Technische Universiteit
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Polarizing Water with Fluctuating Charges

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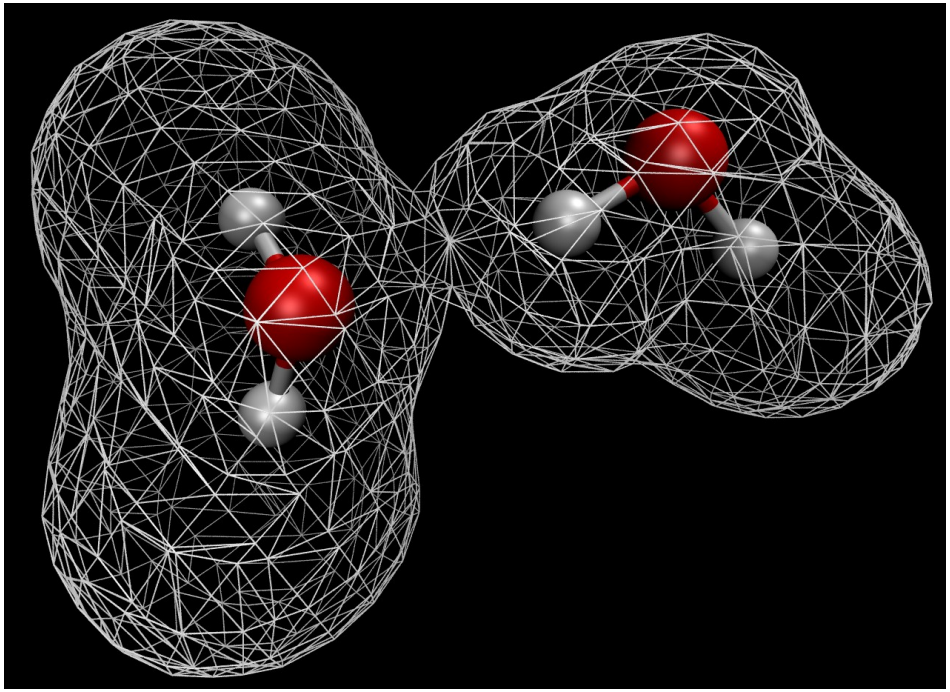


Where innovation starts

Applications of Polarization

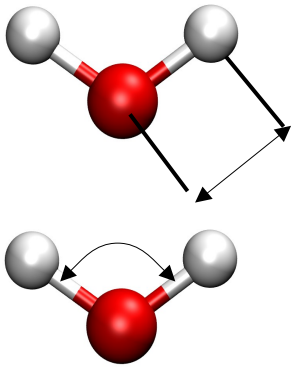
- Polarizable water is necessary for accurate solvation.
- Polarizable proteins: MD simulations of drug binding and enzymatic reactions.
- With dynamic testing for creation/destruction of bonds, can do constant pH simulations.

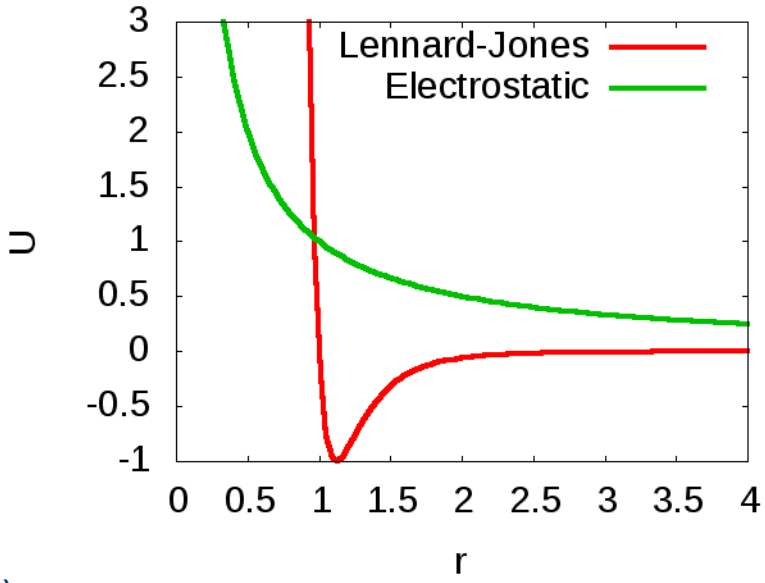
Molecular Dynamics

- Integrate Newton's equations of motion for particles interacting through a potential
- Forcefield components:
  - Non-bonded
  - Bonded
  - Angular
  - Dihedral
  - Electrostatic

$$m_i \ddot{\vec{r}}_i = \vec{F}_i = -\nabla_{\vec{r}_i} U$$

$$U_{LJ} = \sum_{i,j} 4\varepsilon \left(\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right)$$

