 106.66 |
| B3P86 | 1.4891 | 1.8160 | 1.0905 | 1.0906 | 1.0891 | 95.87 | 106.70 |

Table 4: Total dipole moment of dimethyl sulfoxide in the gas phase ($\epsilon=1$) and in the liquid phase (self-consistent reaction-field treatment with $\epsilon=46$ and a cavity radius $a=3.7$ Å; geometries were reoptimised in presence of the reaction field except for MBPT 2). Also given are the relative change in the dipole moment going from the gas to the liquid phase, as well as the reaction field stabilisation energy. All calculation use a 6-311(2d,p) basis. Execution times for one geometry optimisation step using 8 processors of a Silicon Graphics 380 in parallel are given in seconds.

| | μ (debyes) $\epsilon=1$ | μ (debyes) $\epsilon=46$ | μ (% change) | reaction field stabilisation (kJ/mol) | cpu time per optimisation step (s) |
|-----------------|--------------------------------|---------------------------------|---------------------|---|--|
| Experiment [18] | 3.96 (gas phase) | | | | |
| MBPT2 | 3.79 | 4.40 | 16.0 | -9.6 (no geometry reoptimisation) | 19422 |
| HF | 4.32 | 5.01 | 16.1 | -12.5 | 2975 |
| HFS | 3.54 | 4.25 | 20.1 | -8.7 | 2488 |
| X α | 3.62 | 4.31 | 19.1 | -9.0 | 2809 |
| Becke | 3.48 | 4.20 | 20.7 | -8.4 | 2982 |
| BPL | 3.62 | 4.32 | 19.3 | -9.0 | 2856 |
| BVWN | 3.64 | 4.33 | 19.1 | -9.1 | 2668 |
| BVWN5 | 3.62 | 4.32 | 19.3 | -9.0 | 2870 |
| BLYP | 3.59 | 4.28 | 19.4 | -8.8 | 3020 |
| BP86 | 3.63 | 4.32 | 19.2 | -9.0 | 2770 |
| B3LYP | 3.81 | 4.51 | 18.1 | -9.9 | 3462 |
| B3P86 | 3.85 | 4.53 | 17.8 | -10.0 | 3518 |

Table 5: Relative energies (in kJ/mol with respect to the all-trans conformation) of dimethoxy ethane conformers: tgt (gas phase), tgt (solution: self-consistent reaction-field calculation with $\epsilon = 80$ and a cavity radius $a=4.0$ Å), trans-gauche barrier (central dihedral angle O-C-C-O fixed at 120 degrees), tg^+g^- . Also given is the solvent stabilisation energy for the tgt conformer. All calculations have been carried out using the 6-31G** basis set. Unless indicated otherwise, all degrees of freedom were optimised.

| | tgt gas phase | tgt solution (SCRF) | tgt(solution) -tgt(gas phase) | trans-gauche barrier | tg^+g^- |
|-------------------------------|------------------|---------------------------|----------------------------------|-------------------------|--------------------|
| MBPT4 (SDTQ) ^{a)} | 2.56 | | | 12.2 | 0.0255 |
| MBPT4 (SDQ) ^{a)} | 3.15 | | | 12.6 | 1.17 |
| MBPT4 (DQ) ^{a)} | 3.42 | | | 12.8 | 1.86 |
| MBPT3 ^{a)} | 3.41 | | | 12.7 | 1.77 |
| MBPT2 | 2.31 | 0.0155 | -2.29 | 12.4 | 0.0920 |
| CISD ^{a)} | 6.04 | | | 15.7 | 6.41 |
| HF | 5.84 | 4.57 | -1.27 | 15.7 | 6.67 |
| HFS | -1.46 | -2.15 | -0.69 | 8.01 | 4.36 |
| X α | -1.11 | -1.84 | -0.73 | 8.55 | -4.15 |
| Becke | 1.14 | 0.784 ^{b)} | -0.36 ^{b)} | 9.54 | 1.69 ^{b)} |
| BPL | 1.72 | 0.796 | -0.92 | 9.96 | 1.89 |
| BVWN | 1.81 | 0.879 ^{b)} | -0.93 ^{b)} | 10.0 | 1.91 |
| BVWN5 | 1.74 | 0.810 ^{b)} | -0.93 ^{b)} | 10.0 | 1.93 |
| BLYP | 1.62 | -0.0136 ^{b)} | -1.61 ^{b)} | 9.39 | -0.247 |
| BP86 | 0.693 | -0.172 | -0.87 | 9.09 | -0.0752 |
| B3LYP | 2.09 | 1.13 | -0.96 | 10.9 | 1.12 |
| B3P86 | 2.06 | 1.08 | -0.98 | 10.6 | 1.12 |

^{a)} at MBPT2 geometry.

