Ab-initio molecular dynamics:
from the basics up to quantum effects

Roberto Car

Princeton University

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Outline

- *Basics*
- *Why MD with a DFT potential energy surface*
- *CP/BO variations*
- *Path-integral AIMD: quantal nuclei*
- *Open issues*

Basic concepts

Molecular Dynamics

$$M_I \ddot{R}_I = -\frac{\partial \Phi(\{R\})}{\partial R_I} \qquad (I = 1, N)$$

- Nuclei are supposed to obey classical mechanics
- Trajectories are integrated numerically on a computer
- Under ergodic evolution temporal averages are equivalent to ensemble averages
- Correlation functions describing *both* static and dynamic equilibrium properties are evaluated as temporal averages (equilibrium statistical mechanics)

$$C_{AB}(t) \equiv \langle A(t)B(0) \rangle = \overline{A(t)B(0)} \approx \frac{1}{\tau}\int_0^\tau A(t+t')B(t')dt'$$

Potential energy surface without empirical fitting

$$E_{GS}\left(\{R\}\right) = Min_{n(r)} E_V\left[n\right] \qquad n(r) = 2\sum_{i=1,N_e/2} \left|\psi_i(r)\right|^2$$

$$E_V\left[\{\psi^*\},\{\psi\}\right] = 2\sum_{i=1,N_e/2}\left\langle\psi_i\right|\frac{-\hbar^2\nabla^2}{2m}\left|\psi_i\right\rangle + \int V(r)n(r)dr + \frac{1}{2}\iint\frac{n(r)n(r')e^2}{\left|r-r'\right|}drdr' + E_{XC}\left[n\right]$$

$$\frac{\delta E_V\left[\{\psi^*\},\{\psi\}\right]}{\delta\psi_i^*(r)} - \varepsilon_i\psi_i(r) = H_{KS}\psi_i(r) - \varepsilon_i\psi_i(r) = 0$$ Kohn-Sham equations

$$\Phi\left(\{R\}\right) = E_{GS}\left(\{R\}\right) + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J e^2}{\left|R_I - R_J\right|}$$

W. Kohn and L.J. Sham, *Phys Rev* **140**, A1133 (1965)

Ab-initio Molecular Dynamics

- *Parameter-free* molecular dynamics: the potential energy surface is obtained from density functional theory
- The price to pay is that the Kohn-Sham equations need to be solved at all the nuclear configurations in a trajectory
- The problem is greatly simplified (conceptually and in practice) by calculating the electronic structure *on the fly* during nuclear dynamics
- The task is achieved with a generalized molecular dynamics scheme in the *extended* space of nuclear $\{R\}$ and electronic $\{\psi\}$ coordinates

R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985)

Why MD with a DFT potential energy surface?

An example: Hydrogen production from a functionalized pyrite surface immersed in acidified water

