Supplementary Information for

**Toward a Physically-Motivated Force Field: Hydrogen Bond Directionality from a Symmetry-Adapted Perturbation Theory Perspective**

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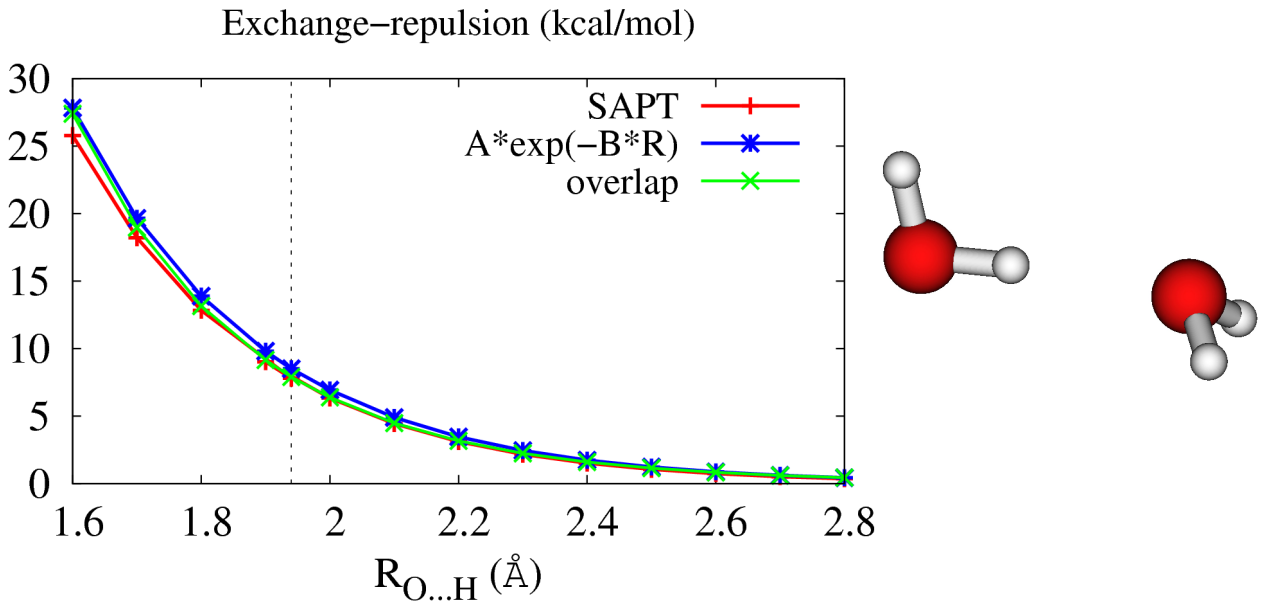
Additional Results

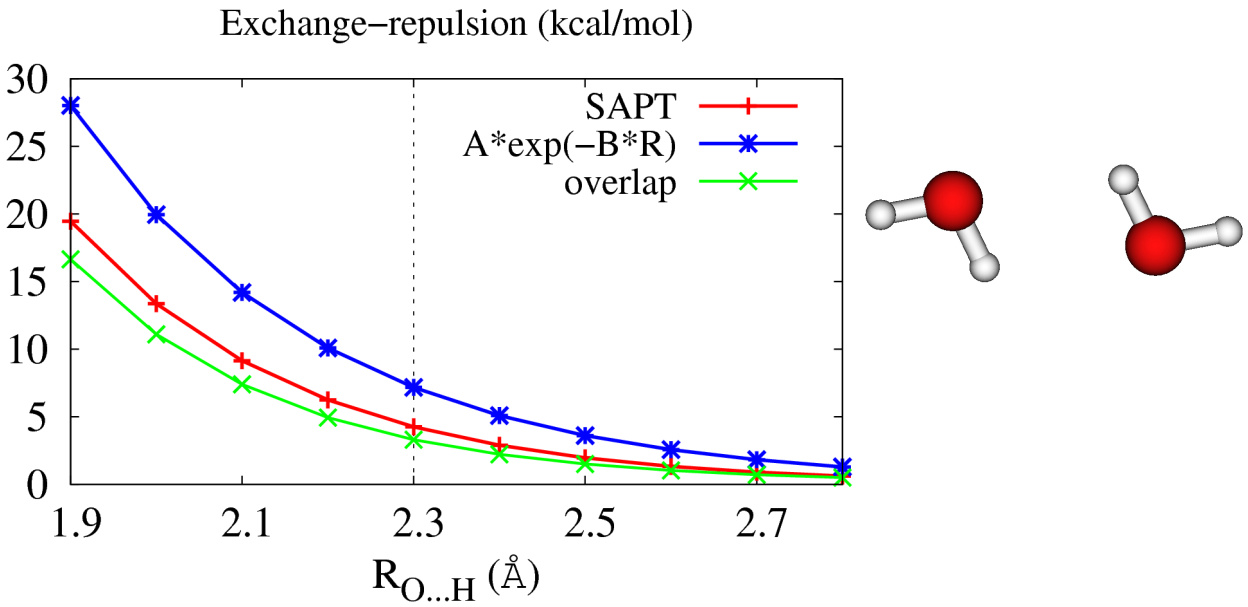
**A**. Exchange-repulsion energy contributions from the fit to a simple exponential function (A*exp(-B*R)) and from valence electron density overlap integrals against the corresponding DFT-SAPT reference data.

