Non-covalent force fields computed \textit{ab initio}

- Supermolecule calculations
- Symmetry-adapted perturbation theory (SAPT)
Supermolecule calculations

\[ \Delta E = E_{AB} - E_A - E_B \]

Requirements:

1. Include electron correlation, intra- and inter-molecular (dispersion energy = intermolecular correlation)

2. Choose good basis, with diffuse orbitals (and “bond functions”) especially to converge the dispersion energy


4. Correct for basis set superposition error (BSSE) by computing \( E_A \) and \( E_B \) in dimer basis
Symmetry-adapted perturbation theory (SAPT)

Combine perturbation theory with antisymmetrization $\mathcal{A}$ (Pauli) to include short-range exchange effects.

Advantages:

1. $\Delta E$ calculated directly.

2. Contributions (electrostatic, induction, dispersion, exchange) computed individually. Useful in analytic fits of potential surface.

Advantage of supermolecule method:

Easy, use any black-box molecular electronic structure program
Problems in SAPT:

1. Pauli: \( AH = HA \).
   Antisymmetrizer commutes with total Hamiltonian \( H = H^{(0)} + H^{(1)} \), but not with \( H^{(0)} \) and \( H^{(1)} \) separately.
   Has led to different definitions of second (and higher) order energies.

2. Free monomer wavefunctions \( \Phi_{A k_1}^A \) and \( \Phi_{B k_2}^B \) not exactly known.
   Use Hartree-Fock wave functions and apply double perturbation theory to include intra-molecular correlation, or use CCSD wave functions of monomers \( \Rightarrow \) Many-body SAPT.

Program packages:

- SAPT2 for pair potentials
- SAPT3 for 3-body interactions
Most difficult: dispersion interactions

First \textit{ab initio} calculation of He–He binding curve:

- H.F. Schaefer, D.R. McLaughlin, F.E. Harris, and B.J. Alder
  page 988: \(D_e = 12.0 \text{ K}\)
- P. Bertoncini and A. C. Wahl
  page 991: \(D_e = 11.4 \text{ K}\)

Present value:
\[
D_e = 11.01 \text{ K} = 7.65 \text{ cm}^{-1}
\approx 0.1 \text{ kJ/mol} \approx 10^{-3} \text{ eV} \approx 3.5 \times 10^{-5} \text{ Hartree}
\]
Can one use DFT methods?

Reviews by Johnson & DiLabio, Zhao & Truhlar

Many different functionals tested with different basis sets

<table>
<thead>
<tr>
<th>type</th>
<th>dimer</th>
<th>mean error in $D_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Van der Waals</td>
<td>$R_g_2$, $(CH_4)_2$, $(C_2H_2)_2$, (benzene)$_2$</td>
<td>40 - 200 %</td>
</tr>
<tr>
<td>dipole-induced dipole</td>
<td>$CH_4$–$HF$, $H_2O$–benzene, etc.</td>
<td>15 - 100 %</td>
</tr>
<tr>
<td>dipole-dipole</td>
<td>$(H_2CO)_2$, etc.</td>
<td>10 - 40 %</td>
</tr>
<tr>
<td>hydrogen bonded</td>
<td>$(NH_3)_2$, $(H_2O)_2$, $(HCOOH)_2$, etc.</td>
<td>3 - 20%</td>
</tr>
</tbody>
</table>

- Some VdW dimers, $(benzene)_2$ for example, not bound
- B971 best, B3LYP worst
- Often best results without BSSE correction, or smaller basis sets
  ⇒ Right for wrong reason
Basic problems with DFT

1. Exchange repulsion

   - Incorrect asymptotic behavior of one-electron potential:
     \[ v(r) \to \exp(-\alpha r) \] instead of \[ -1/r \]

   - In intermolecular Coulomb energy no self-term present
     self-exchange \implies spurious attraction

2. Dispersion

   - Intrinsically non-local:
     cannot be described by local LDA or semi-local GGA methods
DFT with dispersion explicitly included

vdW-DF: M. Dion, H. Rydberg, E. Schroder, D.C. Langreth, B.I. Lundqvist,

Ar–Ar interaction

DFT with dispersion included semi-empirically

Becke, Johnson, and others:

- Include atom-atom $-C_6 R^{-6} - C_8 R^{-8} - C_{10} R^{-10}$ term in addition to the semi-local correlation energy

- Approximate $C_6, C_8, C_{10}$ from atomic squared multipole moment expectation values and (empirical) static polarizabilities

- Empirically optimized damping parameters
Alternative: SAPT-DFT

Implemented by G. Jansen et al. (Essen) and K. Szalewicz et al. (Delaware)

- First order SAPT energy (electrostatic + exchange) computed with monomer densities and density matrices from Kohn-Sham DFT
- Second-order SAPT energy (induction, dispersion + exchange) from (time-dependent) coupled perturbed Kohn-Sham response functions

Only Hartree-Fock like expressions from Many-Body SAPT needed \Rightarrow better scaling
Caution!