F. Zipoli, R.C., M.H. Cohen, A. Selloni,*JACS* **132**, 8593 (2010)

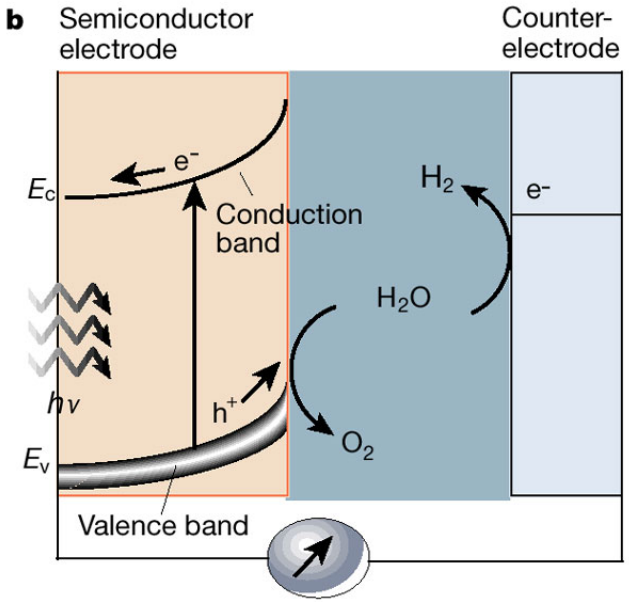
Water splitting in PEC cell

$$H_2O \rightarrow H_2 + \tfrac{1}{2} O_2$$

Oxidation

$H_2O + 2h^+ \rightarrow \frac{1}{2} O_2 + 2H^+$

N-type semiconductor, e.g. TiO_2

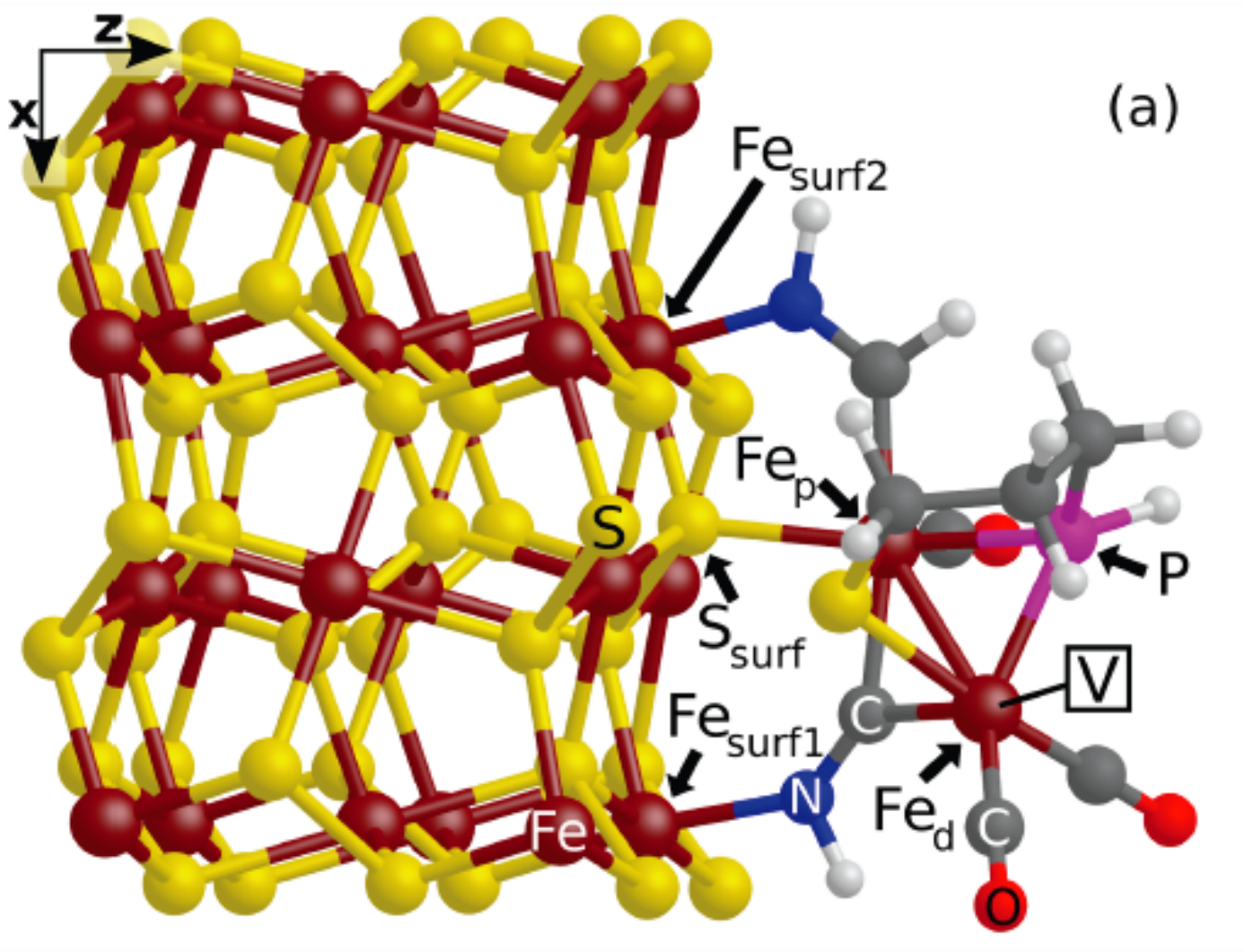


Reduction

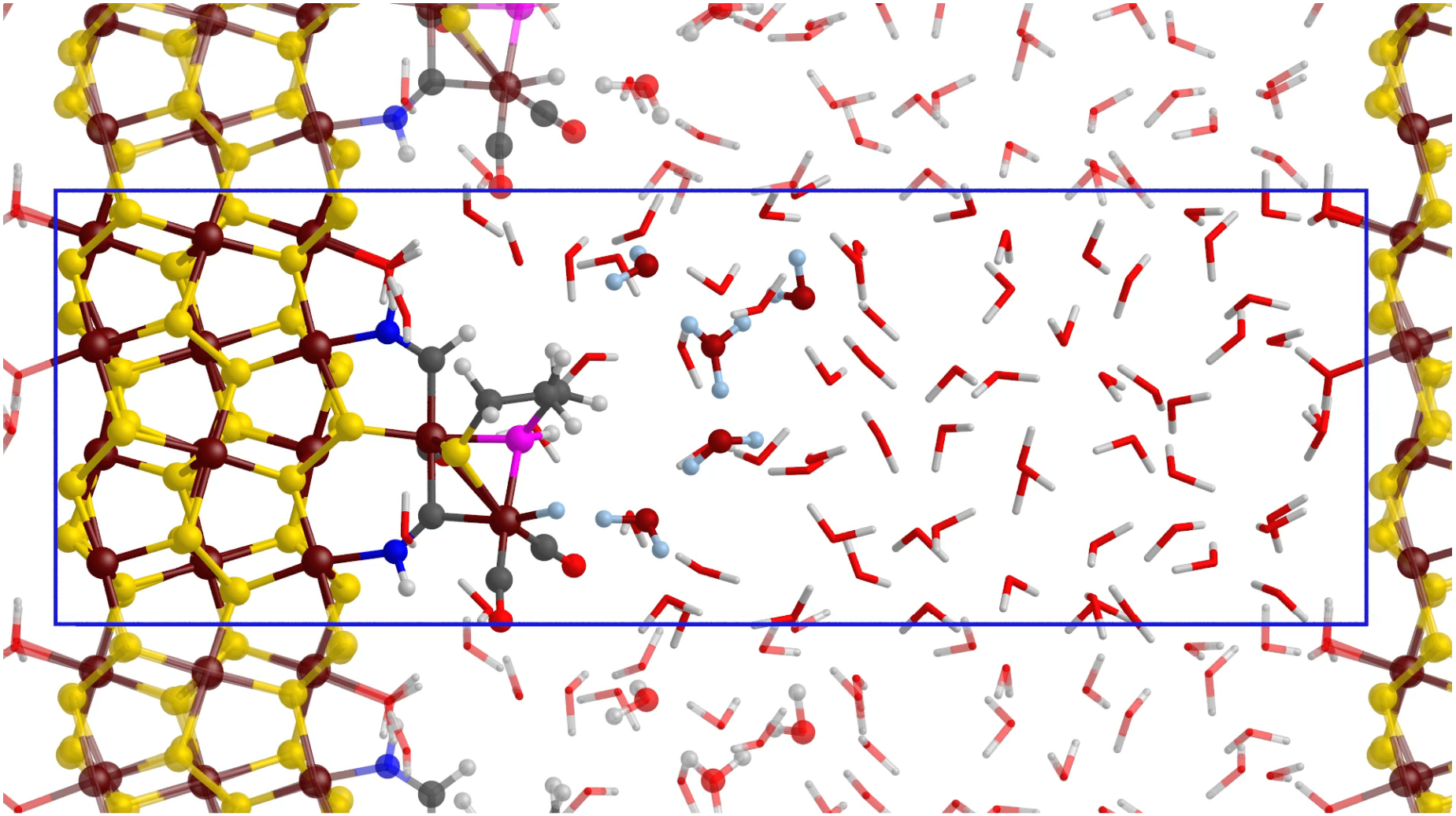
$2H^+ + 2e^- \rightarrow H_2$

Pt typically used as cathode

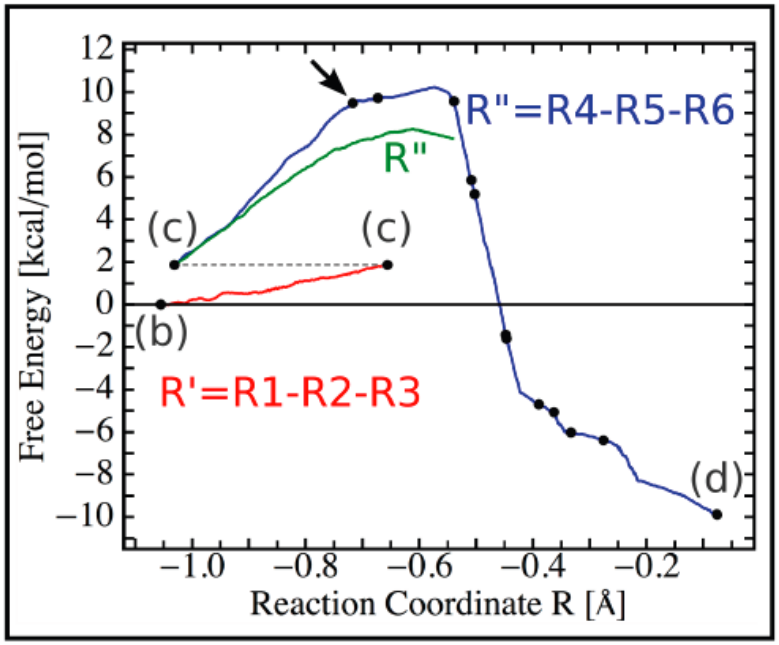
Functionalization of the pyrite surface with a modified $[FeFe]_H$ cluster

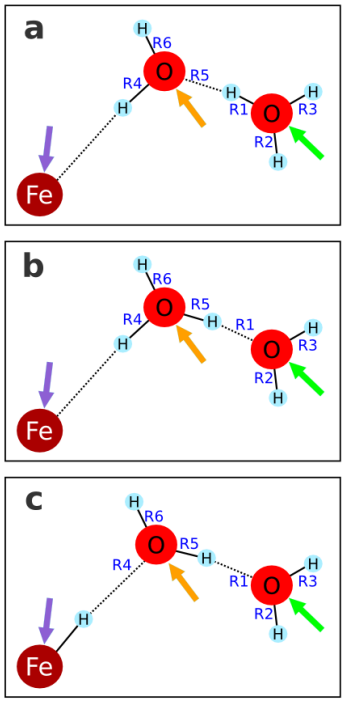


Hydrogen production is easy when the first proton is in place!

