APS physics MARCH MEETING 2022

Exploring Ion Dynamics in Charged Systems using Real-Space Pseudopotential Density Functional Theory

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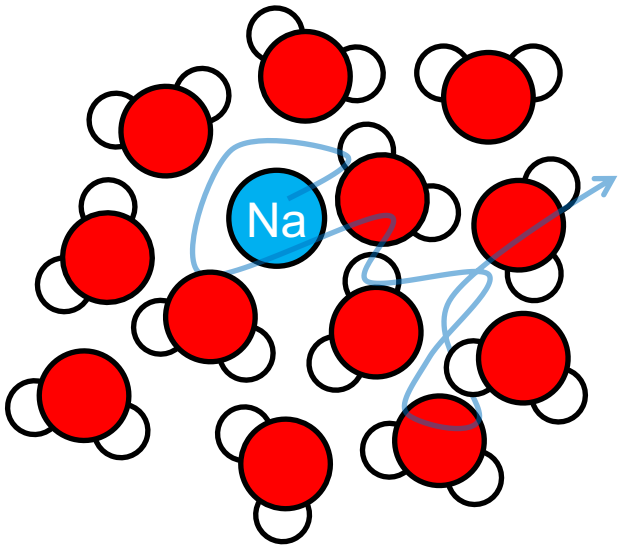
March 15, 2022

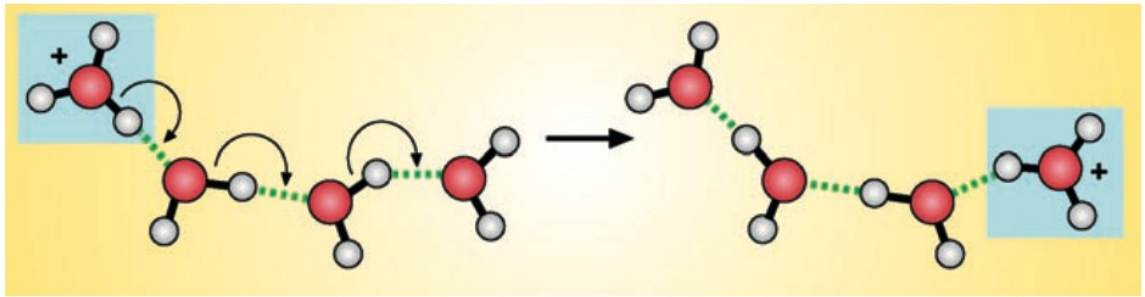
F46.3

Proton transfer in water

Motion of sodium ions in water

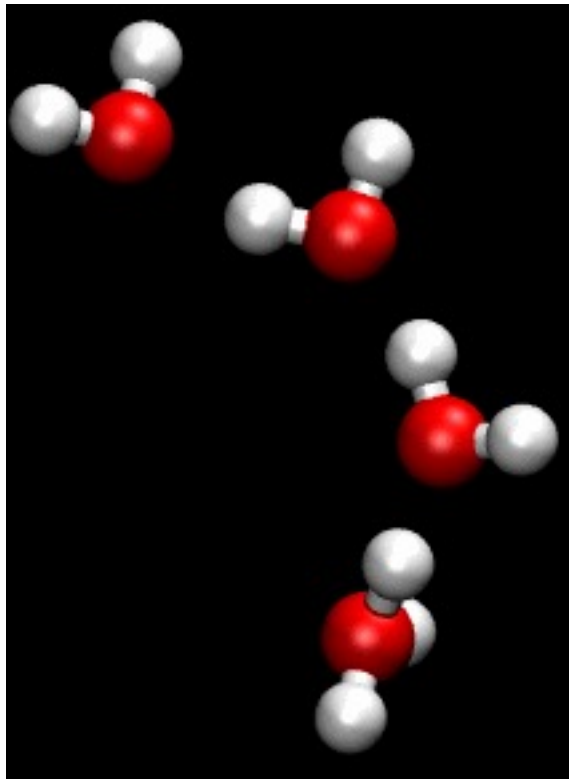


Motion of protons in water
(Grotthuss mechanism)



Marx, D., *ChemPhysChem* **2006,** *7* (9), 1848-70.

