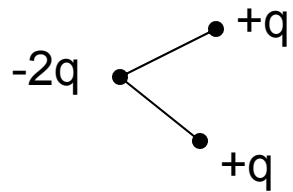
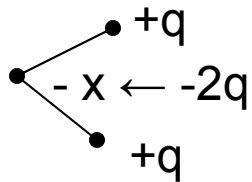


## More on force fields – focus on water



TIP3P  
SPC

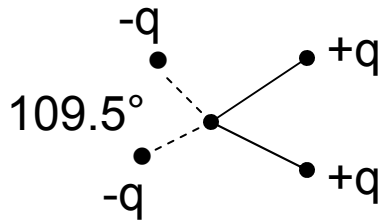
- If  $q$  chosen to give the true dipole moment, the quadrupole moment is way off (poor electrostatics)



TIP4P  
DC  
TTM2  
DPP  
MCY

- By optimizing the location of the minus charge as well as the value of  $q$ , one can reproduce both the dipole and quadrupole moments.

Still sizable errors in the electrostatic potentials at vdW contact.

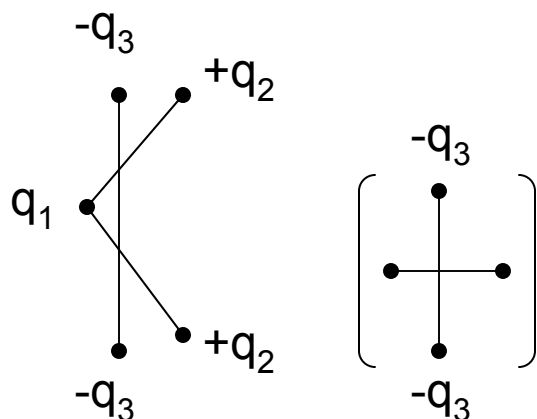


TIP5P  
(Jorgensen  
Group)

- Location of minus charges motivated by shape of lone pairs.
- But comparison of this model with the 4-site models reveals a problem; namely, that the minus charge would "prefer" to be shifted toward the H atoms.

COMMENT:

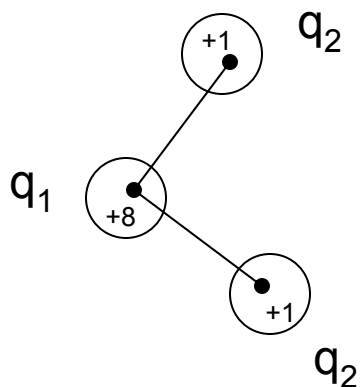
Charges in most of these models are chosen to give enhanced electrostatics ( $\mu = 2.3 - 2.6$  D) to make up for neglect of polarization.



SAPT5S  
(5 symmetry sites)

- 5 point charges – best overall representation of the electrostatics of the models considered. (the  $q_3$  charges are out-of-plane)
- Electrostatic interactions are damped.

Not clear this results in improved electrostatic interactions at short distances (charge penetration!)



- Crude model accounting for 3D spatial distribution of charge  
 $q_1 + 2q_2 + 10 = 0$

electron distribution represented by 3 or more Gaussians

See Piquemal et al., J. Chem. Phys. 125, 104101 (2006); 125, 184101 (2006).  
 also Hall and Tsujinaga, Theor. Chim. Acta. 69, 425 (1986).

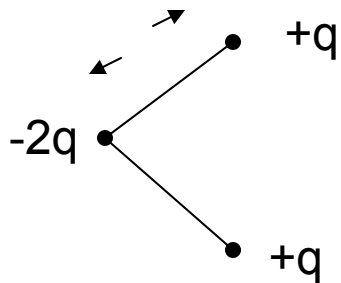
Only the last model accounts for charge penetration

Computational cost of overlap integrals  
can be done over grids

~10x CPU time of simple point-charge models

Not so bad if one is already  
accounting for polarization.

### Charges and flexible models



Most models do not allow the charges  
to adjust when bonds stretch or the  
HOH angle changes

As a result, they do not give the correct vibrational frequencies and intensities of clusters or bulk H<sub>2</sub>O.

One way of addressing this problem is to require that the charges give a dipole moment consistent with the *ab initio* dipole moment surface ( $\mu(r_1, r_2, \theta)$ ).

This strategy was adopted by Xantheas and Burnham in the flexible version of their TTM2 model.

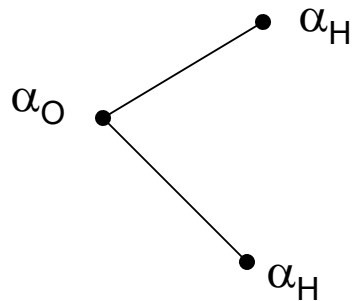
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## Polarizability

Most polarizable models of water employ a single polarizable site, either on or slightly displaced from the O atom

- point inducible dipole moment
- charge-on-spring (Drude osc.) models  
all interactions calculated using point charges

Recently, several models with 3 polarizable sites have appeared.



- If the polarizable sites interact  
 $\alpha_{\text{H}_2\text{O}} \neq 2\alpha_{\text{H}} + \alpha_{\text{O}}$
- Energy diverges if 2 or more polarizable sites are close
- Need to damp  $\sim(1 - e^{-br^2})$

Interaction between polarizable sites → anisotropy

As the geometry changes, so should the atomic polarizabilities.

Recently, a model appeared that allows the atomic polarizabilities to vary so as to reproduce the *ab initio* polarizability surface.

### Repulsion – dispersion

Consider the  $(\text{H}_2\text{O})_2$  dimer

- (1) fit charges of monomer
- (2) determine polarization model for monomer
- (3) subtract  $E^{\text{es}} + E^{\text{ind}}$  of the model from  $E^{\text{MP2}}$
- (4) fit this difference to a repulsion-dispersion model

Most models employ a single repulsion-dispersion site, generally on the O atom

$$\frac{C_{12}}{R^{12}} - \frac{C_6}{R^6}, \text{ or } Ae^{-br} - \frac{C_6}{R^6}$$

Neither the dispersion nor the repulsive terms are really spherically symmetric

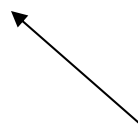
More flexibility is provided by employing repulsion-dispersion terms between all atoms.

SAPT5S also employs out-of-plane repulsion-dispersion sites.



## Dissection of interactions using SAPT of models of the water-graphite system

System	ES	EX	Ind	Ex-Ind	Disp	Ex-disp	$\Delta$	Tot
Benzene-H <sub>2</sub> O	-3.2	4.9	-2.2	1.4	-4.1	0.6	-0.5	-3.1
Coronene-H <sub>2</sub> O	-2.1	5.1	-2.4	1.5	-5.0	0.6	-0.7	-2.9
Circumcoronene-H <sub>2</sub> O	-2.0	5.7	-2.6	1.6	?	?	-0.5	
Graphite-H <sub>2</sub> O	-0.5	2.0	-1.0		-3.4			-2.9
Karapetian/Jordan model								



This work employed the Dang-Chang water model and polarizable sites on each C atom. The polarizable sites on the C atoms were not allowed to interact.

Serious limitation to use of quadrupoles only on C atoms!

Are exch., disp. contributions off in KJ model due to use of combination rules?

$$\varepsilon_{12} = \sqrt{\varepsilon_1 \varepsilon_2} \quad , \quad \sigma_{12} = \frac{\sigma_1 + \sigma_2}{2} \quad \left| \quad E = 4\varepsilon \left( \frac{\sigma^{12}}{R^{12}} - \frac{\sigma^6}{R^6} \right)$$

This is often a rather poor approximation.