Ab initio theory and modeling of water

Mohan Chen Hsin-Yu Ko, Richard C. Remsing, Marcos F. Calegari Andrade, Biswajit Santra, Zhaoru Sun, Annabella Selloni, Roberto Car, Michael L. Klein, and John P. Perdew, and Xifan Wu

Scientific Achievement

We demonstrate that a fully *ab initio* approach, relying on the SCAN density functional, provides such a description of water. SCAN accurately describes the balance among covalent bonds, hydrogen bonds, and van der Waals interactions that dictates the structure and dynamics of liquid water. Notably, SCAN captures the density difference between water and ice at ambient conditions, and many important structural, electronic, and dynamic properties of liquid water.

Significance and Impact

Water is vital to our everyday life, but its structure at a molecular level is still not fully understood from either experiment or theory. The latter is hampered by our inability to construct a purely predictive, first principles model. The difficulty in modeling water lies in capturing the delicate interplay among the many strong and weak forces that govern its behavior and phase diagram. Herein, molecular simulations with a recently proposed nonempirical quantum mechanical approach yield an excellent description of the structural, electronic, and dynamic properties of liquid water. SCAN (strongly constrained and appropriately normed)-based approaches, which describe diverse types of bonds in materials on an equal, accurate footing, will likely enable efficient and reliable modeling of aqueous phase chemistry.

Research Details

(1) Ab initio molecular dynamics calculation based on SCAN density functional theory
(2) NPT ensemble (constant pressure) simulation
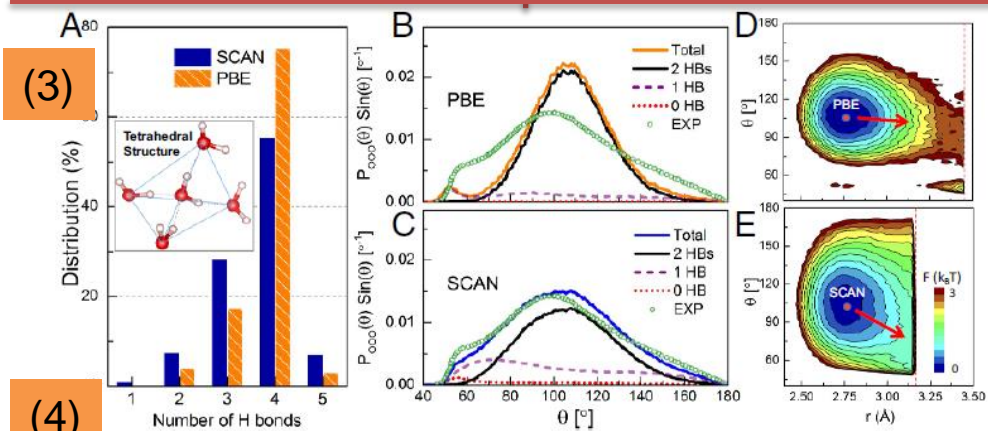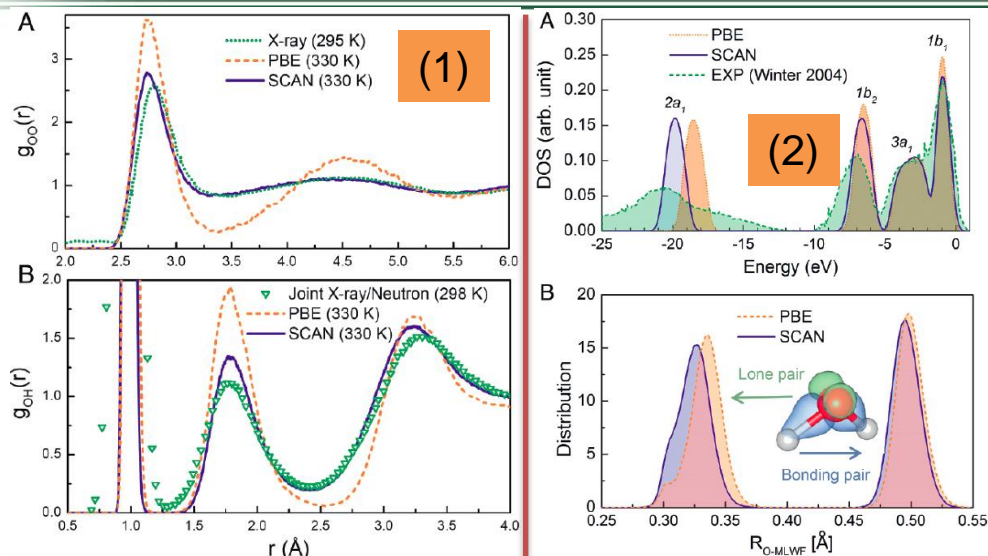(3) Liquid water structures under ambient conditions

