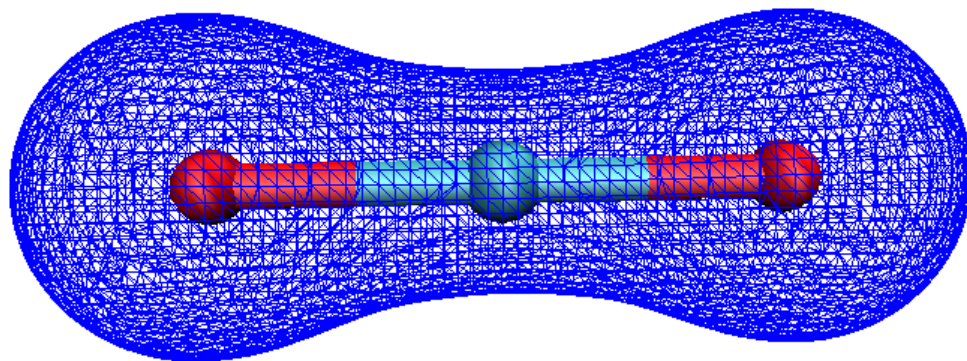
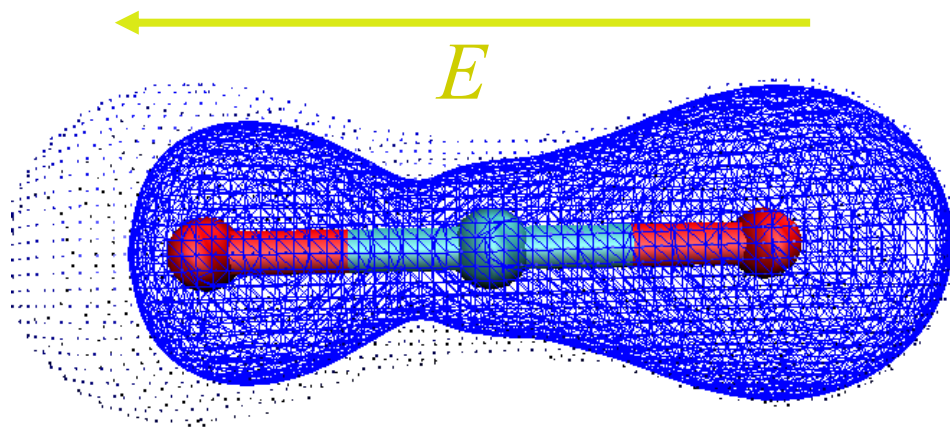


# SAPT-based Force Fields

## Molecular Properties



$$v_{\text{ext}}(\mathbf{r}') = \mathbf{E} \cdot \mathbf{r}'_z$$



Electron (charge) Density  $\rho(\mathbf{r})$

$$v(\mathbf{r}) = \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

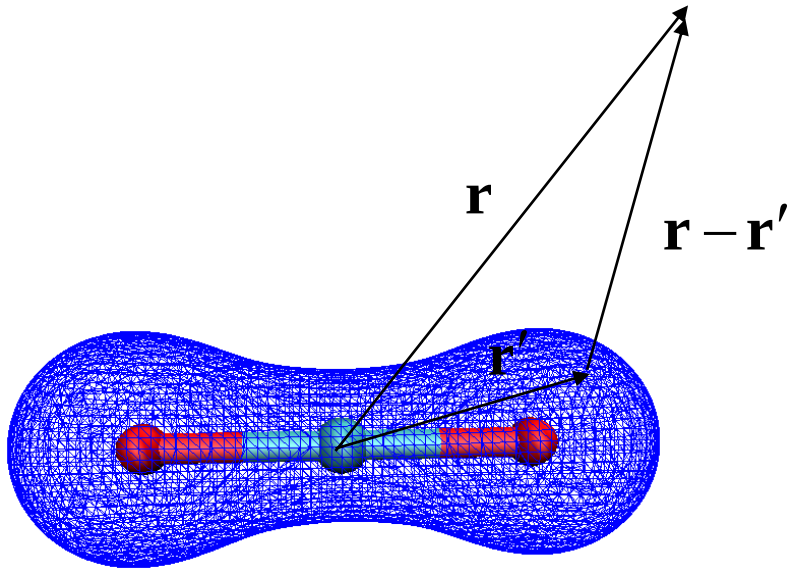
Density Susceptibility  $\chi(\mathbf{r}, \mathbf{r}')$

$$\delta\rho(\mathbf{r}) = \int d\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}') \cdot v_{\text{ext}}(\mathbf{r}')$$

In general, care about the frequency-dependent density susceptibility (FDDS)

$$\chi(\mathbf{r}, \mathbf{r}' | \omega)$$

# Multipole Expansion (note Einstein summation...)



$$v(\mathbf{r}) = \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

for  $r \gg r'$ ,

$$v(\mathbf{r}) = \int d\mathbf{r}' \rho(\mathbf{r}') \left[ \frac{1}{r} + r'_\alpha \left( \frac{\partial}{\partial r'_\alpha} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right)_{\mathbf{r}'=0} + \frac{1}{2} r'_\alpha r'_\beta \left( \frac{\partial}{\partial r'_\alpha r'_\beta} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right)_{\mathbf{r}'=0} + \dots \right]$$

$$= Tq^{tot} - T_\alpha \mu_\alpha + \frac{1}{3} T_{\alpha\beta} \Theta_{\alpha\beta} + \dots$$

where  $T = \frac{1}{r}$ ,  $T_\alpha = \frac{\partial}{\partial r_\alpha} \frac{1}{r}$ , etc.

Multipole Moments

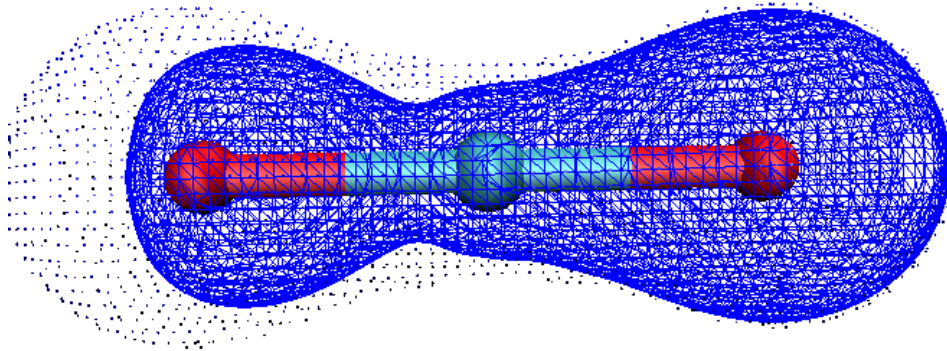
$$\mu_\alpha = \int d\mathbf{r}' \rho(\mathbf{r}') r'_\alpha$$

$$\Theta_{\alpha\beta} = \int d\mathbf{r}' \rho(\mathbf{r}') \left( \frac{3}{2} r'_\alpha r'_\beta - \frac{1}{2} r'^2 \delta_{\alpha\beta} \right)$$

## Polarizabilities

- Analogous to the electron density, we can also characterize density susceptibility by its moments

$$\delta\rho(\mathbf{r}) = \int d\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}') \cdot v_{ext}(\mathbf{r}')$$



*Dipole-dipole* polarizability tensor

$$\alpha_{\alpha\beta} = \int d\mathbf{r} \int d\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}') r_{\alpha} r'_{\beta}$$

*Quadrupole-dipole* polarizability tensor

$$A_{\alpha\beta,\gamma} = \frac{1}{3} \int d\mathbf{r} \int d\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}') \left( \frac{3}{2} r_{\alpha} r_{\beta} - \frac{1}{2} r^2 \delta_{\alpha\beta} \right) r'_{\gamma}$$

## Molecular Properties



## Intermolecular Interactions

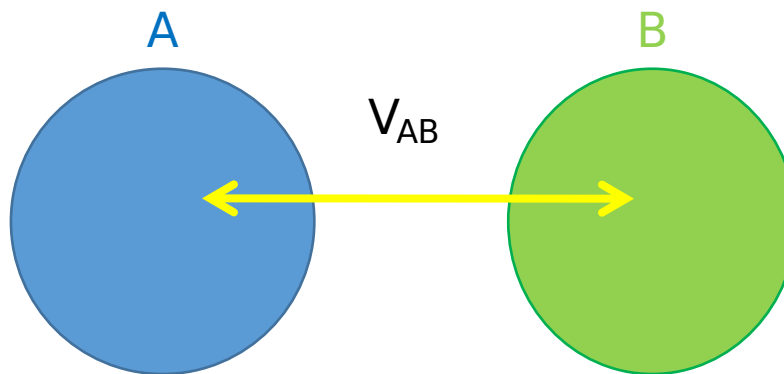
- Rigorous correspondence from perturbation theory!