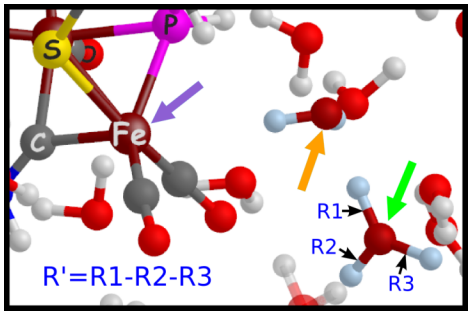


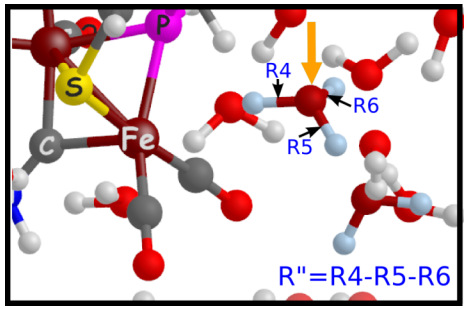
Free energy barrier of 1st protonation





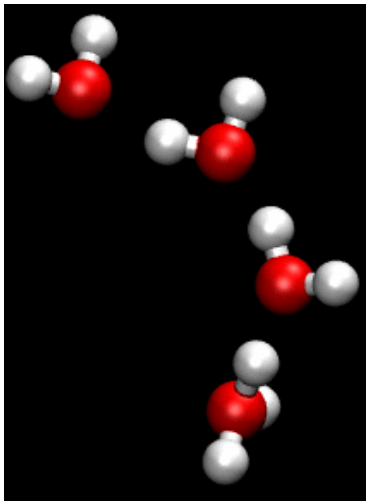
Reaction coordinates:
Leung et al JACS 2009





What did we learn?

a) importance of treating explicitly nuclei and electrons (AIMD)



b) crucial role of the solvating medium: the Grotthuss mechanism

c) rare events are important and require special treatment

CP/BO variations

$$\mathcal{L}_{CP} = \frac{1}{2}\sum_I M_I \dot{R}_I^2 + 2\mu \sum_i \left\langle \dot{\psi}_i \middle| \dot{\psi}_i \right\rangle - \Phi_{CP}\left[\{R\};\{\psi^*\},\{\psi\}\right] + 2\sum_{i,j}\lambda_{ij}\left(\left\langle \psi_j \middle| \psi_i \right\rangle - \delta_{ji}\right)$$

$$\Phi_{CP}\left[\{R\};\{\psi^*\},\{\psi\}\right] = E_{V(\{R\})}\left[\{\psi^*\},\{\psi\}\right] + \frac{1}{2}\sum_{I\neq J}\frac{Z_I^v Z_J^v e^2}{\left|R_I - R_J\right|}$$

$$M_I \ddot{R}_I = -\frac{\partial \Phi_{CP}\left[\{R\};\{\psi^*\},\{\psi\}\right]}{\partial R_I}$$

$$\mu\left|\ddot{\psi}_i\right\rangle = -\frac{\delta \Phi_{CP}\left[\{R\};\{\psi^*\},\{\psi\}\right]}{2\delta\left\langle \psi_i\right|} + \sum_j \left|\psi_j\right\rangle \lambda_{ji} = -H_{KS}\left|\psi_i\right\rangle + \sum_j \left|\psi_j\right\rangle \lambda_{ji}$$

$$\mathcal{H}_{CP} = \mathcal{K} + \mathcal{K}_f + \Phi_{CP} = \frac{1}{2}\sum_I M_I \dot{R}_I^2 + 2\mu\sum_i \left\langle \dot{\psi}_i \middle| \dot{\psi}_i \right\rangle + \Phi_{CP} = \text{const}$$

quasi-BO schemes

$$M\ddot{\mathbf{R}} = \mathbf{F}_{BO}$$

$$\mathbf{F}_{QBO} \approx \mathbf{F}_{BO} - \gamma_E \dot{\mathbf{R}}$$

$$M\ddot{\mathbf{R}} = \mathbf{F}_{QBO} - \gamma\dot{\mathbf{R}} + \zeta \qquad M\ddot{\mathbf{R}} = \mathbf{F}_{BO} - (\gamma_E + \gamma)\dot{\mathbf{R}} + \zeta$$

For Boltzmann sampling: $\left\langle \zeta(0)\zeta(t) \right\rangle = 6(\gamma_E + \gamma)Mk_BT\delta(t)$

γ is arbitrary γ_E fixed by $\left\langle \frac{1}{2}M\dot{\mathbf{R}}^2 \right\rangle = \frac{3}{2}k_BT$

T.D. Kuhne, M. Krack, F.R. Mohamed, M. Parrinello, *PRL* **98**, 066401 (2007)

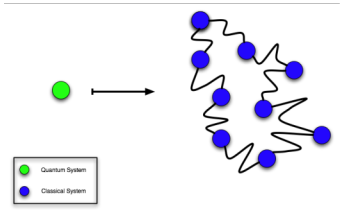
Path Integral AIMD: quantal nuclei

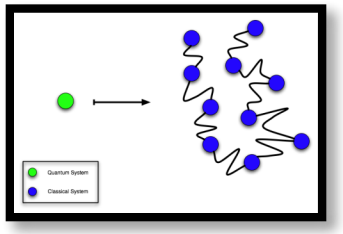
$$\rho_i(\mathbf{r},\mathbf{r}') = \frac{1}{Z}\int \mathrm{d}\mathbf{r}_1 \cdots \mathrm{d}\mathbf{r}_{i-1}\,\mathrm{d}\mathbf{r}_{i+1}\cdots \mathrm{d}\mathbf{r}_M \left\langle \mathbf{R}\left| e^{-\beta\hat{H}} \right| \mathbf{R}' \right\rangle$$

$$\rho_i(\mathbf{r},\mathbf{r}') = \frac{1}{Z}\int_{\mathbf{R}(0)=\mathbf{R},\mathbf{R}(\beta\hbar)=\mathbf{R}'} \mathfrak{D}\mathbf{R}(\tau) e^{-\frac{1}{\hbar}\int_0^{\beta\hbar} d\tau\, \frac{m\dot{\mathbf{R}}^2(\tau)}{2} + V(\mathbf{R}(\tau))}$$

$$Z = \int_{\mathbf{R}(0)=\mathbf{R},\mathbf{R}(\beta\hbar)=\mathbf{R}} \mathfrak{D}\mathbf{R}(\tau) e^{-\frac{1}{\hbar}\int_0^{\beta\hbar} d\tau\, \frac{m\dot{\mathbf{R}}^2(\tau)}{2} + V(\mathbf{R}(\tau))}$$

$$\mathbf{R} = (\mathbf{r}_1,\ldots,\mathbf{r}_{i-1},\mathbf{r},\mathbf{r}_{i+1},\ldots,\mathbf{r}_M),$$
$$\mathbf{R}' = (\mathbf{r}_1,\ldots,\mathbf{r}_{i-1},\mathbf{r}',\mathbf{r}_{i+1},\ldots,\mathbf{r}_M)$$

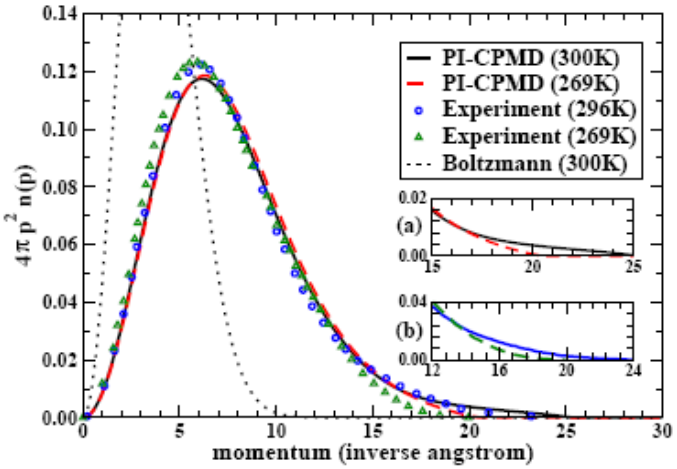




Feynman paths: *closed* and *open*

Protons are light nuclei: how important are quantum effects in their behavior?

