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Quantum Mechanics in a Glass of Water

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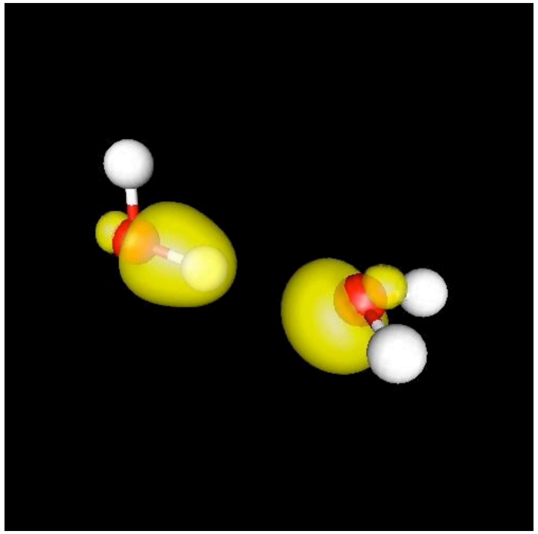
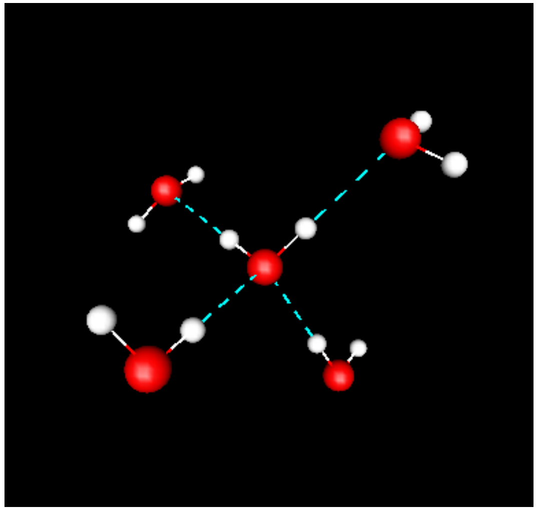
Three Aspects of Computational Physics Research

- *Ab-initio* modeling: realistic simulations
- Physical insight from simulations
- Coarse grained modeling to deepen theoretical insight, go back to simulation

Quantum Mechanics & Water Structure



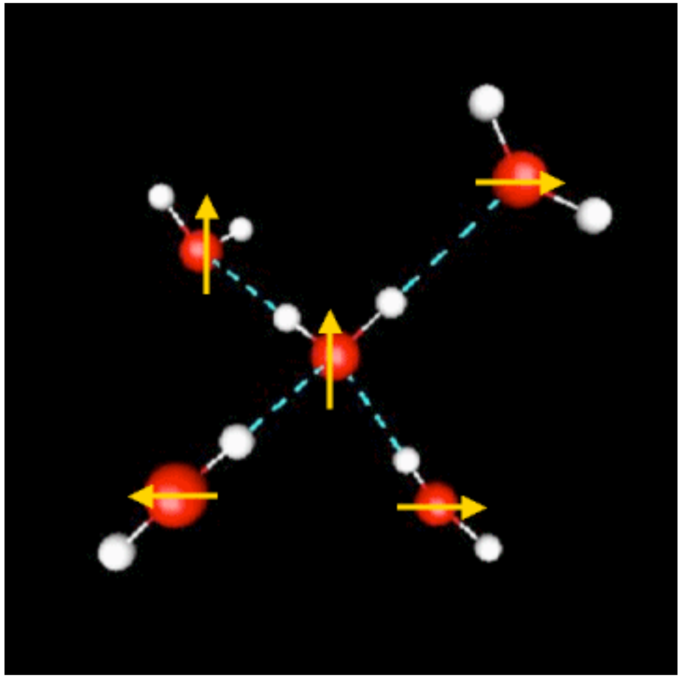


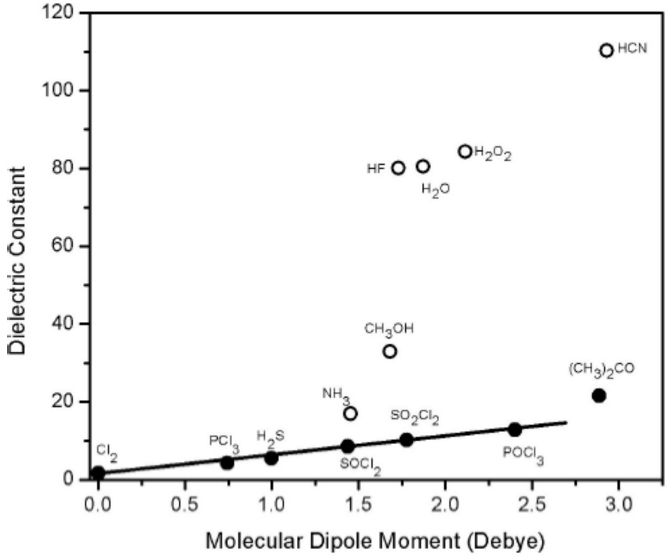
H bonds and electronic structure: H bonds originate from a delicate balance of ionic and covalent effects

Protons are light particles and quantum effects can be important even at room temperature

H bonds are relatively weak (~.2 eV/ bond in water): they break/form easily and thus constitute a sort of universal glue of soft matter