- SAPT-DFT requires XC potential that is good in inner region and has correct $-1/r$ behavior for $r \to \infty$

- Coupled time-dependent DFT must be used for (frequency-dependent) density-density polarizabilities $\alpha(r, r', \omega)$

Both groups, K. Szalewicz (Delaware) and G. Jansen (Essen), further improved efficiency by implementation of density fitting.
Ar–Ar interaction

(benzene)$_2$
1512 GTOs (aug-cc-pVQZ), extrapolation to basis set limit

<table>
<thead>
<tr>
<th>Method</th>
<th>Energy 1 (kJ/mol)</th>
<th>Energy 2 (kJ/mol)</th>
<th>Energy 3 (kJ/mol)</th>
<th>Units</th>
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</thead>
<tbody>
<tr>
<td>MP2</td>
<td>–14.4</td>
<td>–15.1</td>
<td>–20.3</td>
<td>kJ/mol</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>–6.7</td>
<td>–11.8</td>
<td>–11.4</td>
<td></td>
</tr>
<tr>
<td>DF-SAPT-DFT</td>
<td>–7.6</td>
<td>–11.9</td>
<td>–12.7</td>
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<tr>
<td>standard DFT</td>
<td>unbound</td>
<td>metastable</td>
<td>unbound</td>
<td></td>
</tr>
</tbody>
</table>
Adenine-Thymine (G. Jansen et al.)

DF-SAPT-DFT up to aug-cc-pVQZ level
Pair interactions in water trimer

![Diagram of water trimer with pair interactions]

![Bar chart showing energy contributions]

- **exch**: -30 kcal/mole
- **induct**: -20 kcal/mole
- **disper**: -10 kcal/mole
- **elec**: 0 kcal/mole
- **total**: -60 kcal/mole
Many-body interactions (per hydrogen bond)

Trimer

Tetramer

Pentamer

<table>
<thead>
<tr>
<th></th>
<th>pair</th>
<th>3-body</th>
<th>total</th>
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<td>kcal/mole</td>
<td></td>
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<td></td>
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<tr>
<td></td>
<td>0</td>
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<td>-5</td>
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<td></td>
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<td>-6</td>
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<tr>
<td></td>
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<th>3-body</th>
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<td>kcal/mole</td>
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<tr>
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<td>-7</td>
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<td>-7</td>
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</tbody>
</table>
Illustration:

New water potential

- Tested by spectroscopy on dimer and trimer
- Used in MD simulations for liquid water

New polarizable water pair potential: CC-pol

- From CCSD(T) calculations in aug-cc-pVTZ + bond function basis

- Extrapolated to complete basis set (CBS) limit at MP2 level

- 2510 carefully selected water dimer geometries

- Estimated uncertainty < 0.07 kcal/mol
  (same as best single-point calculations published)
**CC-pol**: Analytic representation

- Site-site model with 8 sites (5 symmetry distinct) per molecule
  - Coulomb interaction,
  - dispersion interaction,
  - exponential ‘overlap’ terms: first-order exchange repulsion, second-order exchange induction + dispersion

- Extra polarizability site for induction interaction

- Long range $R^{-n}$ contributions computed by perturbation theory, subtracted before fit of short range terms

- Good compromise between accuracy of reproducing computed points (rmsd of 0.09 kcal/mol for $\Delta E < 0$) and simplicity needed for molecular simulations
How to test non-covalent force fields?
Molecular beam spectroscopy of Van der Waals molecules
Experimental Set-Up

W.L. Meerts, Molecular and Laser Physics, Nijmegen
Intermolecular potential

\[ \downarrow \]

Cluster (Van der Waals molecule) quantum levels, i.e., eigenstates of nuclear motion Hamiltonian

\[ \downarrow \]

Van der Waals spectra
Nuclear motion Hamiltonian $H = T + V$ for “normal” (semi-rigid) molecules

- single equilibrium structure
- small amplitude vibrations

Use rigid rotor/harmonic oscillator model

For (harmonic) vibrations

- Wilson $GF$-matrix method $\Rightarrow$ frequencies, normal coordinates

Rigid rotor model $\Rightarrow$ fine structure (high resolution spectra)
Nuclear motion Hamiltonian $H = T + V$ for weakly bound complexes (Van der Waals or hydrogen bonded)