Quantal protons in water and ice



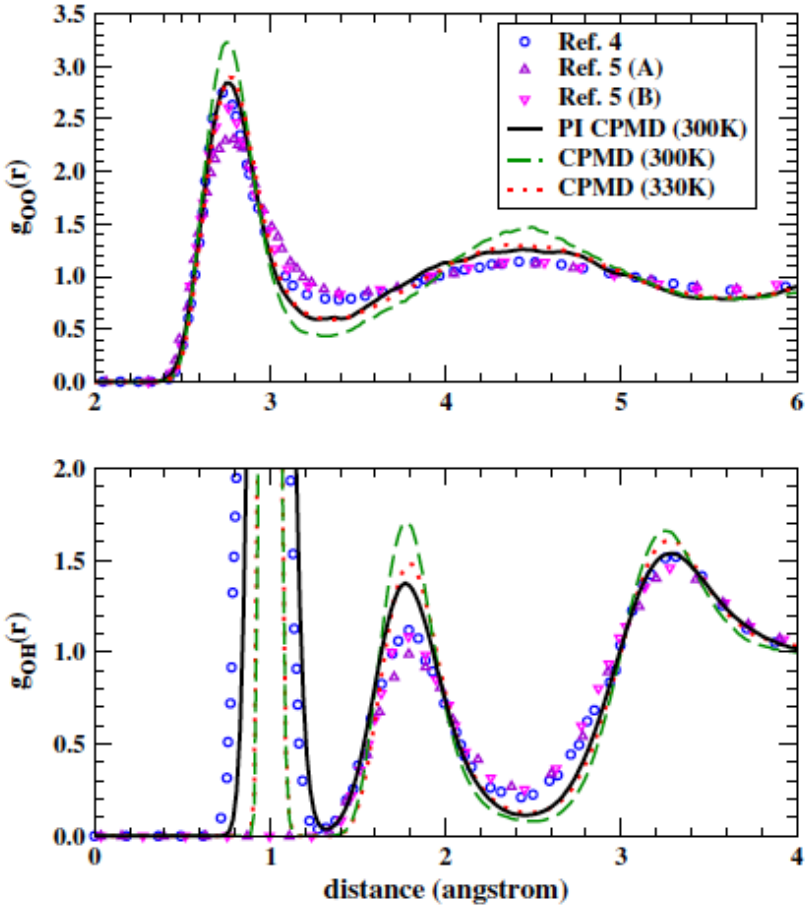
The momentum distribution differs considerably from the classical equilibrium distribution

Path integral simulations: J. Morrone, RC, *PRL* 2008

Experiment: deep inelastic neutron scattering (DINS)

Quantum delocalization of the nuclei affects structural and spectroscopic properties

Quantum (path integral) ab-initio simulations improve substantially the structure



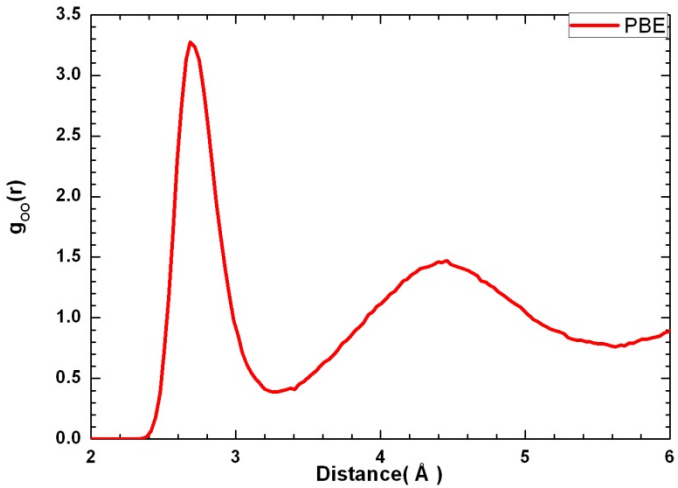
From J. Morrone and RC, *Phys. Rev. Lett.* **101**, 107801 (2008)

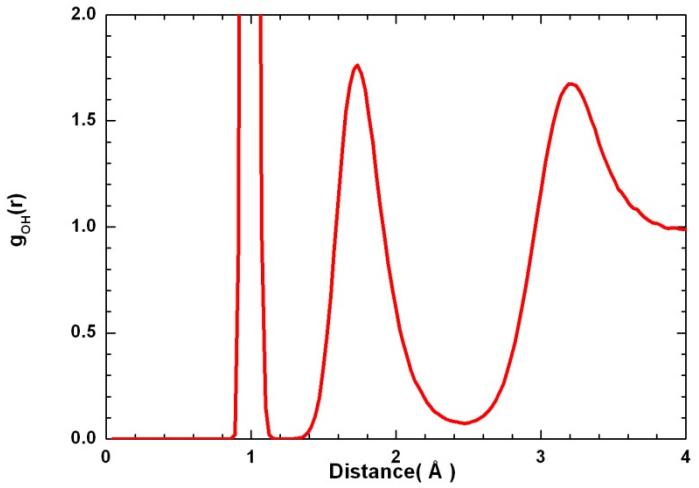
Experiment: Joint structure refinement (x-ray and neutron) A. Soper, *J. Phys.: Condens. Matter* **19**, 335206 (2007)

... but systematic deviations remain.

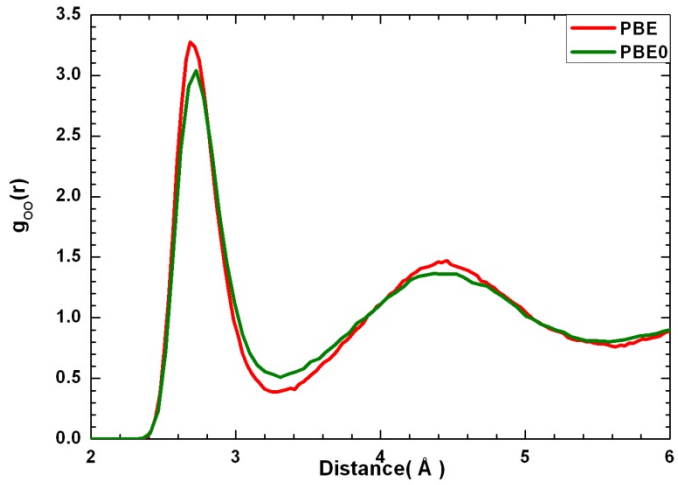
Quantum effect seems to be roughly mimicked by an increase of T

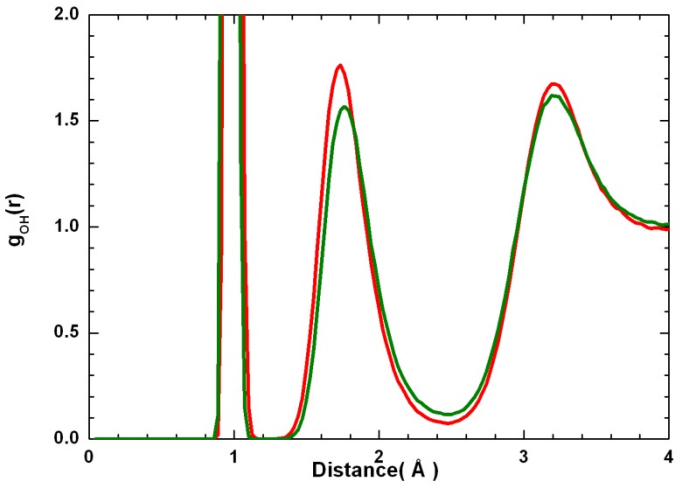
Effect of functional approximations and quantum nuclei





