Electronically coarse grained water

Andrew Jones **Flaviu Cipcigan** Vlad Sokhan Jason Crain Glenn Martyna

THE UNIVERSITY *of* EDINBURGH

NPL National Physical Laboratory

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Problem

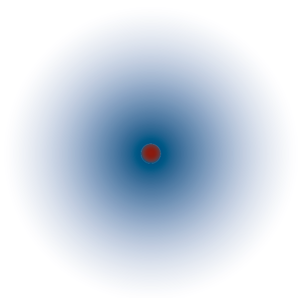
Intermolecular interactions depend on **environment**

Challenge

Develop simplest water model with **electronic responses**

1. Quantum Drude Oscillator (QDO)

Light **negative particle** tethered **harmonically** to **heavy positive**, oppositely charged nucleus



Free parameters

μ reduced mass

ω spring constant

q charge

1. Quantum Drude Oscillator (QDO)

Polarisabilities

$$\alpha_l = \underbrace{\left[\frac{q^2}{\mu\omega^2}\right]}_{\text{dipole}} \left[\frac{(2l-1)!!}{l}\right] \left[\frac{\hbar}{2\mu\omega}\right]^{l-1}$$

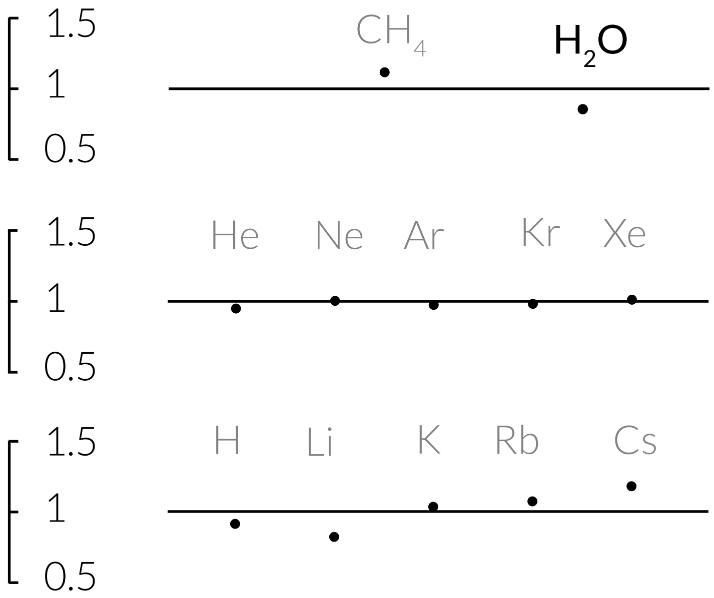
Dispersion coefficients

$$C_6 = \tfrac{3}{4}\alpha_1\alpha_1\hbar\omega$$ | dipole–dipole

$$C_8 = 5\alpha_1\alpha_2\hbar\omega$$ | dipole–quadrupole

$\ldots$

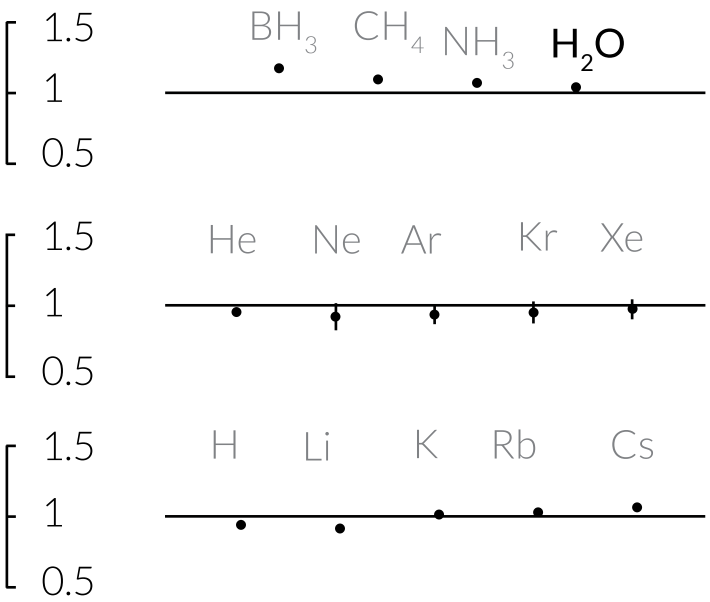
2. The responses of QDOs are realistic



Polarisation

$$\sqrt{\frac{20}{9}}\frac{\alpha_2}{\sqrt{\alpha_1\alpha_3}} = 1$$

2. The responses of QDOs are realistic

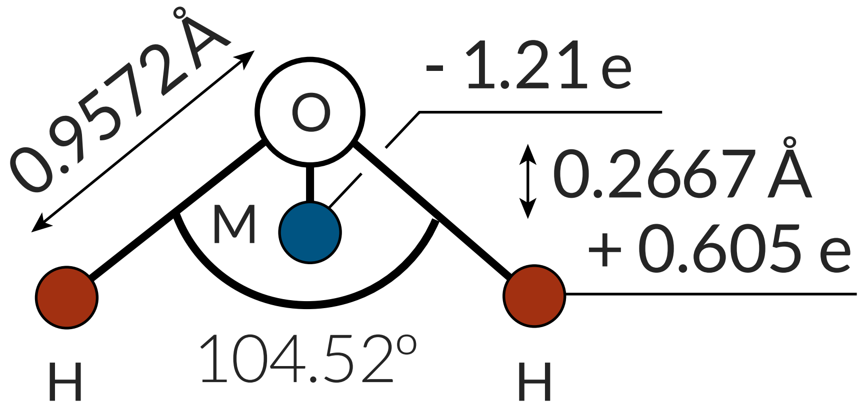


Dispersion

$$\sqrt{\frac{49}{40}}\frac{C_8}{\sqrt{C_6 C_{10}}} = 1$$

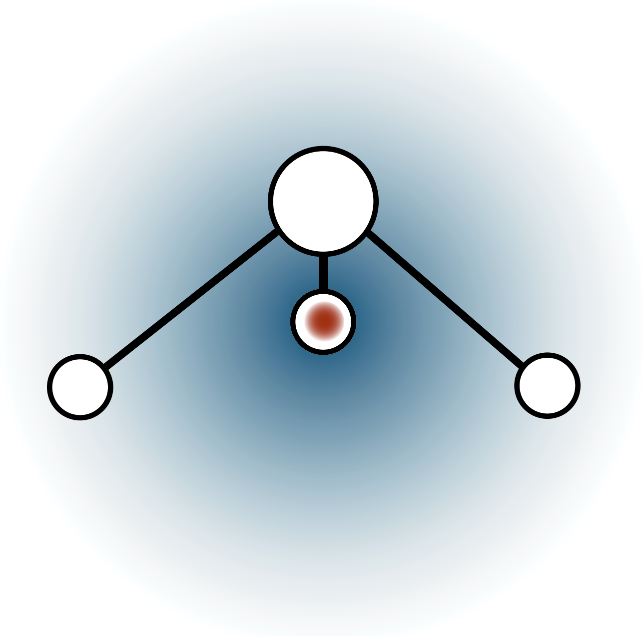
3. QDO water

Frame: ground state charge distribution



3. QDO water

QDO: responses



μ = 0.3656 amu