Table 1. Properties of water (330 K) and ice Ih (273 K) predicted by SCAN and PBE functionals in the isobaric-isothermal ensemble

Method	ρ_w (g/mL)	ρ_{Ih} (g/mL)	$\Delta\rho$ (g/mL)	ρ_w/ρ_{Ih}	μ_w (D)	μ_{Ih} (D)	E_g (eV)	q	D (Å^2/ps)	τ_2 (ps)
SCAN	1.050 ± 0.027	0.964 ± 0.023	0.086 ± 0.035	1.089 ± 0.038	2.97 ± 0.29	3.29 ± 0.21	4.92 ± 0.14	0.68 ± 0.18	0.190 ± 0.025	2.9 ± 0.4
PBE	0.850 ± 0.016	0.936 ± 0.013	-0.086 ± 0.021	0.908 ± 0.021	3.12 ± 0.28	3.35 ± 0.21	4.43 ± 0.13	0.83 ± 0.11	0.018 ± 0.002	7.1 ± 0.5
EXP	0.99656 (36)	0.9167 (37)	0.080	1.087	2.9 ± 0.6 (38)		8.7 ± 0.6 (42)	0.593 (4)	0.187 (39)	2.4 (40)

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Water is of the utmost importance for life and technology. However, a genuinely predictive ab initio model of water has eluded scientists. We demonstrate that a fully ab initio approach, relying on the strongly constrained and appropriately normed (SCAN) density functional, provides such a description of water. SCAN accurately describes the balance among covalent bonds, hydrogen bonds, and van der Waals interactions that dictates the structure and dynamics of liquid water. Notably, SCAN captures the density difference between water and ice I*h* at ambient conditions, as well as many important structural, electronic, and dynamic properties of liquid water. These successful predictions of the versatile SCAN functional open the gates to study complex processes in aqueous phase chemistry and the interactions of water with other materials in an efficient, accurate, and predictive, ab initio manner.

water | ab initio theory | hydrogen bonding | density functional theory | molecular dynamics

body effects, included in the exchange-correlation (XC) functional. XC functionals can be conceptually arranged, by accuracy and computational efficiency, according to Jacob's ladder (14), with the simplest local density approximation (LDA) (15, 16) on the bottom rung of the ladder, followed by generalized gradient approximations (GGAs) (17–19), meta-GGAs, hybrid functionals (20, 21), and so on.