Effect of functional approximations and quantum nuclei





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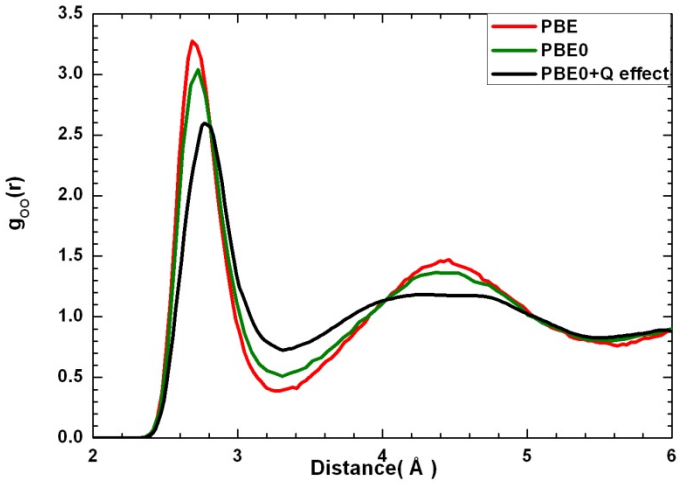

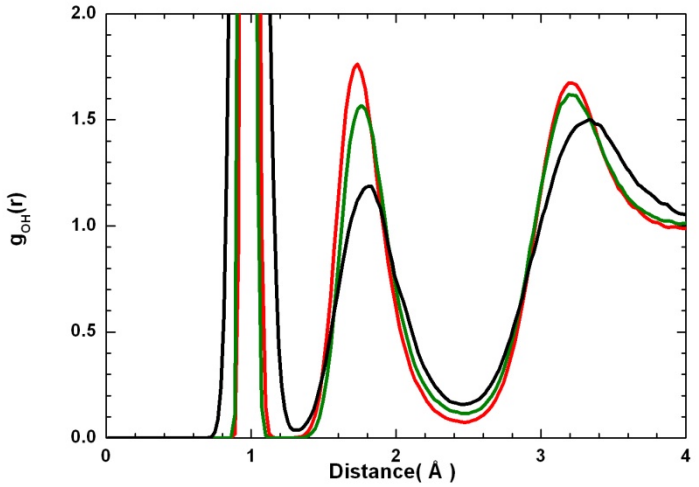

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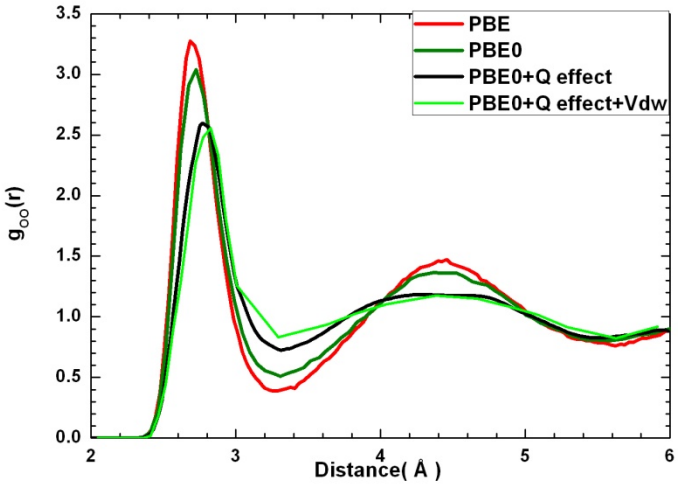
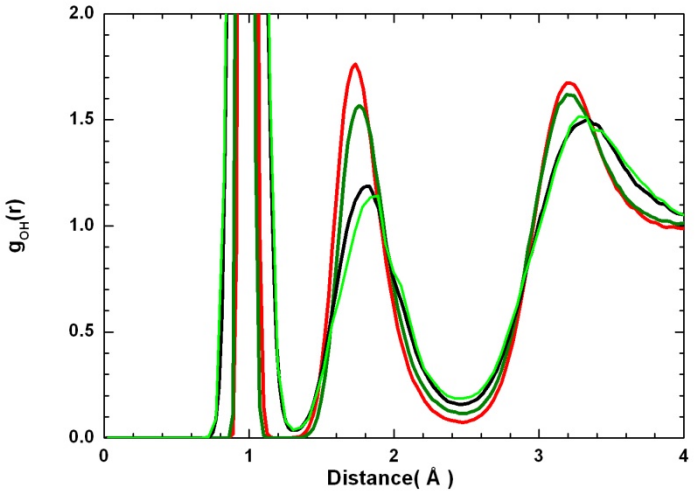
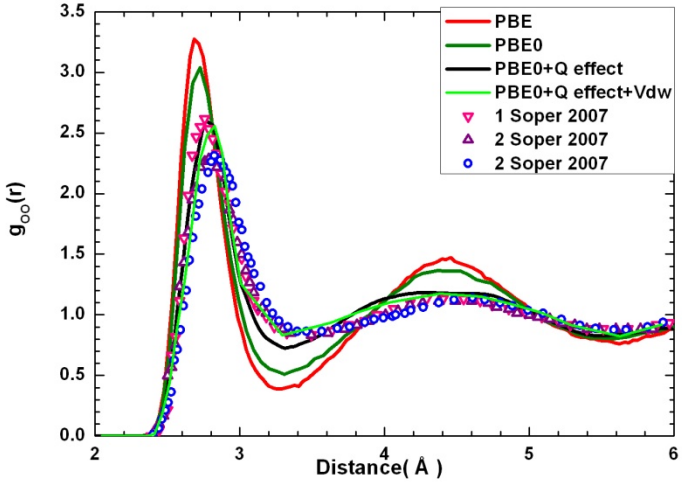
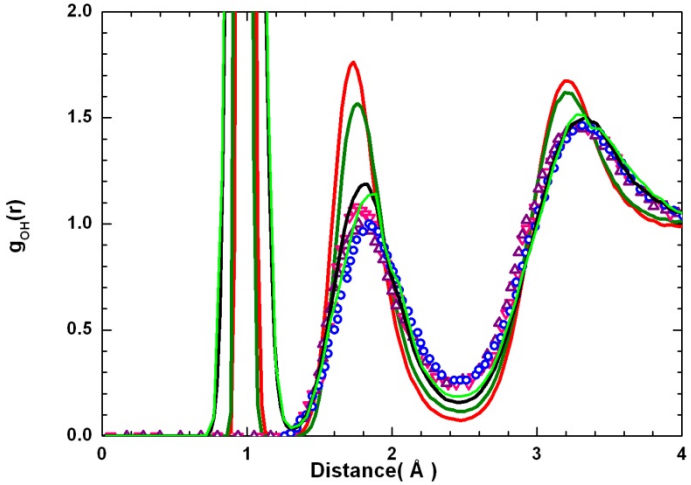




Functional approximations and experiment





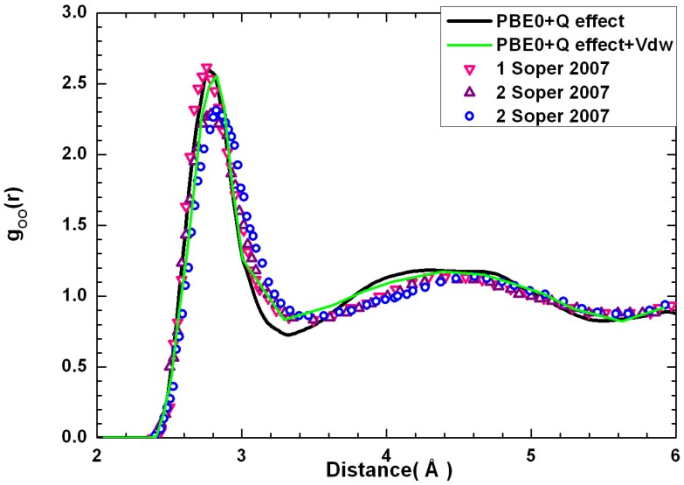
Soper 2007: Joint structure refinement of X-ray and neutron diffraction data from:

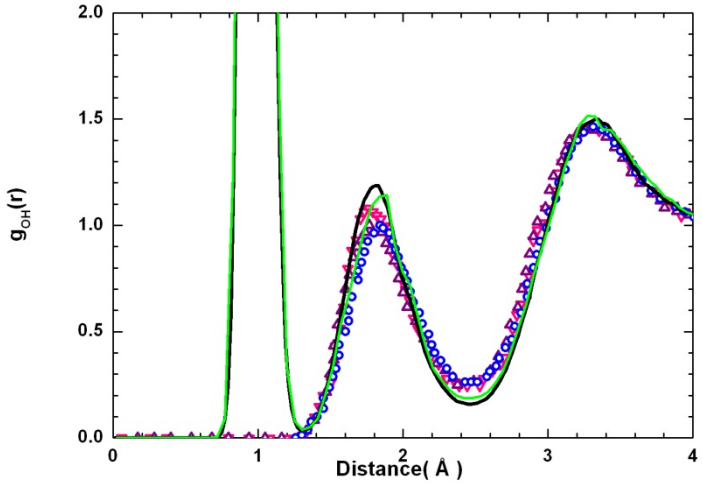
1. Hart et al, PRL 2005 ; 2. Hura et al, PCCP 2003 ; 3. Narten-Levy, JCP 1971

VdW use Tkatchenko-Scheffler theory, *PRL* 2009

In the end comparison to experiment is good

From Z. Li, R. Di Stasio, X. Wu, and RC (preliminary results)

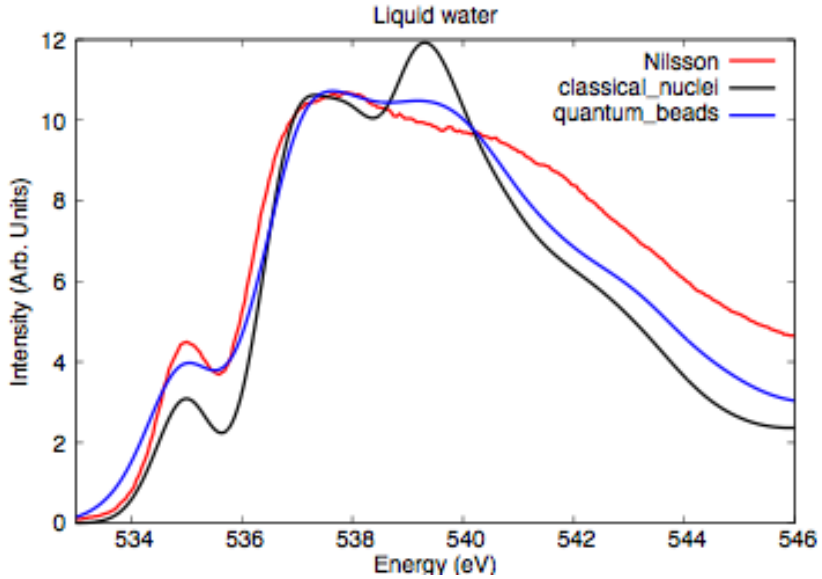




The approach is not entirely consistent: quantum corrections have been calculated at the BLYP level of DFT, VdW corrections to the PBE0 energy have been used to reweigh the g(r)'s, a procedure that is affected by large statistical errors.

However, fully consistent calculations should be available soon. Based on the current results a promising outcome should be expected.

Effect of quantum nuclei on XAS spectra: liquid water at 300K



Expt (Nilsson): Wernet et al., *Science* (2004)

Theory: L. Kong, X. Wu, R.C., (work in progress, 2011)

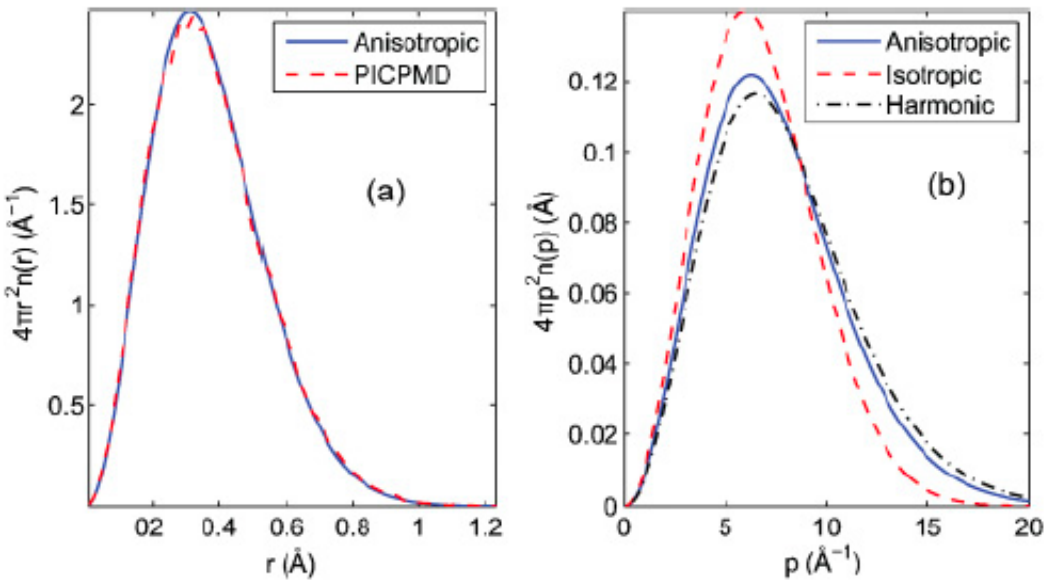
COHSEX self-energy expression as in

W. Chen, X. Wu, R.C., *Phys. Rev. Lett.* (2010)

nuclear configurations from J. Morrone, R.C., *Phys. Rev. Lett. (2008)*

The residual deviation from experiment at high energy calls for improvements in the self-energy approximation

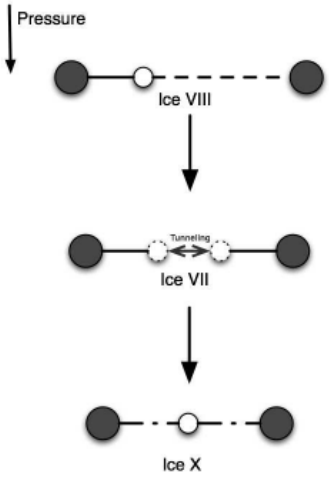
Zero-point motion in ice Ih



L. Lin, J. Morrone, RC, M. Parrinello, *PRB 2011*

Quasi-harmonic model fits the data well: **zero-point motion is large but still semi-classical in nature**

New physics occurs when tunnel driven phase transitions happen



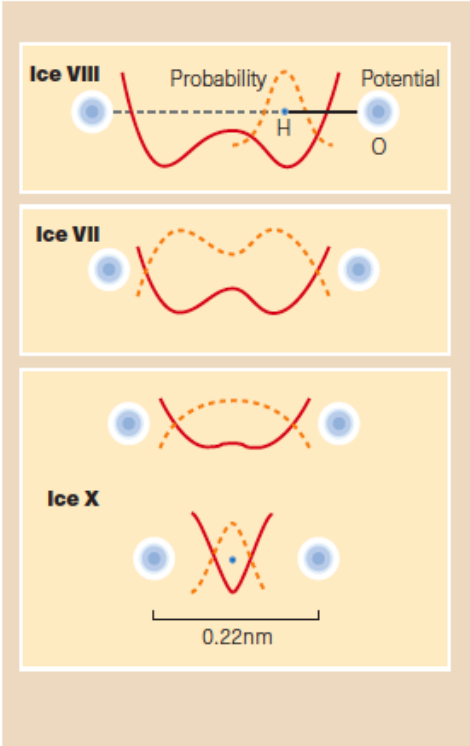


Figure 2 **Proton density in ice under pressure. As the oxygen atoms are forced together, the potential energy changes from a double to a single well; but a new simulation shows that a form of ice with the proton midway between the oxygens occurs even before that happens.**

