

(Towards) Quantitative Materials Science from Quantum Chemistry

Hong-Zhou Ye

Department of Chemistry & IPST
University of Maryland, College Park

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Prof. Timothy C. Berkelbach
Columbia University

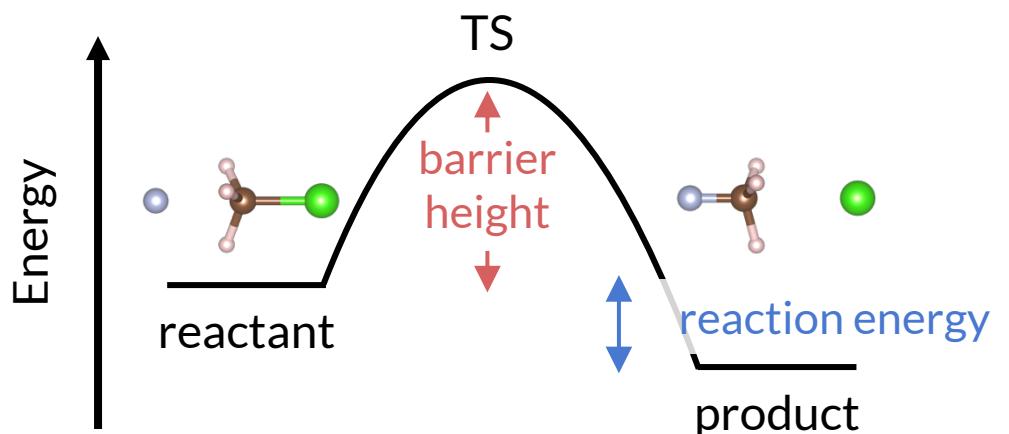


Quantum chemistry in a nutshell

The electronic structure problem

$\Psi \rightarrow$ Density, bond order, dipole, ...

$E(\mathbf{R}^M)$ → Potential energy surface



Quantum chemistry is making (strategic) *approximations*

1. “enough” accuracy for chemistry
 2. computationally affordable

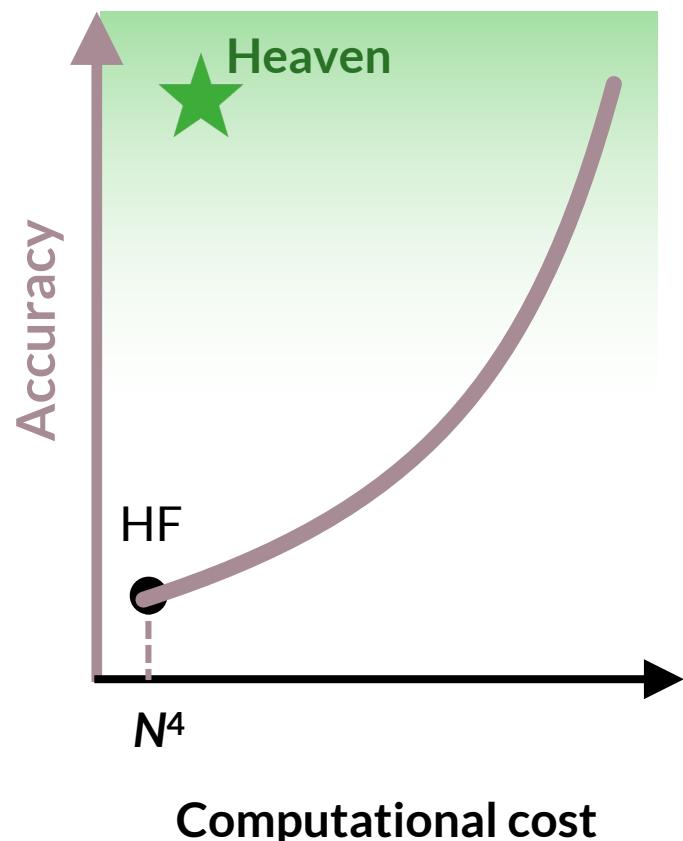
- Density functional theory

PBE, SCAN, B3LYP, HSE, ...

- Correlated wavefunction theory (TODAY!)

MP2, CCSD, CCSD(T), ...

Correlated wavefunction theory



Hartree-Fock (HF) approximation

- 1e problem:

$$\{\hat{h}(\mathbf{r}) + v_{\text{HF}}(\mathbf{r})\} \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

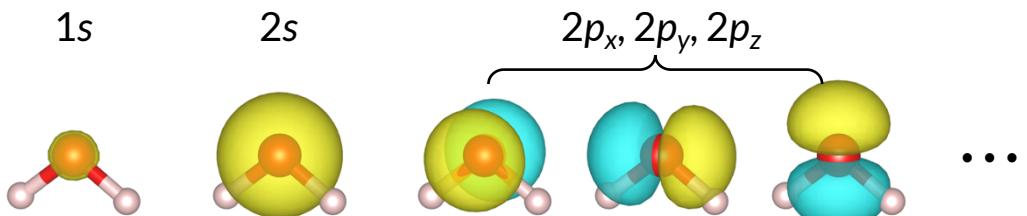
"mean-field"

orbitals

- Gaussian basis:

$$\phi_i(\mathbf{r}) = \sum_{\mu}^{N_{\text{basis}}} C_{\mu i} \chi_{\mu}(\mathbf{r})$$

E.g., O atom
in a water
molecule

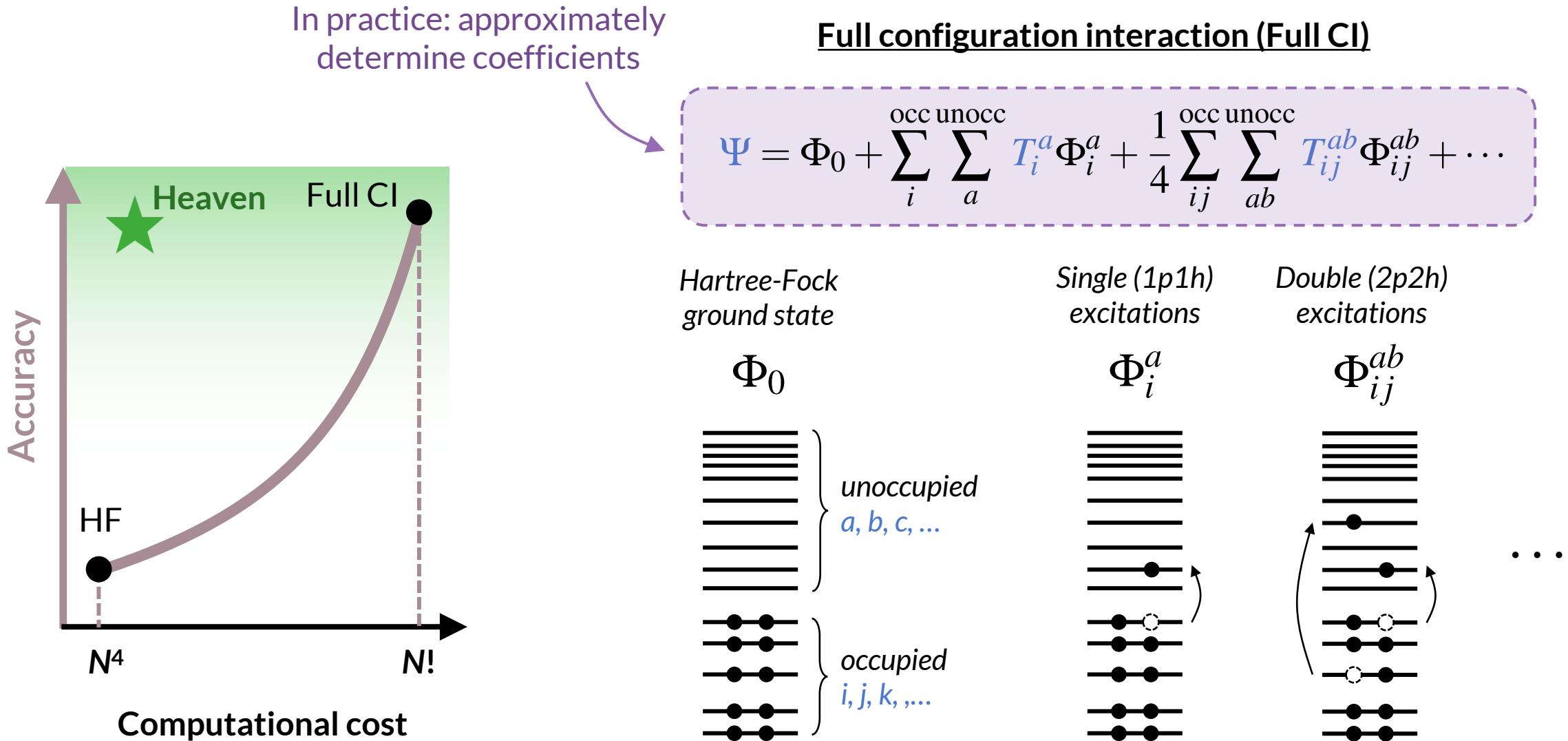


- Eigval. Eqn.:

$$(h_{\mu\nu} + v_{\mu\nu}^{\text{HF}}) C_{\mu i} = \epsilon_i C_{\mu i}$$

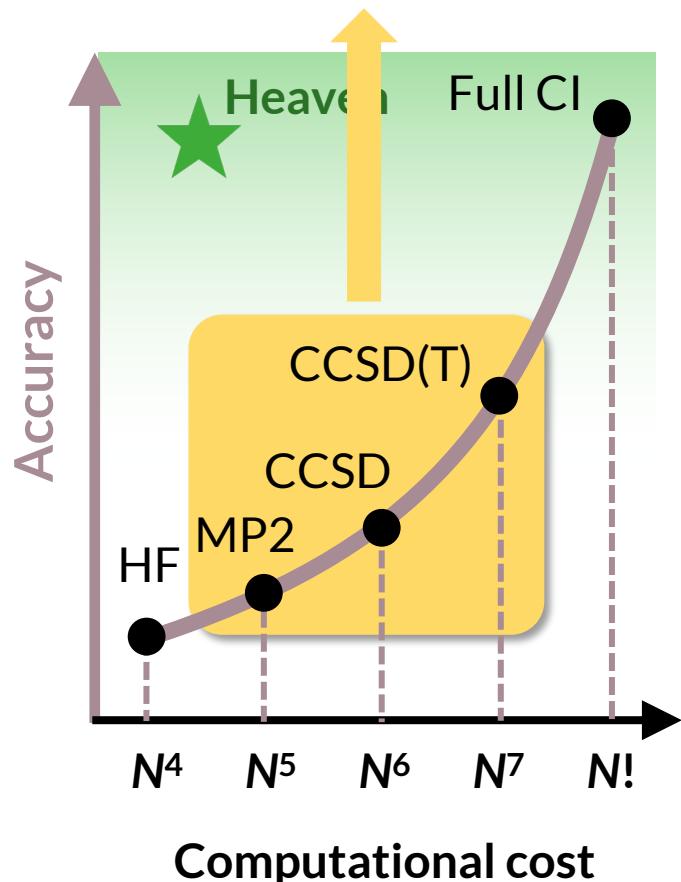
$$h_{\mu\nu} = \int d\mathbf{r} \chi_{\mu}(\mathbf{r}) \hat{h}(\mathbf{r}) \chi_{\nu}(\mathbf{r})$$

Correlated wavefunction theory



Correlated wavefunction theory

Commonly used as reference for ML
– at least for molecules!



2nd-order perturbation theory (MP2)
Cheapest correlated wavefunction theory

$$\hat{H} = \hat{H}_0 + \hat{V} \quad \longrightarrow \quad T_{ij}^{ab} \approx \frac{V_{iajb}}{\epsilon_i - \epsilon_a + \epsilon_j - \epsilon_b}$$

Brute-force MP3/4/5/6 ... often leads to *divergence*!

Coupled-cluster theory (CC)

“Resummation” of selected terms to infinite order

$$\Psi_{\text{CC}} = e^{\hat{T}} \Phi_0 = \left(1 + \hat{T} + \frac{1}{2} \hat{T}^2 + \dots \right) \Phi_0$$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 \quad \longrightarrow \quad \text{CCSD}$$

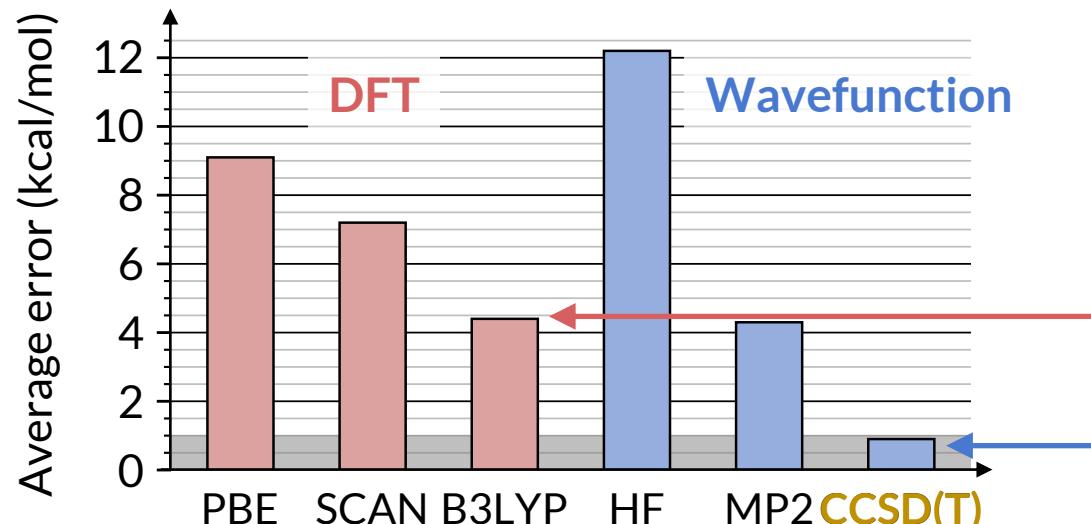
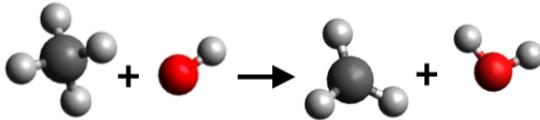
$$\hat{T} = \hat{T}_1 + \hat{T}_2 + (\hat{T}_3)_{\text{perturb}} \quad \longrightarrow \quad \text{CCSD(T)}$$

Relevant energy scale: “chemical accuracy”

Database of gas-phase barrier heights

Lynch & Truhlar *J. Phys. Chem. A*, 107, 2003

Example:



Can we achieve “chemical accuracy”
for materials?

$$\text{Rate} \sim \exp(-\Delta E/kT)$$

300 K ~ 0.5 kcal/mol

4 kcal/mol error

1 kcal/mol error = factor of 5 error in rate

“chemical accuracy”