Hydrogen bond cooperativity

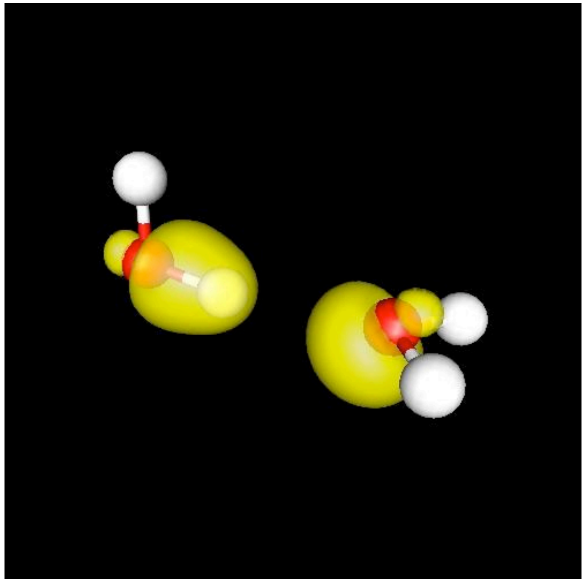




Reproduced from L. Pauling, *General Chemistry* (1970)

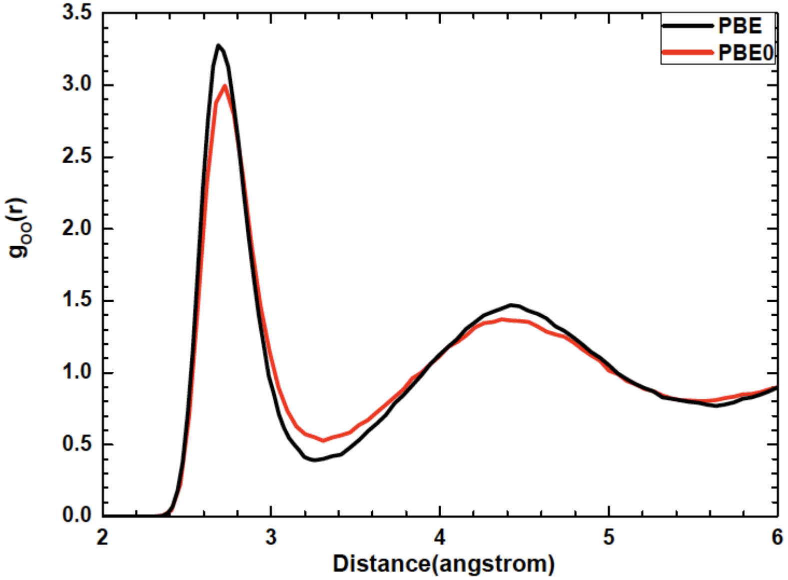
Protons in condensed water phases are **strongly correlated**

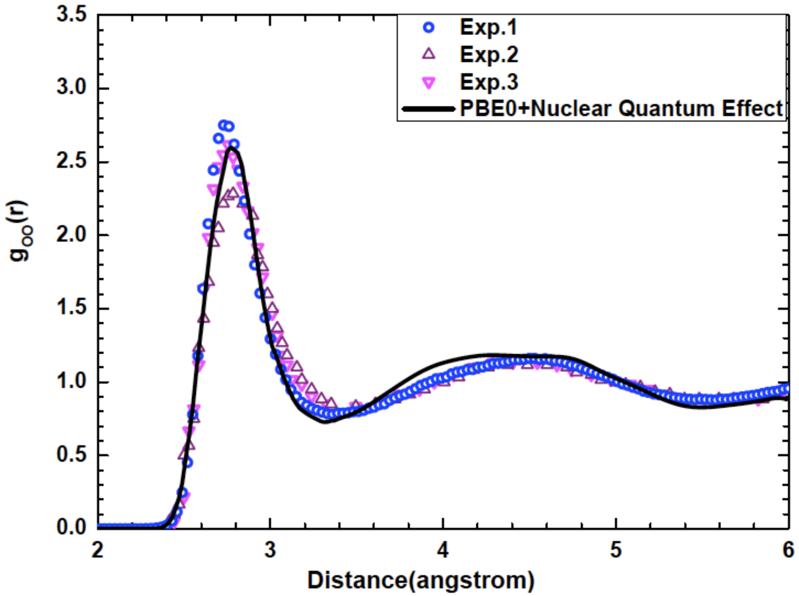
The role of the electrons



The self-interaction error of DFT approximations favors H-bond donation enhancing the H-bond network

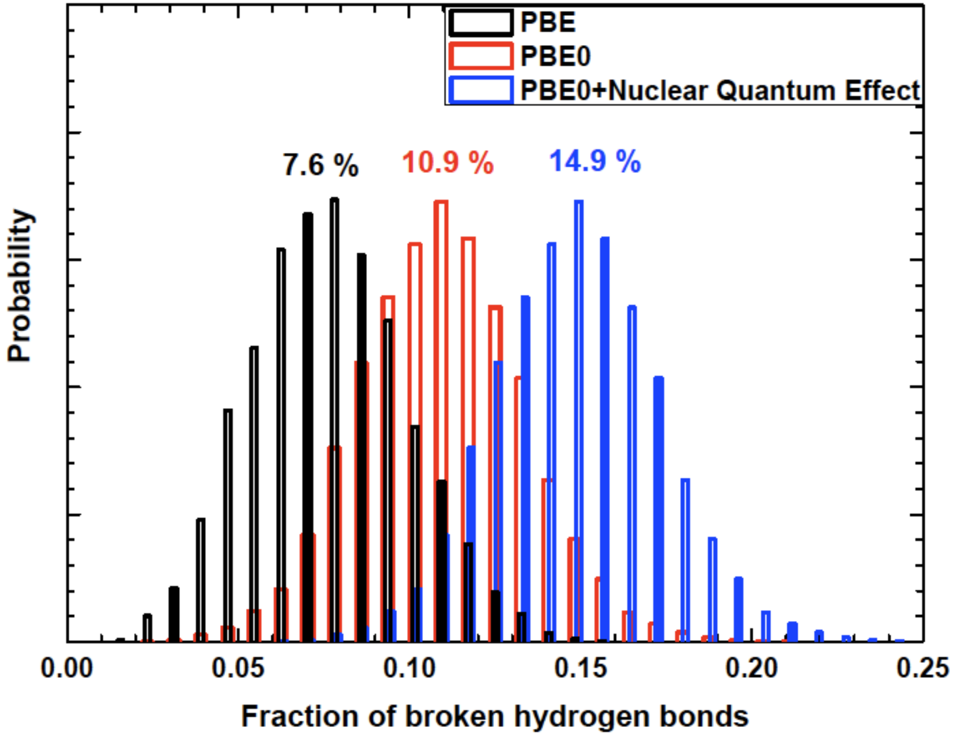
RDFs: DFT approximations and quantum nuclei