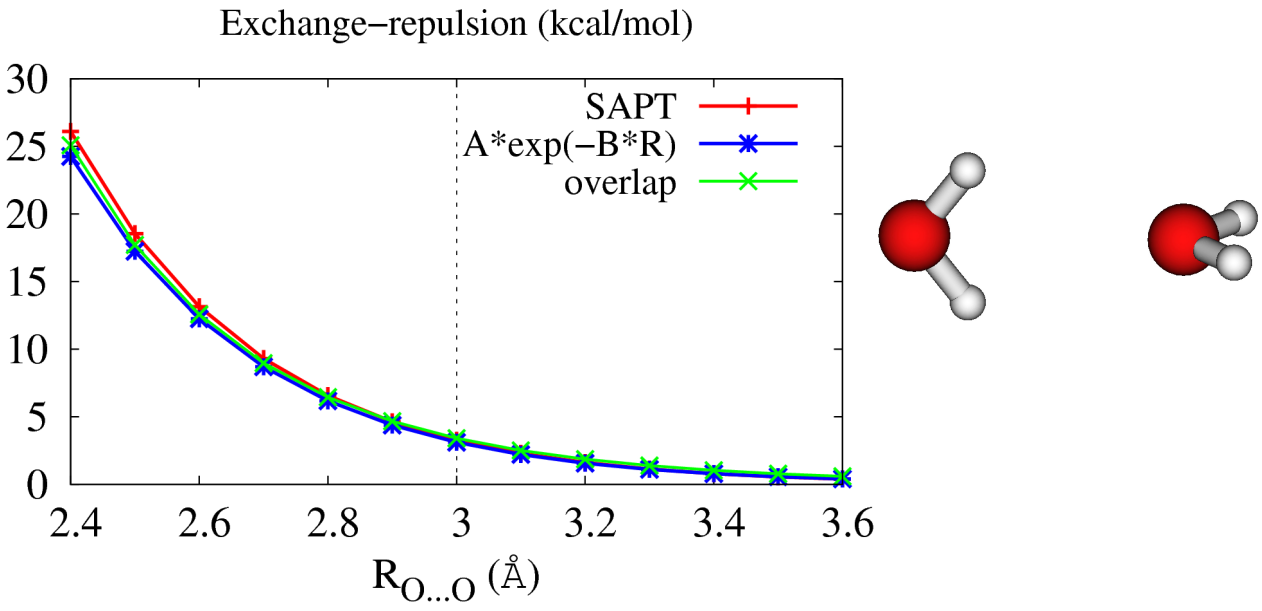
Table: Parameters for the exchange-repulsion energy term