- multiple equivalent equilibrium structures
  (= global minima in the potential surface $V$)

- small barriers $\Rightarrow$ tunneling between minima

- large amplitude (VRT) motions:
  vibrations, internal rotations, tunneling
  (more or less rigid monomers)

- curvilinear coordinates
  $\Rightarrow$ complicated kinetic energy operator $T$
Method for molecule-molecule dimers

\( \text{H}_2\text{O–H}_2\text{O, NH}_3–\text{NH}_3, \text{etc.} \)

Hamiltonian

\[
H = T_A + T_B - \frac{\hbar^2}{2\mu R} \frac{\partial^2}{\partial R^2} R + \frac{(J - j_A - j_B)^2}{2\mu R^2} + V(R, \omega_A, \omega_B)
\]

Monomer Hamiltonians \( X = A, B \):

\[
T_X = A_X (j_X)_a + B_X (j_X)_b + C_X (j_X)_c
\]

Basis for bound level calculations

\[
\chi_n(R) \ D^{(J)}_{MK}(\alpha, \beta, 0) \sum_{m_A, m_B} D^{(j_A)}_{m_A k_A}(\omega_A) \ D^{(j_B)}_{m_B k_B}(\omega_B) \langle j_A, m_A; j_B, m_B | j_{AB}, K \rangle
\]
The permutation-inversion (PI) symmetry group

For semi-rigid molecules

Use *Point Group of Equilibrium Geometry* to describe the (normal coordinate) vibrations

N.B. This point group is isomorphic to the *PI* group, which contains all “feasible” permutations of identical nuclei, combined with inversion $E^*$. 

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Point group</th>
<th>PI group</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Molecule 1" /></td>
<td>$C_{2v}$</td>
<td>{E, E*, (12), (12)*}</td>
</tr>
<tr>
<td><img src="image2.png" alt="Molecule 2" /></td>
<td>$C_{3v}$</td>
<td>{E, (123), (132), (12)<em>, (13)</em>, (23)*}</td>
</tr>
</tbody>
</table>
Example: $\text{H}_2\text{O}$

<table>
<thead>
<tr>
<th>$PI$ operation</th>
<th>frame rotation</th>
<th>point group operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(12)$</td>
<td>$R_z(\pi) = C_{2z}$</td>
<td>$C_{2z}$</td>
</tr>
<tr>
<td>$E^*$</td>
<td>$R_y(\pi) = C_{2y}$</td>
<td>$\sigma_{xz}$ reflection</td>
</tr>
<tr>
<td>$(12)^*$</td>
<td>$R_x(\pi) = C_{2x}$</td>
<td>$\sigma_{yz}$ reflection</td>
</tr>
</tbody>
</table>

permutation $\Rightarrow$ frame rotation $+$ point group rotation

permutation-inversion $\Rightarrow$ frame rotation $+$ reflection

Hence: $PI$-group $\simeq$ point group
For “floppy” molecules/complexes

- multiple equivalent minima in $V$
- low barriers: tunneling between these minima is “feasible”.

$\Rightarrow$ additional “feasible” $PI$-operations

**Example**  $\text{NH}_3$

<table>
<thead>
<tr>
<th>Semi-rigid $\text{NH}_3$</th>
<th>$PI(C_{3v}) = {E, (123), (132), (12)^<em>, (13)^</em>, (23)^*}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ inversion tunneling</td>
<td>$PI(D_{3h}) = PI(C_{3v}) \otimes {E, E^*}$</td>
</tr>
<tr>
<td>(umbrella up $\leftrightarrow$ down)</td>
<td>Also (12), (13), (23) and $E^*$ are feasible</td>
</tr>
</tbody>
</table>

Additional feasible $PI$-operations $\iff$ observable tunneling splittings in spectrum
For $\text{H}_2\text{O} \text{–H}_2\text{O}$

PI group $G_{16} = \{E, P_{12}\} \otimes \{E, P_{34}\} \otimes \{E, P_{AB}\} \otimes \{E, E^*\}$

Equilibrium geometry has $C_s$ symmetry

$\Rightarrow$ 8-fold tunneling splitting of rovib levels
Water cluster spectra (far-infrared, high-resolution) from Saykally group (UC Berkeley)

Used for test of potential:

Pair potential $\Rightarrow$ Dimer VRT levels $\Rightarrow$ Dimer spectrum

Pair + 3-body potential $\Rightarrow$ Trimer VRT levels $\Rightarrow$ Trimer spectrum
Water dimer tunneling pathways