“Gold standard” of molecular quantum chemistry

Gaussian-based periodic quantum chemistry

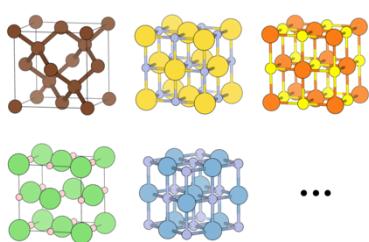


- Translationally adapted Gaussian basis functions

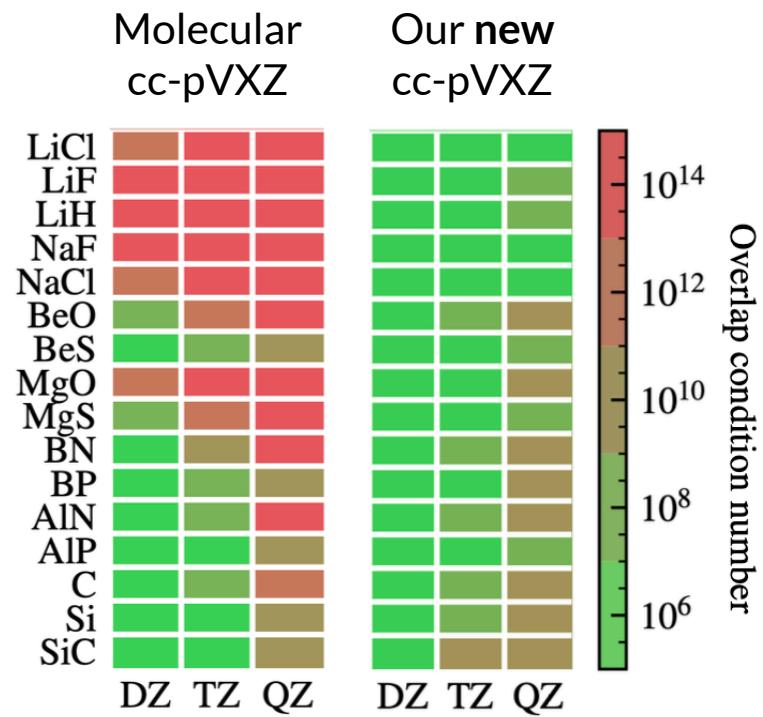
$$\phi_{\mu\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}} \phi_{\mu}(\mathbf{r} - \mathbf{T}) \quad \begin{matrix} \mathbf{k} & 1^{\text{st}} \text{ BZ} \\ \mathbf{T} & \text{lattice vector} \end{matrix}$$

Gaussian basis sets for solids

[HY](#) and TCB, JCTC, **18** (2022)



- ✓ Lattice constant
- ✓ Bulk modulus
- ✓ Cohesive energy
- ✓ Band structure
- ✓ Bulk/defect excitons



- Hamiltonian (e.g., Coulomb integrals)

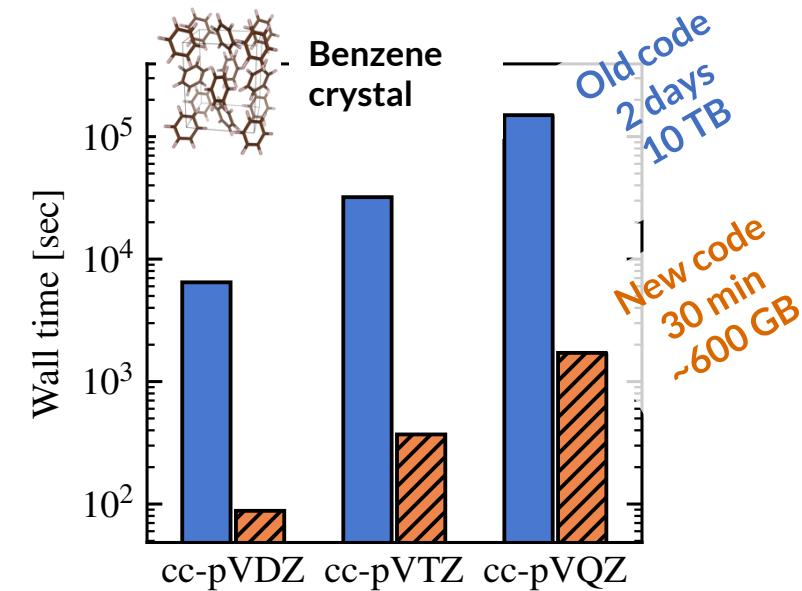
$$V_{\mu\nu\lambda\sigma}^{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3\mathbf{k}_4} = \sum_{\mathbf{T}_2\mathbf{T}_3\mathbf{T}_4} e^{-i(\mathbf{k}_2\cdot\mathbf{T}_2-\mathbf{k}_3\cdot\mathbf{T}_3+\mathbf{k}_4\cdot\mathbf{T}_4)} V_{\mu\nu\lambda\sigma}^{0\mathbf{T}_1\mathbf{T}_2\mathbf{T}_3}$$

Fast and robust periodic density fitting

[HY](#) and TCB, JCP, **154** (2021); [HY](#) and TCB, JCP, **155** (2022); Bintrim, TCB and [HY](#) JCTC, **18** (2022)

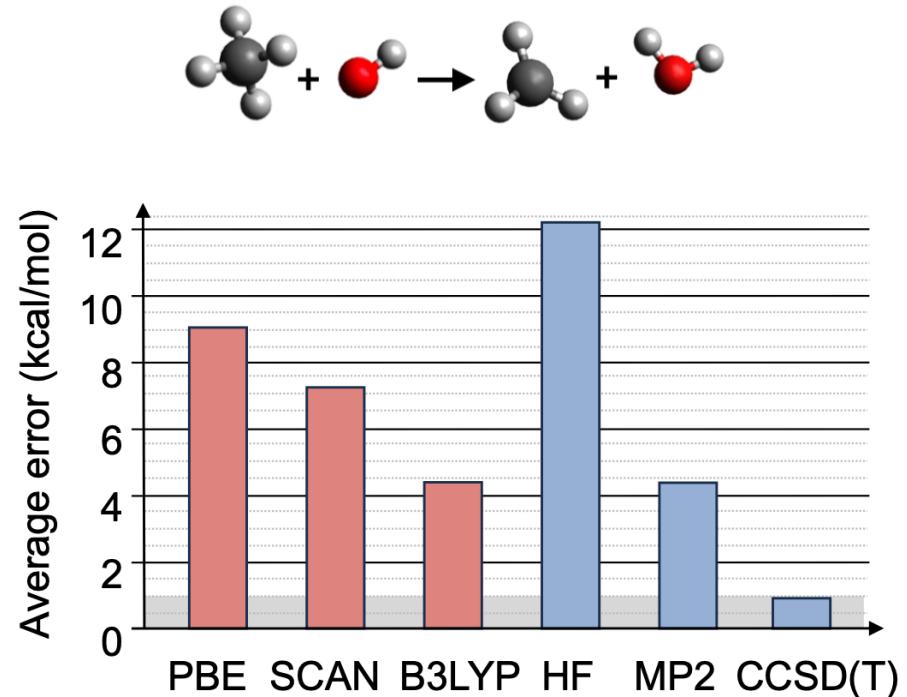
$$(P|\mu\nu) = (P|\mu\nu)_{\text{SR}} + (P|\mu\nu)_{\text{LR}}$$

