EX19706 (大阪大学推薦課題)

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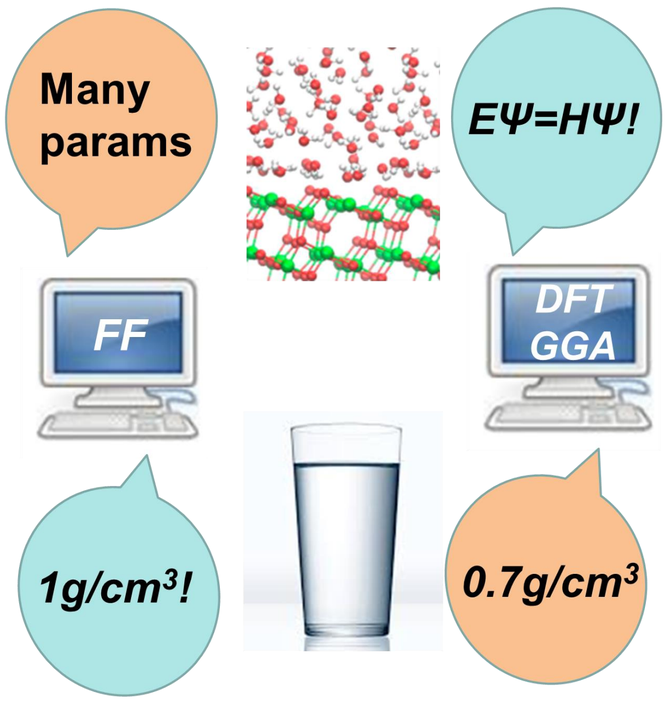
研究課題名　ハイブリッド汎関数を用いた水界面物性の第一原理分子動力学シミュレーション

DFT-MD Simulation



Advantage:
No need for force field modelling

Disadvantage:
often not realistic
- bulk density
- surface tension
- melting point

Three Drawbacks of GGA

1. *Lack of vdW interactions* → *vdW correction!*
2. *Self-Interaction Error* → *Hybrid GGA!*
3. *Beyond gradient approximation* → *Meta-GGA!*

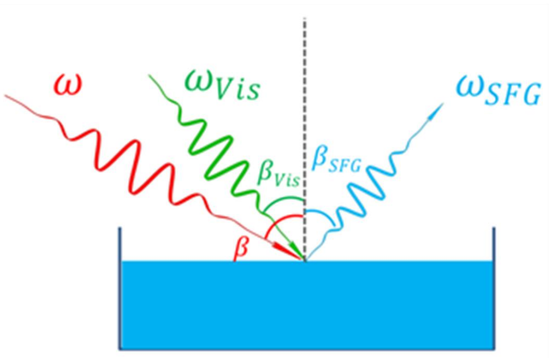
Can these techniques provide better description of water?

Why Water-Air Interface?

	Ambient Condition?	Interaction?
Gas-phase	No	Heterogeneous
Bulk-phase	Yes	Homogeneous
Interface	Yes	Heterogeneous

Sum-Frequency Generation (SFG)