Z. Li, X. Wu and RC, (2010); quantum nuclei: J.Morrone and RC, *PRL* (2008)

The distribution of broken bonds



Quantum nuclei in water: isotopic effects in thermodynamic equilibrium properties

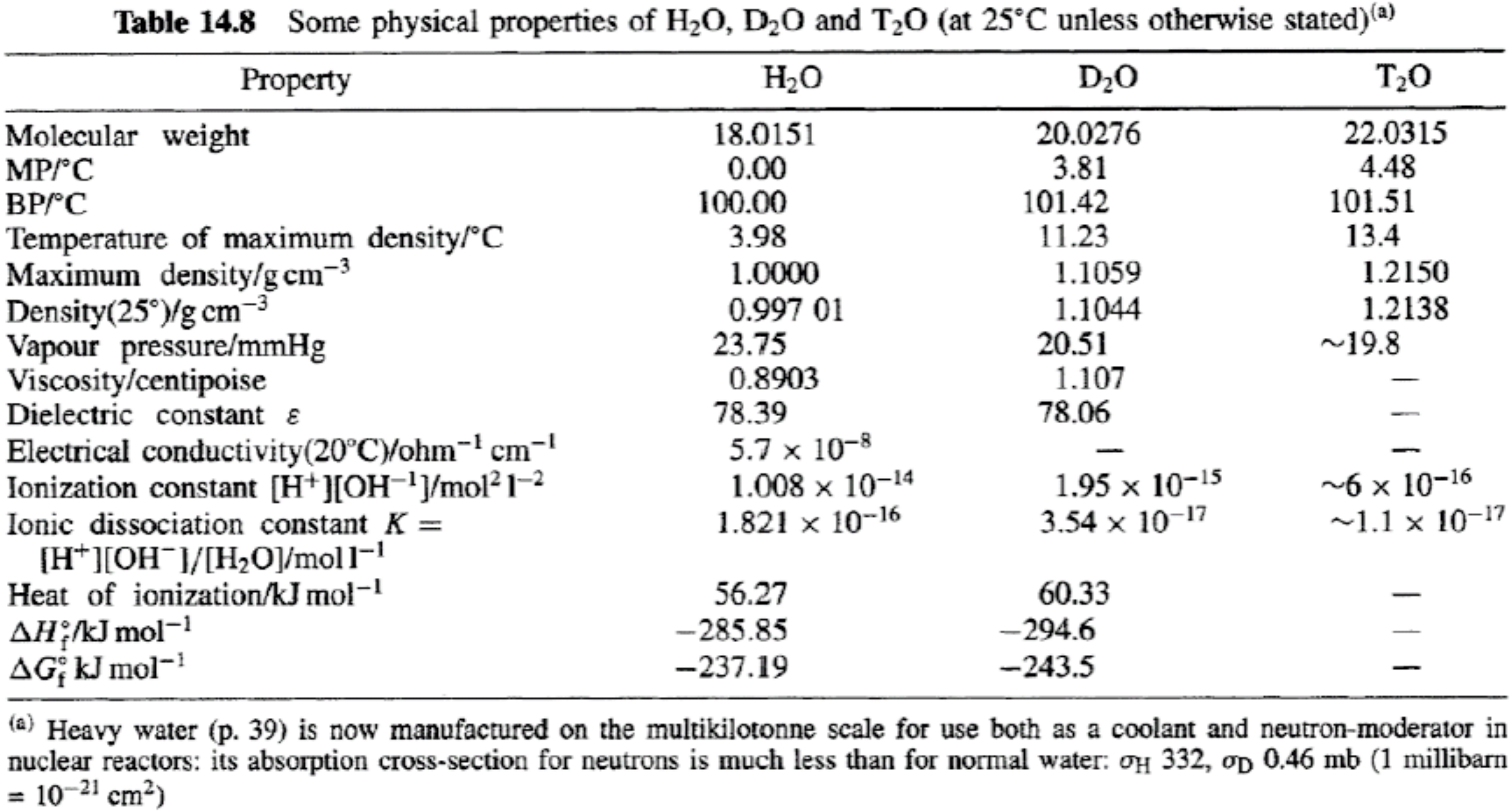
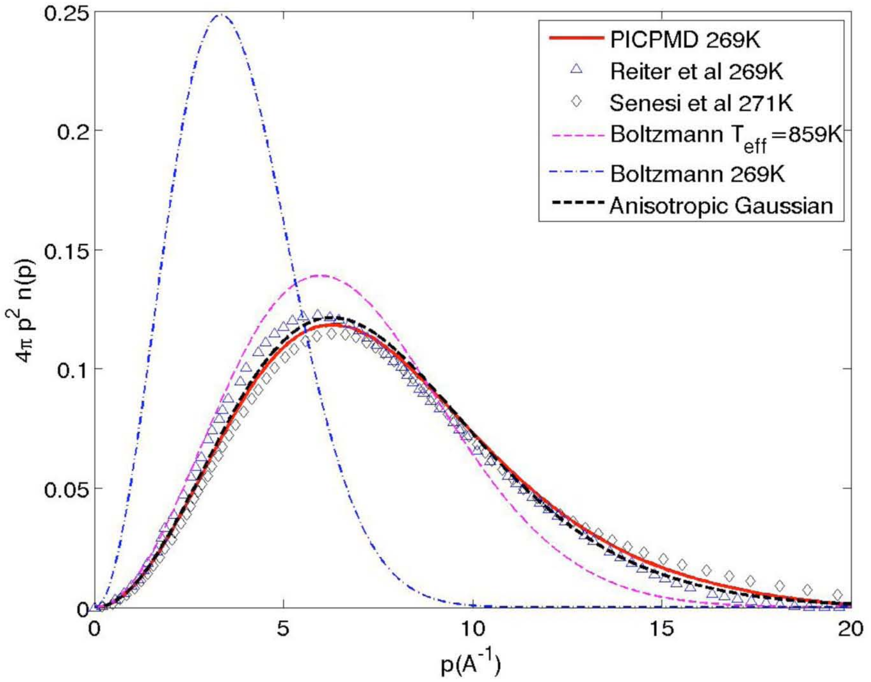