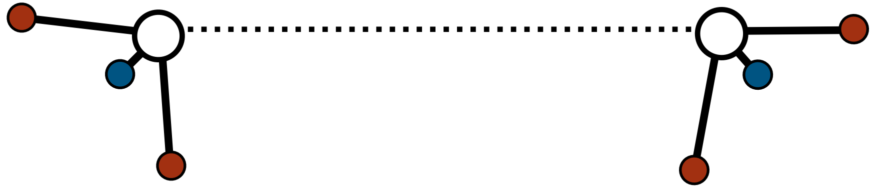
ω = 0.6287 ω_h

q = -1.1973 e

3. QDO water

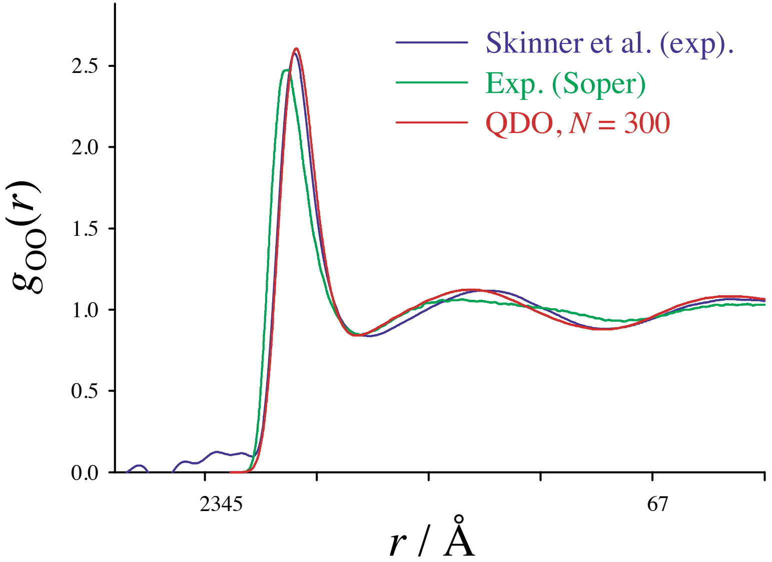
Short range: empirical repulsion

$$\lambda_1 e^{k_1} + \lambda_2 e^{k_2}$$



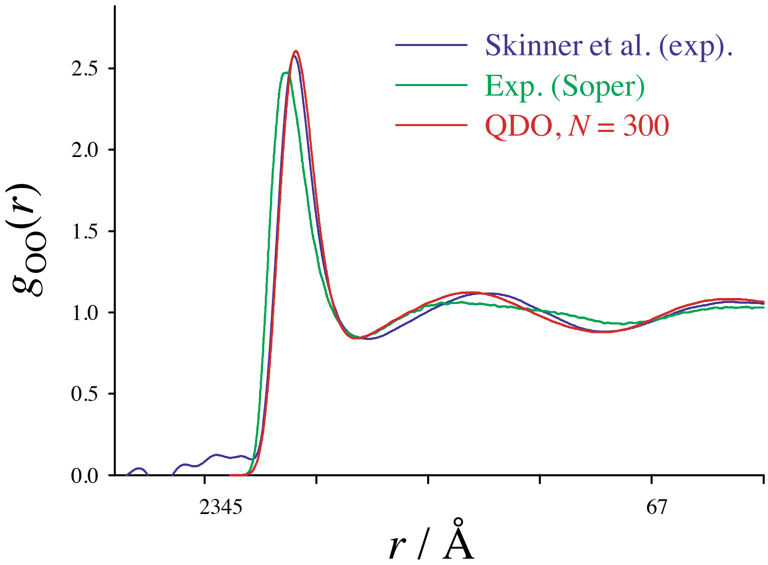
4. Liquid QDO water

Radial distribution function



4. Liquid QDO water

Radial distribution function



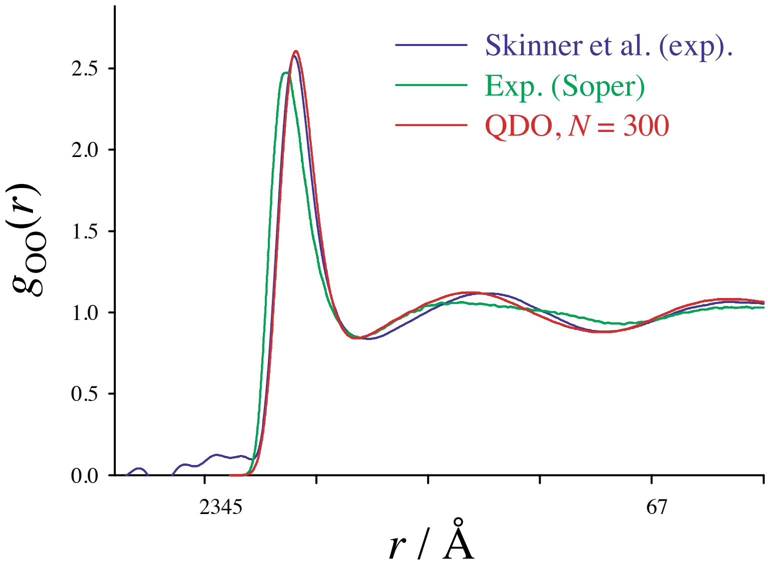
Vapour pressure

46 ± 2 kJ / mol

exp: 43.91 kJ/mol

4. Liquid QDO water

Radial distribution function



Vapour pressure

46 ± 2 kJ / mol

exp: 43.91 kJ/mol

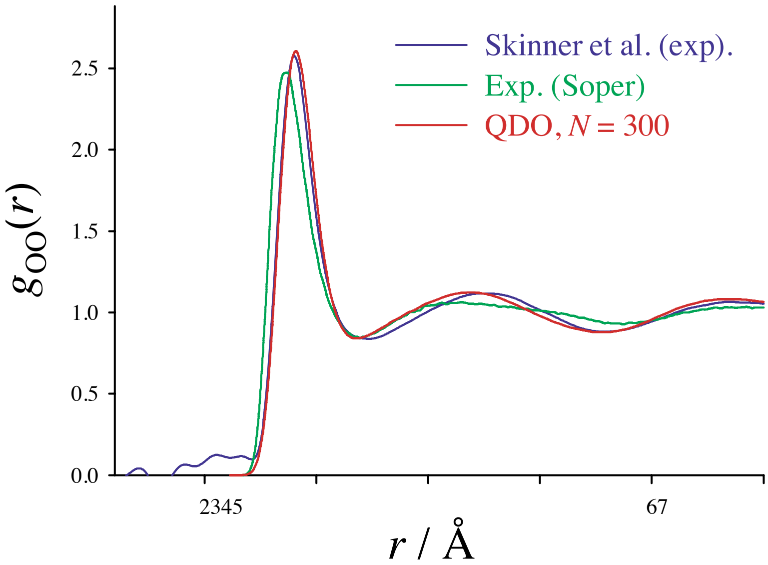
Dielectric constant

79 ± 2

exp: 78

4. Liquid QDO water

Radial distribution function



Vapour pressure

46 ± 2 kJ / mol

exp: 43.91 kJ/mol

Dielectric constant