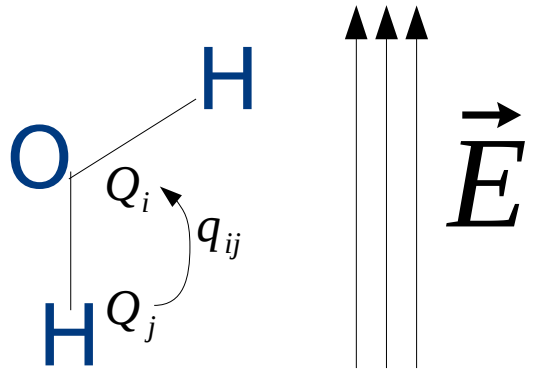


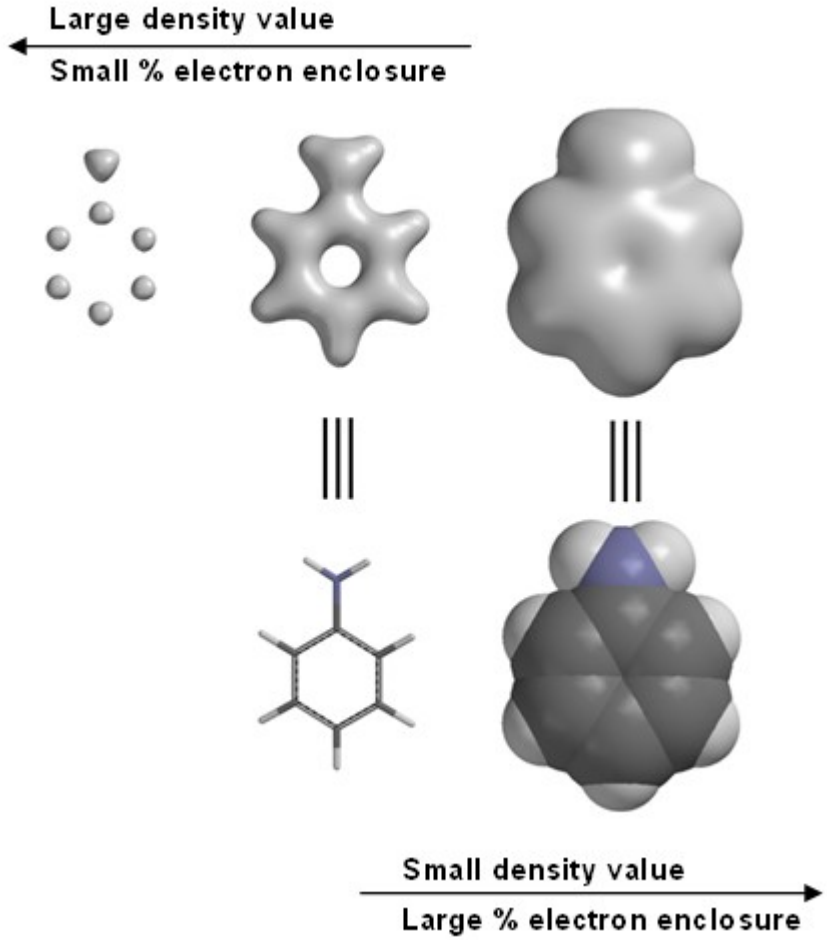


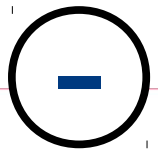
Picture by Bagheri (2016).