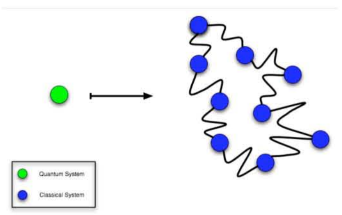
Table 14.8 Some physical properties of H_2O, D_2O and T_2O (at 25°C unless otherwise stated)(a)

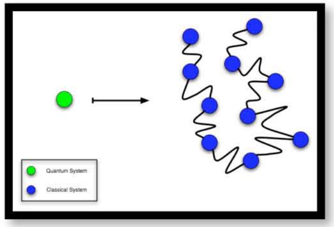
Property	H_2O	D_2O	T_2O
Molecular weight	18.0151	20.0276	22.0315
MP/°C	0.00	3.81	4.48
BP/°C	100.00	101.42	101.51
Temperature of maximum density/°C	3.98	11.23	13.4
Maximum density/g cm^{-3}	1.0000	1.1059	1.2150
Density(25°)/g cm^{-3}	0.997 01	1.1044	1.2138
Vapour pressure/mmHg	23.75	20.51	~19.8
Viscosity/centipoise	0.8903	1.107	—
Dielectric constant ε	78.39	78.06	—
Electrical conductivity(20°C)/ohm^{-1} cm^{-1}	5.7×10^{-8}	—	—
Ionization constant $[H^+][OH^{-1}]/mol^2\,l^{-2}$	1.008×10^{-14}	1.95×10^{-15}	$\sim 6 \times 10^{-16}$
Ionic dissociation constant $K = [H^+][OH^-]/[H_2O]/mol\,l^{-1}$	1.821×10^{-16}	3.54×10^{-17}	$\sim 1.1 \times 10^{-17}$
Heat of ionization/kJ mol^{-1}	56.27	60.33	—
ΔH_f°/kJ mol^{-1}	−285.85	−294.6	—
ΔG_f° kJ mol^{-1}	−237.19	−243.5	—

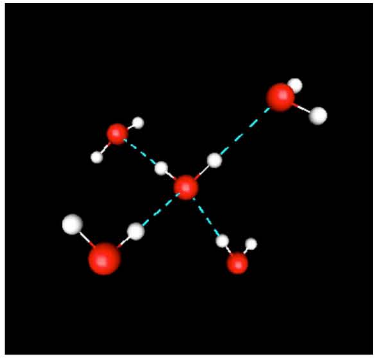
(a) Heavy water (p. 39) is now manufactured on the multikilotonne scale for use both as a coolant and neutron-moderator in nuclear reactors: its absorption cross-section for neutrons is much less than for normal water: σ_H 332, σ_D 0.46 mb (1 millibarn = 10^{-21} cm^2)

The proton momentum distribution in ice; theory and experiment (deep inelastic neutron scattering)









Harmonic isotropic distribution (Landau-Lifchitz):

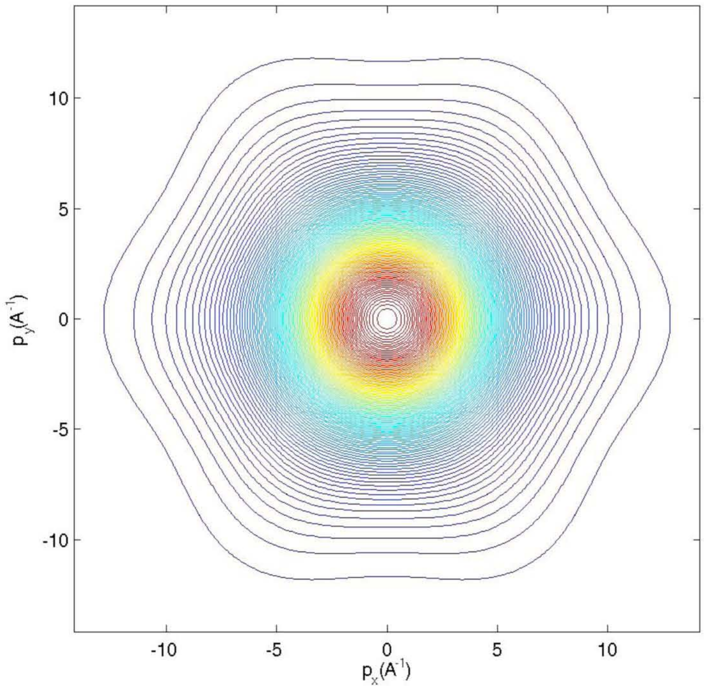
$$T_{i,\mathrm{eff}} \approx T + \frac{\beta^2 \hbar^2}{12 k_{\mathrm{B}} m_i} \langle (\nabla_i U)^2 \rangle_{\mathrm{cl}}$$

