Force field development

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Nonbonded intermolecular interactions

- Electrostatic
- Induction
- Repulsion
- Dispersion

QM energy decomposition

- SAPT – perturbative approach
  - Electrostatic
  - Induction
  - Exchange repulsion
  - Dispersion
- ALMO – SCF-based approach
  - Electrostatic
  - Polarization
  - Charge transfer

Absolutely localized molecular orbitals (ALMO)

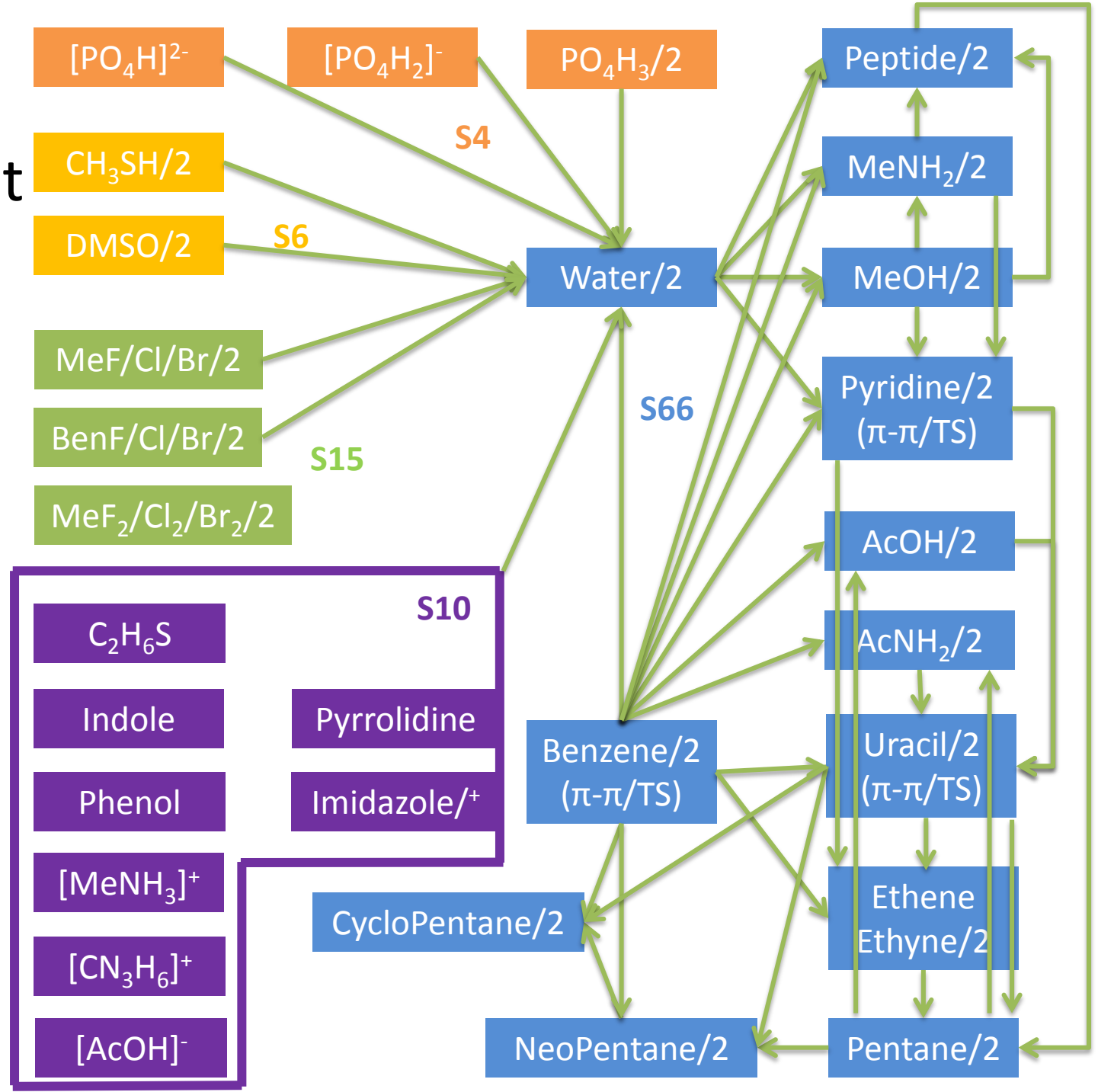
$$E_{int} = E_{AB} - {E^0}_A - {E^0}_B = E_{frz} + E_{pol} + E_{ct}$$

$$\begin{aligned} E_{frz} &= {E^0}_{AB} - {E^0}_A - {E^0}_B \\ &= \langle {\Psi^0}_A {\Psi^0}_B | H_{AB} | {\Psi^0}_A {\Psi^0}_B \rangle - \langle {\Psi^0}_A | H_A | {\Psi^0}_A \rangle - \langle {\Psi^0}_B | H_B | {\Psi^0}_B \rangle \end{aligned}$$