Cartoon from J. Texeira, *Nature N&V* commenting

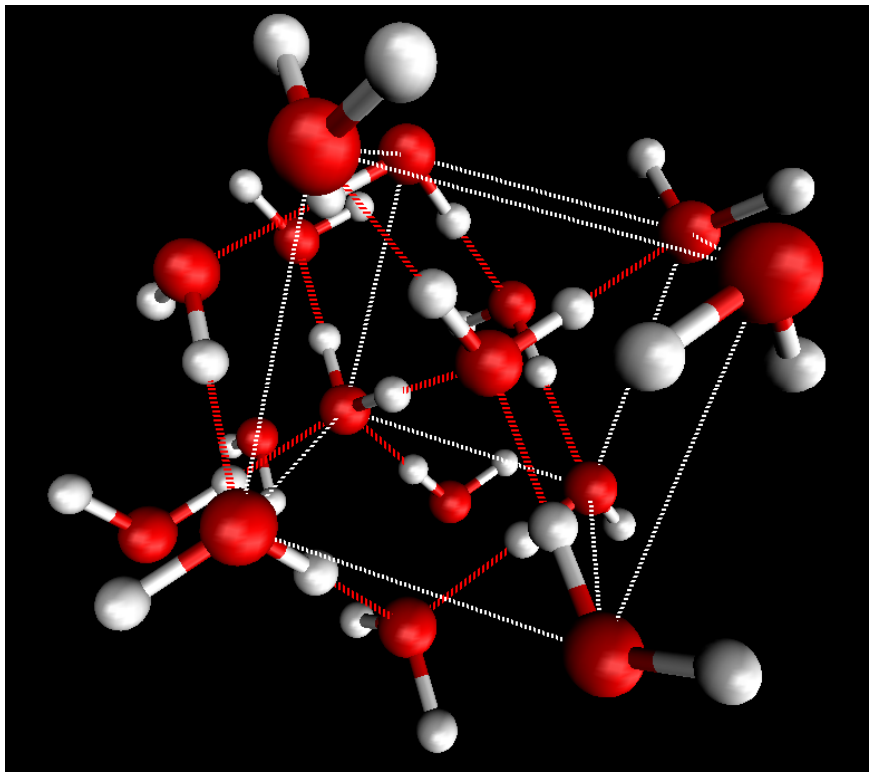
Benoit, Marx, and Parrinello, *Nature* 1998

Picture is suggestive but rooted in Mean Field Theory

ice VIII -> ice VII: *antiferroelectric* to *disordered* proton sublattice
Another transition driven by quantum fluctuations occurs in KDP: *ferroelectric* to *disordered*

Reduced longitudinal model

Motions along and orthogonal to the bond are *uncorrelated* in all ice structures considered in this study (Ih, VIII, VII, X)



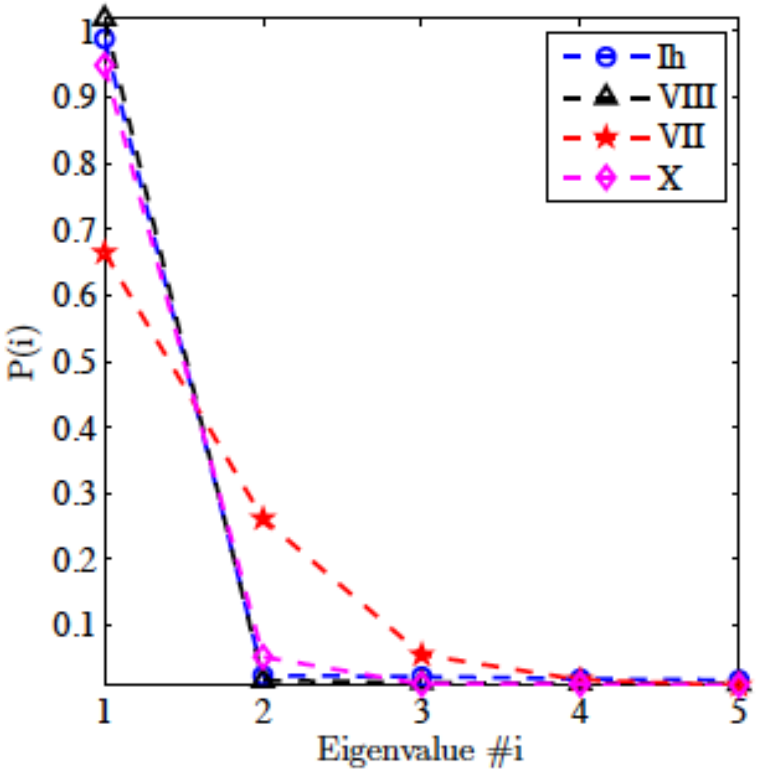
$$\rho(\mathbf{r},\mathbf{r}') \sim \rho(\bar{x},x')\rho(\mathbf{b},\mathbf{b}')$$

$$\rho(x,x')$$

The longitudinal density matrix contains the interesting physics

L. Lin, J.A. Morrone, RC (2011)

Entangled protons



From Lin, Morrone, RC (preprint 2011)

$$\rho = \sum_i |\phi(i)\rangle P(i) \langle \phi(i)|$$

Von Neumann entanglement entropy

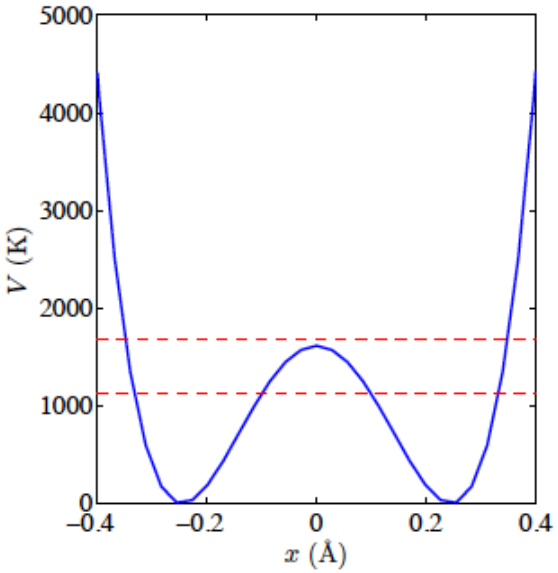
$$S = -\mathrm{Tr}[\rho \log \rho]$$

S is essentially 0 in ice Ih and VIII

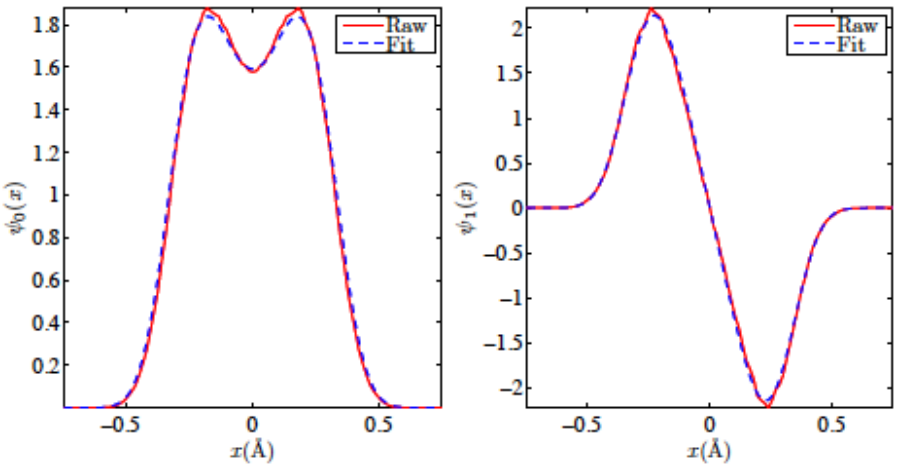
$S = 0.60$ in ice VII and $S = 0.20$ in ice X

What is the origin of the entanglement? Why does it occur in ice VII and X?