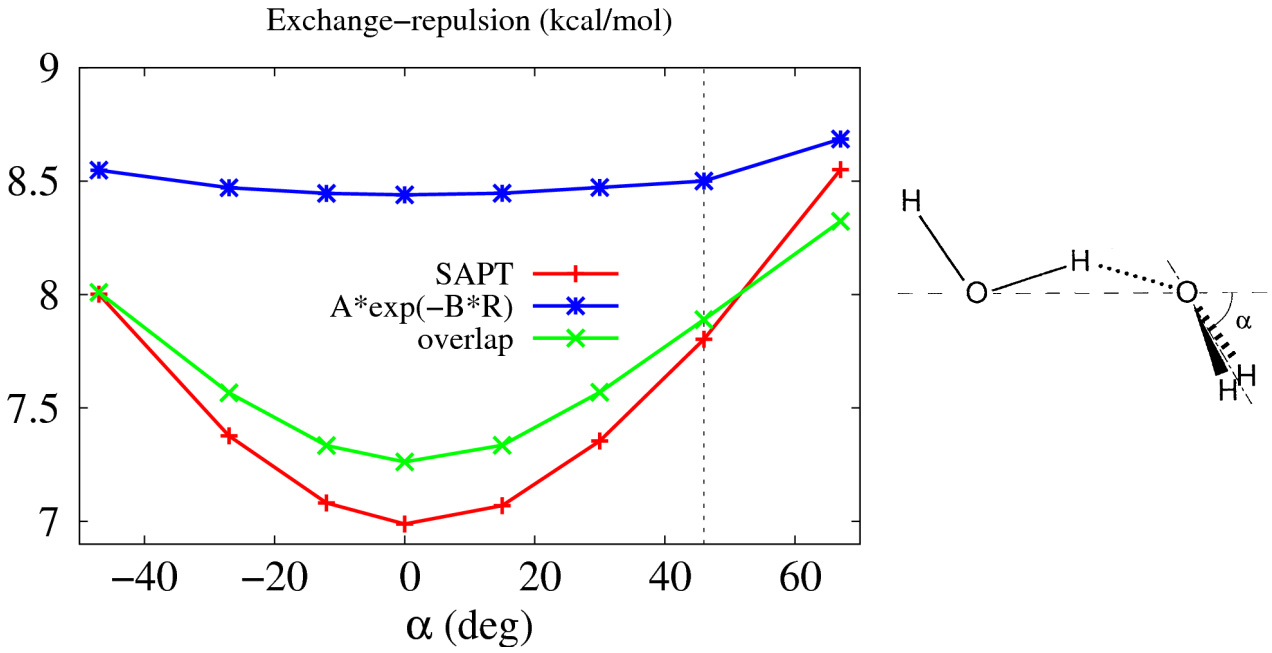
| Atom class | **A,** kcal/mol* | **B**, 1/Å** |
|---|---|---|
| O | 0.2719 | 3.662 |
| H | 0.0011 | 3.240 |

* The geometric mean combination rule is used for the unlike atoms.
** The harmonic mean combination rule is used for the unlike atoms.