$$\begin{aligned} E_{pol} &= {E^1}_A - {E^0}_A + {E^1}_B - {E^0}_B \\ &= \langle ({\Psi^1}_A {\Psi^0}_B) | H_A | ({\Psi^1}_A {\Psi^0}_B) \rangle - \langle {\Psi^0}_A | H_A | {\Psi^0}_A \rangle \\ &\quad + \langle ({\Psi^0}_A {\Psi^1}_B) | H_B | ({\Psi^0}_A {\Psi^1}_B) \rangle - \langle {\Psi^0}_B | H_B | {\Psi^0}_B \rangle \end{aligned}$$

$$E_{ct} = E_{AB} - {E^0}_{AB} - {E^1}_A - {E^1}_B = \langle \Psi_{AB} | H_{AB} | \Psi_{AB} \rangle - {E^0}_{AB} - E_{pol}$$

Database development (S101x7)



Parameters (fitted alpha, uracil H(N) polar H optimized, c2)

Training set (94x7 pairs)	MUE	MSE	RMSE
Overall	1.327	0.007	2.492
R (0.90~1.10)	0.720	-0.173	1.038
R (0.70~0.80)	2.844	0.456	4.364

Training 547x: R(eq) : MUE 0.621
Testing 0.855

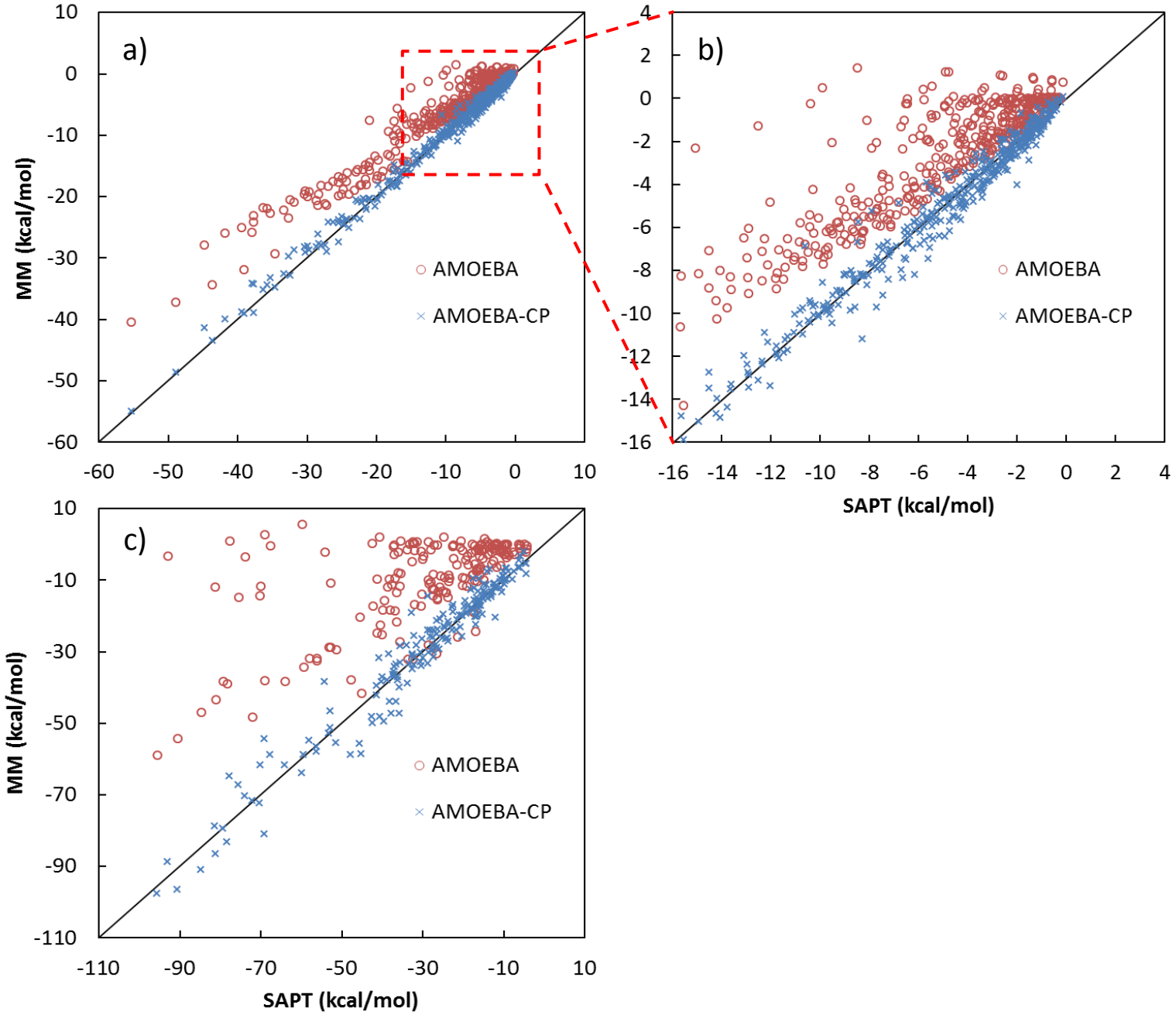
	Z	α (Å^{-1})	β (Å^{-1})
H (non-polar)	1	3.3	2.924
H (aromatic)	1	3.3	3.064
H (polar, water)	1	3.3	3.178
C (SP3)	4	3.8	2.934
C (aromatic)	4	3.8	2.764
C (SP2)	4	3.8	2.673
N (SP3)	5	3.1	2.790
N (aromatic)	5	3.1	2.784
N (SP2)	5	3.1	2.761
O (SP3, hydroxyl, water)	6	3.5	3.131
O (aromatic)	6	3.5	3.188
O (SP2, carbonyl)	6	3.5	3.213
P (phosphate)	5	2.4	2.603
S (sulfide, e.g. R-SH)	6	2.6	2.382
S (sulfur IV, e.g. DMSO)	6	2.6	2.230
F (organofluorine)	7	4.2	4.030
Cl (organochloride)	7	3.0	2.594
Br (organobromine)	7	2.7	2.336