Proton transfer in water



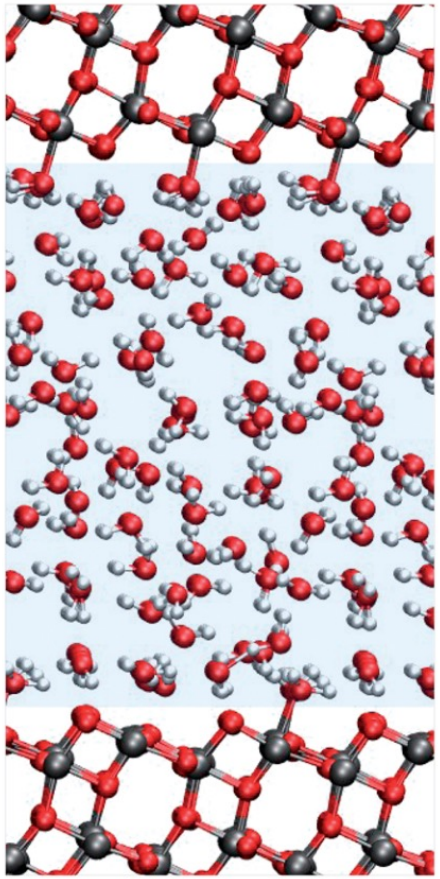
Wikipedia “Grotthuss mechanism”

Diffusivity of common ions in aqueous solution at 298 K

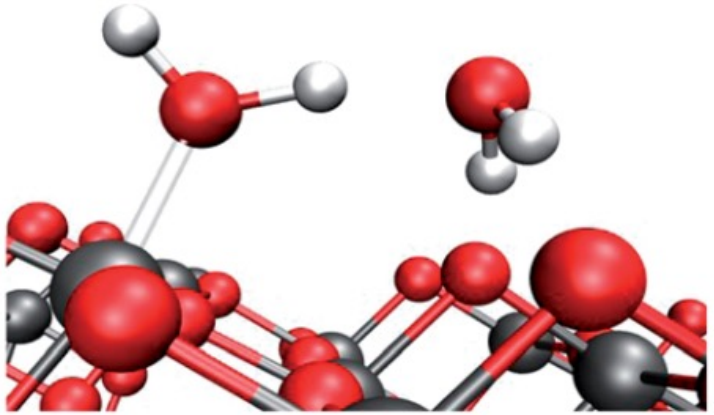
Ion	D (ang^2 ps^{-1})
H^+	0.9311
D^+	0.6655
Li^+	0.1029
Na^+	0.1334
K^+	0.1957
NH_4^+	0.1957

Haynes, W. M., *CRC Handbook of Chemistry and Physics*. CRC Press: 2016.

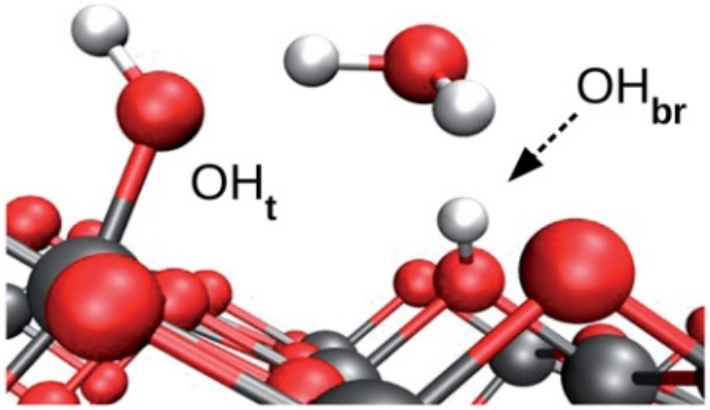
Interfaces between TiO_2 and liquid water