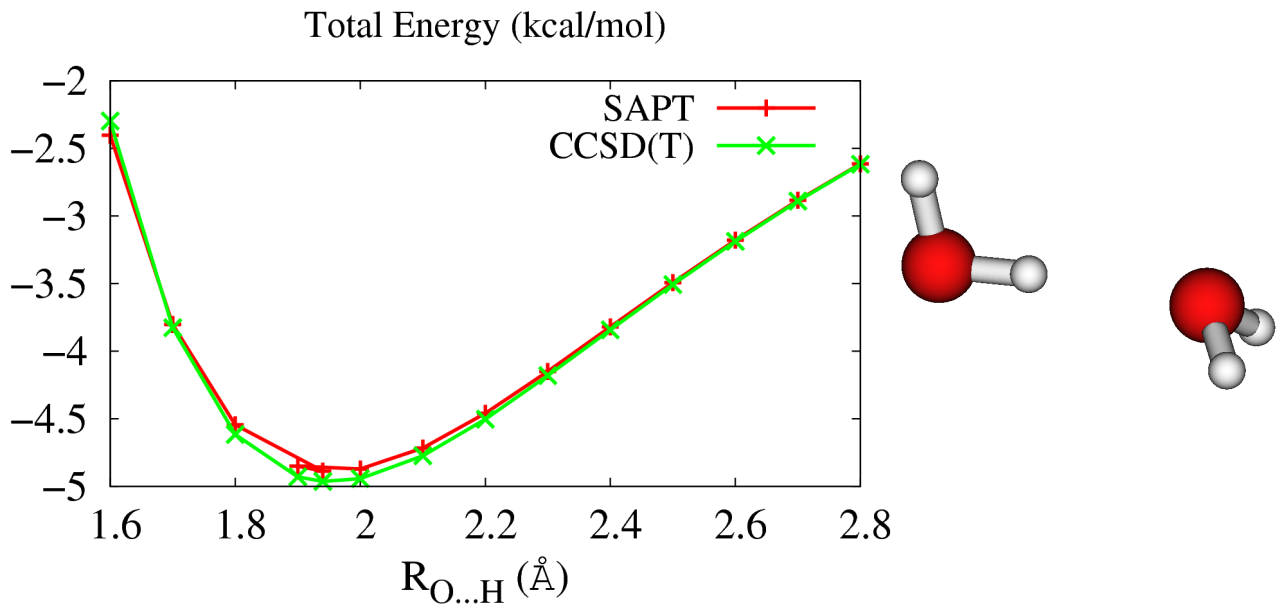


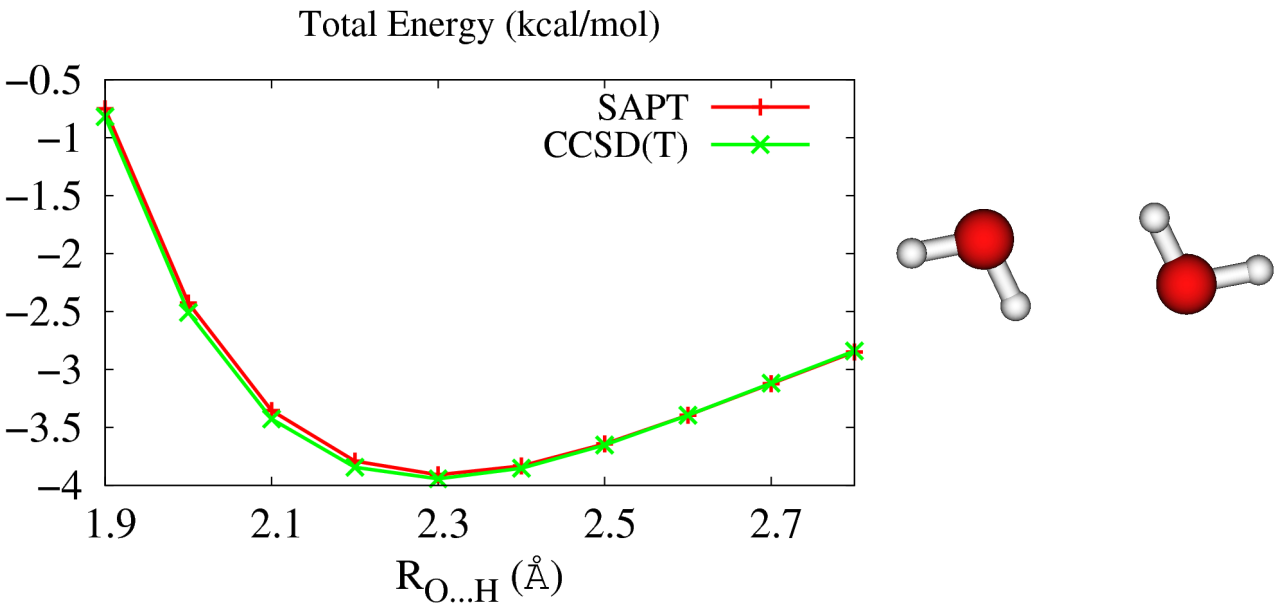

Exchange−repulsion (kcal/mol)
30
25
20
15
10
5
0
1.9
2.1
2.3
2.5
2.7
SAPT
A*exp(−B*R)
overlap
R_O...H (Å)