^{b)} geometry optimization not fully converged.

ergy does not change significantly (so we can take it as converged and report it in Table 5) none of these configurations satisfies the convergence criteria (average or maximum residual force). This behaviour might indicate a technical problem in the calculation of gradients which might lead to calculated gradients not strictly being derivatives of the calculated energy. This suspicion is fostered by the fact that the problem seems to be aggravated in the self-consistent reaction-field method which requires energy derivatives not only with respect to atom positions but also with respect to an external electric field.

The failure of the DFT methods to provide reliable electric moments has already been mentioned (Table 6. Average quadrupole moments are only included for the record; they are too uncertain to be discussed here). The trend observed for *tgt*, namely that DFT methods provide too low dipole moments, continues for the other conformers. For most conformations of DME, DFT methods are less reliable than HF. Exceptions are B3LYP and B3P86 at the barrier conformation, where they have about the same absolute error as HF, but with a different sign.

In Table 7, we try to compare the reliability of the different methods in predicting the geometries of the various conformers of dimethoxy ethane. Again, MBPT2 results are taken as reference (there seems to be no experimental data available). There is a wealth of geometrical information in our calculations from which one can try in many ways to extract the reliability of the method. We concentrate on the heavy atoms, deeming the geometrical data relating to hydrogen atoms less important, at least for our work. We also believe that in trying to assess the reliability of a method one should not use the average deviation from a reference value, but the largest deviation found. Therefore we list for the different types of bonds, bond angles and torsional angles the largest deviations found in any conformer. Looking at the data this way, one finds surprising results: the CO bond length are most reliably reproduced by methods as different in spirit as B3LYP and HFS, most other DFT methods are of similar reliability as HF, and the otherwise very successful BLYP method is the worst of all, by far. The central CC bond is most reliably reproduced by B3LYP, B3P86, $X\alpha$ and HF;

BLYP is again the least reliable method. The COC bond angle is reliably calculated by all DFT methods (with HFS and $X\alpha$ sticking out as particularly good methods): all DFT methods outperform HF. The COO bond angles are reproduced by all methods (including HF) to within a degree. The values for the COCC dihedral are in almost all cases the deviation of the gauche⁻ outer dihedral of the *tg*⁺*g*⁻ conformer from its MBPT2 value. For this dihedral, HF clearly performs worst, whereas of the DFT methods the simplest (HFS and $X\alpha$) and most sophisticated methods (BLYP, BP86, B3LYP, B3P86) yield the smallest largest absolute deviation, however, with different signs. The central dihedral OCCO is again well reproduced by all methods, with HFS and $X\alpha$ being most reliable and HF somewhere in the middle. The worst deviation for dipole moments (where available) is also given. This confirms our previous discovery that HF is by far the most reliable method for this property. The worst deviation among all cartesian quadrupole tensor elements is also given, and - without putting too much emphasis on this property - we note that all methods are of roughly the same quality.

VI. Summary

Based on the benchmark cases reported in this paper, unfortunately, we can make only a few comments about the use of local-density methods in molecular calculations.

- For energetic aspects, most LSDA methods provide results more reliable than Hartree-Fock. Particularly, the combined functionals B3LYP and B3P86 appear to be an inexpensive way of improving upon HF estimates.
- For geometries, the picture is mixed: among the reliable methods are not only the sophisticated ones (B3LYP and B3P86) but also very simple ones (HFS and $X\alpha$) and - for bond distances - Hartree-Fock.
- We would not rely on any LSDA method for the calculation of electric moments. The least unreliable seem to be B3LYP and B3P86.

Table 6: Static electric moments of dimethoxy ethane, for details of the calculation, see Table 5. Dipole moments are in debyes, average quadrupole moments $(Q_{xx} + Q_{yy} + Q_{zz})/3$ are in D Å. Also given are the CPU times per geometry optimisation step of the tg^+g^- conformer which has C_1 symmetry (Silicon Graphics 380, parallelised version).