Molecular adsorption



Dissociative adsorption

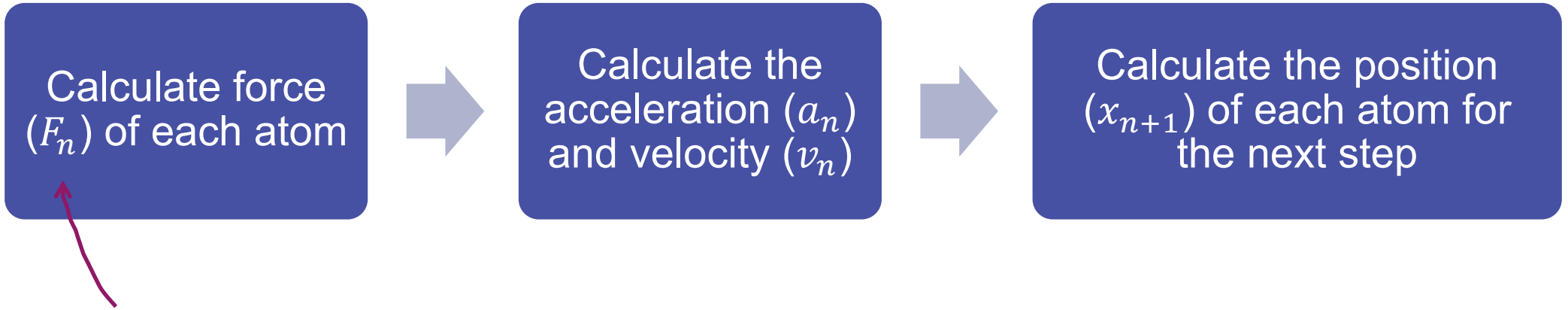


Calegari Andrade, M. F.; Ko, H.-Y.; Zhang, L.; Car, R.; Selloni, A., *Chemical Science* **2020,** *11* (9), 2335-2341.

ab-initio molecular dynamics

at step n

to step $n + 1$



From first-principles calculations

Real-space pseudopotential density functional theory

The Kohn–Sham equations:

$$\left[-\frac{1}{2}\nabla^2 + \hat{V}_{\text{ion}} + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r})\right]\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$$

$\hat{V}_{\text{ion}}$	ionic pseudopotential
$V_{\text{H}}(\mathbf{r})$	Hartree potential
$V_{\text{xc}}(\mathbf{r})$	exchange-correlation potential

Chebyshev-filtered subspace iteration method

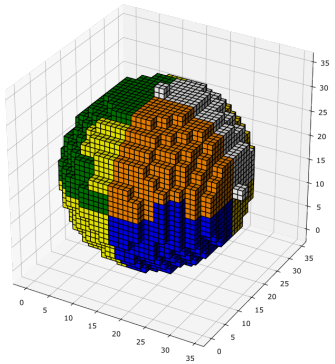
$$\overbrace{\left[-\frac{1}{2}\nabla^2 + V_{\text{eff}}\right]}^{H_{\text{KS}}}\phi_i = \varepsilon_i\phi_i$$

$$\{\phi_i\}_{i=1,\ldots,N_s}$$

The subspace of the lowest-energy states

1. **Filtering** the subspace to amplify the lowest-energy states
2. **Orthonormalizing** the subspace
3. Obtaining the approximate eigenpairs from the subspace via **Rayleigh–Ritz method**

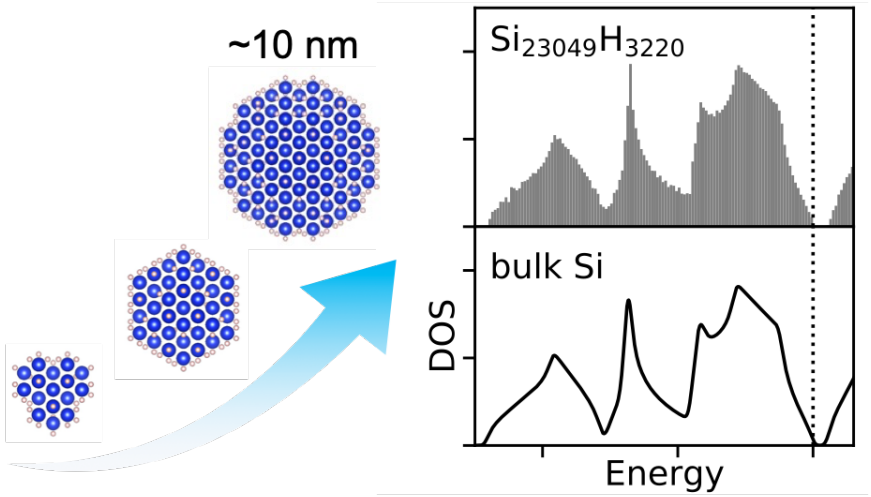
Zhou, Y.; Chelikowsky, J. R.; Saad, Y., *Journal of Computational Physics* **2014,** *274*, 770--782.