The past three decades have witnessed widespread successes of DFT in elucidating and predicting properties of materials. However, water still presents a major challenge, with many DFT-based simulations yielding results that are not even qualitatively consistent with experimental measurements. The H-bonds formed between gas-phase water clusters were first treated within the LDA (22, 23), which overestimates H-bond strengths and yields interwater distances that are too close. This overbinding is largely corrected by GGA-level functionals, which became a class of popular functionals to study liquid water within the last two decades (10). Despite the improvements over LDA that are provided by GGAs, H-bond strengths are overestimated and
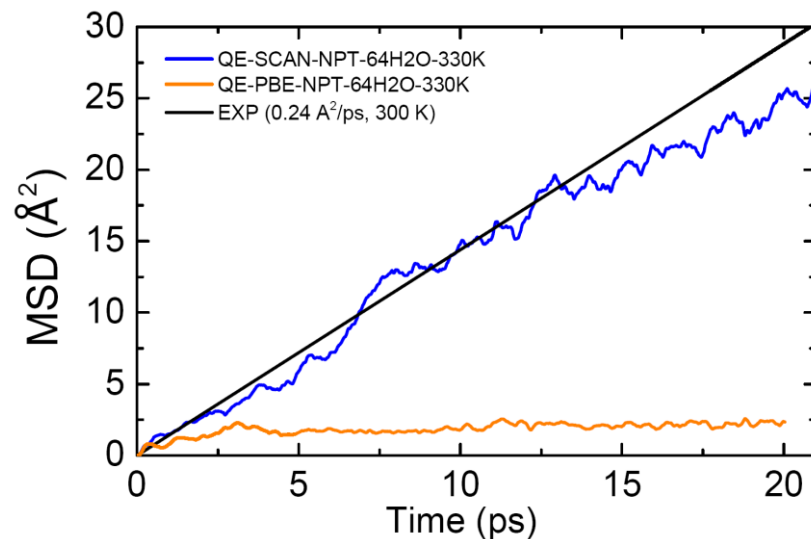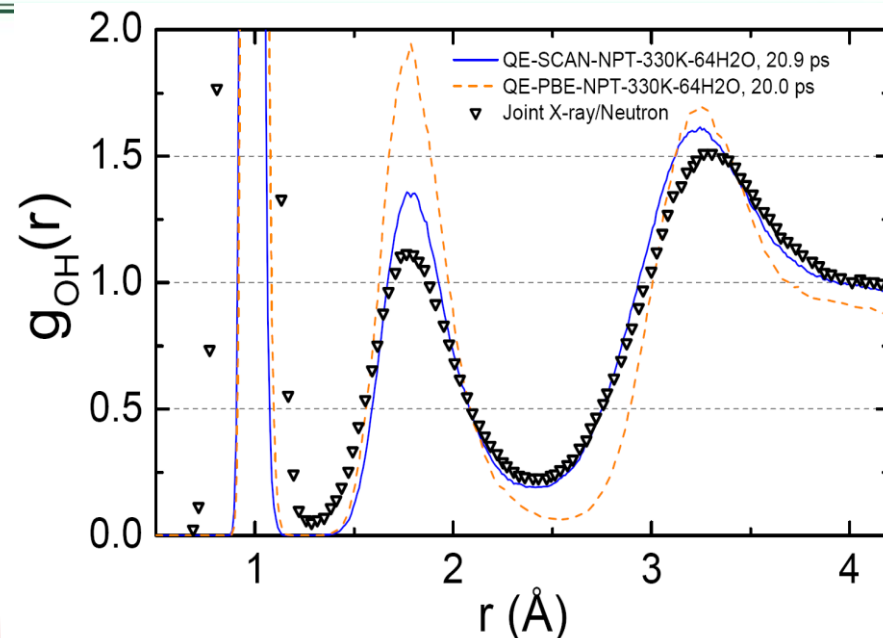
CHEMISTRY

PNAS

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Method	$D \ (10^{-9}m^2/s)$	$\tau_2 (ps)$
PBE	0.4 ± 0.12	7.1 ± 0.5
SCAN	2.14 ± 0.22	2.9 ± 0.4
Experiment	1.8 (D_2O) 2.4 (H_2O)	2.4

τ_2: rotational correlation time
D: diffusion constant

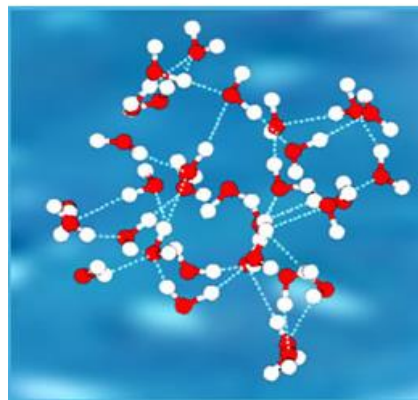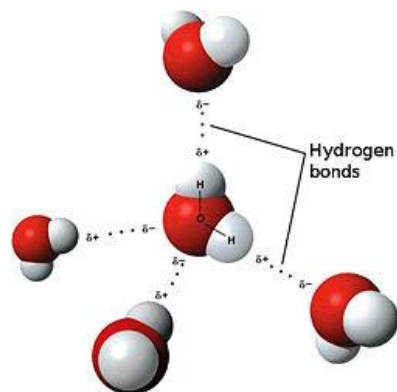# *Ab initio* theory and modeling of water

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Challenges of DFT for liquid water structure

1. Light atom of proton
➤   Nuclear quantum effect

2. Nature of H-bonding
➤   Much weaker than covalent
➤   Electrostatic, mixed with covalency
➤   Delicate balance of the above

3. van der Waals (vdW)
➤   Nonlocal exchange-correlation effect
➤   Missing vdW in intermediate and long-range

SCAN + nuclear quantum effect simulations !!