Polarization

- QM:
  - Electrons as clouds
  - Electron clouds deform due to electric fields



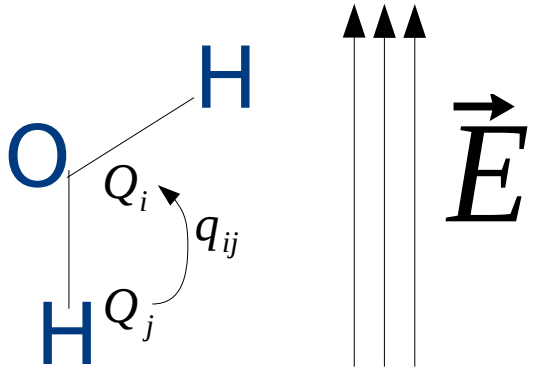


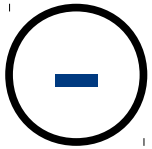


http://en.wikipedia.org/wiki/File:ElectronDensityAniline.PNG

Fluctuating Charge

- Split Charge Equilibration (SQE):
  - Charge moves between atoms
  - Charge can't move too far: long organic molecules don't conduct electricity





$$Q_i = \sum_{j \neq i} q_{ij} \qquad q_{ij} = -q_{ji}$$

$$U = U_0 + \sum_i \chi_i Q_i + \frac{1}{2}\sum_i \kappa_i Q_i^2 + \frac{1}{2}\sum_{i,j} \kappa_{sij} q_{ij}^2 + \frac{1}{2}\sum_{i,j \neq i} Q_i \boldsymbol{J_{ij}} Q_j$$

Nistor *et al*. (2006). *JCP*

Finding Atomic Charges

- Find minimal energy charge distribution

$$F_{ij} = -\frac{dU}{dq_{ij}} = 0 \; \forall \left\{ i, j \right\} \text{ bonded pairs}$$

- Optimize using Newton-Raphson

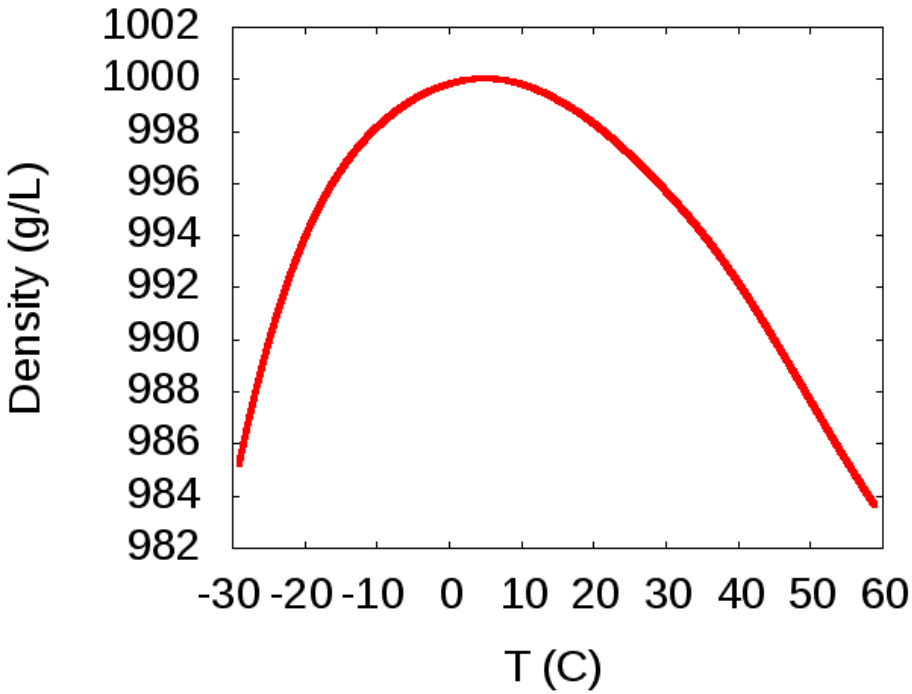
$$Q_i = \sum_{j \neq i} q_{ij} \qquad q_{ij} = -q_{ji}$$

$$U = U_0 + \sum_i \chi_i Q_i + \frac{1}{2} \sum_i \kappa_i Q_i^2 + \frac{1}{2} \sum_{i,j} \kappa_{sij} q_{ij}^2 + \frac{1}{2} \sum_{i,j \neq i} Q_i \boldsymbol{J_{ij}} Q_j$$