Parameters (valence alpha, set f4.g1; same as set f4.g1, Uracil H(N) polar)

Training set (94x7 pairs)	MUE	MSE	RMSE
Overall	1.345	-0.068	2.572
R (0.90~1.10)	0.571	-0.036	0.834
R (0.70~0.80)	3.282	-0.149	4.627

Training 54x7: R(eq) : MUE 0.526
Testing 0.630

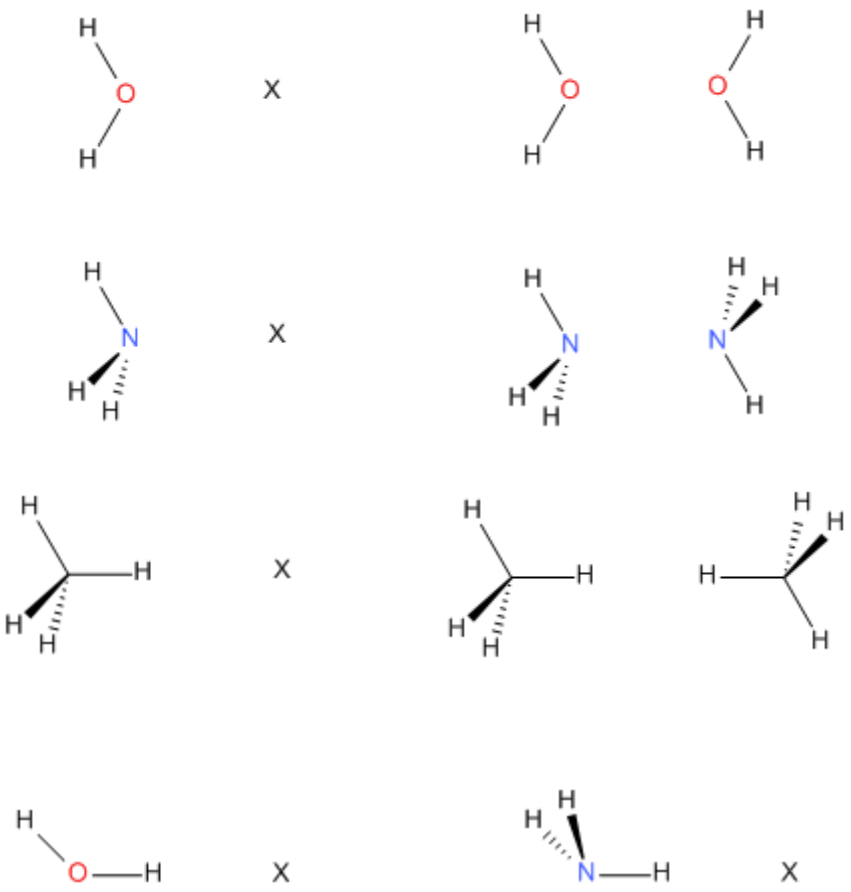
	Z	α (Å^{-1})	β (Å^{-1})
H (non-polar)	1	2.0	1.999
H (aromatic)	1	2.0	2.010
H (polar, water)	1	2.0	2.004
C (SP3)	4	4.0	2.646
C (aromatic)	4	4.0	2.708
C (SP2)	4	4.0	2.685
N (SP3)	5	5.0	3.097
N (aromatic)	5	5.0	3.072
N (SP2)	5	5.0	3.054
O (SP3, hydroxyl, water)	6	6.0	3.661
O (aromatic)	6	6.0	4.282
O (SP2, carbonyl)	6	6.0	4.469
P (phosphate)	5	5.0	2.360
S (sulfide, e.g. R-SH)	6	6.0	2.770
S (sulfur IV, e.g. DMSO)	6	6.0	2.381
F (organofluorine)	7	7.0	4.275
Cl (organochloride)	7	7.0	2.830
Br (organobromine)	7	7.0	2.564


a)
b)
c)
AMOEBA
AMOEBA-CP
MM (kcal/mol)
SAPT (kcal/mol)