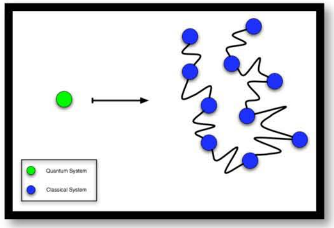
Principal frequencies

$$2624 \quad 1150 \quad 764 \quad \mathrm{cm}^{-1}$$

The potential of mean force is harmonic but anisotropic

Hexagonal protons: the directional “momentum distribution” in the basal plane of ice Ih





$$n(p) = FT\left[\tilde{n}(x)\right]$$

$$\tilde{n}_0(\mathbf{x}) = e^{-\frac{m\mathbf{x}^2}{2\beta\hbar^2}}$$

$$\tilde{n}(x) = \tilde{n}_0(x)\tilde{n}_V(x)$$

From L Lin, J Morrone, RC and M Parrinello (2010)

Question

When distributions of position and momentum of the protons are **both** accessible (from simulation or experiment) **what do they tell us?**

Short Answer

At low T if the protons act as independent particles the two distributions convey the same information;

If the protons do not act as independent particles the two distributions tell us about their correlation

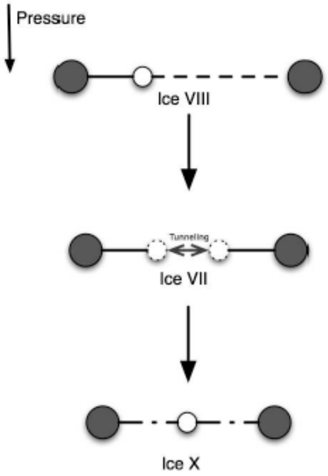
Basic quantum mechanics

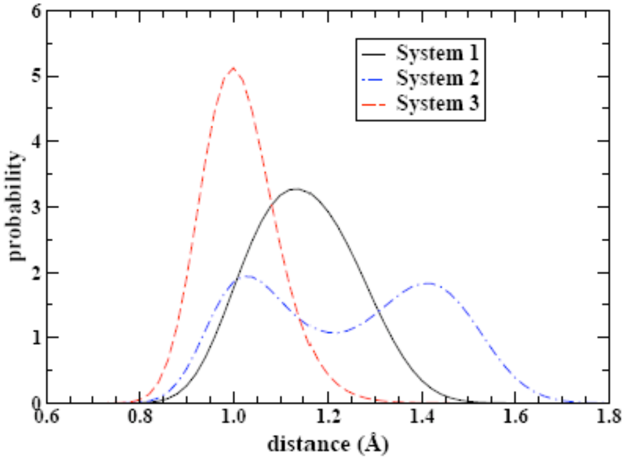
$$\rho_1(x,x') = \psi(x)\psi(x') \qquad \rho(x) = \psi^2(x) \qquad n(p) = \psi^2(p) \qquad \rho_1^2 = \rho$$

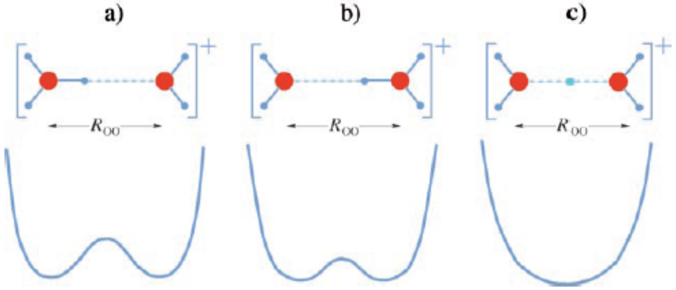
$$\rho_1(x,x') = Z^{-1}\int dx_2, dx_3 ... dx_N \left\langle x, x_2, ..., x_N \middle| \exp(-\beta H) \middle| x', x_2, ..., x_N \right\rangle \qquad \rho_1^2 < \rho_1$$

$$\tilde{n}(x) = \int dr\, dr'\, \delta(r - r' - x)\rho_1(r,r') \qquad n(p) = \left(2\pi\right)^{-3}\int dx \exp(ipx)\tilde{n}(x)$$

H bonds in crystalline ice under under pressure



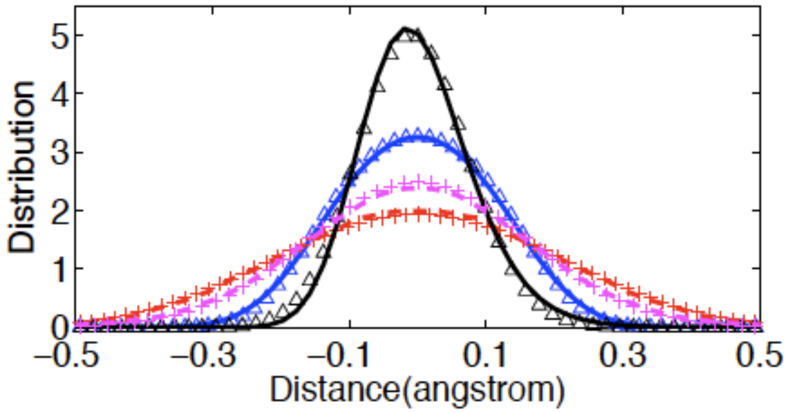




From J.Morrone, L.Lin, R.C., *JCP* (2009)