Nistor *et al*. (2006). *JCP*

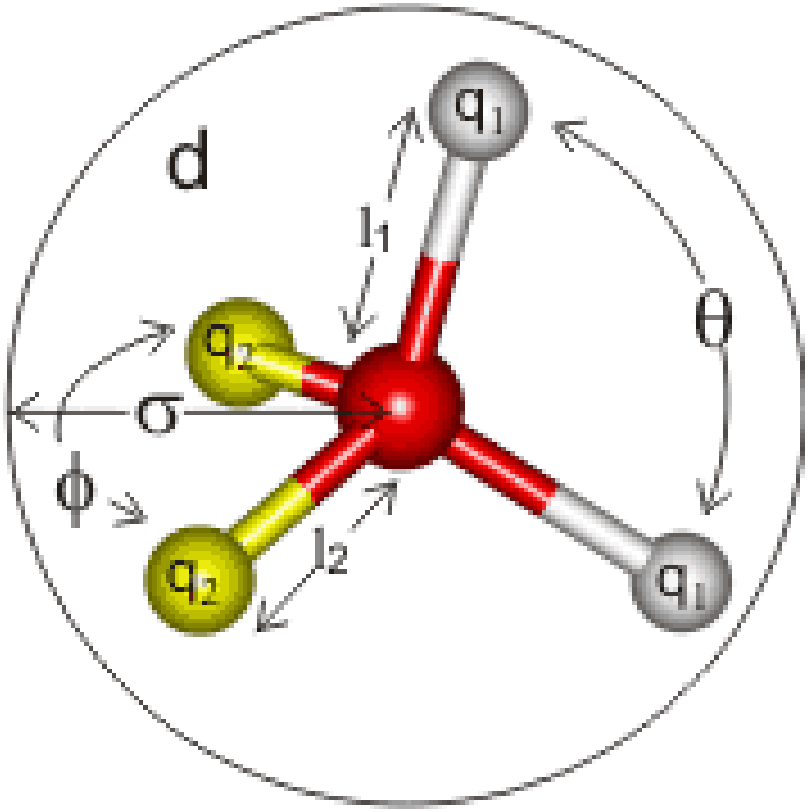
Water

- Chosen as proof of concept
- Density peak at 4 °C
- Highly tetrahedral order
- Different dipole moments in gas and liquid phases
  - To describe liquid, need periodic boundary conditions