$$\omega_{SFG} = \omega_{IR} + \omega_{VIS}$$

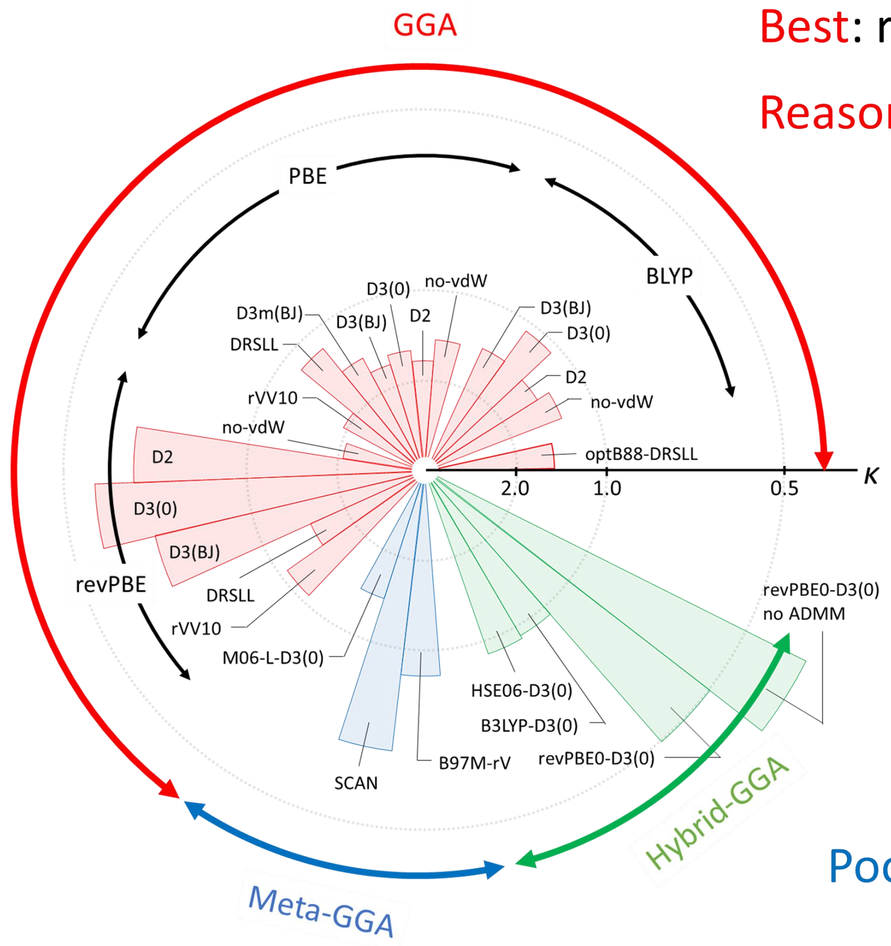


Static SFG:
Fraction of free O-H = **20-25 %**

Polarization-dependent SFG:
Angle of free O-H = **~60°**

Time-resolved SFG:
Free O-H lifetime = **1.1 ps**

Accuracy of DFT Methods



Best: revPBE0-D3(0)

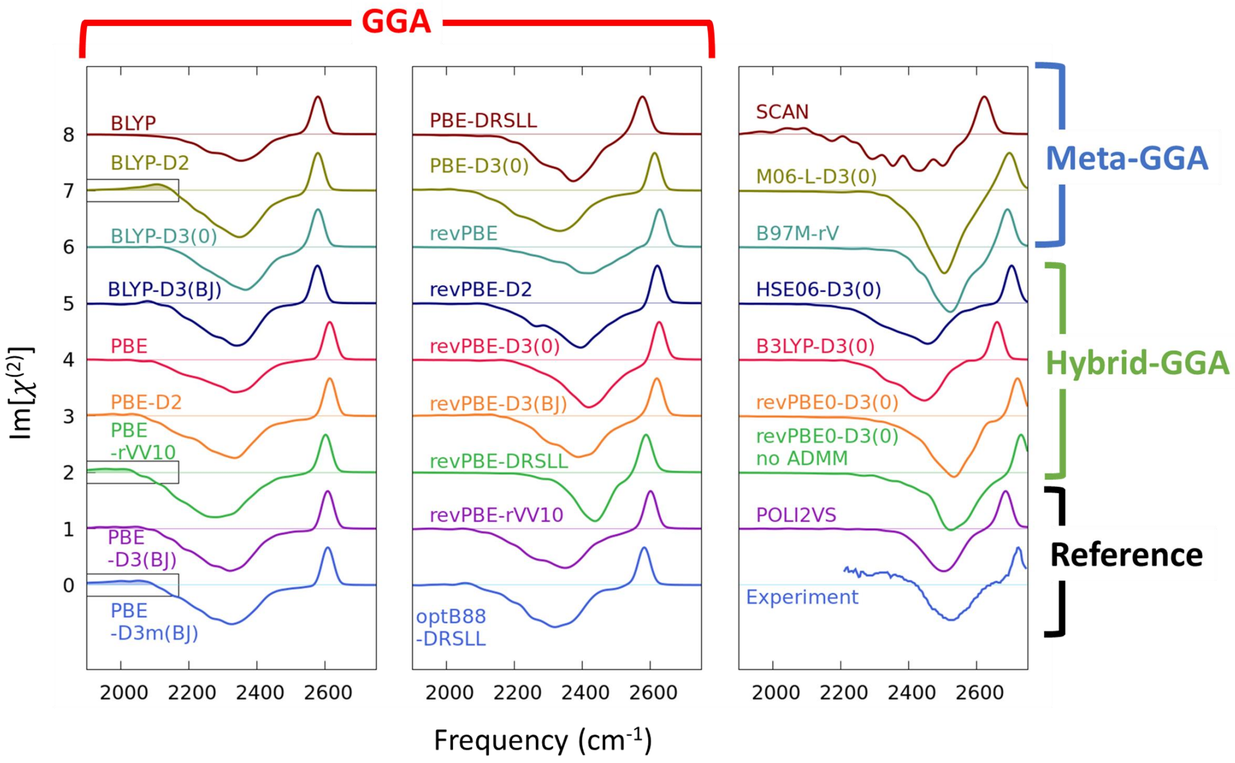
Reasonably good: revPBE-D3(0)

Poor: M06-L-D3(0)

poor M06 = *physics more important than data?*
Right answers for the wrong reasons?

"theoretical advances, until the early 2000s, was reversed by unconstrained functionals sacrificing physical rigor for the flexibility of empirical fitting" Medvedev, *et al.*, Science **2017**, 355, 49.

SFG Spectra of O-D Stretch



- Spectral shapes with meta-GGA functionals differ significantly from experiment, while hybrid-GGA provides spectra in agreement with experiment.

- Positive peak around 2100 cm^{-1} is linked with poor description of water.