$$H_{AB} = H^0 + \lambda V_{AB}$$

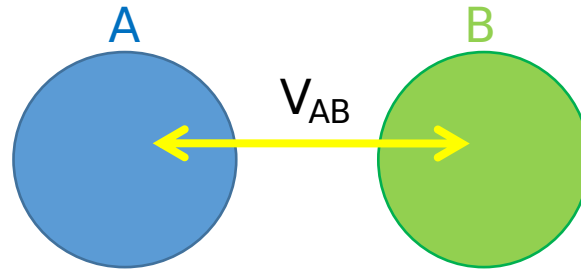
$$H^0 = H_A + H_B$$

$$\Psi^0 = \Psi_A \Psi_B$$

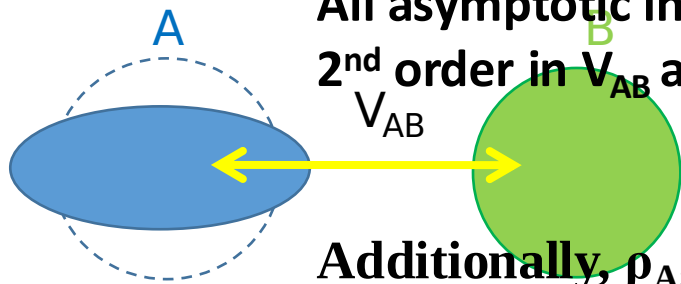
$$E_{\text{int}} = E^1 + E^2 + \dots = E_{\text{Elec}}^1 + E_{\text{ind}}^2 + E_{\text{disp}}^2$$



$$E_{Elec}^{(1)} = \int \frac{\rho_A(\mathbf{r})\rho_B(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}'$$

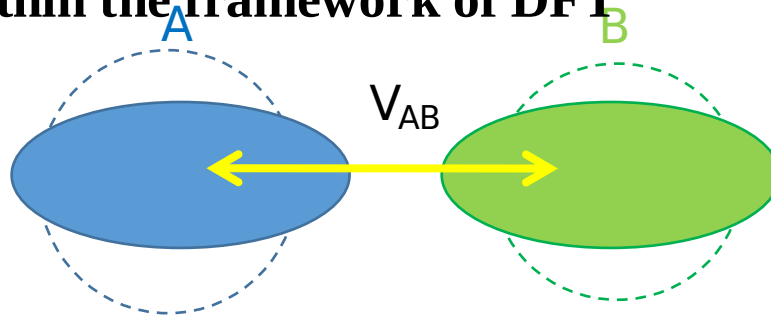


**All asymptotic intermolecular interactions up to 2<sup>nd</sup> order in  $V_{AB}$  are determined by  $\rho_A, \rho_B, \chi_A, \chi_B$  !!!**



$$E_{ind}^{(2)}(B \rightarrow A) = -\frac{1}{2} \int d\mathbf{r}d\mathbf{r}' v_B(\mathbf{r}) \overbrace{\chi_A(\mathbf{r}, \mathbf{r}') \delta\rho_A(\mathbf{r})}^{v_B(\mathbf{r})} v_B(\mathbf{r}')$$

**Additionally,  $\rho_A, \rho_B, \chi_A, \chi_B$  can in principle be calculated exactly within the framework of DFT**



$$E_{disp}^{(2)} = -\frac{1}{2\pi} \int_0^\infty d\omega \int d\mathbf{r}_A d\mathbf{r}'_A d\mathbf{r}_B d\mathbf{r}'_B \frac{1}{|\mathbf{r}_A - \mathbf{r}_B|} \frac{1}{|\mathbf{r}'_A - \mathbf{r}'_B|} \chi_A(\mathbf{r}_A, \mathbf{r}'_A | i\omega) \chi_B(\mathbf{r}_B, \mathbf{r}'_B | i\omega)$$

Example: VDWs  $C_6/R^6$  interaction ...

perturbation theory

$$E_{disp}^{(2)} = -\frac{1}{2\pi} \int_0^\infty d\omega \int d\mathbf{r}_A d\mathbf{r}'_A d\mathbf{r}_B d\mathbf{r}'_B \frac{1}{|\mathbf{r}_A - \mathbf{r}_B|} \frac{1}{|\mathbf{r}'_A - \mathbf{r}'_B|} \chi_A(\mathbf{r}_A, \mathbf{r}'_A | i\omega) \chi_B(\mathbf{r}_B, \mathbf{r}'_B | i\omega)$$

multipole expansion

$$E_{disp,6}^{(2)} = -\frac{1}{2\pi} T_{\alpha\beta} T_{\gamma\delta} \int_0^\infty d\omega \int d\mathbf{a} d\mathbf{a}' d\mathbf{b} d\mathbf{b}' \chi_A(\mathbf{a}, \mathbf{a}' | i\omega) \chi_B(\mathbf{b}, \mathbf{b}' | i\omega) a_\alpha b_\beta a'_\gamma b'_\delta$$

compute moments

$$\alpha_{\alpha\beta} = \int d\mathbf{r} \int d\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}') r_\alpha r'_\beta$$

$$E_{disp,6}^{(2)} = -\frac{1}{2\pi} T_{\alpha\beta} T_{\gamma\delta} \int_0^\infty d\omega \alpha_{\alpha\gamma}^A(i\omega) \alpha_{\beta\delta}^B(i\omega)$$

Isotropic ...

$$T_{\alpha\beta} T_{\alpha\beta} = \frac{6}{R^6} \rightarrow C_6 = \frac{3}{\pi} \int_0^\infty d\omega \bar{\alpha}_1^A(i\omega) \bar{\alpha}_1^B(i\omega)$$

Force Field Development:

Intermolecular interactions

$$E_{Elec}, E_{Ind}, E_{Disp}$$

Perturbation theory

Molecular properties

$$\rho(\mathbf{r}), \chi(\mathbf{r}, \mathbf{r}'), \chi(\mathbf{r}, \mathbf{r}' | i\omega)$$

???

Atomic parameters

$$\{q_i, \mu_i\}, \{\alpha_i\}, C_{6,i}$$

$$C_6 = \frac{3}{\pi} \int_0^\infty d\omega \alpha(i\omega) \alpha(i\omega)$$



Mapping:  $\rho(\mathbf{r}) \rightarrow \{q_i, \mu_i\}, \quad \chi(\mathbf{r}, \mathbf{r}') \rightarrow \{\alpha_i\}$

## 1) Partitioning schemes:

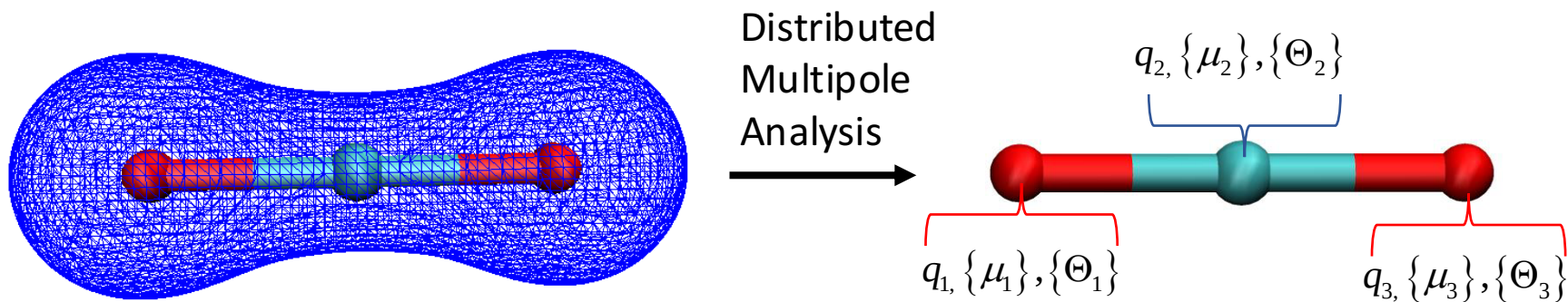
Density	Susceptibility
<ul style="list-style-type: none"> <li>• Distributed Multipole Analysis (DMA)</li> <li>• Natural Atomic Orbitals (NAO)</li> <li>• Bader</li> <li>• Hirshfeld</li> </ul>	<ul style="list-style-type: none"> <li>• LoProp</li> <li>• Misquitta-Stone</li> </ul> <p>Disadvantages: Non-local polarizabilities. E.g. non-zero for CO<sub>2</sub></p> <p><math>\alpha^{C,O}</math></p>

## 2) “Field” fitting schemes

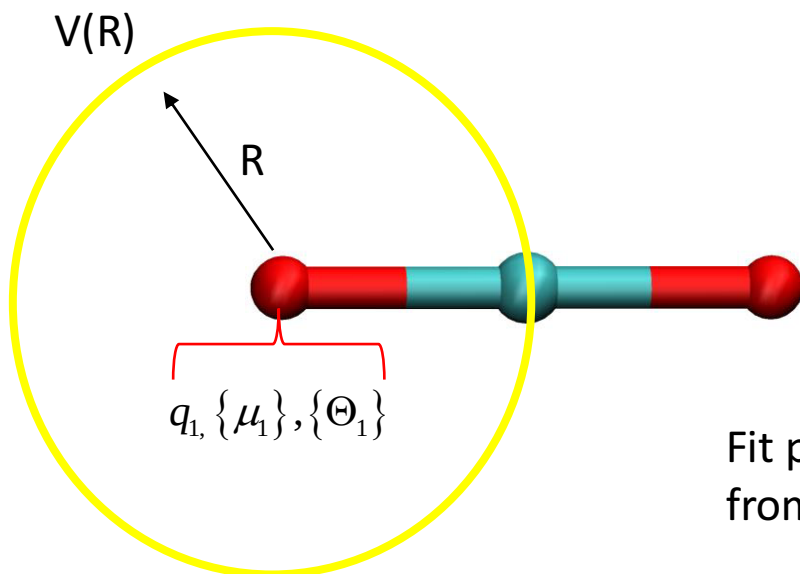
Electrostatic Potential	Linear Response
<ul style="list-style-type: none"> <li>• CHELPG</li> </ul> <p>Disadvantages: Unphysical charges on “buried” atoms</p>	<ul style="list-style-type: none"> <li>• Point-to-point fitting (Williams-Stone)</li> </ul>

# Charges:

- Very important, less work than other parameters
- Charges are probably least transferable force field parameters (most sensitive to chemical environment)



(A.J. Stone: Gaussian, Molpro, etc.)



