Modeling of biological systems, exercises

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Contents

Abstract

Exercises for the Modeling of Biological Systems course, University of Helsinki

1. Fitting of a Ryckaert-Bellemans potential to HF/DFT results

2. Calculation of RESP charges

1 Dihedral parameters

1.1 Constrained scan

The O-C-C-O dihedral angle was scanned from 0 to 180 degrees at 10 degree intervals, requiring 18 geometry optimizations per level of theory. Altogether 32 geometry optimizations would be needed, which would be slow using the aug-cc-pVTZ basis set.

For this reason, the geometries were optimized using the PBEh-3c method, which is a fast and accurate method for molecular geometries [1]. It combines the PBEh density functional with three empirical corrections (3c) and a minimal basis set. These dihedral scans were performed using the ORCA 4.0.1 program [2].

The input and output files for the scan are in `.qc_calculations/scan/pbeh-3c`

1.2 Single point calculations

The single point energies of the obtained structures were computed with the HF and B3LYP [3, 4] SCF-methods with the aug-cc-pVTZ [5] basis set. The PBEh-3c orbitals were read to speed up the SCF convergance. The input and output files for these calculations are in `.qc_calculations/scan/{b3lyp,hf}`. Single point calculations were also done using the MMFF94 [6] force field using the Open Babel library [7].

The barrier height $\mathcal{E}$ is defined as the energy relative to the energy of the most stable structure:

$$\mathcal{E} = E - \min(E) \tag{1}$$

The barrier heights for the PBEh-3c, HF, B3LYP quantum chemical methods and the MMFF94 force field are shown in figure 1.

One can see that the the the barriers are qualitatively very similar. The MMFF94 predicts too large barrier hights relative to the minimum energy. The difference between B3LYP and PBEh-3C may be accounted by the lack of dispersion correction of the B3LYP/aug-cc-pVTZ method.

1.3 Fitting the potential

The torsional energy was substracted from the total energy of the MMFF94 force field calculations:

$$E_{\text{MD-tors}} = E_{\text{MD}} - E_{\text{tors}} \tag{2}$$
$$\tag{3}$$

The barrier heights of this were then substracted from the barrier heights obtained using the B3LYP and SCF methods, yielding V_{fit}.
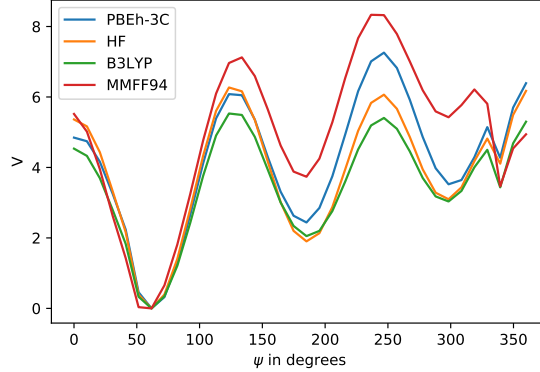
Figure 1: Energy (in kcal/mol) relative to the lowest energy geometry as a function of the dihedral angle (in degrees) with the PBEh-3c, HF, B3LYP quantum chemical methods and with the MMFF94 force field.

The Ryckaert-Bellemans potential is a 5th order trigonometric polynomial.

$$V_{rb}(\phi_{ijkl}) = \sum_{n=0}^{5} C_n (\cos(si))^n \tag{4}$$

It was fit using the calculated (V_{fit}, ϕ) pairs using the $polyfit$ function of the $numpy$ library [8]. The fitting, data manipulation, and visualizations are all contained in the `./analysis/potential_fit.ipynb` Jupyter notebook[1]. The expansion coefficients C_n are tabulated in table 1 and the Ryckaert-Bellemans potentials as the function of dihedral angle are shown in figure 2.

Coefficient	B3LYP	HF
C_1	1.563306	1.486257
C_2	1.668620	1.575792
C_3	-8.396610	-9.882902
C_4	1.109764	1.209000
C_5	3.310302	4.355467
C_6	1.543540	1.830176

Table 1: Fitted coefficients C_n of the RB potential.
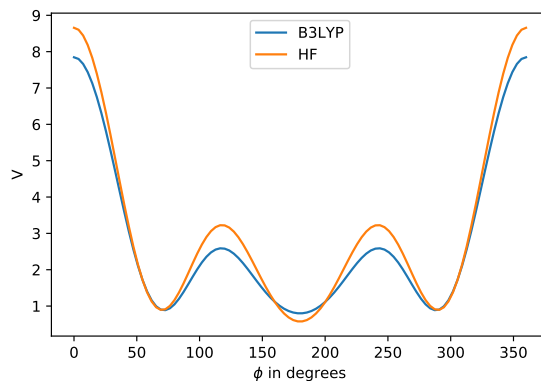
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[1] Also as a pdf, `./analysis/potential_fit.pdf`

Figure 2: Ryckaert-Bellemans potential (in kcal/mol) as a function of dihedral angle.

2 RESP charges

The RESP charges were calculated with Turbomole 7.2 using the B3LYP and SCF methods using the PBEh-3c geometries of the minimum energy structure. The input and output files are in `./qc_calculations/resp/b3lyp,hf`. They are tabulated in table 3 and shown in figure 3.

atom	B3LYP	HF
1C	0.204987	0.222241
2C	0.37251	0.403284
3C	-0.385143	-0.406909
4H	0.103488	0.107139
5H	0.086909	0.091056
6H	0.101354	0.110429
7O	-0.662389	-0.704385
8H	-0.043494	-0.044339
9H	0.398354	0.417985
10O	-0.597586	-0.637468
11H	0.000034	0.001739
12H	0.034103	0.031094
13H	0.386872	0.408134

Table 2: RESP charges using the B3LYP and HF methods with aug-cc-pVTZ basis set.

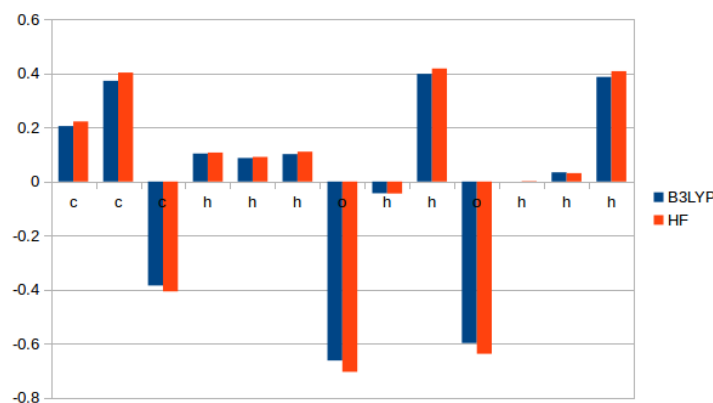Figure 3: RESP charges using the B3LYP and HF methods with aug-cc-pVTZ basis set.

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