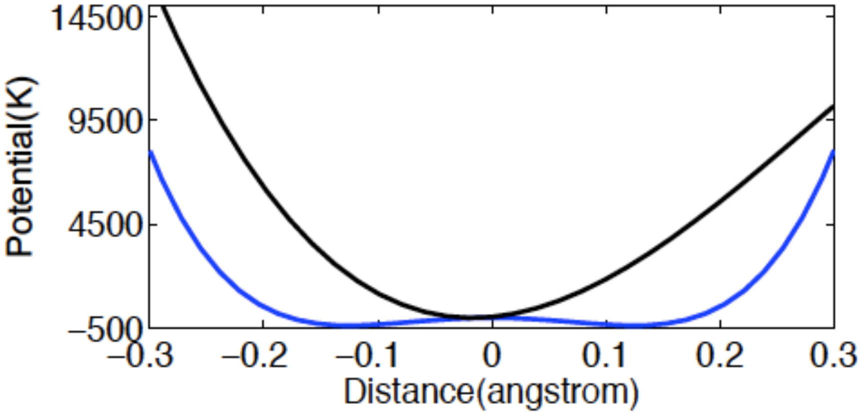
When ice VIII -> ice VII the protons go from an *antiferroelectric* ordered to a *disordered* distribution (order-disorder transition)

Ice VIII and ice X: space and end-to-end distributions with underlying 1-particle potentials



Position (black: ice VIII, blue: ice X)

End-to-end (magenta: ice VIII, red: ice X)

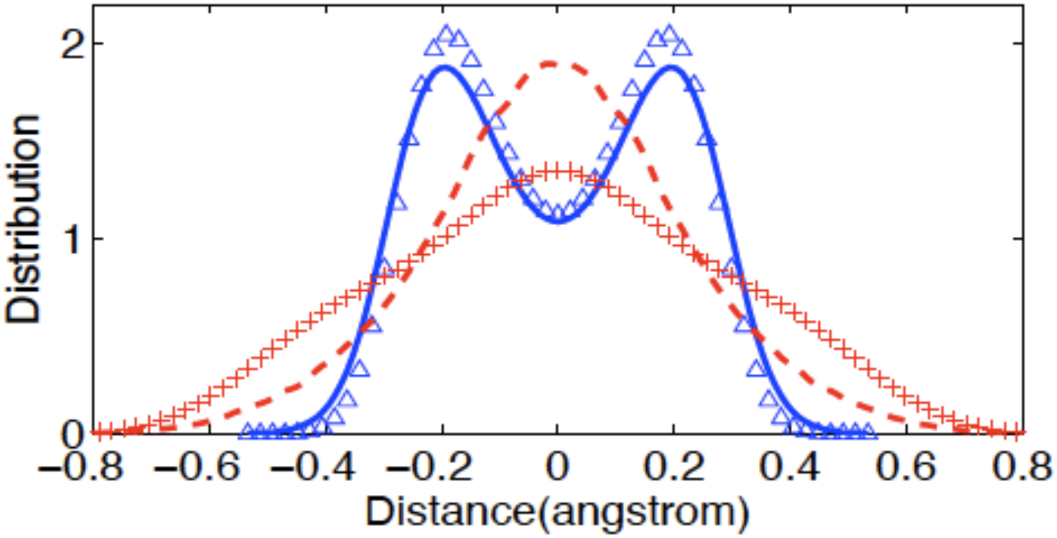


Effective one particle potential along the bond direction:

black: ice VIII, blue: ice X

Anharmonicity is present but the protons behave as independent particles

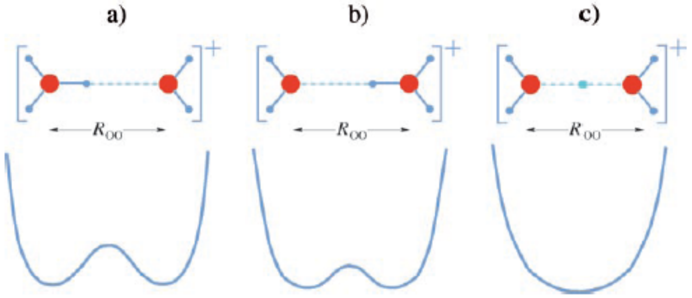
Ice VIII: tunneling protons



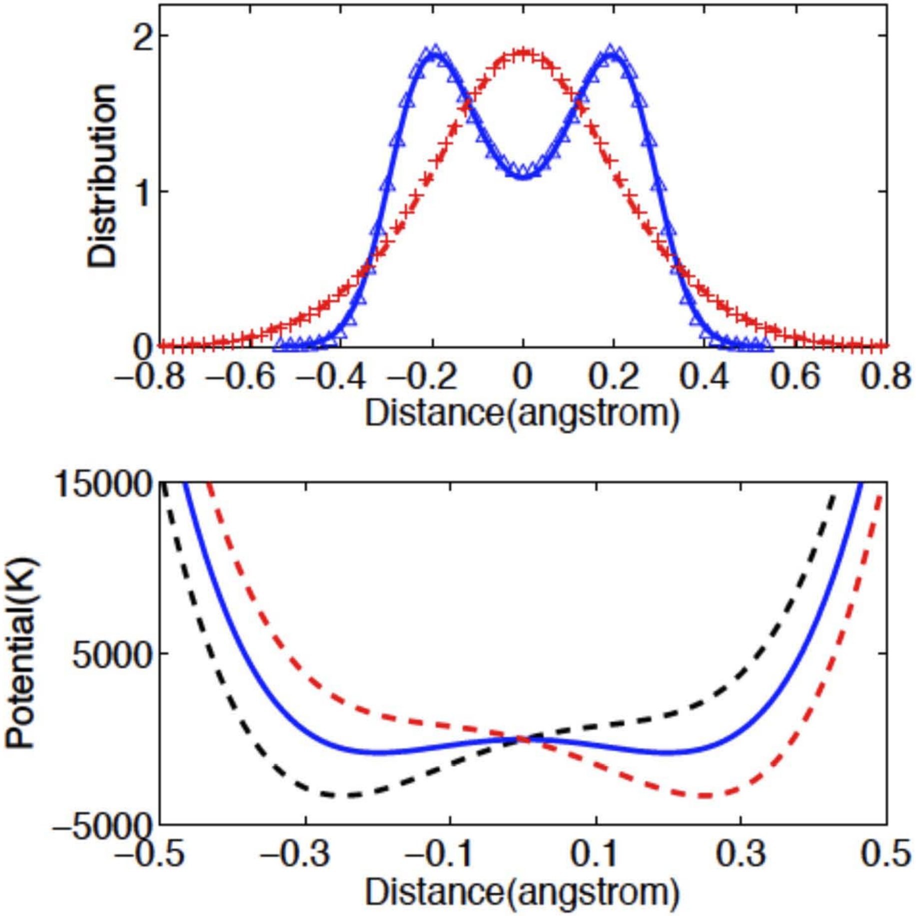
Blue: space distribution (triangles=fit)