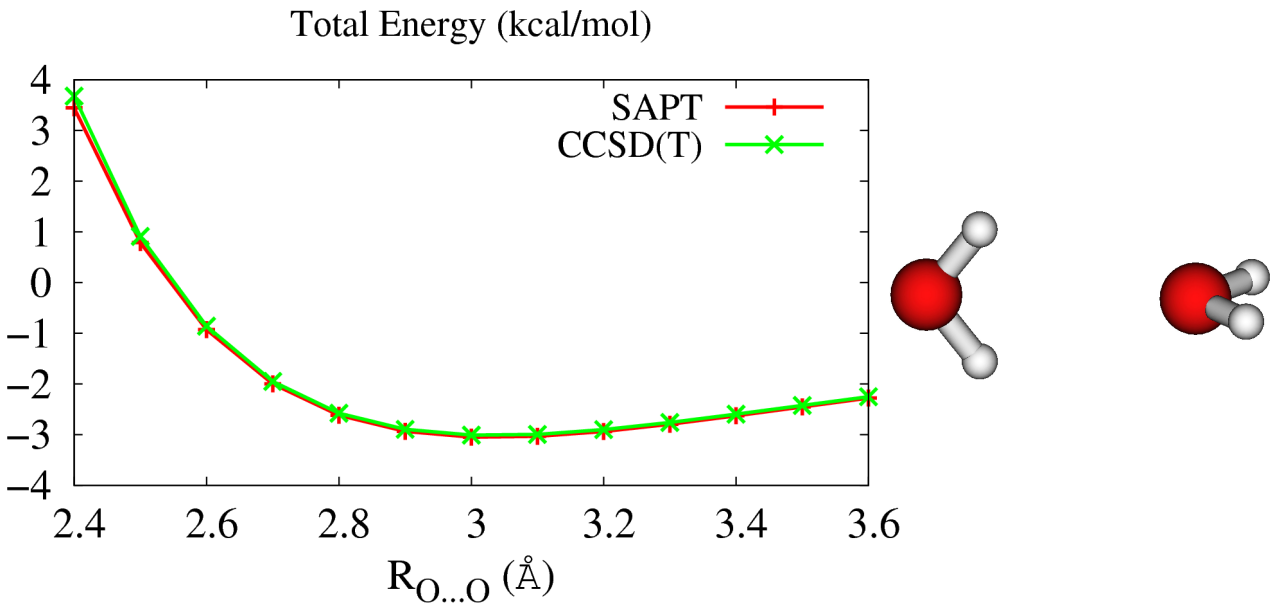

Exchange−repulsion (kcal/mol)
30
25
20
15
10
5
0
2.4
2.6
2.8
3
3.2
3.4
3.6
SAPT
A*exp(−B*R)
overlap
R_O...O (Å)

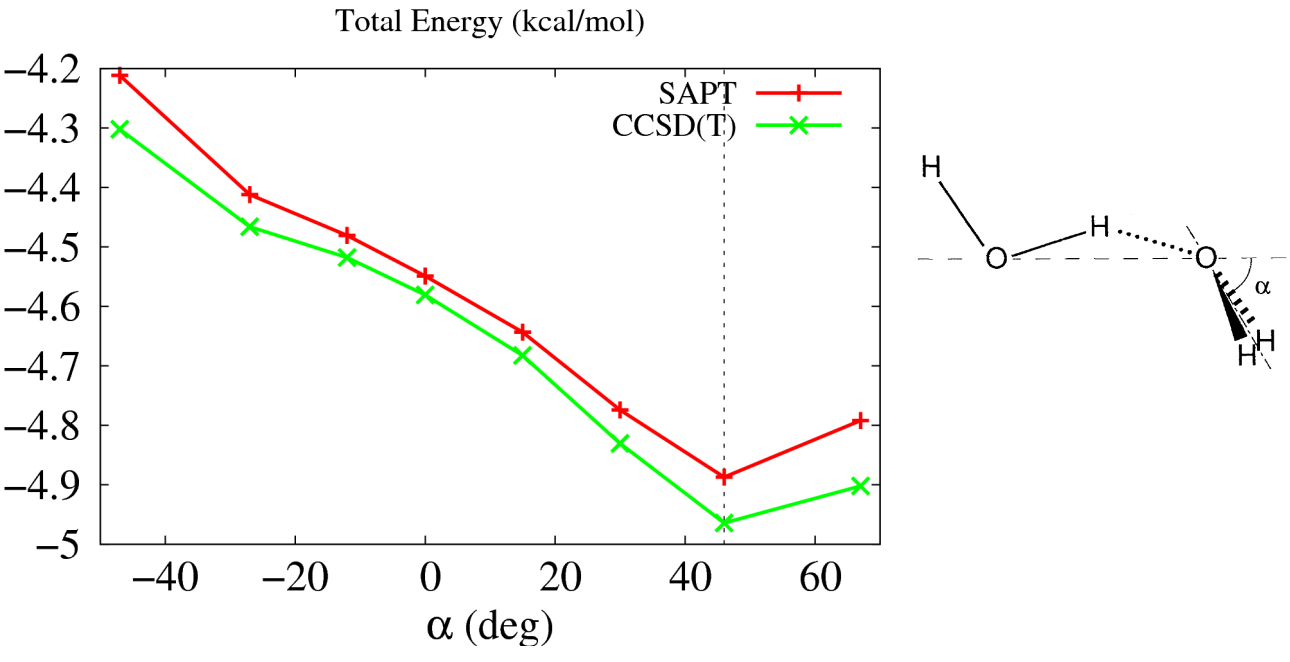

Exchange−repulsion (kcal/mol)
9
8.5
8
7.5
7
−40
−20
0
20
40
60
α (deg)
SAPT
A*exp(−B*R)
overlap
H
O
H
O
α
H
H

**B**. Total interaction energy: DFT-SAPT/aug-cc-pVQZ against CCSD(T)/aug-cc-pVQZ.




Total Energy (kcal/mol)
SAPT
CCSD(T)
4
3
2
1
0
−1
−2
−3
−4
2.4
2.6
2.8
3
3.2
3.4
3.6
R_O...O (Å)


Total Energy (kcal/mol)
SAPT
CCSD(T)
−4.2
−4.3
−4.4
−4.5
−4.6
−4.7
−4.8
−4.9
−5
−40
−20
0
20
40
60
α (deg)
H
O
H
O
α
H
H