real space *reciprocal space*

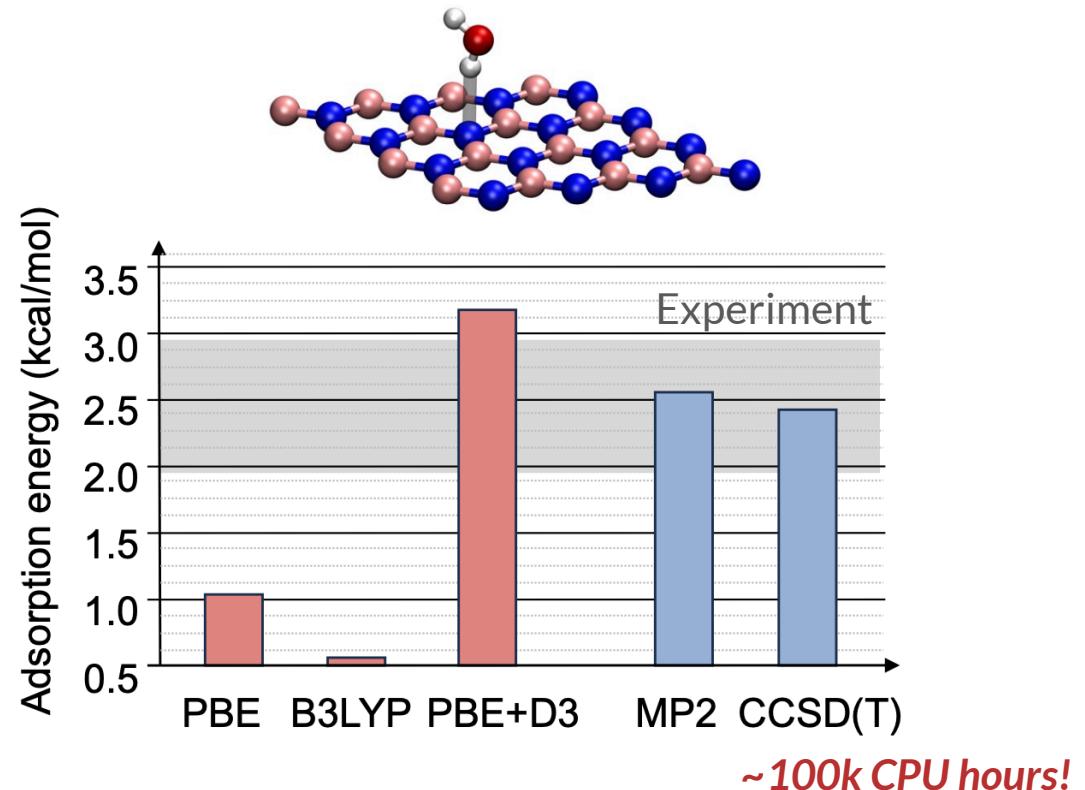


Achieving “chemical accuracy” for materials science?

Database of gas-phase barrier heights



Adsorption energy of water on h-BN



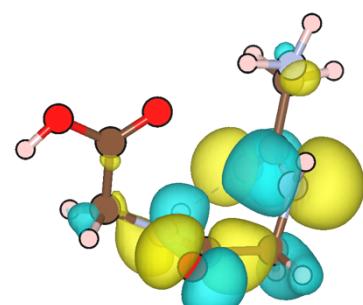
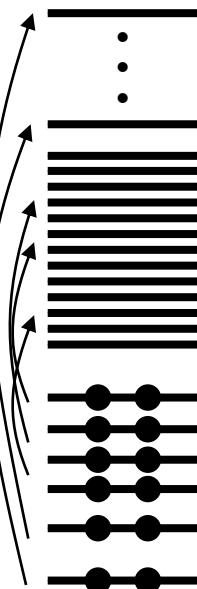
Can we reduce the cost of periodic CCSD(T)?

- reliably converge calculations (basis set size, k-points/supercell size, ...)
- explore PES (barrier heights, vibrations, molecular dynamics, ...)

Reducing the cost of CCSD(T)

CCSD(T): $O(N^7)$

All unoccupied



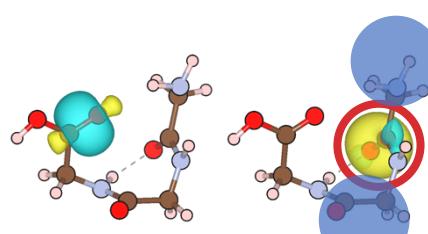
Molecular orbitals are usually *delocalized*

Local CCSD(T): $O(N)$

S. Li, W. Li, Piecuch, Kállay, Nagy, ...

All occupied

$$E = E_1 + E_2 + \dots$$



Molecular orbitals can be *localized*



Improved accuracy w/ more orbitals

Nearby unoccupieds

Localized orbital

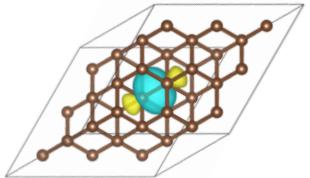
Nearby occupieds

Now implemented for materials with periodic boundary conditions

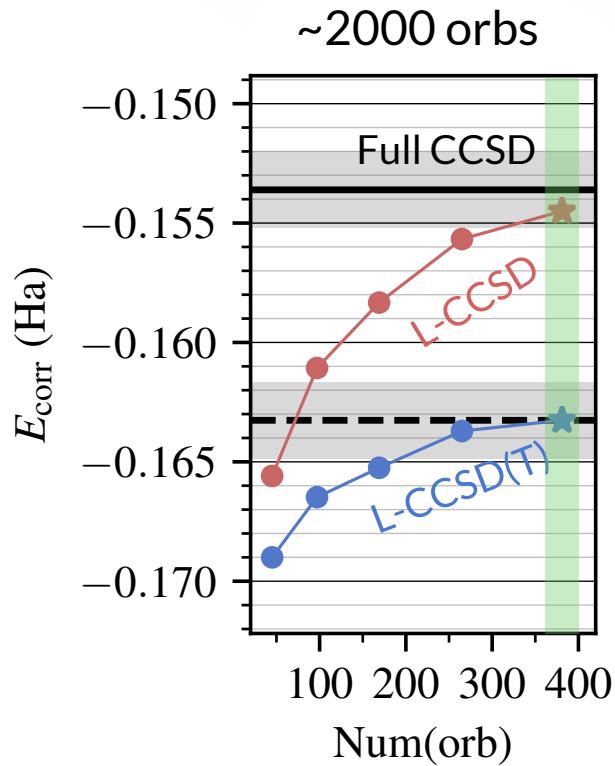
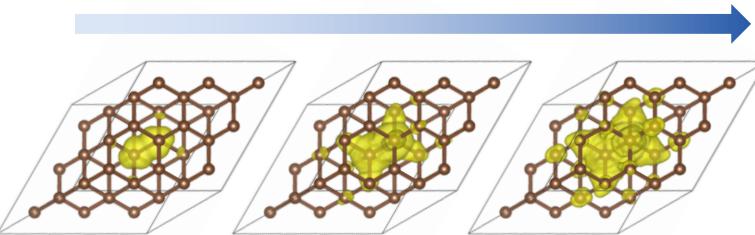


Diamond with local coupled cluster

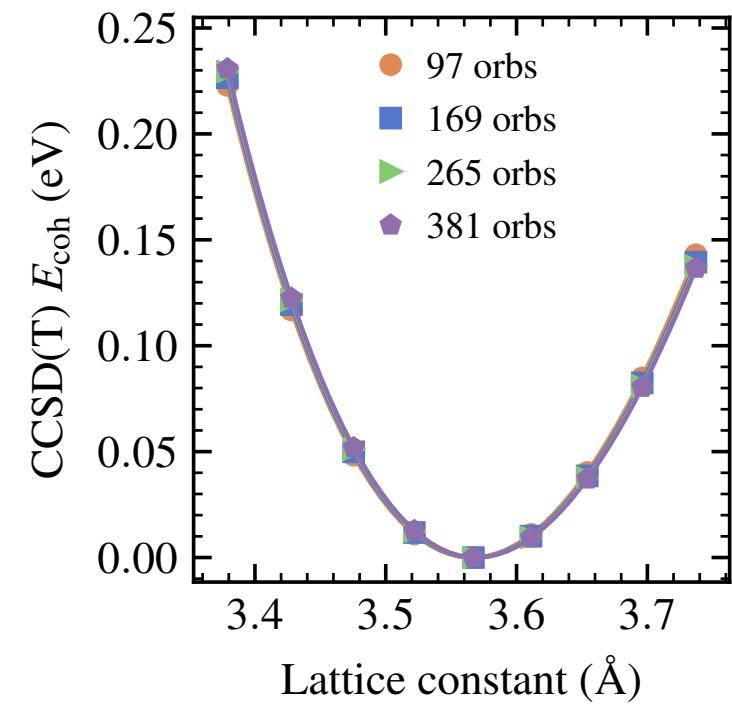
Localized orbital
(C-C single bond)