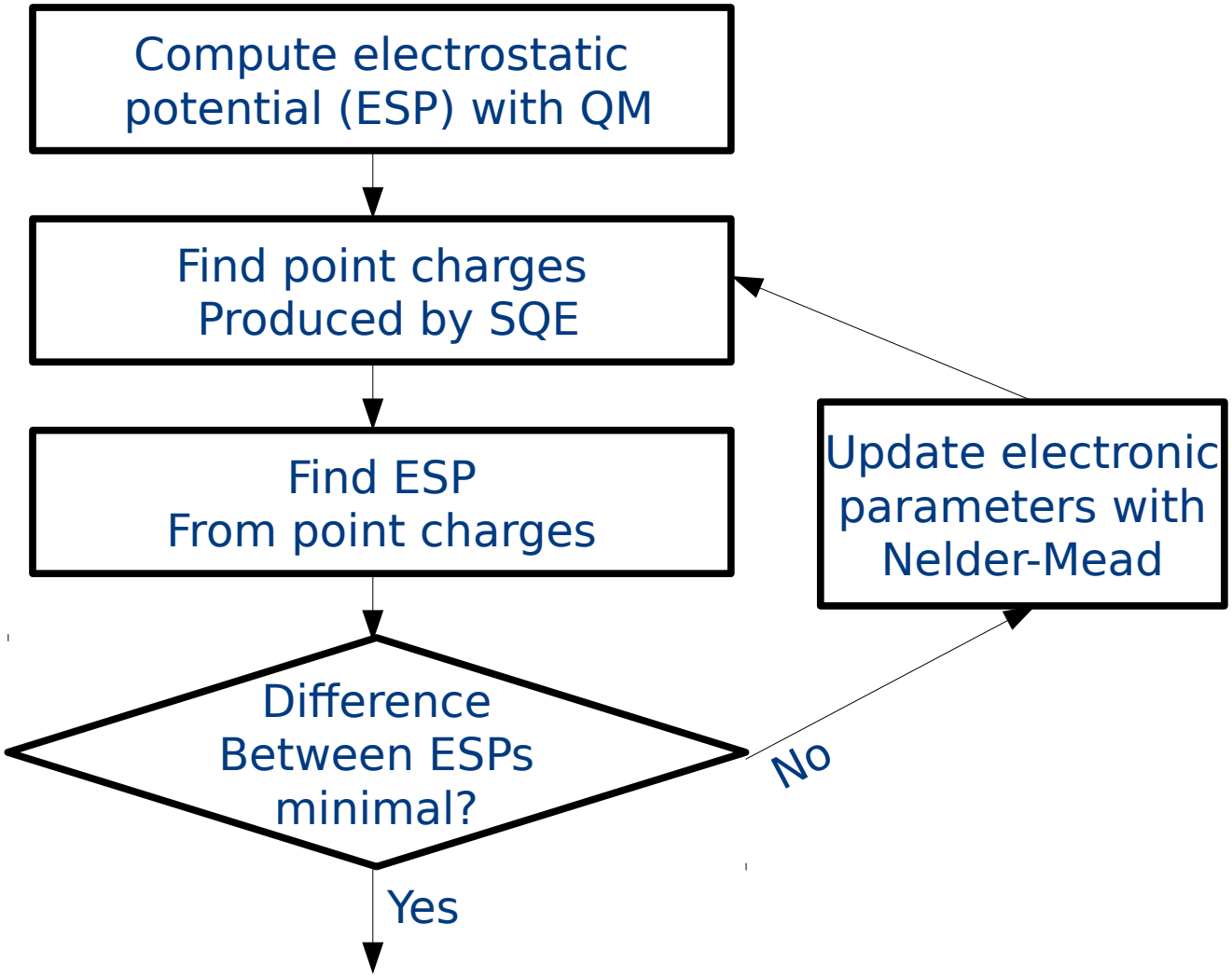


Lide (1990). *CRC Handbook of Chemistry and Physics.*

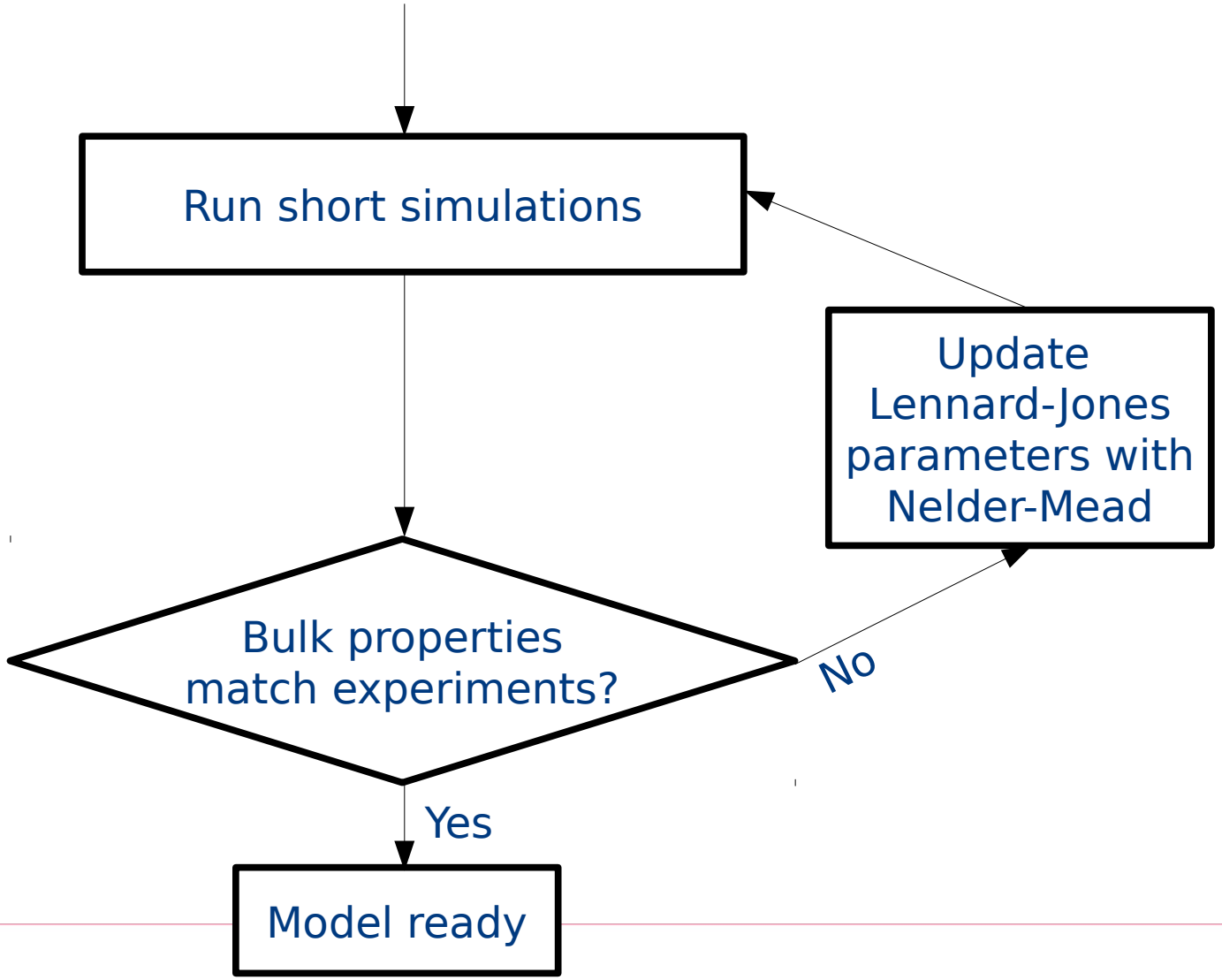
Water Geometry



