Electronic Structure and Molecular Dynamics in Disordered Water Phases at Low and High Pressure

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Water and Water Systems

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The challenge of ab-initio water

- Molecular interactions in condensed water phases depend on a delicate balance of electronic effects (cooperative polarization, dispersion interactions) that are difficult to model with standard DFT approximations
- Quantum corrections to the nuclear dynamics cannot be ignored even at room temperature and beyond

Background

- Ab-initio molecular dynamics
- Density functionals
- Maximally Localized Wannier Functions
- Path Integrals

Potential energy surface without empirical fitting

$$E_{GS}(\{R\}) = Min_{n(r)}E_{V}[n] \qquad n(r) = 2\sum_{i=1,N_{e}/2} |\psi_{i}(r)|^{2}$$
$$E_{V}[\{\psi^{*}\},\{\psi\}] = 2\sum_{i=1,N_{e}/2} \langle\psi_{i}|\frac{-\hbar^{2}\nabla^{2}}{2m}|\psi_{i}\rangle + \int V(r)n(r)dr + \frac{1}{2}\int\int\frac{n(r)n(r')e^{2}}{|r-r'|}drdr' + E_{XC}[n]$$

 $\frac{\delta E_{V}\left[\{\psi^{*}\},\{\psi\}\right]}{\delta\psi_{i}^{*}(r)} - \varepsilon_{i}\psi_{i}(r) = H_{KS}\psi_{i}(r) - \varepsilon_{i}\psi_{i}(r) = 0 \quad \text{Kohn-Sham equations}$

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

The forces $-\frac{\partial \Phi(\{R\})}{\partial R_I}$ are calculated *analytically* (Hellman-Feynman)

Ab-initio Molecular Dynamics on the Fly: The Car-Parrinello Lagrangian (1985)

$$\mathcal{L}_{CP} = \frac{1}{2} \sum_{I} M_{I} \dot{R}_{I}^{2} + \mu \sum_{i} \left\langle \dot{\psi}_{i} \middle| \dot{\psi}_{i} \right\rangle - E_{DFT} \Big[\{R\}; \{\psi^{*}\}, \{\psi\} \Big] \\ + \sum_{i,j} \lambda_{ij} \Big(\left\langle \psi_{j} \middle| \psi_{i} \right\rangle - \delta_{ji} \Big) \\ M_{I} \ddot{R}_{I} = -\frac{\partial E_{DFT} \Big[\{R\}; \{\psi^{*}\}, \{\psi\} \Big]}{\partial R_{I}} \\ \mu \middle| \ddot{\psi}_{i} \right\rangle = -\frac{\delta E_{DFT} \Big[\{R\}; \{\psi^{*}\}, \{\psi\} \Big]}{\delta \left\langle \psi_{i} \middle|} + \sum_{j} \middle| \psi_{j} \right\rangle \lambda_{ji} = -H_{KS} \middle| \psi_{i} \right\rangle + \sum_{j} \middle| \psi_{j} \right\rangle \lambda_{ji}$$

$$\mathcal{H}_{CP} = \mathcal{K} + \mathcal{K}_{f} + E_{DFT} = \frac{1}{2} \sum_{I} M_{I} \dot{R}_{I}^{2} + \mu \sum_{i} \left\langle \dot{\psi}_{i} \middle| \dot{\psi}_{i} \right\rangle + E_{DFT} = \text{const}$$

Density functionals

GGA
$$E_{xc}^{(1)} = \int f^{(1)}(n(r), |\nabla n(r)|)n(r)dr$$

Hybrid
$$E_{xc}^{hyb} = \alpha E_x^{KS} + (1-\alpha) E_{xc}^{GGA}$$

van der Waals

$$E_{\text{TS-vdW}}[\rho(\mathbf{r})] = -\frac{1}{2} \sum_{AB} \frac{f_{AB}[\rho(\mathbf{r})]C_{6,AB}[\rho(\mathbf{r})]}{R_{AB}^6}$$

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Hydrogen bonds: some basic background



Maximally Localized Wannier Functions (Boys Orbitals) in H_2O : bond and lone pairs. The molecule is polar

The water dimer: the hydrogen bond between two water molecules originates from simple electrostatics



Hydrogen Bonds



Local tetrahedral H-bond order :

Donors (D) and Acceptors (A)

Bernal-Fowler-Pauling ice rule: 2D + 2A

Proton disorder & residual entropy in ice

water dimer



Path integral simulations

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

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

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

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





Feynman paths: *closed* and *open*

DFT functionals & H-bonding in water



R.A. DiStasio, B. Santra, Z. Li, X. Wu, R. Car, J. Chem. Phys. 141, 084502 (2014)