Local subspace of increasing size



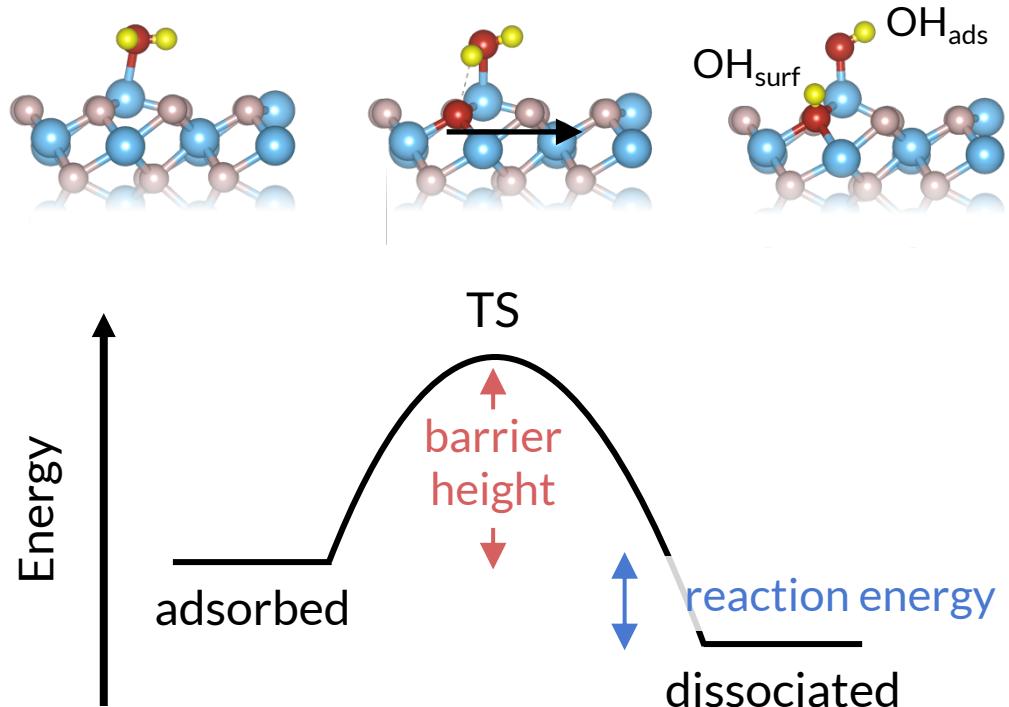
	E_{coh} eV	Cost CPUh	Bulk mod. GPa
Full CCSD	7.3	3000	
L-CCSD	7.3	10	466
L-CCSD(T)	7.5	100	448
Expt	7.5		453



Water on Al_2O_3

Al_2O_3 is a non-magnetic insulator and common catalyst support

Does water dissociate upon adsorption?



The Chemistry of Water on Alumina Surface:
Reaction Dynamics from First Principles

Andreoni and co-workers, *Science* **282** (1998)

Computational: CPMD with DFT@BLYP

... free energy profiles established that **molecularly adsorbed water is metastable and dissociates readily.**

Confirmed by many other DFT@GGA+vdW studies

Molecular Water Adsorption and Reactions on $\alpha\text{-Al}_2\text{O}_3(0001)$ and α -Alumina Particles

Kimmel and co-workers, *J. Phys. Chem. C* **122** (2018)

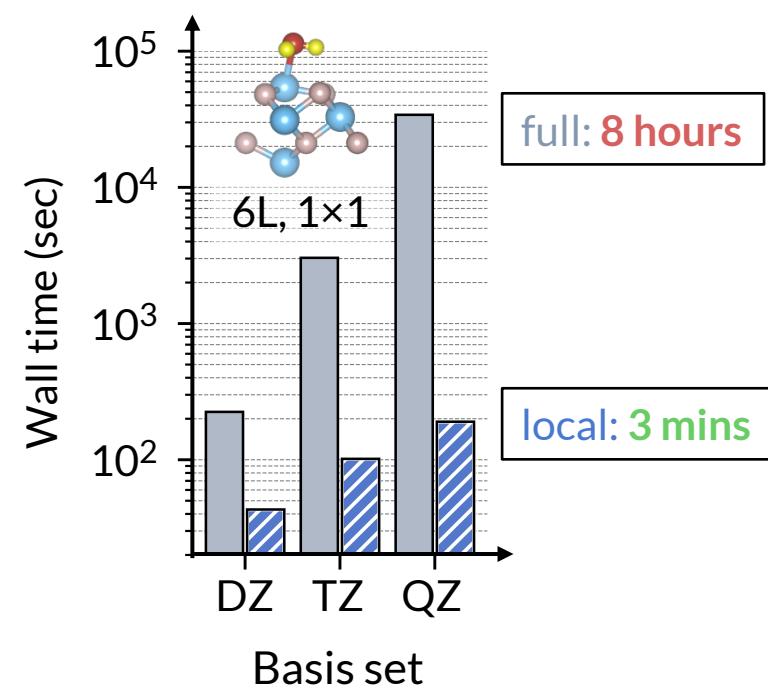
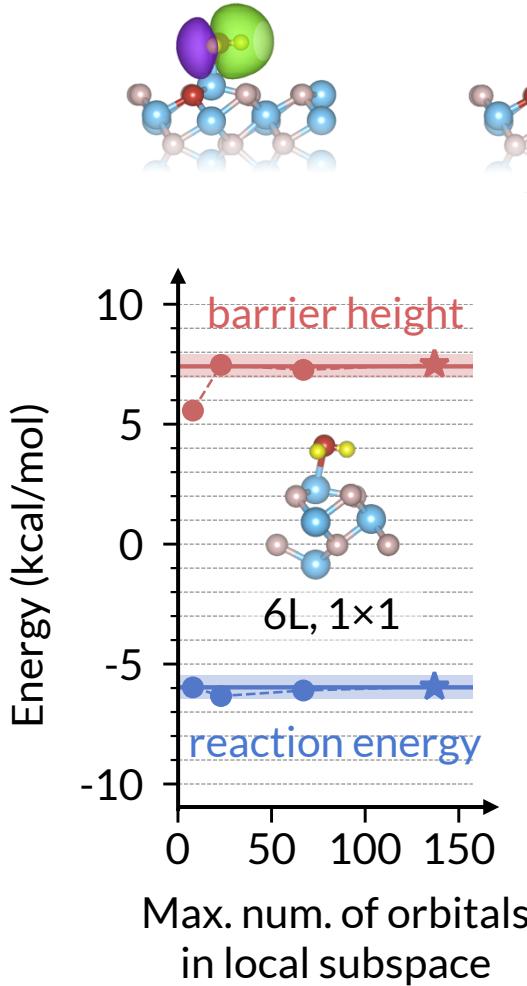
Experimental: TPD and vibrational spectroscopy in UHV

... at most a **small amount of water dissociation** ...
difficult to reconcile with calculations suggesting
that the barrier to dissociation is small.

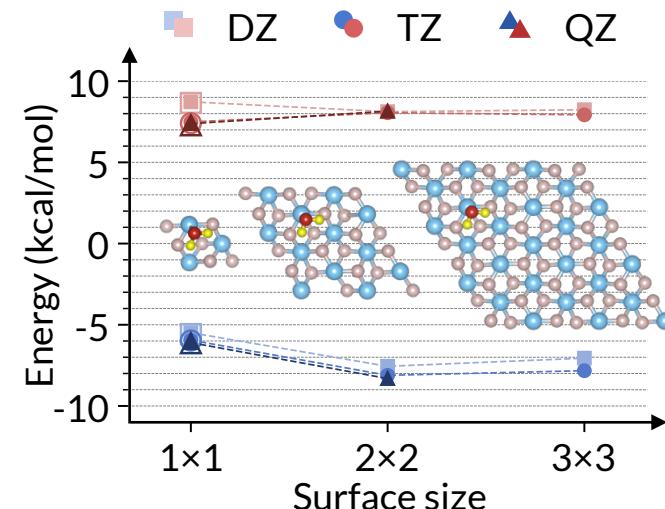
Water on Al_2O_3 from local CCSD(T)