PARSEC

http://real-space.org/

Pseudopotential Algorithm for Real-Space Electronic Structure Calculation



System	# of grid points	# of states	# of Cori KNL nodes	Wall time (hrs)
$Si_{849}H_{348}$	812,112	2,000	1	1.3
$Si_{4001}H_{1012}$	2,707,504	9,216	8	4.0
$Si_{10869}H_{1924}$	6,377,184	24,576	64	8.4
$Si_{23049}H_{3220}$	15,180,904	61,440	256	27.9

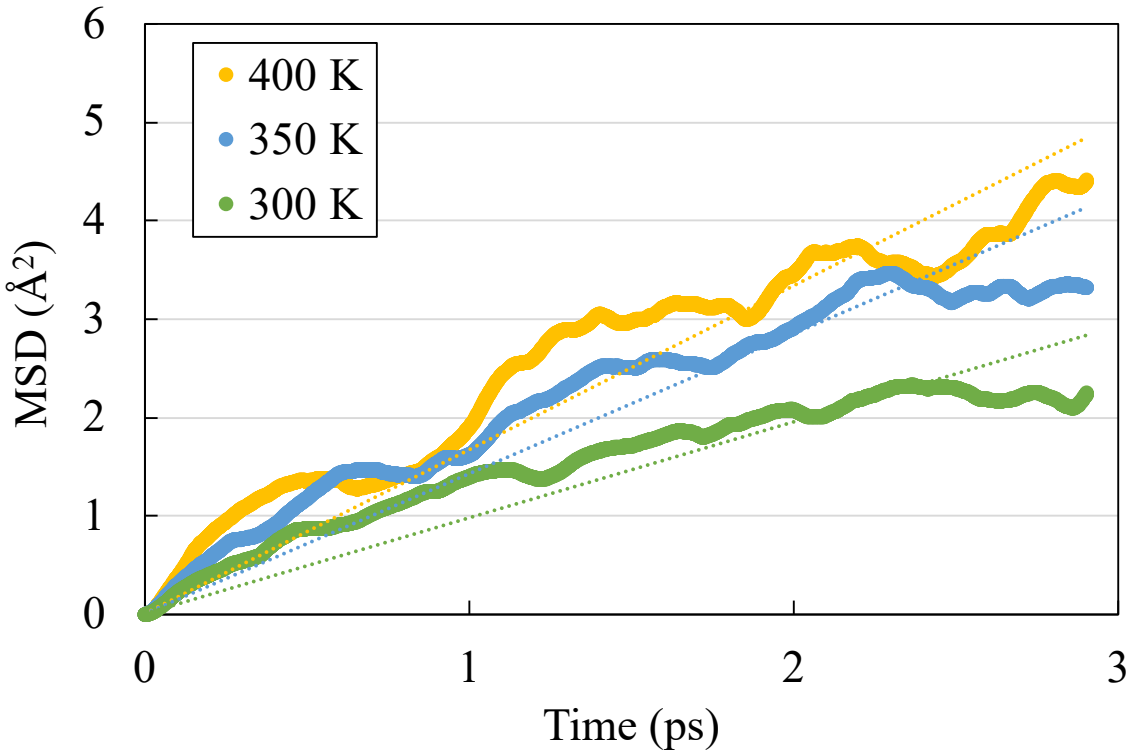
Kronik, L. *et al.*, *physica status solidi (b)* **2006,** *243* (5), 1063-1079.

Liou, K. H.; Biller, A.; Kronik, L.; Chelikowsky, J. R., *Journal of Chemical Theory and Computation* **2021,** *17* (7), 4039-4048.