Robust, no problems with “buried atoms”

Fit point charges separately to potential from each multipole expansion site

## Dispersion coefficients (polarizabilities):

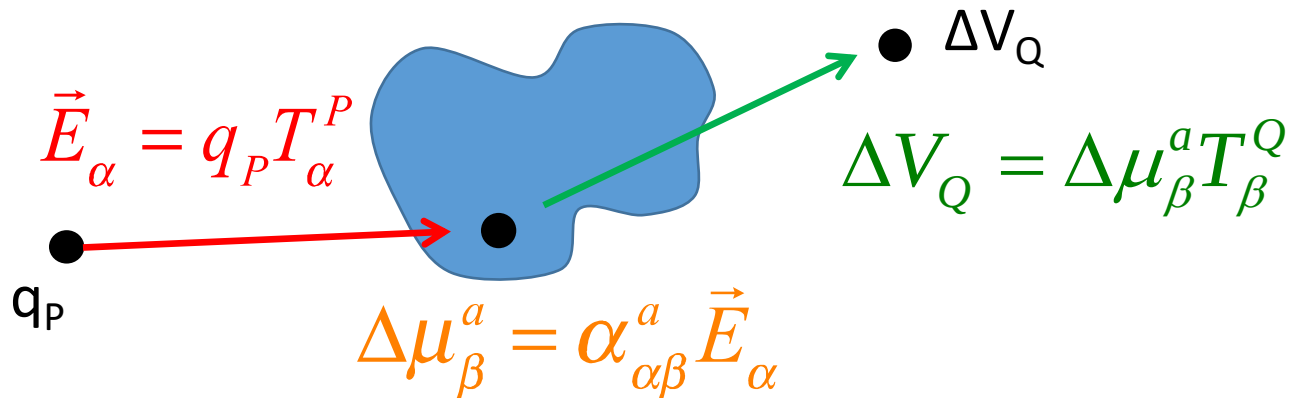
- These are harder...
- “Potentially” extremely transferable (if parameterized correctly)
- Higher order terms ( $C_8$ ,  $C_{10}$  ...) only accessible from ab initio calculations (impossible to fit empirically)

Bear with me for next few slides...

“Point-to-point response” (Williams and Stone)

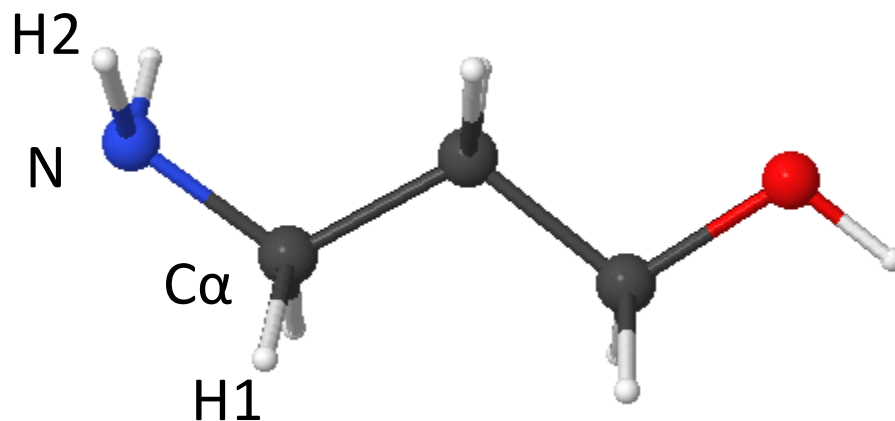
Ab Initio  $\alpha_{PQ}(\omega) = \int d\mathbf{r} d\mathbf{r}' \frac{1}{r_Q} \chi(\mathbf{r}, \mathbf{r}' | \omega) \frac{q_P}{r'_P}$

Model  $\tilde{\alpha}_{PQ}(\omega) = - \sum_a^{atoms} q_P T_\alpha^P \alpha_{\alpha\beta}^a(\omega) T_\beta^Q$



## Williams and Stone method (continued)

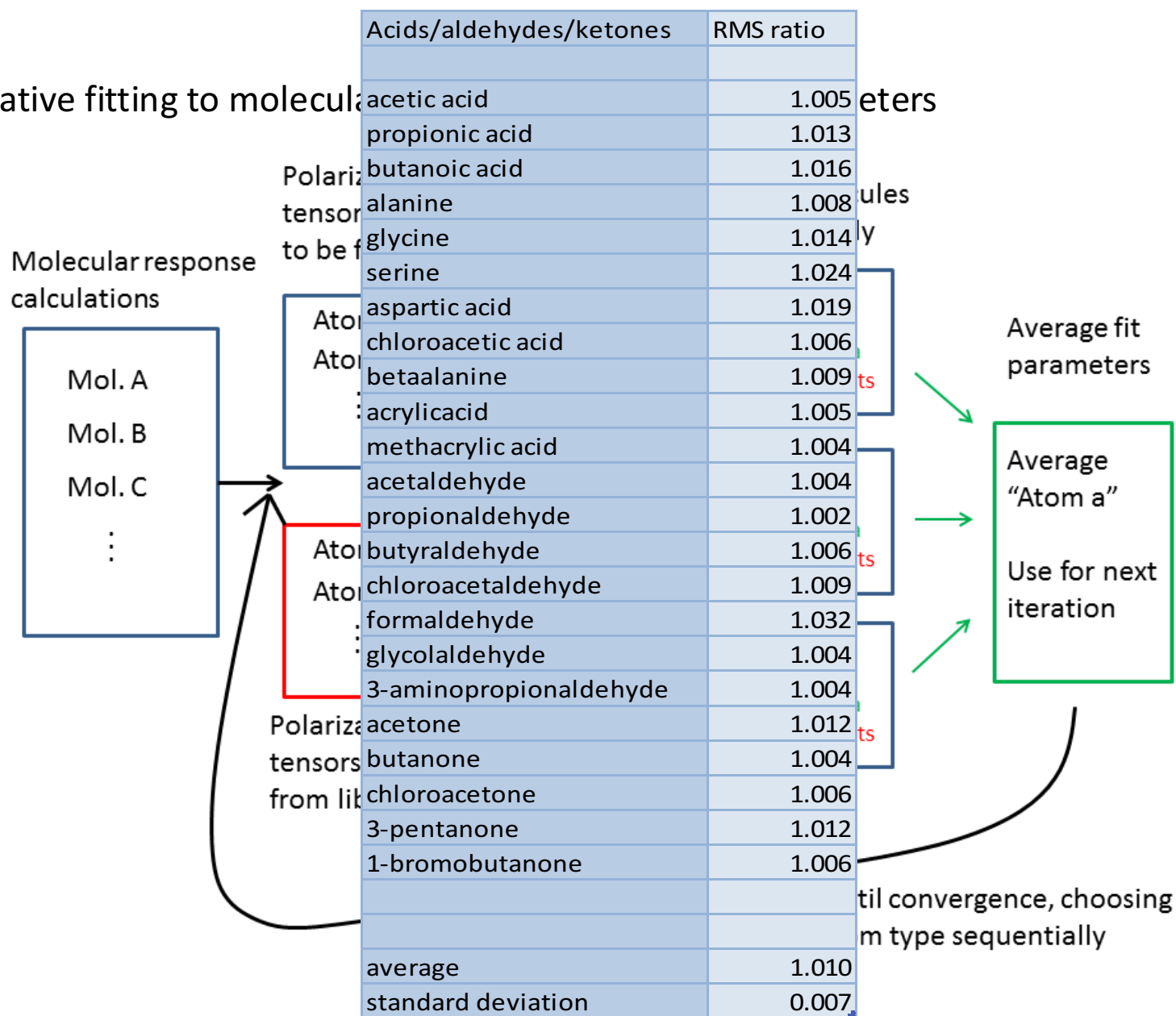
- Parameter coupling in molecules is problematic for transferability



Unconstrained fit:

$$\frac{C_6^N}{C_6^{C\alpha}} \sim 8 \qquad \frac{C_6^{H2}}{C_6^{H1}} \sim \frac{1}{5}$$