For each
localized orbital

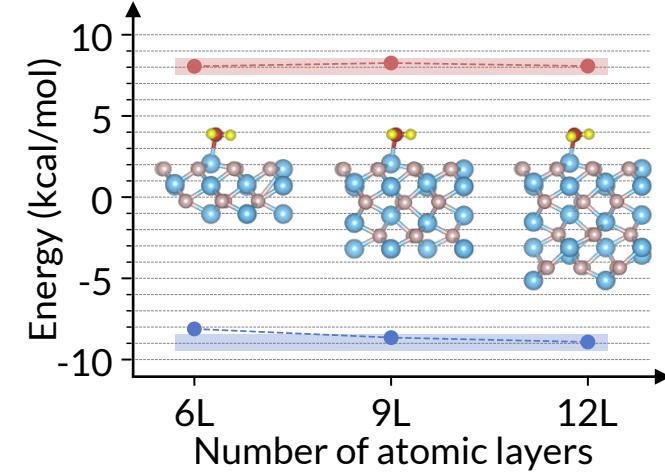
Local subspace of increasing size



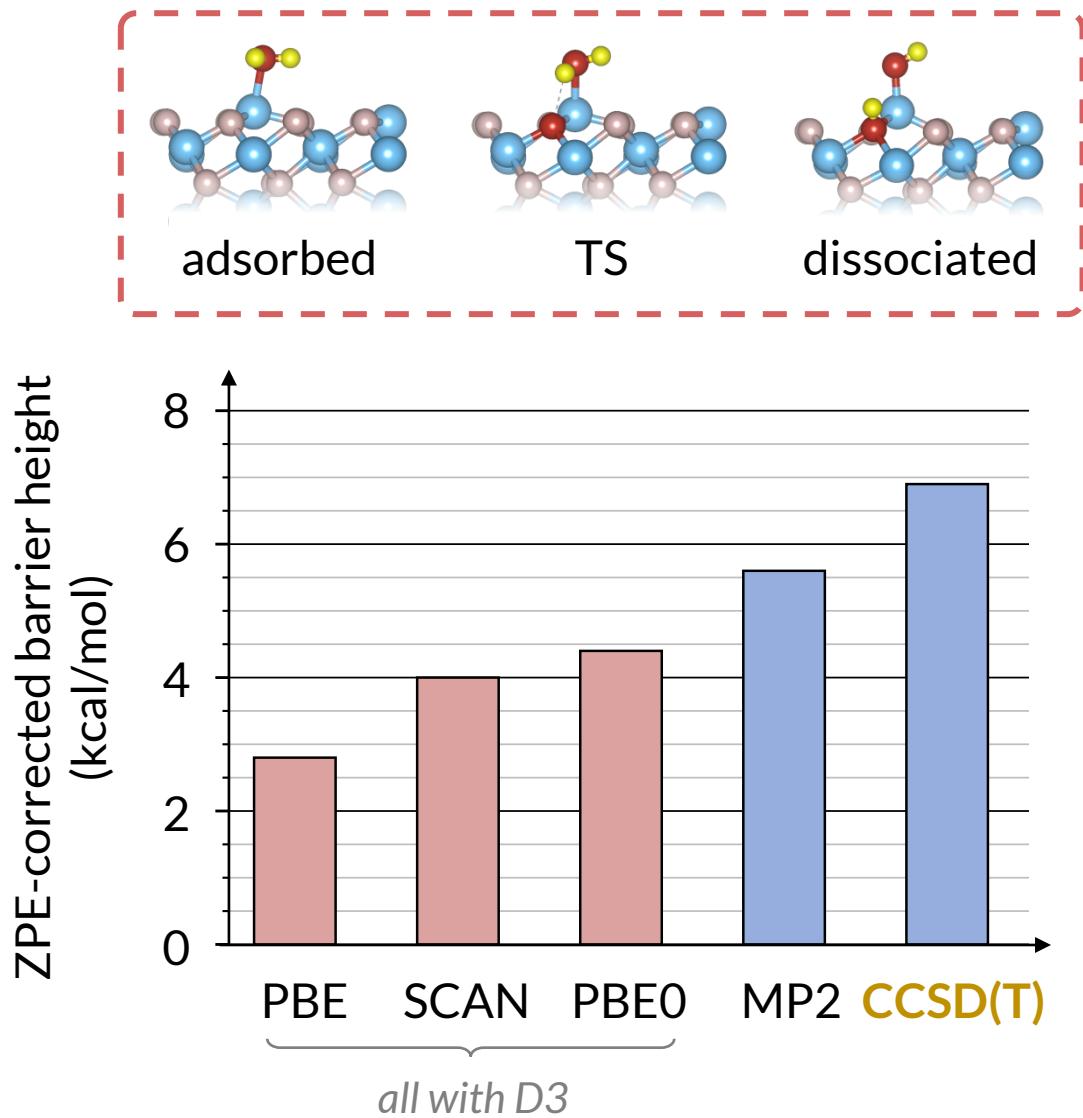
Converge with surface & basis size



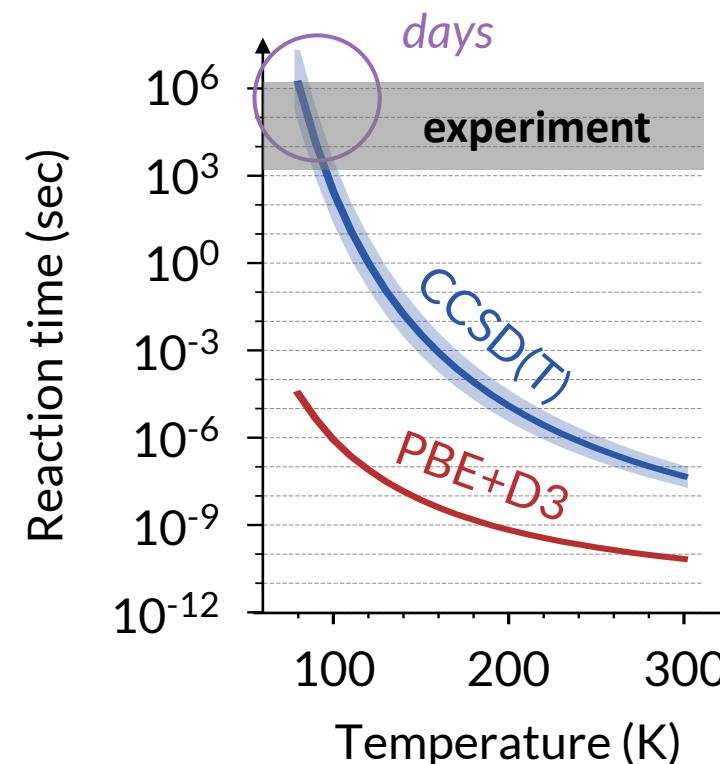
Converge with slab thickness



Water on Al_2O_3

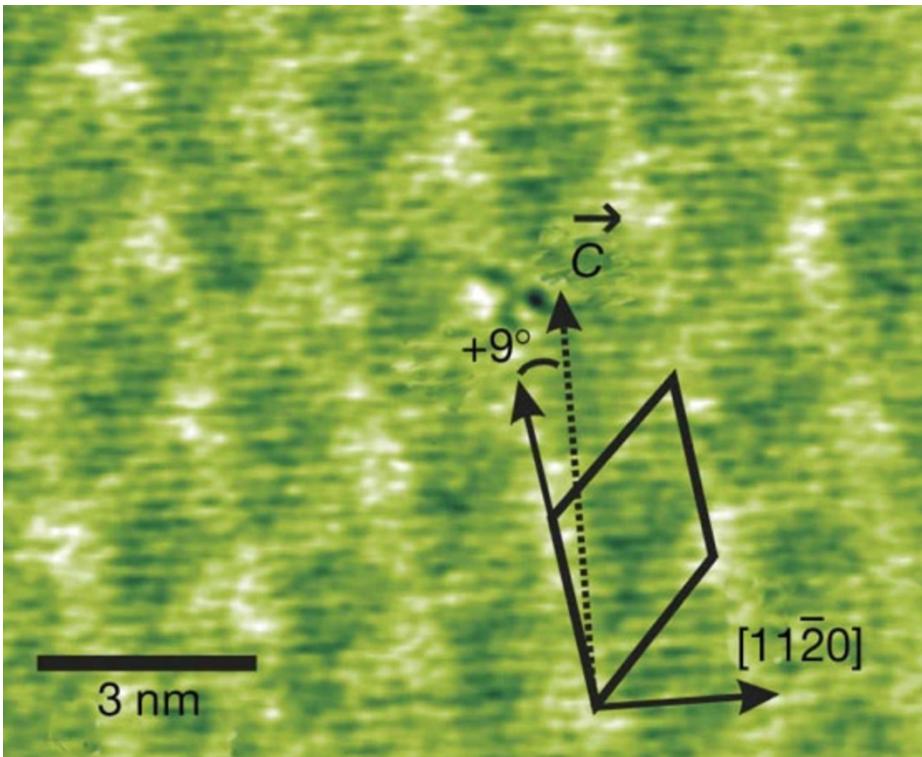


Does this explain experiments?
Not really.