Setup for liquid water simulations

Number of H_2O	64
Density (g cm^{-3})	0.996
Grid spacing (bohr)	0.25 (~158 Ry of kinetic energy cutoff)
Time step (fs)	0.5
XC functional	GGA-PBE
Pseudopotential	Troullier–Martins norm-conserving
Coefficient of the Langevin thermostat, β	0.01

Diffusivity of H_2O in liquid water



Simulations

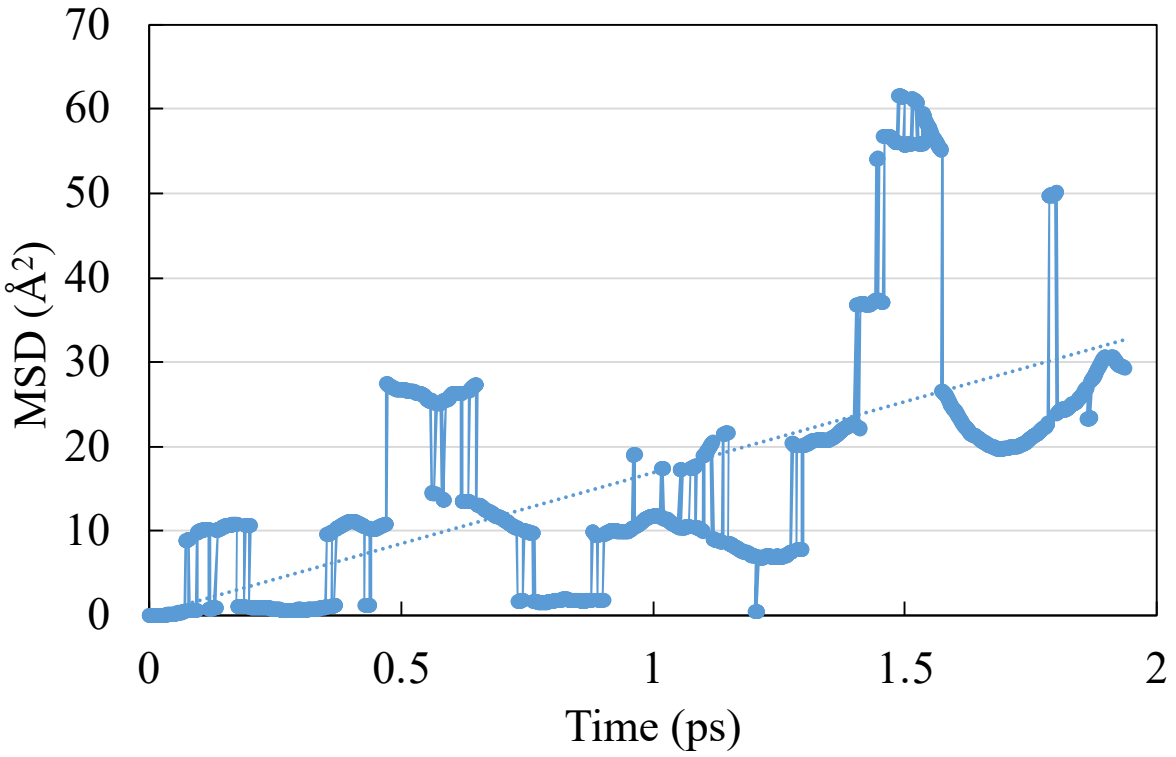
Temperature (K)	D (ang^2 ps^{-1})
400	0.278
350	0.237
300	0.163

Experiments

Temperature (K)	D (ang^2 ps^{-1})
318	0.3575
308	0.2919
298	**0.2299**
288	0.1777
278	0.1313

Mills, R., *The Journal of Physical Chemistry* **1973,** *77* (5), 685-688.