Strict BO, isobaric-isothermal simulation, PBE0-TS(sc) exchange-correlation functional



Kinetic Energy of the nuclei & zero-point motion

Current calculation:

Ice Ih (273K 1bar): ~ 161 meV (H) ~56 meV(O) 3/2 kT ~ 35meV

Phase	T [K]	$\langle E_K \rangle^{DINS}$	$\langle E_K \rangle^{INS}$	$\langle E_K \rangle^M$
		[meV]	[meV]	[meV]
SW	269	$(199\pm2)^{26}$	$(152\pm 4)^{24}$	
	270			$(148.1\pm0.5)^{6}$
	271	$156.0{\pm}2.0$	$(152\pm 4)^{24}$	
		$(228\pm 2)^{26}$		
	273	$(150\pm 2)^{27}$	$(153\pm 4)^{24}$	
Ice	270			$(149.5\pm0.5)^{6}$
	271	$157.0{\pm}2.0$	$(158 \pm 4)^{24}$	$(155\pm3)^9$
		$(156\pm 2)^{25}$		
Liquid	296	$(146\pm3)^{27}$	$(150\pm 4)^{24}$	
	300	(146 ± 3)		$(155\pm3)^9$
		$(143\pm3)^4$		

Table 2. Values of $\langle E_{\rm K} \rangle$ for SW, Ice, and Water^{*a*}

From C. Andreani, G. Romanelli, R. Senesi:

DOI: 10.1021/acs.jpclett.6b00926 J. Phys. Chem. Lett. 2016, 7, 2216-2220

Thermal and quantum fluctuations affect differently the electronic properties



Electron-lattice coupling cannot be neglected when estimating the electron excitation gap

Urbach tail and electron localization



Ice-Ih @ 273 K, 1 Bar

Liquid Water @ 300 K, 1 Bar

The states at the top of the valence band are (Anderson) localized by disorder: the effect is more pronounced in presence of quantum fluctuations

Top valence band states correspond to "autoprotolysis" configurations



Liquid Water @ 300 K, 1 Bar



Local environment and Inherent Potential Energy Surface



From Santra, DiStasio, Martelli, RC, *Mol Phys* (2015)

The local structure index *I* (Shiratani and Sasai (1996))

On the Inherent Potential Energy Surface (IPES, Stillinger and Weber (1984)) the LSI distribution is *bimodal*: I_{min} is the "isosbestic" point



A site with $I > I_{min}$ is in a low density environment A site with $I < I_{min}$ is in a high density environment

The IPES of ambient water: clusters of low density water (red) in a sea of high density water (blue)





The ring distribution in red/blue clusters



6-fold rings in crystalline ice



The IRO of the red and blue clusters on the IPES bears similarity with that of LDA and HDA: the seeds of water polyamorphism are present in ambient water

Water "No Man's Land" may hold the clue for understanding water anomalies



Metastable undercooled water is currently unaccessible to ab-initio simulations because the time scales of network relaxation are in the microsecond domain: coarse grained models are necessary. Here we use the ST2 model potential (Stillinger and Rahman (1974))

Does the 1st order LDA-HDA boundary continue into deeply supercooled water? LDL-HDL boundary would terminate at a critical point. Second critical point hypothesis (Poole et al. (1992)) would provide an elegant explanation of the water anomalies such as the observed large increase in density and entropy fluctuations upon cooling

Results with ST2 potential from: *Metastable liquid-liquid transition in a molecular model of water* (J. C. Palmer *et al. Nature* (2014))

Sampling the free energy surface of liquid and ice



NPT Monte Carlo + Umbrella Sampling

- 1,000,000+ CPU hours...and counting
- Other efficiency techniques
 - Parallel Tempering (228 282 K)
 - Configurational Pre-sampling
 - Collective Moves (Force Bias)
 - Metadynamics

Liquid-liquid coexistence in water "No Man's Land"

Simulations with the ST2 model potential (Stillinger and Rahman (1974)) for water shows HDL/LDL coexistence under deeply undercooled conditions



Red/blue clusters at HDL/ LDL coexistence span the length of the simulation box (green box)

Why two network structures in the IPES?