79 ± 2

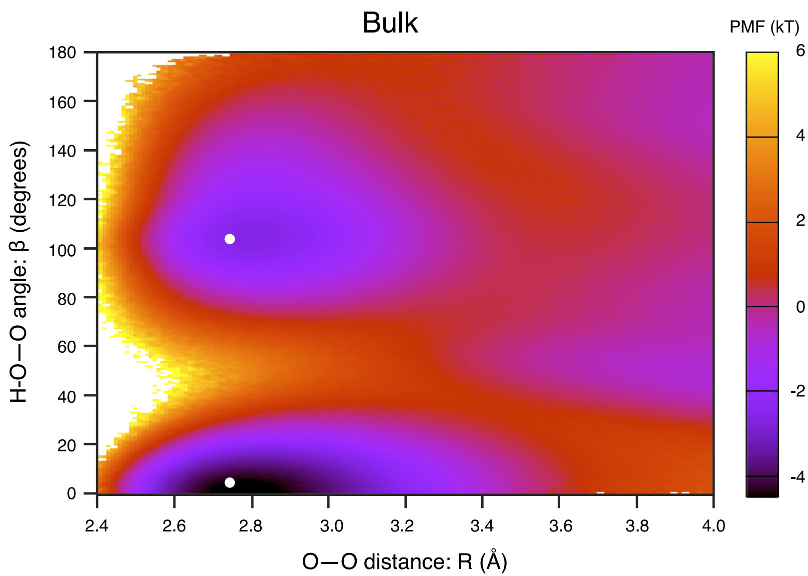
exp: 78

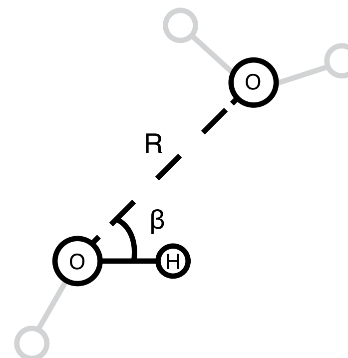
Surface tension

72.6 ± 1 mN / m

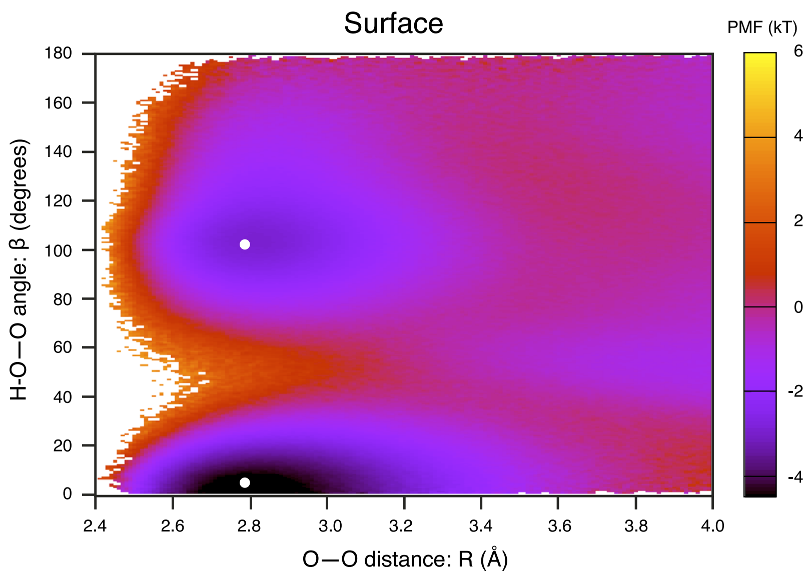
exp: 71.73 mN / m

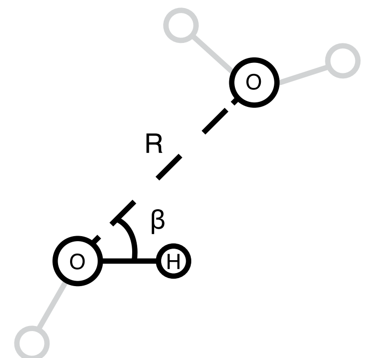
5. Liquid–vapour interface of QDO water



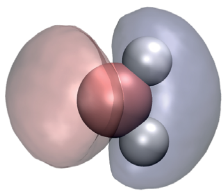


5. Liquid–vapour interface of QDO water



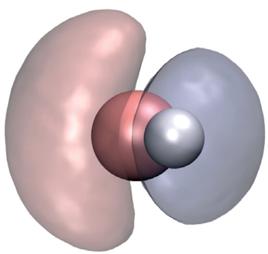


5. Liquid–vapour interface of QDO water

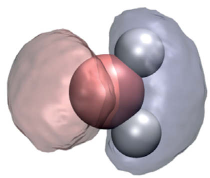


loss & gain of electronic charge

in bulk

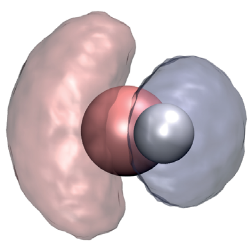


5. Liquid–vapour interface of QDO water

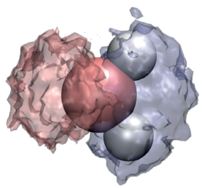


loss & gain of electronic charge

at surface

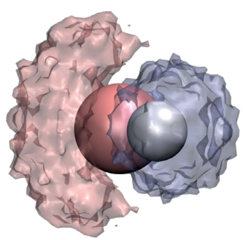


5. Liquid–vapour interface of QDO water



loss & gain of electronic charge

last surface layer



6. Conclusions

QDO water

model of the **isolated molecule**, condensed properties **emerge naturally**

simple, but with a **complex electronic structure**

transferability may be good, **under investigation**

Electronically coarse grained water

Andrew Jones **Flaviu Cipcigan** Vlad Sokhan Jason Crain Glenn Martyna

A. Jones, **Quantum drude oscillators for accurate many-body intermolecular forces**, PhD thesis, The University of Edinburgh

A. Jones, F. Cipcigan, V. Sokhan, J. Crain, G. Martyna, Electronically coarse grained model for water, **PRL 110, 227801 (2013)**

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