Red: end-to-end distribution (crosses=fit)

What’s wrong with this picture?



A model that works: 2 order parameters

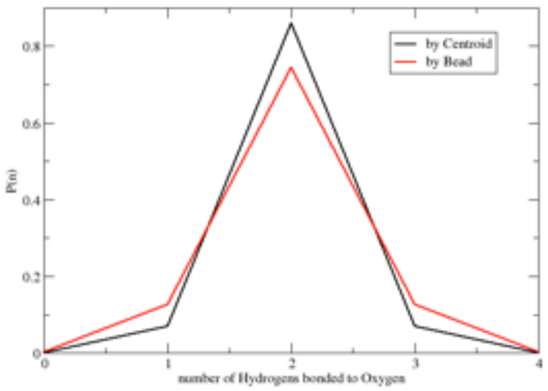


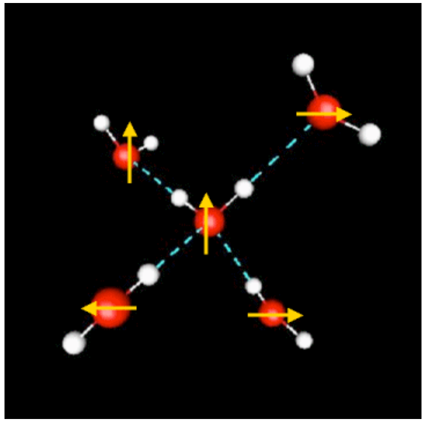
$\psi(x,\mu)$ μ=staggered displacement field

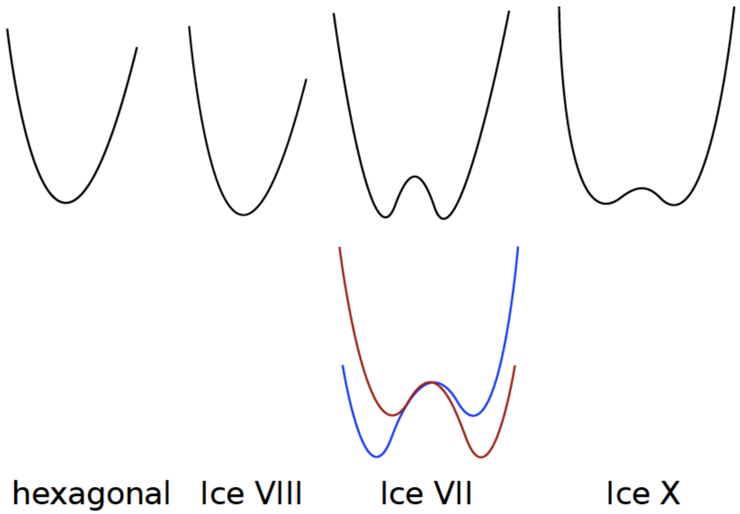
$$\rho_1(x,x') = \sum_\mu \psi(x,\mu)\psi(x',\mu) \qquad \rho_1^2 < \rho_1$$

$$\begin{aligned} V_{+1}(z) &= az^4 + bz^2 + cz, \\ V_0(z) &= az^4 + bz^2, \\ V_{-1}(z) &= az^4 + bz^2 - cz. \end{aligned}$$

Proton correlations arise from ice rules





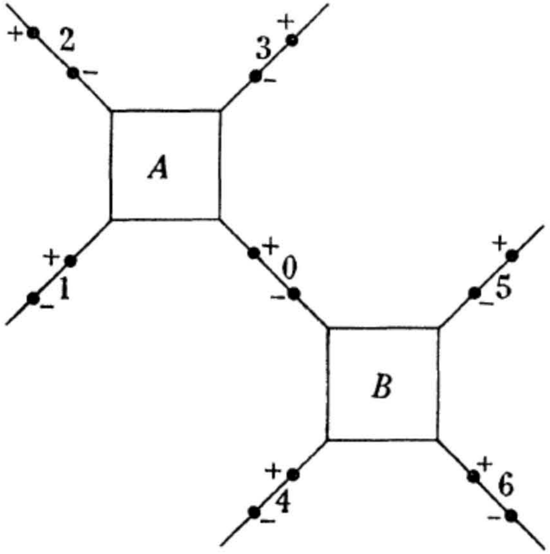


Tunneling probes the ice rules

Quantum effects: some remarks

- In typical H bonded systems where no tunneling occurs the effective potential experienced by the protons is largely harmonic and separability holds confirming the usefulness of simple 1D models
- Quasi-harmonic behavior suggests that semi-classical models should provide an accurate representation of quantum effects (anisotropic zero-point motion). Thus it should be possible to model accurately quantum effects at a lower cost than required by full PI calculations
- In tunneling situations this simple picture fails: more than one order parameter is necessary