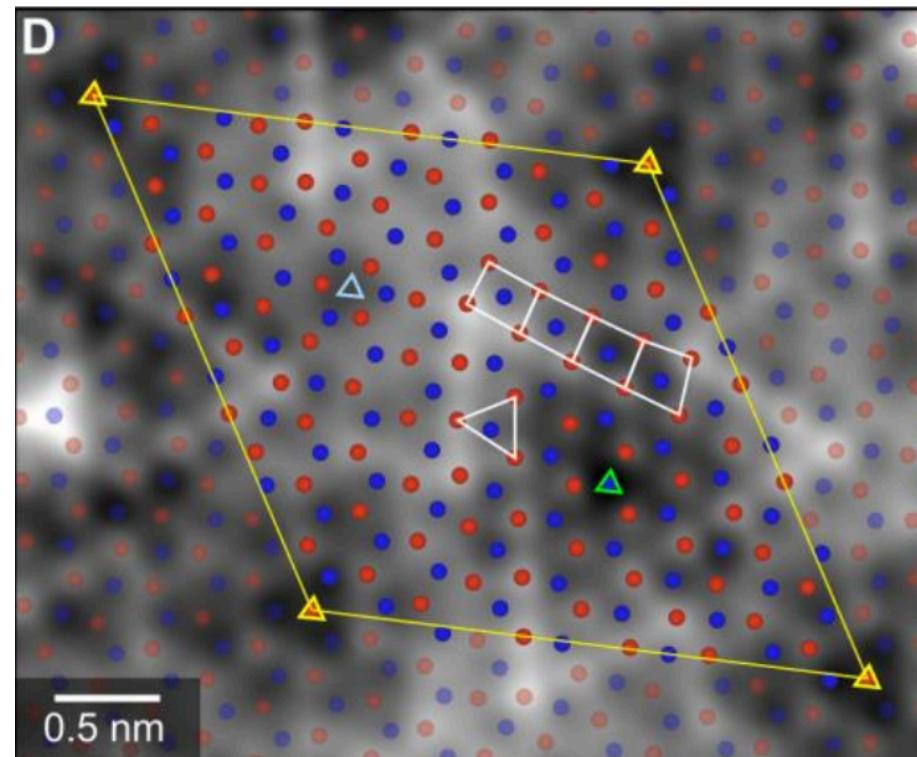


Evidence for surface reorganization

Effect on water dissociation has not been characterized yet
May be good target for DP-based dynamics



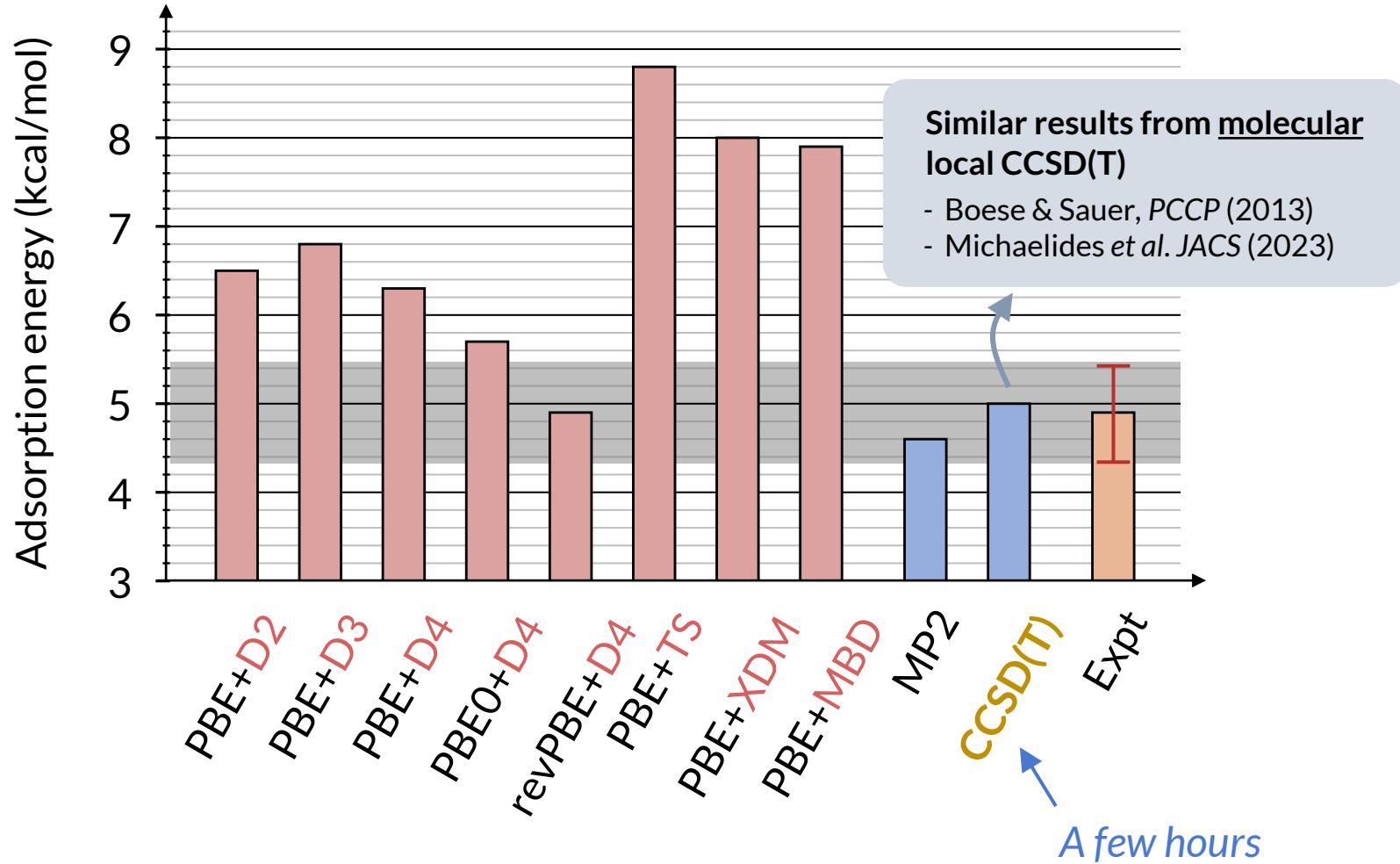
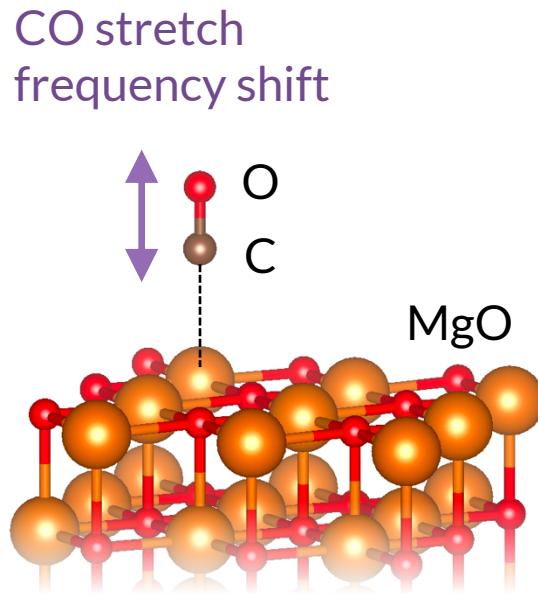
Barth & Reichling, Nature, 414 (2001)