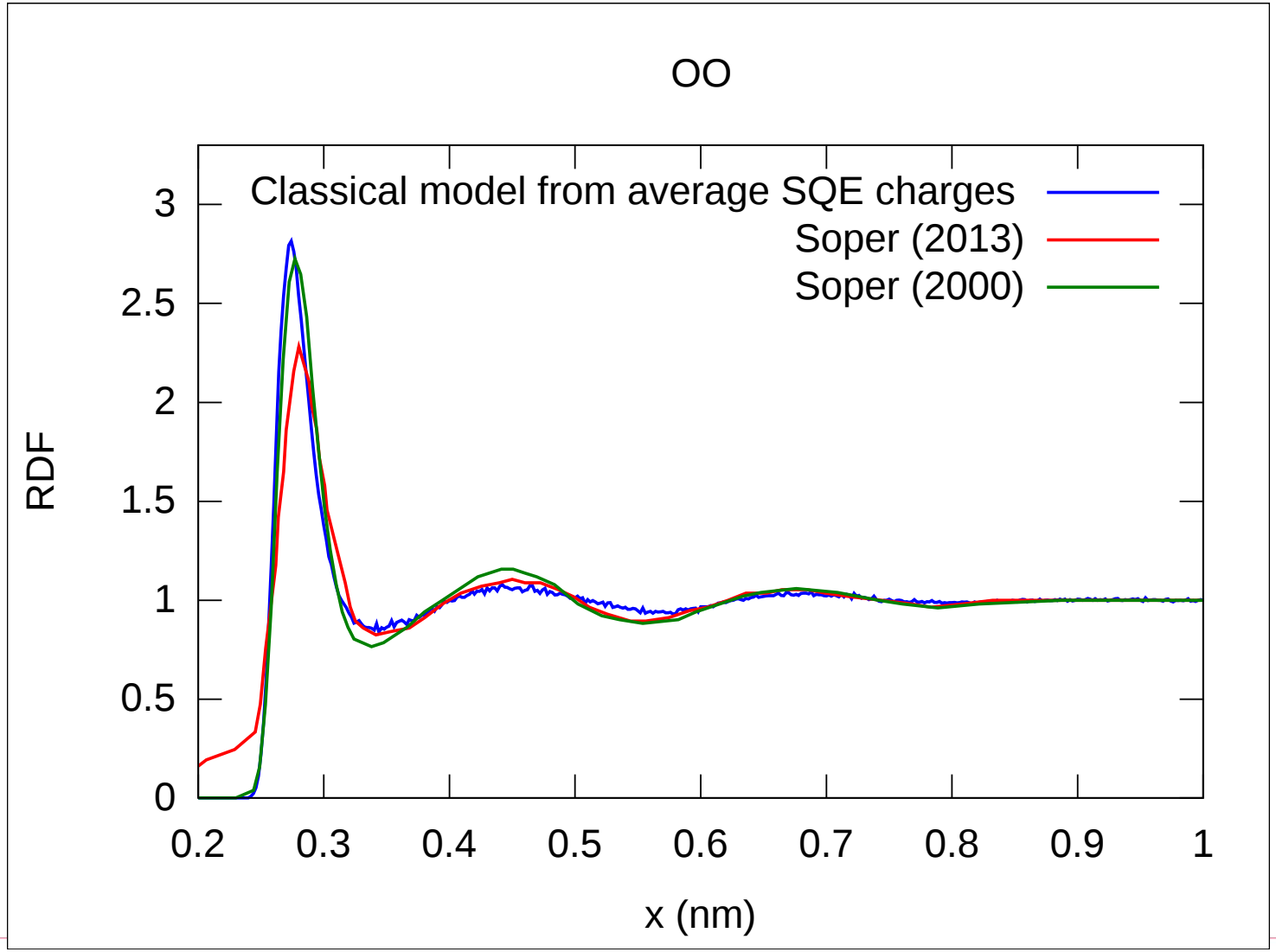
Optimizing Parameters



Optimizing Parameters



Current State of the Model



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Acknowledgements