Noble gases

Rm and E predicted from SAPT2+/aug-cc-pV5Z calculations

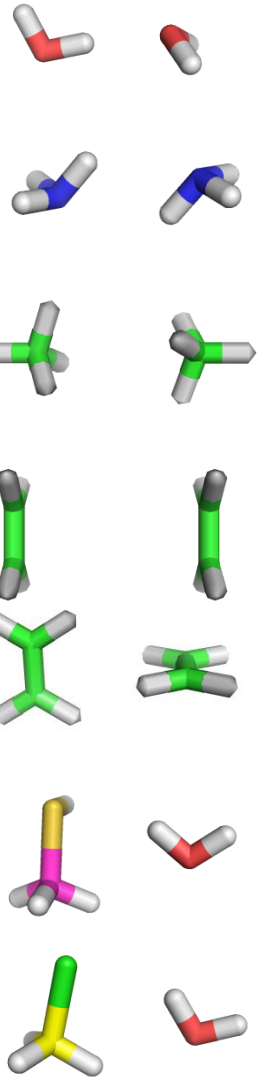
	R (Å)	ε (kcal/mol)
He2	3.11	-0.0138
Ne2	3.31	-0.0480
Ar2	4.07	-0.1597
Kr2	4.38	-0.2180
He-Ne	3.21	-0.0255
He-Ar	3.71	-0.0361
He-Kr	3.93	-0.0366
Ne-Ar	3.76	-0.0738
Ne-Kr	3.96	-0.0769
Ar-Kr	4.23	-0.1840
Wat-Ne	3.58	-0.0640
Wat-Ar	3.87	-0.1446
Amm-Ne	4.11	-0.0398
Amm-Ar	4.27	-0.1160



X = Ne, Ar;
Monomers optimized at
MP2/cc-pVTZ

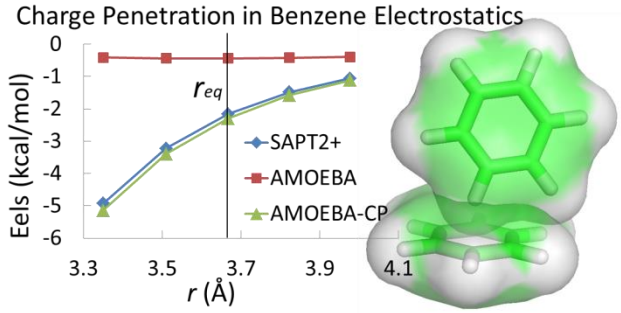
Dimers will be used in vdW study

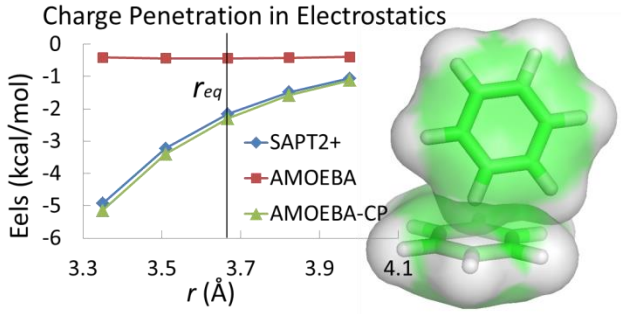
- Water-Water (S66)
- Ammonia-Ammonia (S22)
- CH4-CH4 (S22)
- Ethene-Ethene (pi-pi, new)
- Ethene-Ethene (S22)
- CH3SH-Water (S101)
- CH3Cl-Water (S101)
- Water-Li+/Na+/Mg2+ (new)



Future work

- vdW
  - Mixing rules
  - Functional forms
    - Repulsion
    - Dispersion
- Polarization
  - Defining the reference
  - Damping


Charge Penetration in Benzene Electrostatics
Eels (kcal/mol)
0
-1
-2
-3
-4
-5
-6
r_{eq}
SAPT2+
AMOEBA
AMOEBA-CP
3.3
3.5
3.7
3.9
4.1
r (Å)


Charge Penetration in Electrostatics
Eels (kcal/mol)
0
-1
-2
-3
-4
-5
-6
r_{eq}
SAPT2+
AMOEBA
AMOEBA-CP
3.3
3.5
3.7
3.9
4.1
r (Å)