A Theory of Water and Ionic Solution, with Particular Reference to Hydrogen and Hydroxyl Ions

> J. D. BERNAL AND R. H. FOWLER, University of Cambridge, England (Received April 29, 1933)

Bernal and Fowler (1933) suggested that water was characterized by a continuous transformation from a denser quartz-like structure (4-coordinated) to a less dense ice tridymite structure (4-coordinated) upon lowering T



WWW bond switches

A simple continuous random network tetrahedral model shows an abrupt transition in the amorphous structures generated by simulated annealing upon increasing the density

Molecular interactions and intrinsic water defects (H₃O⁺, OH⁻, OH)

- Pioneering AIMD studies on the Grotthuss mechanism of proton transfer by Parrinello, Tuckerman, Marx and coworkers
- Pioneering force-field studies using the empirical valence bond formalism on the Grotthus mechanism by Voth and coworkers
- Recently a paradigm changing paper by Hassanali, Giberti, Kuhne, and Parrinello (*PNAS* (2013)) pointed out the crucial role of dynamic correlation in successful proton jumps (overlooked in earlier studies adopting a transition state theory framework) and its connection with the topology of the H-bond network
- How do molecular interactions at the PBE0-TS(sc) level affect charged and neutral water defects?

Effect of the interactions on the proton jump distribution



Diffusion PBE0 vdW Exp.^{2, 3, 4} Coefficient (10⁻⁹ m²/s) 3.73 OH-3.12 H₃O⁺ 8.31 6.69 $D(OH^{-})/D(H_{3}O^{+})$ 0.47 0.45

OH-

Why does PBE0-TS(sc) (substantially) reduce multiple jumps for the hydroxide ion?

(Princeton-Temple collaboration)

Exact exchange and vdW increase the relative concentration of hypercoordinated OH⁻ configurations



Hypercoordinat ed: not able to transfer



Tetrahedral: able to transfer



Exact exchange makes the lone pair side more hydrophilic and the hydrogen site more hydrophobic as indicated by Wannier function analysis. vdW modifies the intermediate range order favoring more disordered configurations (low LSI) and this again favors hypercoordination

Effect of exact exchange on the solvation structure of the OH radical



By reducing the self-interaction error PBE0 eliminates the unphysical hemi-bond present at the GGA level of theory

Schematic band structure showing that the minority spin hole level is moved deep into the gap by exact exchange (eliminating the metallic character of the defect complex evident at the GGA level)

Upon electron capture the hole level moves close to the valence band maximum after a substantial network rearrangement associated to the formation of a hydroxide ion. The greater stability of the hydroxide ion versus the hydroxyl radical indicates the Anderson negative U character of this defect complex

Ice at extreme pressure is very different from low pressure ice



The phase diagram of superionic ice according to J. Sun, B. Clark, S. Torquato and R. C. (2015)

Superionic ice and ionic water may explain the unusual magnetic fields of Uranus and Neptune where nearby patches of the surface can have magnetic fields of opposite polarity

At extreme pressure (>50 Gpa) the H-bond network is disrupted, water molecules cease to be the basic constituents and ice becomes an ionic compound that may exhibit superionic behavior

Weird water lurking inside giant planets | New Scientist

A layer of superionic water seems to lie around the rocky cores of both Neptune and Uranus. It may not undergo convection, which could help explain the planets' strange magnetic fields



Ice at extreme pressure is very different from low pressure ice



The superionic phase diagram is predicted from single phase *NPT* ab-initio MD simulations (PBE functional) using the Parrinello-Rahman variable cell technique

From *Superionic ices at ultrahigh pressure* (J. Sun *et al. Nature Commun.* (2015))

The newly predicted monoclinic (P21/c) superionic phase



From molecules to ions: a dramatic change in the electronic structure



The distribution of the Maximally Localized Wannier function Centers (MLWC) shows vividly the change in chemical bond promoted by pressure: from H-bonds to ionic bonds

Character of the superionic transition



The conductivity shows that FCC (DHCP) superionic ice is type I, whereas P21/c superionic ice is type II. Type I-II character correlates with the behavior of the mean squared displacement (MSD) of the O sublattice

$$\sigma = n \left(Z^* e \right)^2 D / k_B T$$



Typical conductivity data for superionic conductors (from Boyce and Huberman, *Phys. Rep.* (1979))

Locating the melting line for the SI transition in a type II system





Colored plots: phonon DOS from A. Herman, N. Ashcroft and R. Hoffmann (2013); Black lines: power spectrum of dynamics from our calculations

Large zero point motion effects expected !

Are nuclear quantum effects important?



Qualitatively NQE on the phase diagram can be understood using the lowest order (2nd order) expansion of the free energy in the Planck constant

Concluding remarks

- Trends are more important than perfect agreement with experiment
- It is reassuring that the qualitative agreement with experiment improves for many properties when more accurate functionals and NQE are included
- AIMD provides a unified description not only of pure water but also of solvation processes and is able to describe different environments (e.g. interfaces, effect of pressure, solvation phenomena etc.)
- From the electronic structure point of view the low pressure phases are more challenging than the phases at ultrahigh pressure due to the important role of electron correlations.

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