Spectrum of the longitudinal density matrix



Effective potential and tunnel splitting

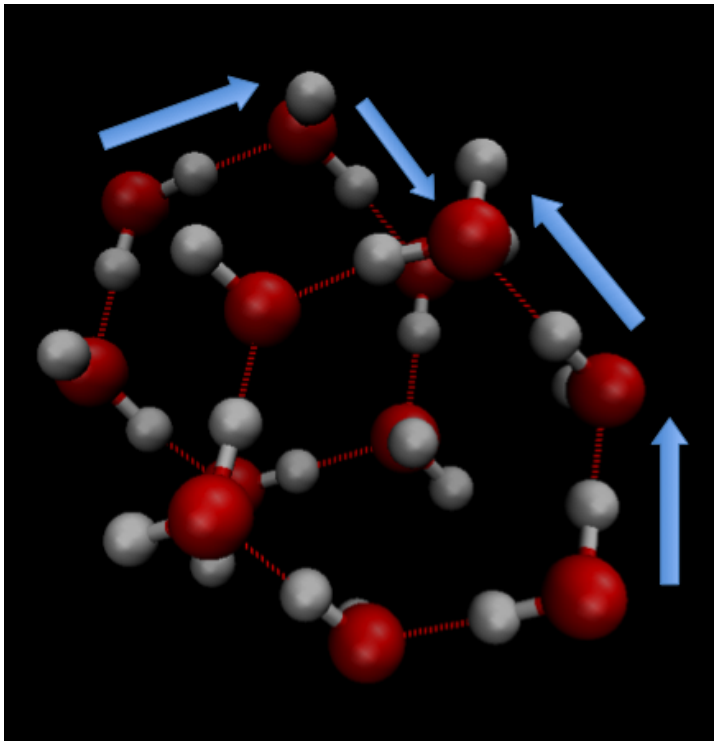


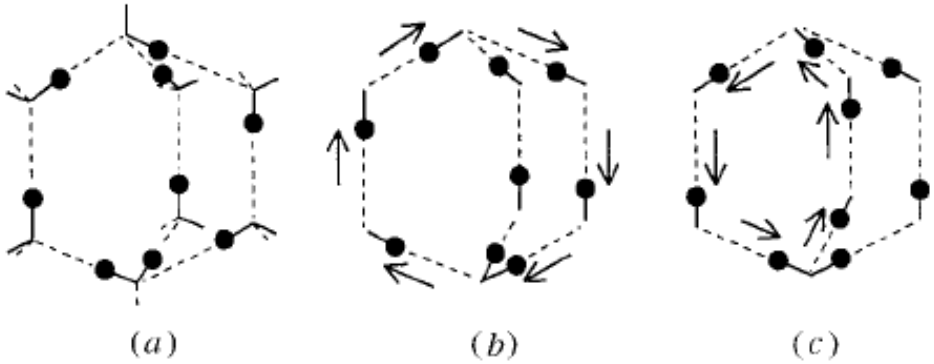
The first 2 eigenstates in ice VII: these are the **natural orbitals** of the proton

Tunnel splitting $547K$ *T* of simulation $100K$

Entanglement is due to ***correlations***

Ring tunneling does not violate ice rules

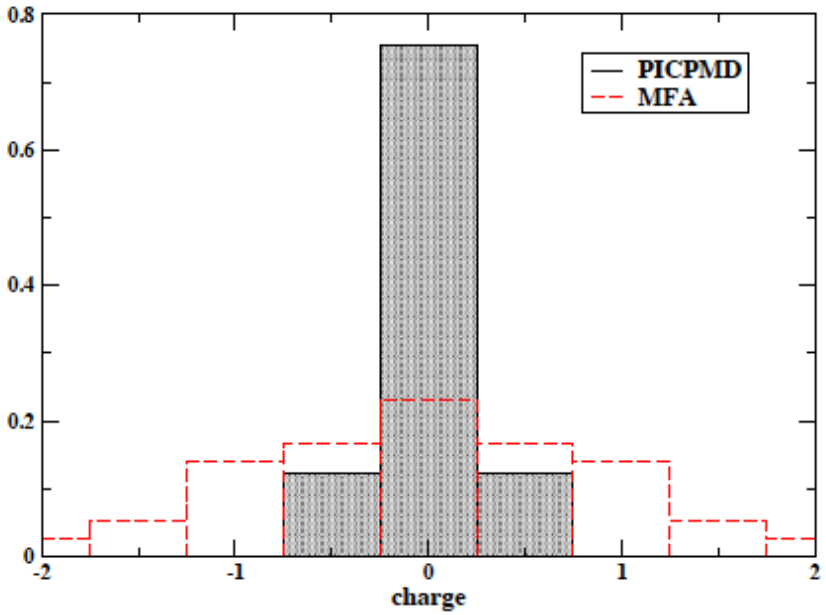




Mapping to a spin model: spin 1/2 or spin 1?

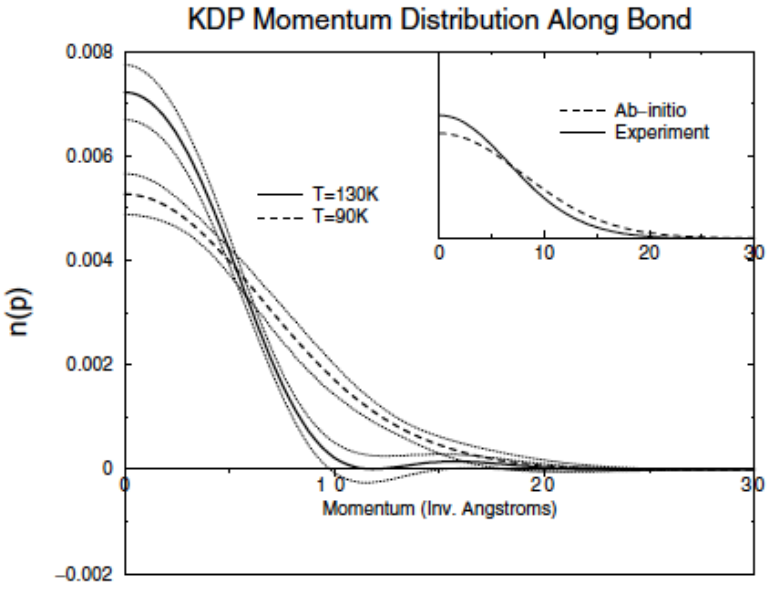
A quantum spin liquid

Simulation versus Mean Field



The distribution of local charge fluctuations in a 3-state (spin 1) model with N,C, and F states

MFA leads to a ionization catastrophe that severely violates local charge neutrality



(from Reiter, Mayers, Platzman, *PRL (*2002)

Is there a **node** in the proton momentum distribution of KDP in the paraeletric phase?

Ring tunneling does occur but is not the only process as some ionized configurations do occur

Consider, however: small cell size, T of the simulation, chosen lattice parameter (applied pressure)

Open issues

- 1-particle density matrix vs density: a possible way beyond DFT

- Quantum dynamics vs equilibrium statistical sampling

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