- Iterative fitting to molecular



- All asymptotic intermolecular interactions (2<sup>nd</sup> order) determined by *monomer* properties :

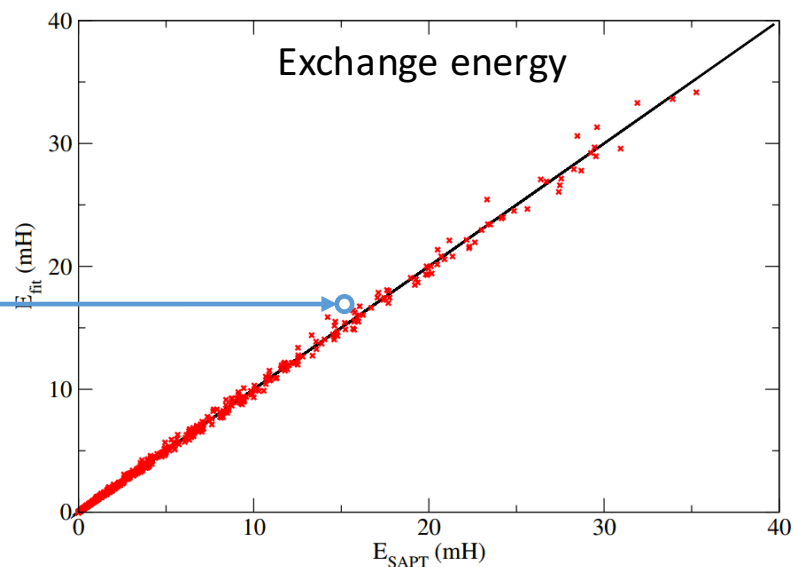
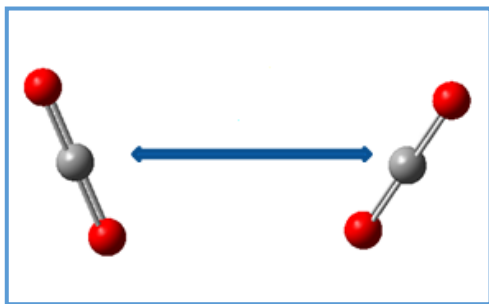
$$\rho(\mathbf{r}), \chi(\mathbf{r}, \mathbf{r}' | \omega)$$

- These properties can be computed with DFT, giving rise to SAPT(DFT) method
- Force fields can be developed by representing these *molecular* properties in terms of *atomic* parameters



## Why SAPT?

- allows for seamless transition between asymptotic and short-range interactions
- Parameters describing asymptotic electrostatic, induction, and dispersion interactions fit to monomer properties
  - Parameters describing the short-range exchange, charge-penetration (electrostatic, induction) interactions fit explicitly to **SAPT** homo-molecular dimer energies



## Problem with “regular” perturbation theory

- Only asymptotically correct (no charge overlap)
- No repulsive terms!


$$\Psi^0 = \Psi_A \Psi_B$$

$$\Psi_A(3,2)\Psi_B(1,4) \neq -\Psi_A(1,2)\Psi_B(3,4)$$

The exchange anti-symmetry of Fermions is broken

symmetry-adapt the wavefunction...

$$E^{(1)} = \langle \Psi_A \Psi_B | V_{\text{int}} | \Psi_A \Psi_B \rangle$$

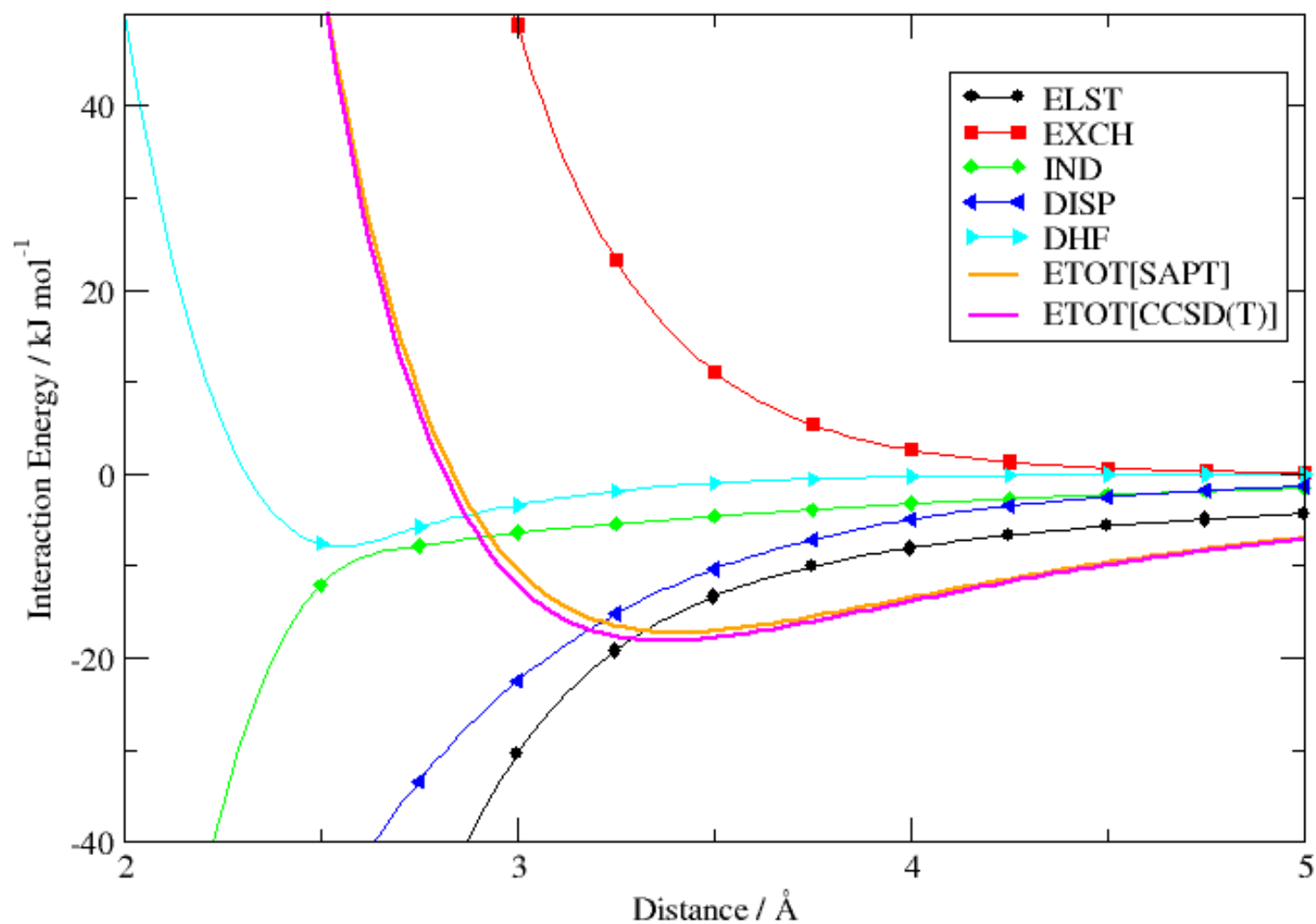


$$E^{(1)} = \langle \Psi_A \Psi_B | V_{\text{int}} \mathcal{A} | \Psi_A \Psi_B \rangle$$
$$= E_{\text{elec}}^{(1)} + E_{\text{exch}}^{(1)}$$

In general, SAPT gives interaction energy as...

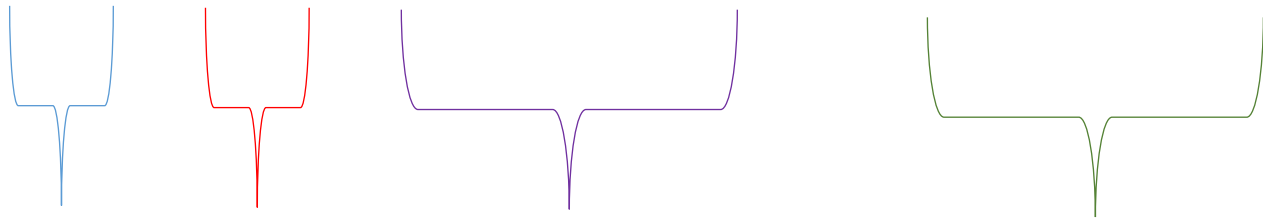
$$E_{\text{int}} = E_{\text{elec}}^{(1)} + E_{\text{exch}}^{(1)} + E_{\text{ind}}^{(2)} + E_{\text{exch-ind}}^{(2)} + E_{\text{disp}}^{(2)} + E_{\text{exch-disp}}^{(2)}$$