Acceptor Tunneling

Donor-Acceptor Interchange Tunneling

Donor (Bifurcation) Tunneling
Water dimer tunneling levels

\((J = K = 0)\)
(H$_2$O)$_2$ levels computed from various potentials (J=K=0)

H$_2$O dimer
tunneling levels
from CC-pol (red)
experiment (black)

\begin{align*}
\text{Acceptor tunneling} \\
a(K=0) + a(K=1) & = 16.58 \text{ (ab initio)} \\
& = 13.92 \text{ (experiment)} \\
\end{align*}

\begin{align*}
\text{Rotational constants} \\
A = \Delta - (B+C)/2 & = 7.34 \\
& = 7.44 \\
B+C & = 0.423 \\
& = 0.411 \\
\end{align*}

$J=K=0$ $\begin{array}{c} 
B_1^+,A^-_1 \\
E^+,E^- \\
0.47 \\
0.41 \\
A^+_1,B^-_1 \\
\end{array}$

$J=K=1$ $\begin{array}{c} 
B_2^-A^+_2 \\
E^-,E^+ \\
0.37 \\
0.37 \\
A^-_2,B^+_2 \\
\end{array}$

$J=K=2$ $\begin{array}{c} 
B_1^+A^-_1 \\
E^+,E^- \\
0.69 \\
0.75 \\
B_1^-A^+_1 \\
\end{array}$

$\Delta = a_0 + a_1$

$\Delta a_0 = 0.66$

$\Delta a_1 = 0.65$

$\Delta = 0.69$
H$_2$O dimer
intermolecular
vibrations
from CC-pol (red)
experiment (black)
D$_2$O dimer

tunneling levels

from CC-pol (red)

experiment (black)
$\text{D}_2\text{O dimer}$

intermolecular vibrations

from CC-pol (red)

experiment (black)
Second virial coefficient of water vapor
Water trimer tunneling pathways

Torsional tunneling (flipping)

Bifurcation (donor) tunneling
flipping \((G_6)\) + bifurcation tunneling \((G_{48})\)

Water trimer tunneling levels \((J = 0)\)
H$_2$O trimer torsional levels

**Experiment**
- 22.7
- 65.6
- 87.1

**CC-pol**
- 75.9

**TTM2.1**
- 47.6

**VRT(ASP−W)III**
- 108.3
- 109.4

Levels are indicated in cm$^{-1}$.
$D_2O$ trimer torsional levels

<table>
<thead>
<tr>
<th>Level</th>
<th>Experiment</th>
<th>CC-pol</th>
<th>TTM2.1</th>
<th>VRT(ASP-W)III</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.5</td>
<td>8.0</td>
<td></td>
<td>9.8</td>
</tr>
<tr>
<td>±1</td>
<td>28.0</td>
<td>25.1</td>
<td>26.3</td>
<td>7.3</td>
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<tr>
<td>±2</td>
<td>90.3</td>
<td>98.1</td>
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<td>3</td>
<td>41.1</td>
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<td>35.4</td>
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</tr>
<tr>
<td>±2</td>
<td></td>
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<td></td>
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<tr>
<td>±1</td>
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<td></td>
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</tbody>
</table>
MD simulations of liquid water, $T = 298$ K
Atom-atom radial distribution functions
Conclusions

- CC-pol pure *ab initio*
- Predicts dimer spectra better than semi-empirical potentials fitted to these spectra
- Second virial coefficients in excellent agreement with experiment
- CC-pol + 3-body potential gives good trimer spectrum
- Simulations of liquid water with CC-pol + N-body forces predict the neutron and X-ray diffraction data equally well as the best empirical potentials fitted to these data
- Important role of many-body forces in liquid water
  Nearly tetrahedral coordination:
  3.8 hydrogen bonds, only 2.8 with pure pair potential
General conclusion

**CC-pol**, with the accompanying many-body interaction model, provides the first water force field that recovers the dimer, trimer, and liquid properties well.
Latest development

Water pair potential with flexible monomers: 12-dimensional

Improved version (J. Chem. Phys., accepted)

- From CCSD(T) calculations in aug-cc-pVTZ basis.
- 20,000 $\Rightarrow$ 30,000 water dimer geometries.
- Accurate fit in terms of symmetry-adapted polynomials of scaled atom-atom distances.
  
- Produces even more accurate VRT levels of (H$_2$O)$_2$ and (D$_2$O)$_2$. Also acceptor splitting $a_0 + a_1$ accurate in 12d calculations.

- Good VRT levels of (H$_2$O)$_3$ and (D$_2$O)$_3$ when 3-body interactions added.