| | ttt | tgt | | trans-gauche barrier | | tg^+g^- | | cpu (s) |
|------------|---------------------|-------|---------------------|----------------------|---------------------|---------------|---------------------|---------|
| | $\langle Q \rangle$ | μ | $\langle Q \rangle$ | μ | $\langle Q \rangle$ | μ | $\langle Q \rangle$ | |
| MBPT2 | -36.64 | 1.444 | -36.07 | 0.892 | -36.47 | 1.727 | -37.48 | 29142 |
| HF | -36.21 | 1.523 | -35.59 | 0.959 | -36.02 | 1.684 | -36.91 | 2700 |
| HFS | -37.53 | 1.128 | -37.12 | 0.679 | -37.43 | 1.492 | -38.31 | 2858 |
| X α | -36.76 | 1.160 | -36.34 | 0.704 | -36.64 | 1.524 | -37.53 | 2867 |
| Becke | -36.99 | 1.252 | -36.52 | 0.775 | -36.86 | not converged | | |
| BPL | -36.06 | 1.300 | -35.56 | 0.809 | -35.91 | 1.425 | -36.77 | 4349 |
| BVWN | -36.91 | 1.309 | -35.41 | 0.817 | -35.76 | 1.435 | -36.63 | 4025 |
| BVWN5 | -36.03 | 1.304 | -35.52 | 0.812 | -35.87 | 1.425 | -36.73 | 4021 |
| BLYP | -36.44 | 1.256 | -35.86 | 0.775 | -36.30 | not converged | | |
| BP86 | -36.32 | 1.256 | -35.97 | 0.775 | -36.19 | 1.491 | -37.07 | 5115 |
| B3LYP | -36.19 | 1.334 | -35.68 | 0.828 | -36.04 | 1.552 | -36.94 | 4904 |
| B3P86 | -36.98 | 1.342 | -35.47 | 0.830 | -35.83 | 1.582 | -36.74 | 4677 |

Table 7: "Worst" deviation of calculated geometrical and electrostatic parameters from the reference value (MBPT2). For example, the values under R_n designate the largest deviation from the MBPT2 value of all CO bond lengths in all conformers of dimethoxy ethane studied here (ttt, tgt(gas phase), tgt(solvent), trans-gauche barrier and tg^+g^-). Deviations are in Å (bond distance R), in degrees (bond angles ϕ and dihedral angles τ), debyes (total dipole moment μ), and in DÅ (any component of the cartesian quadrupole tensor Q). For details of the calculations, see Table 5.

| | R _{CO} | R _{CC} | ϕ_{COC} | ϕ_{CCO} | τ_{COCC} | τ_{OCCO} | μ | Q _{$\alpha\beta$} |
|---------------------|-----------------|-----------------|--------------|--------------|---------------|---------------|--------|---------------------------------------|
| HF | -0.0234 | 0.0044 | 2.92 | 0.97 | -7.27 | -2.18 | 0.080 | 0.99 |
| HFS | -0.0044 | 0.0133 | -0.14 | 0.93 | 1.94 | -0.70 | -0.315 | -1.92 |
| X α | -0.0223 | -0.0065 | 0.34 | 1.08 | 1.90 | -1.08 | -0.284 | -1.10 |
| Becke ^{a)} | 0.0438 | 0.0503 | 1.45 | 0.96 | -3.66 | 2.89 | -0.192 | -0.95 |
| BPL | 0.0225 | 0.0276 | 1.53 | 0.91 | -3.94 | 2.97 | -0.302 | 0.98 |
| BVWN ^{a)} | 0.0197 | 0.0242 | 1.55 | 0.95 | -3.77 | 3.08 | -0.292 | 1.10 |
| BVWN5 ^{a)} | 0.0212 | 0.0266 | 1.57 | 0.94 | -4.02 | 3.04 | -0.302 | 1.11 |
| BLYP ^{a)} | 0.1148 | -0.0776 | 0.96 | 0.85 | -2.34 | 2.53 | -0.187 | 0.75 |
| BP86 | 0.0153 | 0.0193 | 1.02 | 0.81 | -1.23 | 2.22 | -0.236 | 0.90 |
| B3LYP | -0.0052 | 0.0091 | 1.44 | 0.85 | -2.23 | 1.75 | -0.175 | 0.79 |
| B3P86 | -0.0125 | 0.0021 | 0.97 | 0.93 | -1.66 | 1.94 | -0.146 | -1.31 |

a) The geometries of some conformers are not completely converged, see Table 5. Those conformations are not part of this compilation.

- The use of LSDA methods in connection with the self-consistent reaction-field method is questionable, because either the permanent dipole moments are off (as for dimethoxy ethane) or the dipole moments induced by the reaction field are wrong (as for dimethyl sulfoxide) which is most likely due to the dipole polarisabilities being incorrect, too. (Although we have not yet calculated polarisabilities using DFT methods.)
- While most DFT methods require CPU times of a similar order of magnitude (within a factor of 2 or so) as HF, they are significantly faster than conventional post-HF methods. However, in geometry optimisations we found that some DFT methods converge so slowly (or not at all) that the relative speed for a single configuration (which is reported in our tables) is partly off-set by the need to perform many more optimisation steps (30-50 vs. half a dozen for MBPT2). This feature might, however, be implementation-dependent.
- There is no method that we can wholeheartedly recommend for all types of molecules, basis sets and properties. In some cases, LSDA method show a terrific performance when compared to conventional moderately-correlated methods such as MBPT2, in other cases they are unacceptable. Hence, the probing will have to continue. Meanwhile, we will use LSDA methods only for systems for which MBPT calculations are totally out of the question, not if it is just a matter of convenience.

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