## Imidazolate + CO<sub>2</sub>



- *Fit distinct force field terms to individual SAPT energies*

$$E_{Total}^{SAPT} = E_{elec}^{(1)} + E_{exch}^{(1)} + E_{ind}^{(2)} + E_{exch-ind}^{(2)} + E_{disp}^{(2)} + E_{exch-disp}^{(2)}$$



$$E_{Total}^{force\ field} = E_{elec} + E_{exch} + E_{ind} + E_{disp}$$

#### Advantages:

- Force field contains the correct balance of different physical interactions by construction.
- Physically-motivated functional forms can be used to describe each type of interaction
- Simple and accurate combination rules for hetero-molecular interactions can be developed

$$E_{exch} = \sum_{i,j} A_{ij}^{exch} \exp(-B_{ij} r_{ij})$$

$$E_{elec} = \sum_{i,j} f_1 \frac{q_i q_j}{r_{ij}} + \sum_{i,j} A_{ij}^{elec} \exp(-B_{ij} r_{ij})$$

$$E_{ind} = U_{shell} + \sum_{i,j} A_{ij}^{ind} \exp(-B_{ij} r_{ij})$$

$$E_{disp} = \sum_{n=6,8,10,12} \sum_{i,j} -f_n \frac{C_n^{ij}}{r_{ij}^n}$$

$$E_{Total} = E_{exch} + E_{elec} + E_{ind} + E_{disp}$$

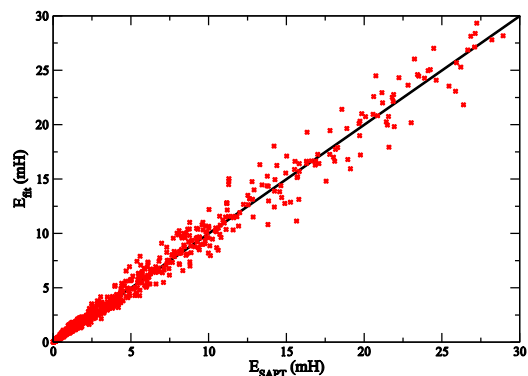
$$E_{Total} = \sum_{i,j} f_1 \frac{q_i q_j}{r_{ij}} + \sum_{i,j} \left( A_{ij}^{tot} \exp(-B_{ij} r_{ij}) - \sum_{n=6,8,10,12} f_n \frac{C_n^{ij}}{r_{ij}^n} \right) + U_{shell}$$

Two important things to evaluate:

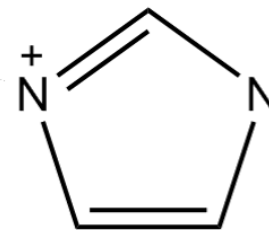
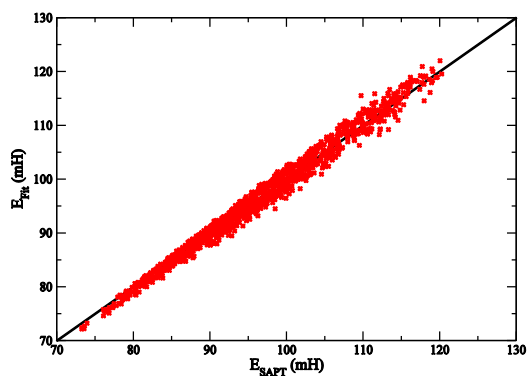
- 1) Functional form (isotropic!). What error does this introduce?
- 2) Transferability for hetero-molecular interactions  
(without explicit parameterization)

## Example 1: Imidazolium dimer (isotropic functional form works well)

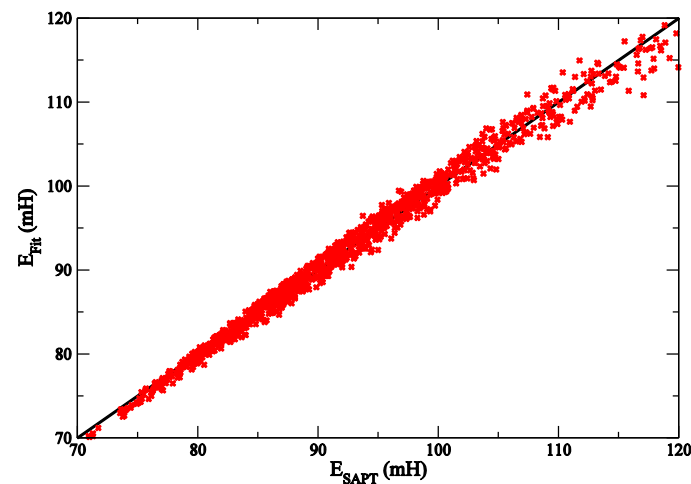
Exchange



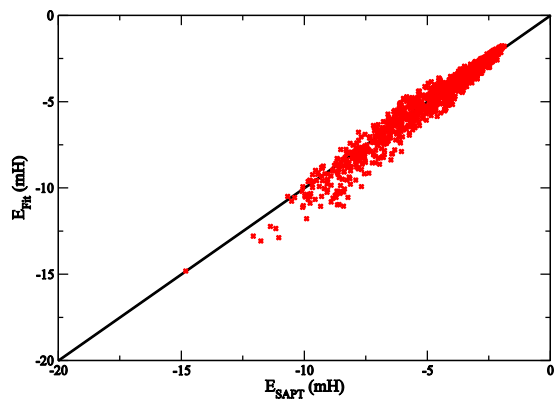
Electrostatics



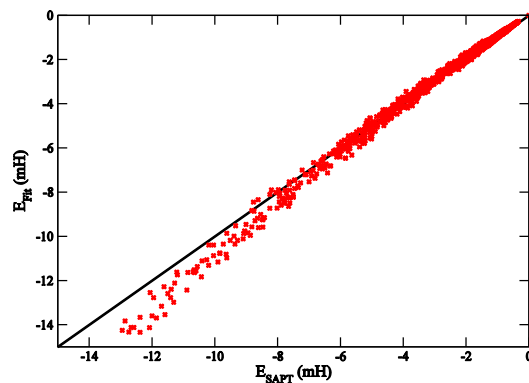
Total



Induction

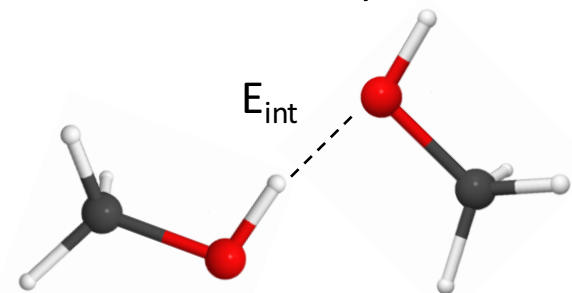
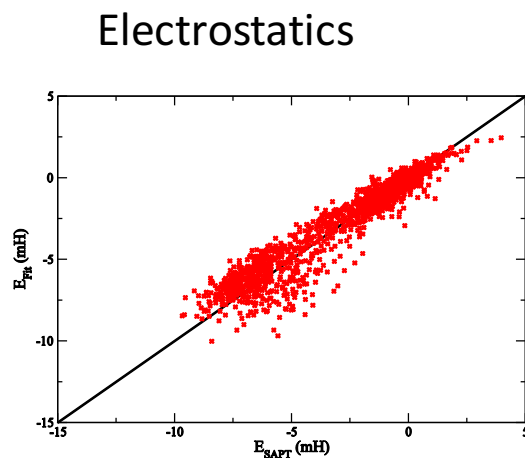
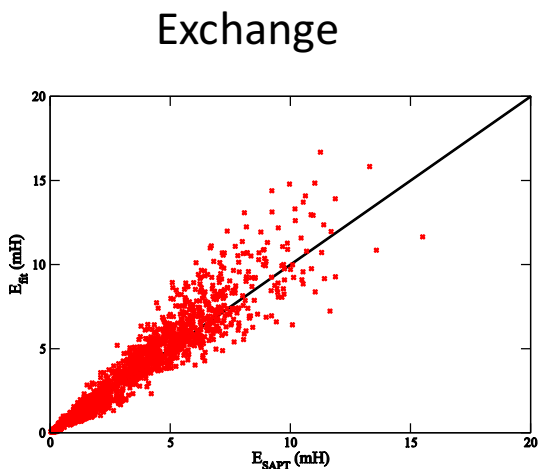


