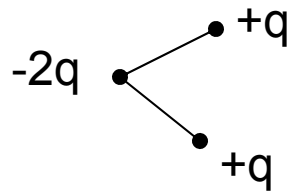
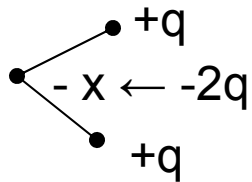


More on force fields – focus on water



TIP3P
SPC

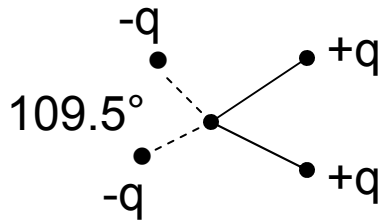
- If q chosen to give the true dipole moment, the quadrupole moment is way off (poor electrostatics)



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.

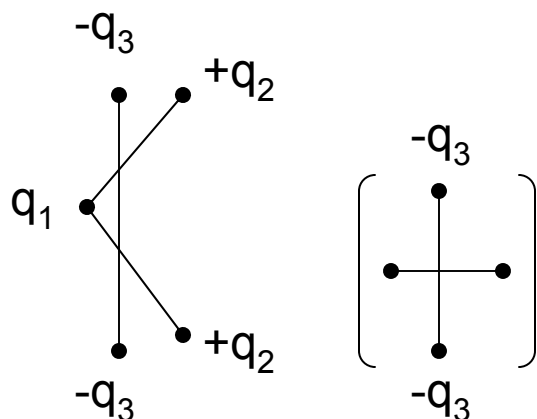


TIP5P
(Jorgensen
Group)

- 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:

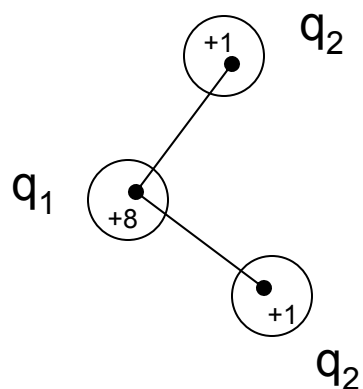
Charges in most of these models are chosen to give enhanced electrostatics ($\mu = 2.3 - 2.6$ D) to make up for neglect of polarization.



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).

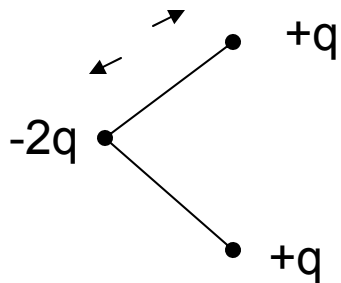
Only the last model accounts for charge penetration

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 H₂O.

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

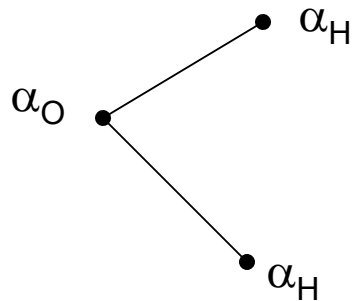
This strategy was adopted by Xantheas and Burnham in the flexible version of their TTM2 model.

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
 $\alpha_{\text{H}_2\text{O}} \neq 2\alpha_H + \alpha_O$
- 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^{MP2}
- (4) fit this difference to a repulsion-dispersion model

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

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

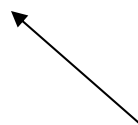
Neither the dispersion nor the repulsive terms are really spherically symmetric

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	Δ	Tot
Benzene-H ₂ O	-3.2	4.9	-2.2	1.4	-4.1	0.6	-0.5	-3.1
Coronene-H ₂ O	-2.1	5.1	-2.4	1.5	-5.0	0.6	-0.7	-2.9
Circumcoronene-H ₂ O	-2.0	5.7	-2.6	1.6	?	?	-0.5	
Graphite-H ₂ 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.