- Thank you all for listening

University of Waterloo

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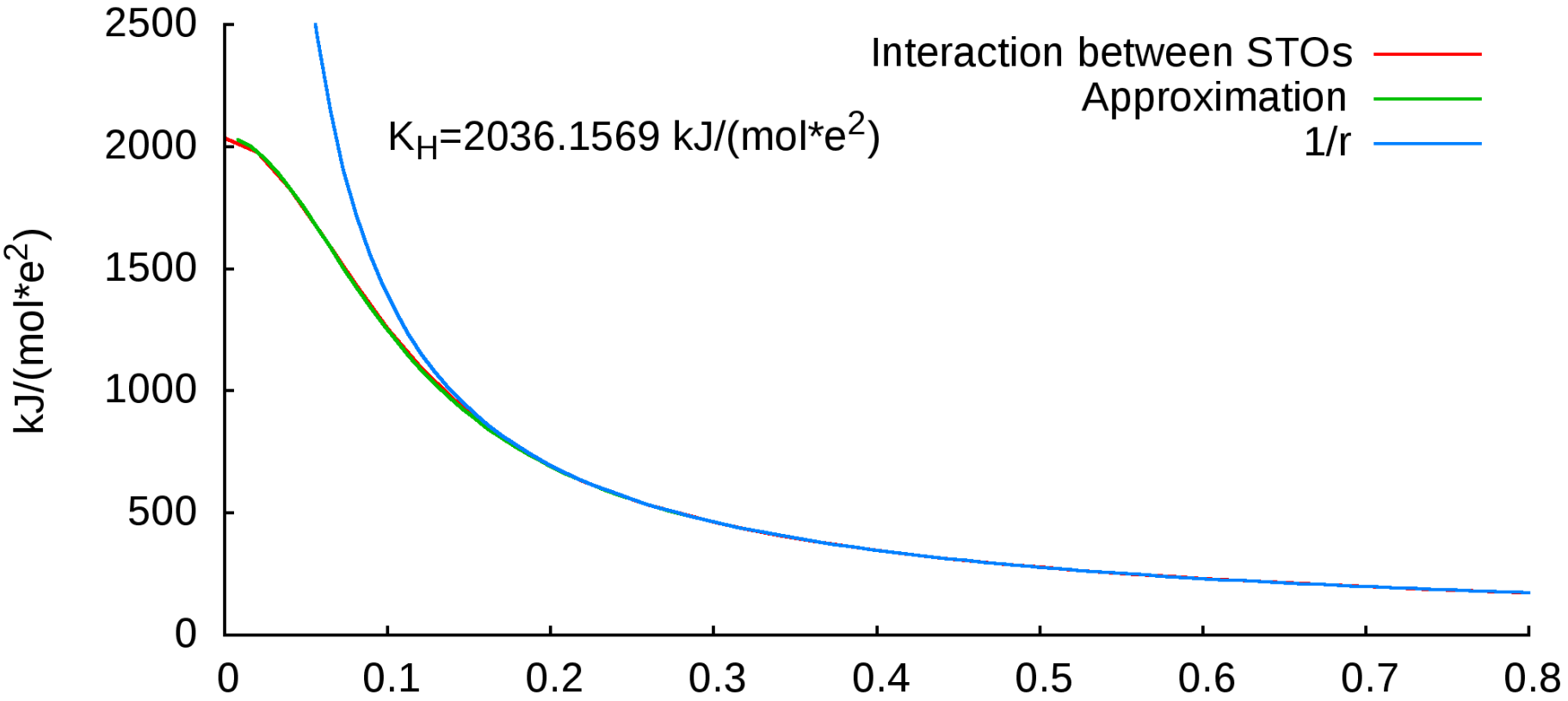
Where innovation starts