Diffusivity of H^+ in liquid water



Simulations

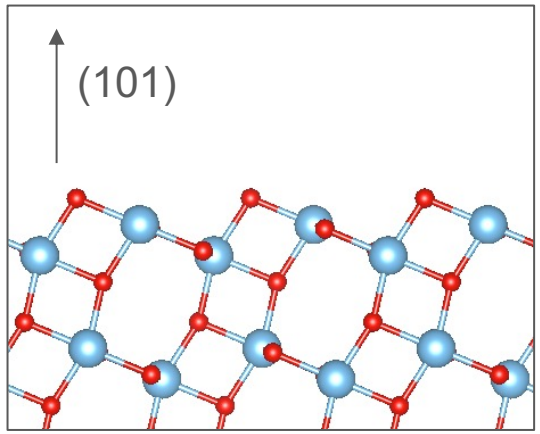
Temperature (K)	D (ang² ps⁻¹)	D_{H+}/D_{H2O}
440	3.00 [1]	5.4 [1]
350	2.69 ± 1.33	11.4
300	1.02 [1]	23.1 [1]

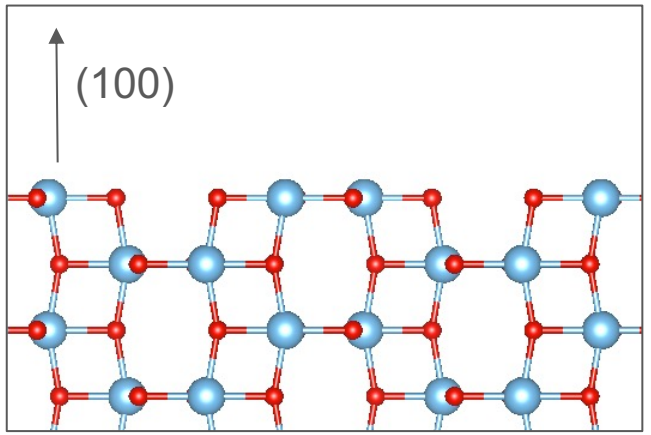
Experiments

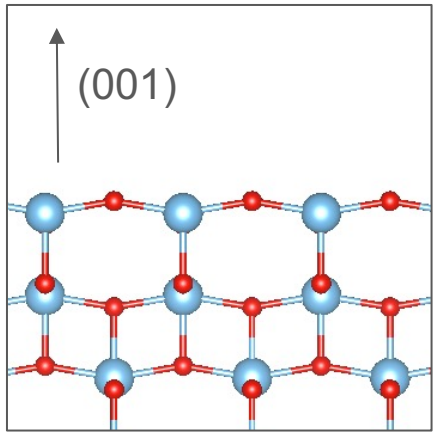
Temperature (K)	D (ang² ps⁻¹)	D_{H+}/D_{H2O}
298	0.9311 [2]	4.05 [3]

[1] Fischer, S. A.; Dunlap, B. I.; Gunlycke, D., *Chemical Science* **2018,** *9* (35), 7126-7132.
[2] Haynes, W. M., *CRC Handbook of Chemistry and Physics*. CRC Press: 2016.
[3] R. Mills and V. M. M. Lobo, Elsevier, New York, NY, 1989, vol. 36.

Surface energy of anatase TiO_2





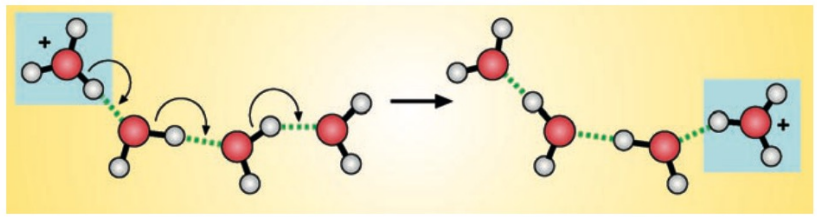


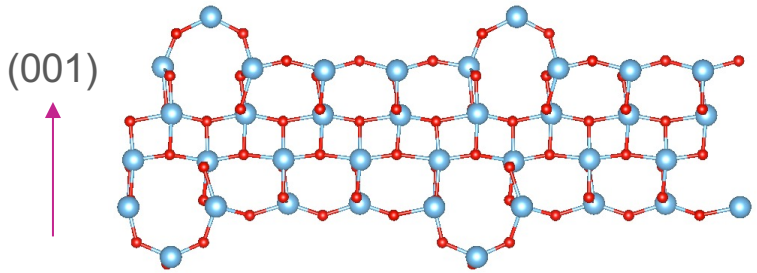
Surface	Surface energy (J/m^2)	
	PARSEC	Literature[1]
(101)	0.55	0.49
(100)	0.59	0.58
(001)	1.10	0.98