Dispersion

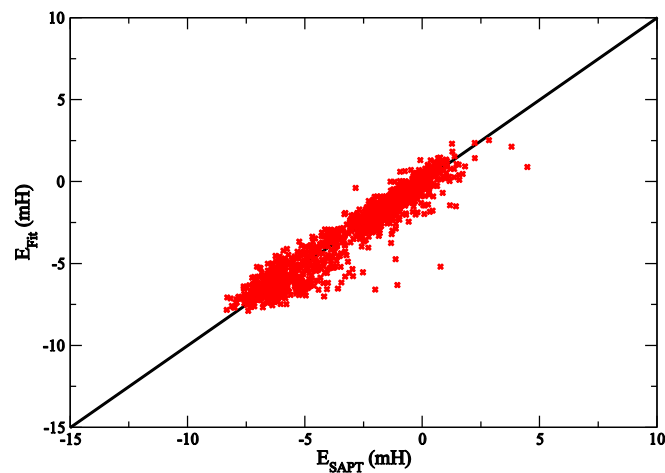
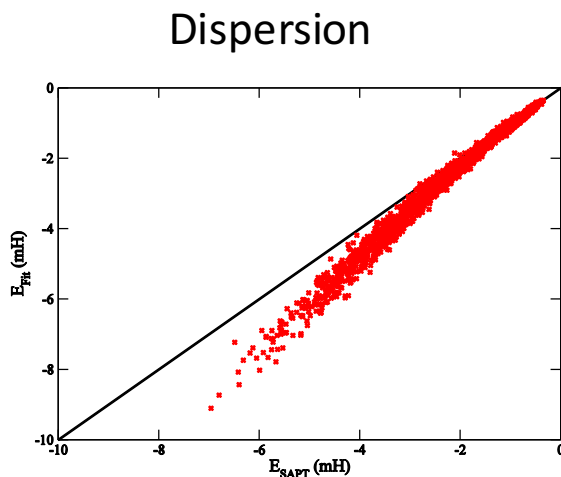
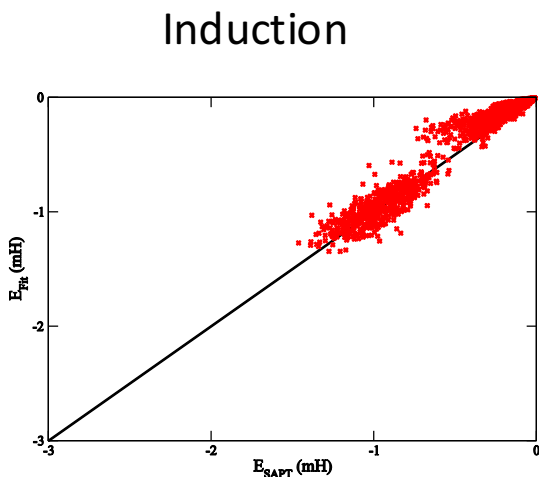




## Example 2: Methanol dimer (isotropic functional form introduces error)



Total



Two important things to evaluate:

1) Functional form (isotropic!). What error does this introduce?

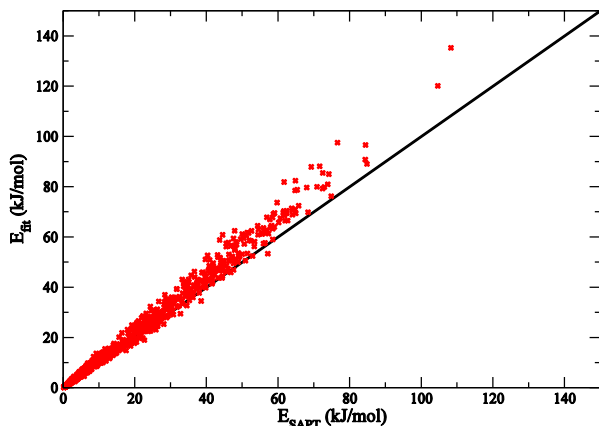
2) Transferability for hetero-molecular interactions  
(without explicit parameterization)

Transferability to hetero-molecular interactions

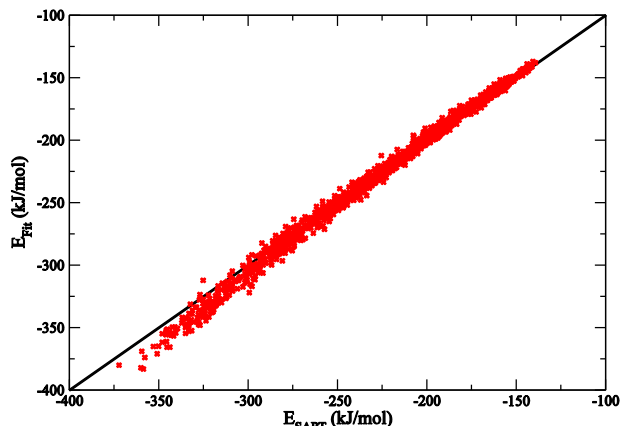
e.g. alkylimidazolium<sup>+</sup>, BF<sub>4</sub><sup>-</sup>

**No parameters are fit to the cross interaction!**

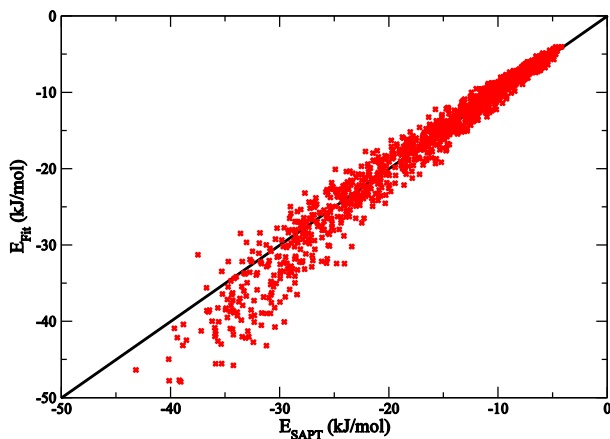
Exchange



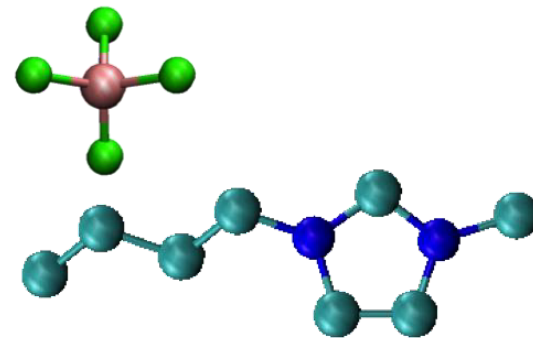
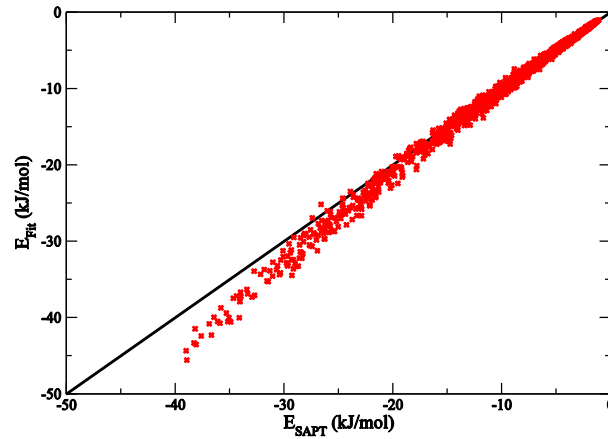
Electrostatics



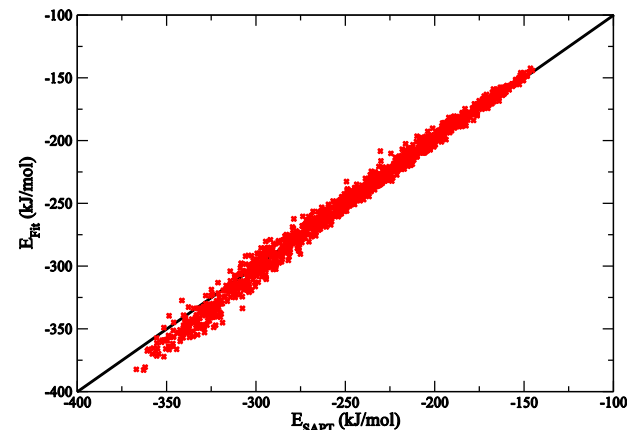
Induction



Dispersion



Total



- SAPT fixes the incorrect behavior of intermolecular perturbation theory at short distances by anti-symmetrizing the product wavefunction
- Force fields can be developed by fitting distinct, physically-motivated functional forms separately to each type of intermolecular interaction given by SAPT
- Correct asymptotic behavior is preserved by parameterizing much of the force field based on monomer properties (1<sup>st</sup> part of talk)

Including many-body interactions to predict condensed-phase properties.

Look at

- 1) Virial coefficients
- 2) Bulk liquid properties

Ideal Gas Law

Corrections...