NWO

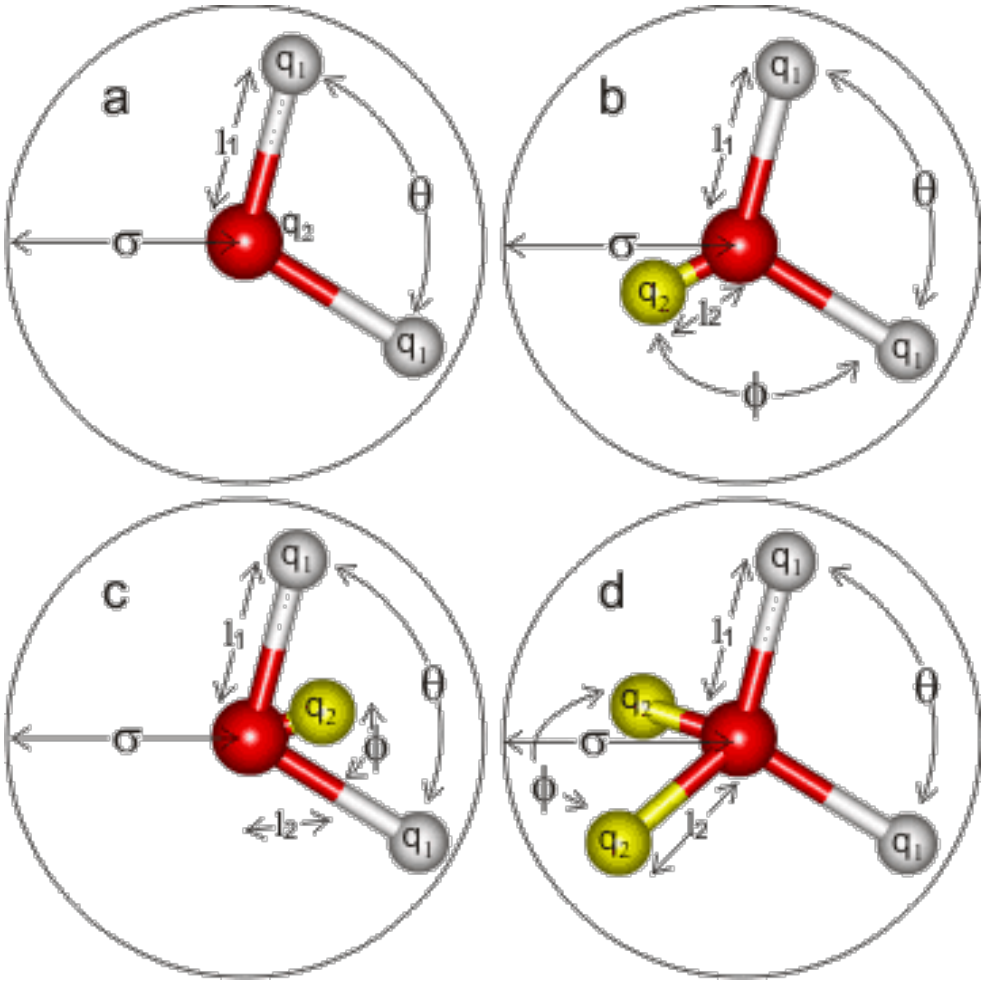
NSERC CRSNG

Shielding



$$J_{ij}(r) = \frac{1}{4\pi\epsilon_0} \frac{2/\left(1+e^{-k_{ij}r}\right)-1}{r}$$

Water Geometries



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