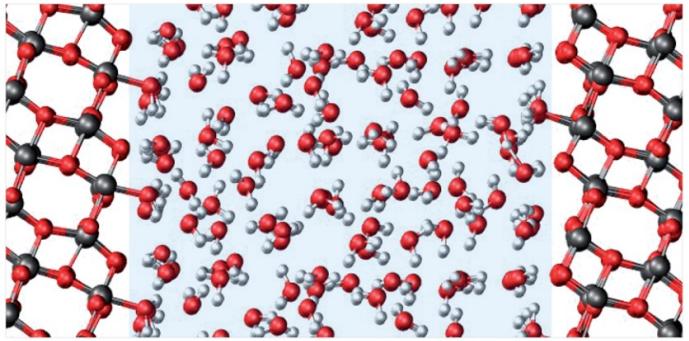
[1] Lazzeri, M.; Vittadini, A.; Selloni, A., *Physical Review B* **2001,** *63* (15), 155409.

Summary and future work

- *ab-initio* MD using real-space pseudopotential density functional theory
- Proton transfer in liquid water
- Reconstruction and energetics of TiO_2 surfaces
- Dynamics at TiO_2–liquid water interfaces and their optical responses

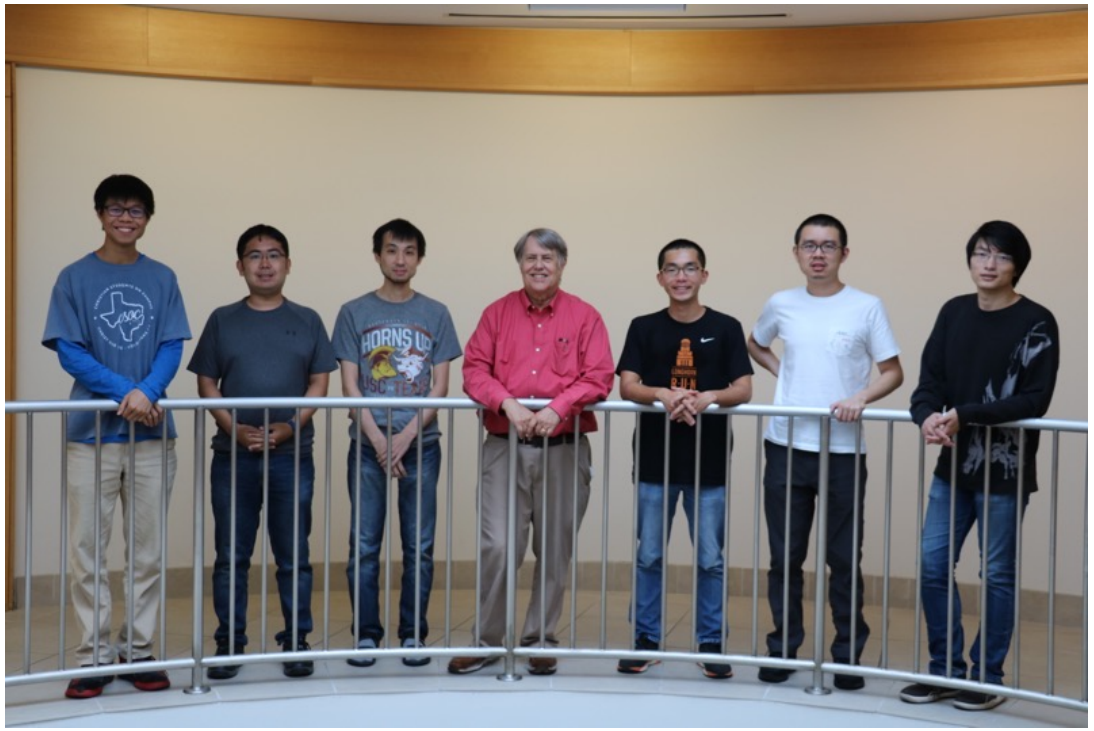






Feel free to send me emails if you have any questions or comments! lioukaihsin@utexas.edu

Acknowledgements



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