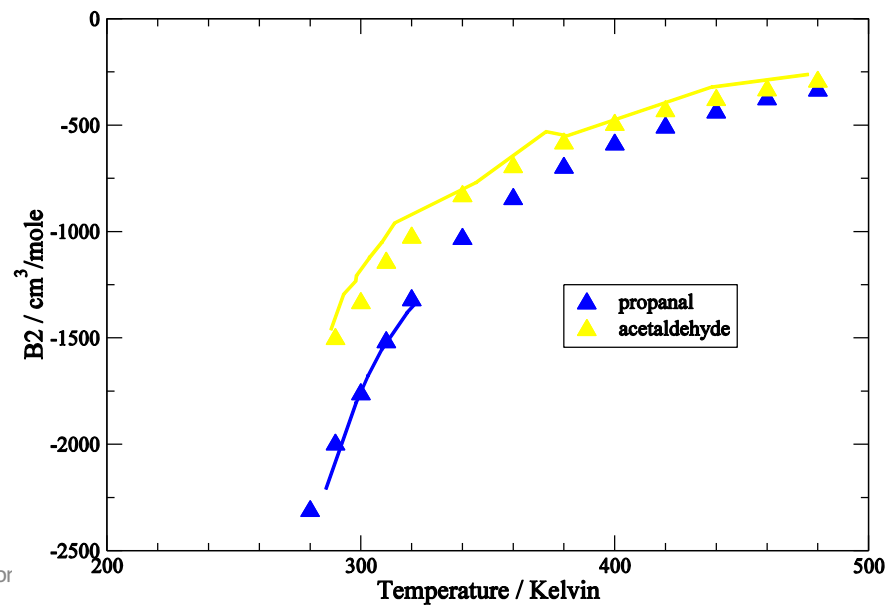
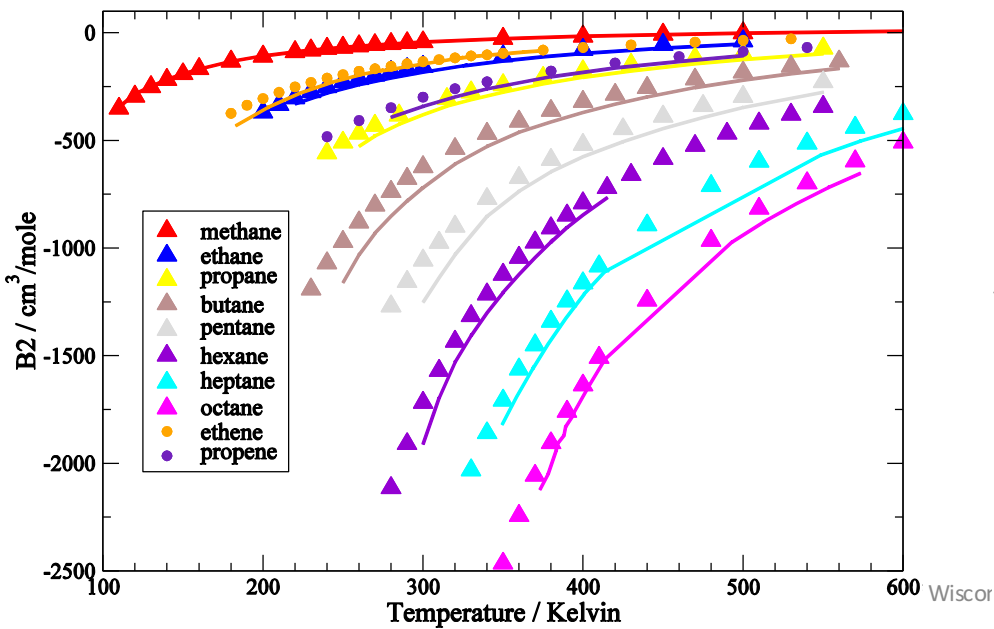
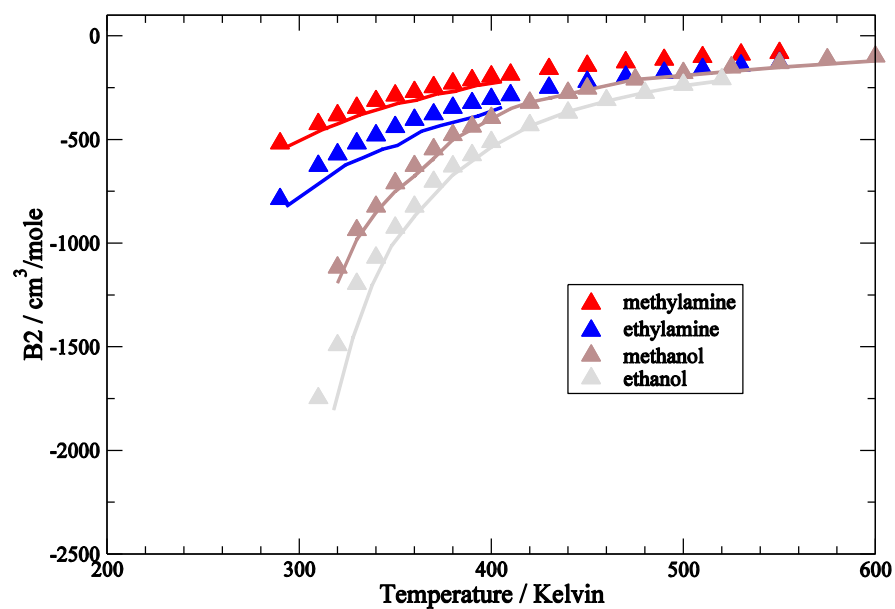
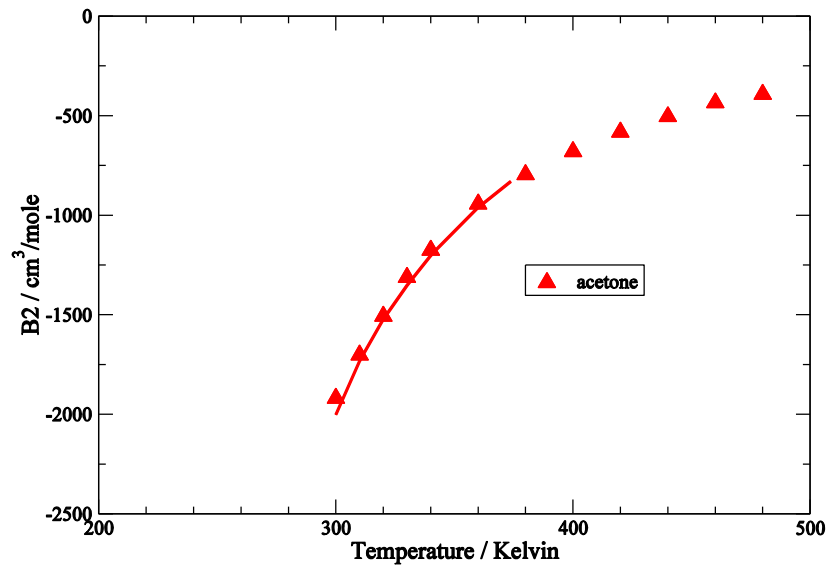
$$\frac{p}{k_B T} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \dots$$

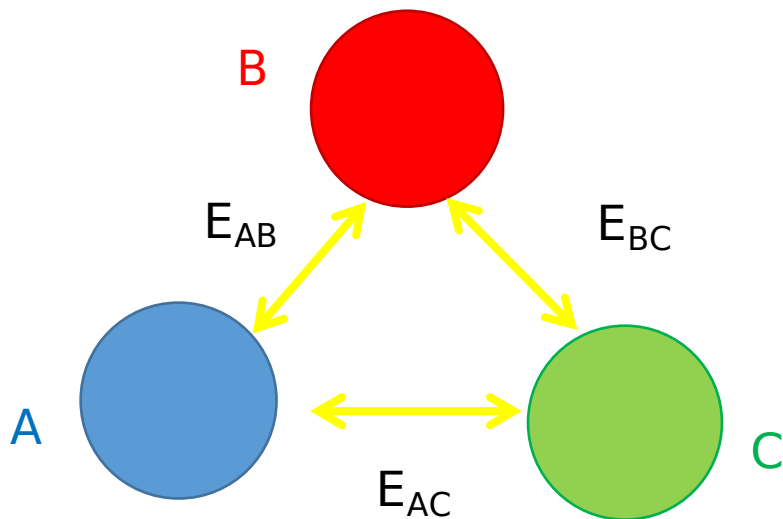
**Second Virial Coefficient—two body interactions**

$$B_2(T) = -2\pi \int_0^{\infty} f_{12}(r_{12}) r_{12}^2 dr_{12} \quad f_{12} = e^{-E_{12}/kT} - 1$$

**Third Virial Coefficient—three (and two) body interactions**

$$B_3(T) = -\frac{1}{3} \int \int \left[ \left( e^{-\Delta E_{123}/kT} - 1 \right) e^{-(E_{12} + E_{13} + E_{23})/kT} + f_{12} f_{13} f_{23} \right] \mathbf{dr}_{12} \mathbf{dr}_{13}$$





$$E_{ABC} \neq E_{AB} + E_{AC} + E_{BC}$$

*Non-additive* contributions include:

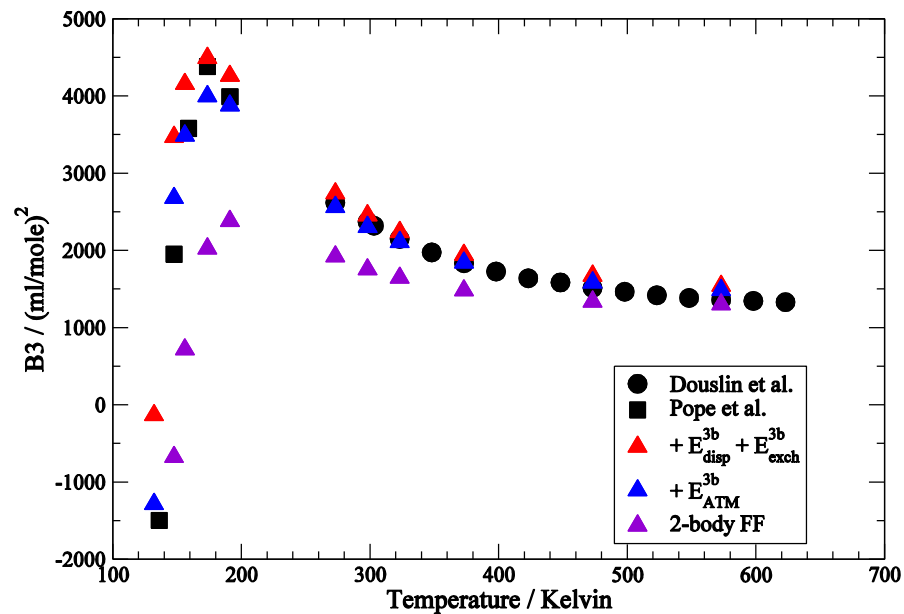
$$E_{ind}^{3b}, E_{disp}^{3b}, E_{exch}^{3b}$$