A coarse grained model



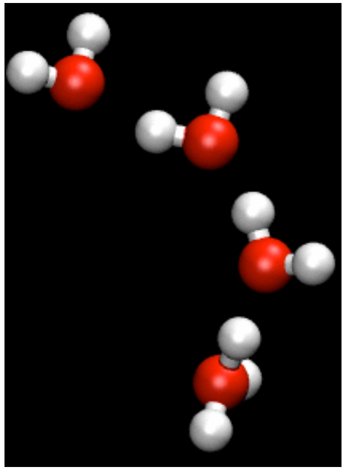
Grindlay and Ter Haar (Proc. R. Soc. Lond. 1959) propose a simple spin model to explain ferroelectric to paralelectric transition in KDP

Model includes Ising spin interaction and a penalty U for creating charged defects - when U $\rightarrow \infty$ it reduces to a model previously introduced by Slater (1941)

Quantum fluctuations may be introduced in such a model by coupling to a transverse magnetic field: this could allow to study more in detail the order-disorder transition in the proton network both in ice and in KDP, overcoming size etc. limitations of *ab-initio* simulations

Does all that matter in everyday life?

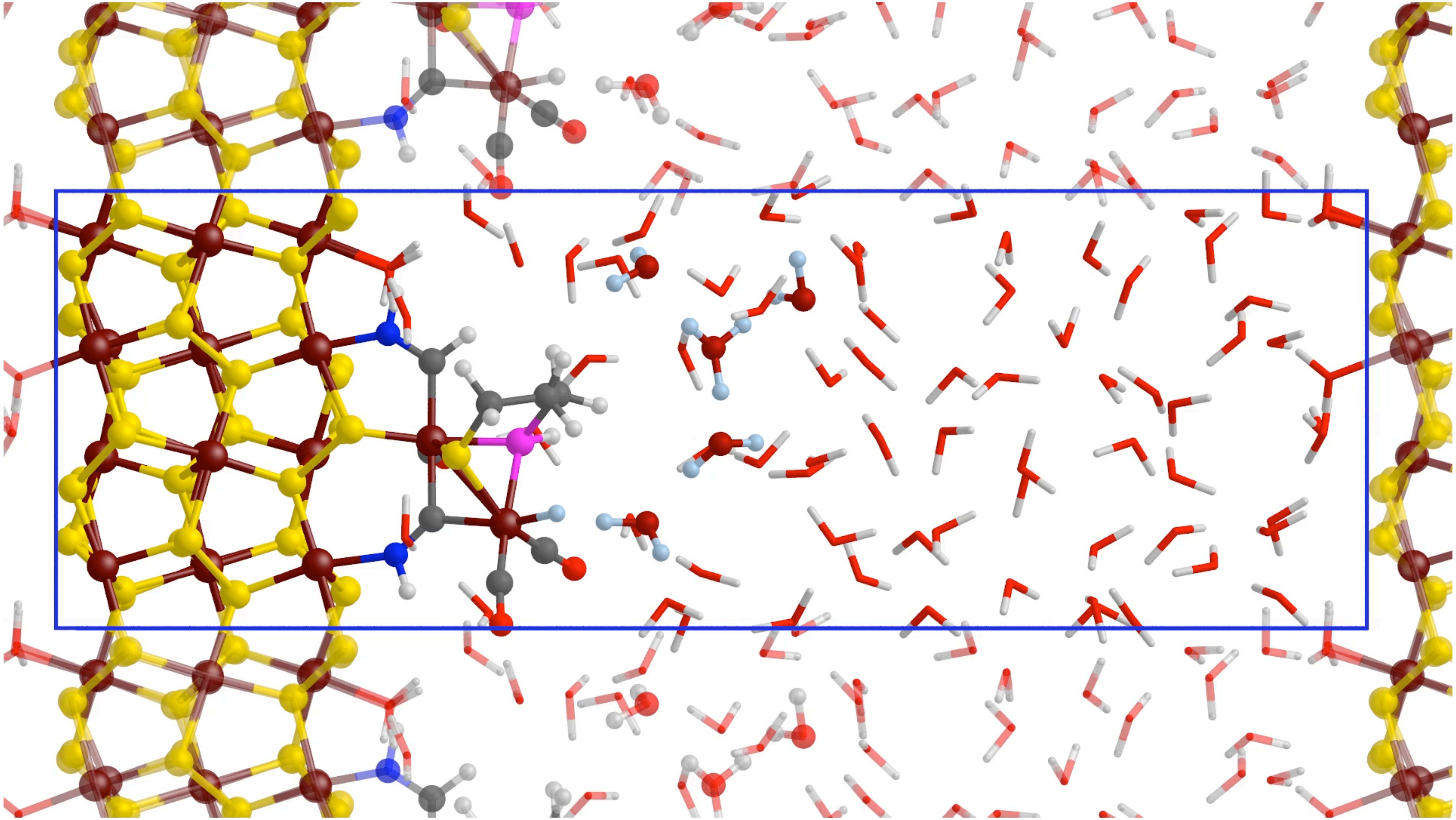
Breaking and forming of H-bonds allows for efficient charge transfer



The Grotthuss mechanism

Ab-initio Molecular Dynamics in action: H_2 production!

(F Zipoli, RC, M Cohen, A Selloni, *JACS* (2010))



Acknowledgements

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