Standard Approaches  
(Drude oscillators)

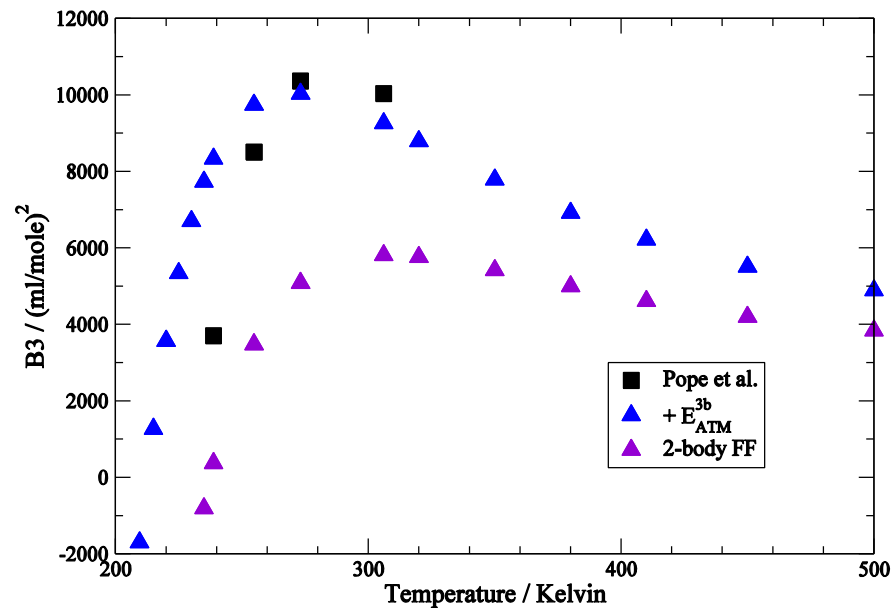
Axilrod-Teller Muto (ATM)  
potential



## Methane



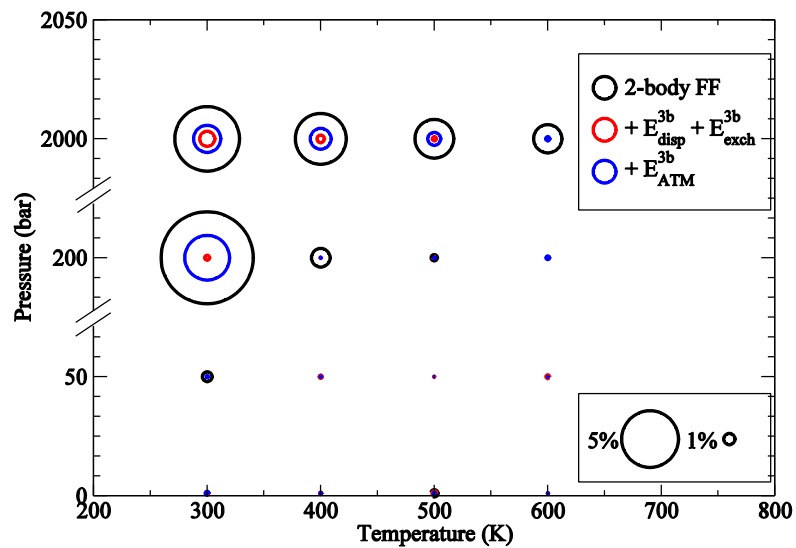
## Ethane



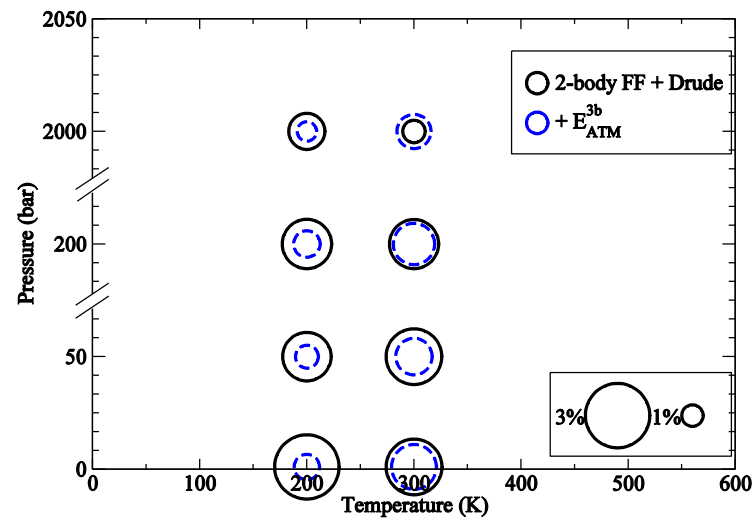
$$E_{\text{ATM}} = C_9^{ABC} \frac{1 + 3 \cos \phi_A \cos \phi_B \cos \phi_C}{R_{AB}^3 R_{AC}^3 R_{BC}^3}$$

$$C_9^{ABC} = \frac{3}{\pi} \int_0^\infty d\omega \alpha^A(i\omega) \alpha^B(i\omega) \alpha^C(i\omega)$$

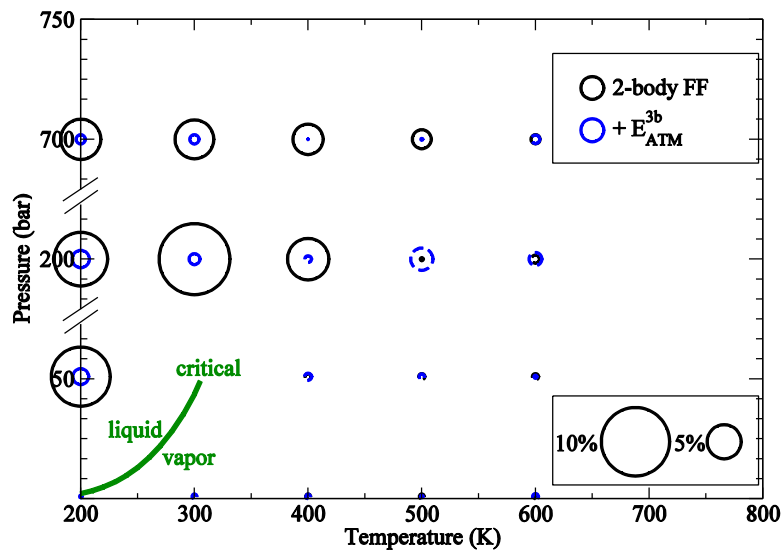
# Methane



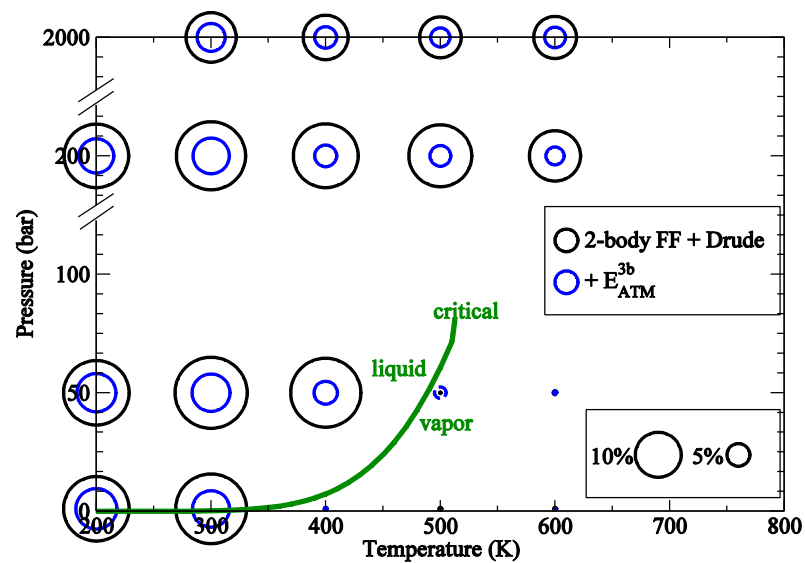
# Acetone



# Ethane



# Methanol



Don't really need Axilrod-Teller terms for Ionic Liquids because the cohesive Energy is so high!!

Organic Solvents:	10-40 kJ/mol
Ionic Liquids:	450-500 kJ/mol
Axilrod Teller	: ~ 1 kJ/mol

What about electrolyte mixtures? I added correction for acetonitrile..., error cancellation for dichloroethane, acetone...