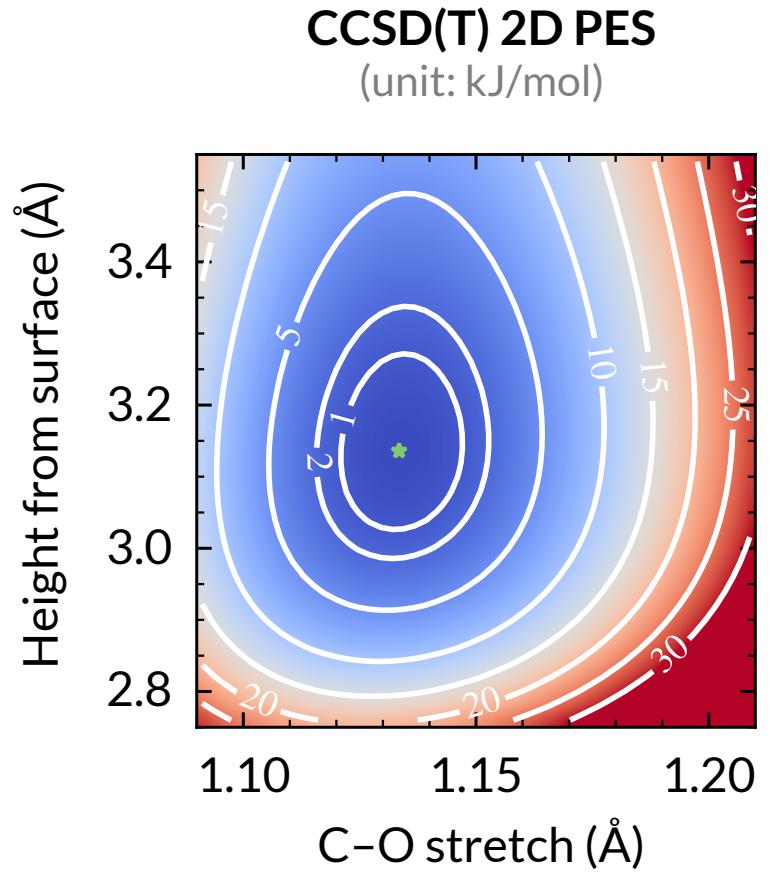
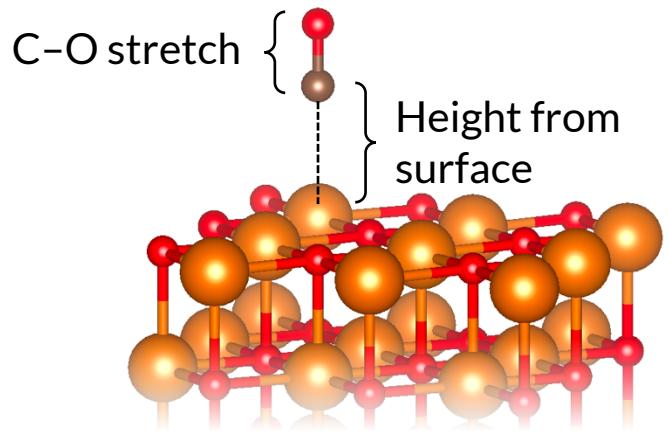
Balajka and co-workers, arXiv:2405.19263

CO on MgO

Can we predict the adsorption energy of CO on MgO?

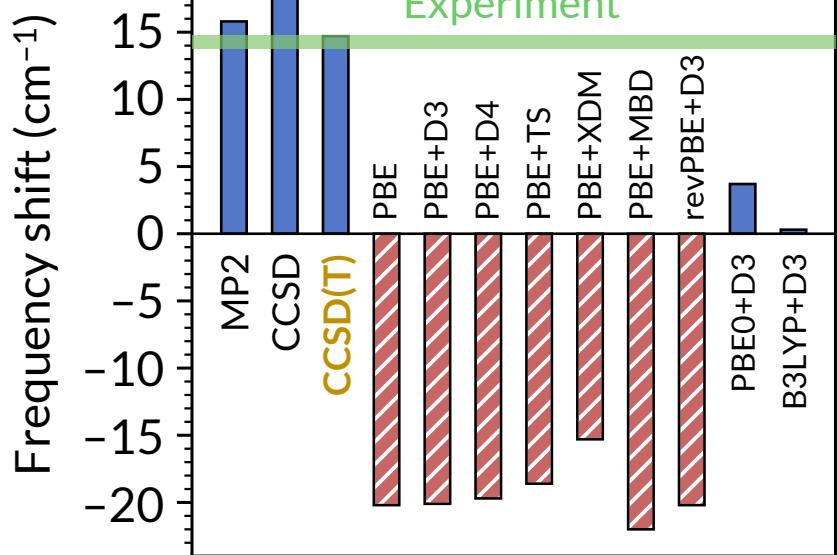
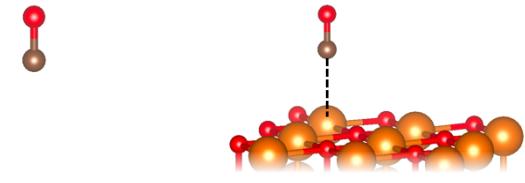


CO on MgO



C-O stretch frequency shift

gas \longrightarrow surface

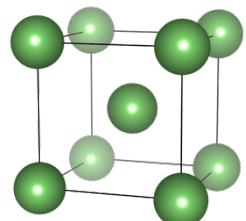


Metals

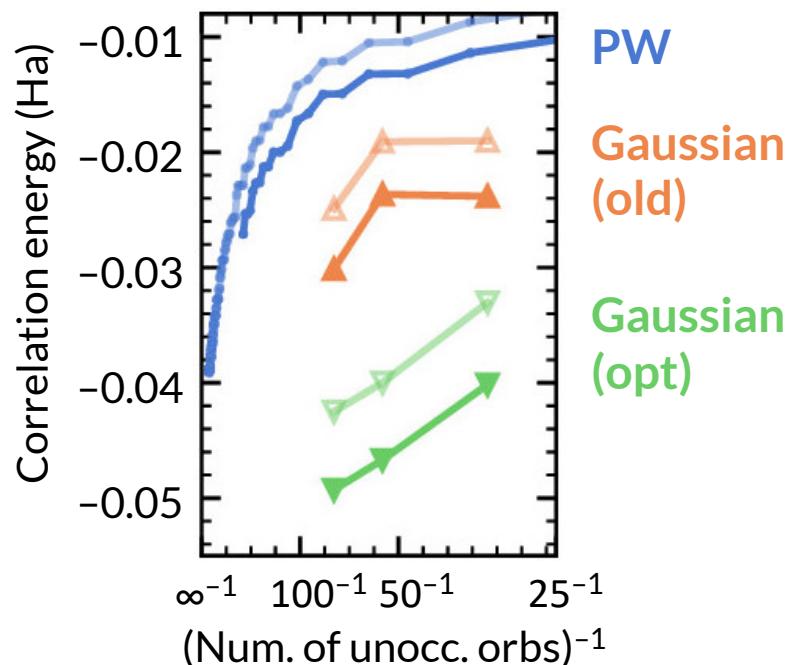
Most industrial catalysts are based on transitional metals

Can coupled cluster theory describe metals?

Neufeld, HY and TCB, *J. Phys. Chem. Lett.* **13**, 2022



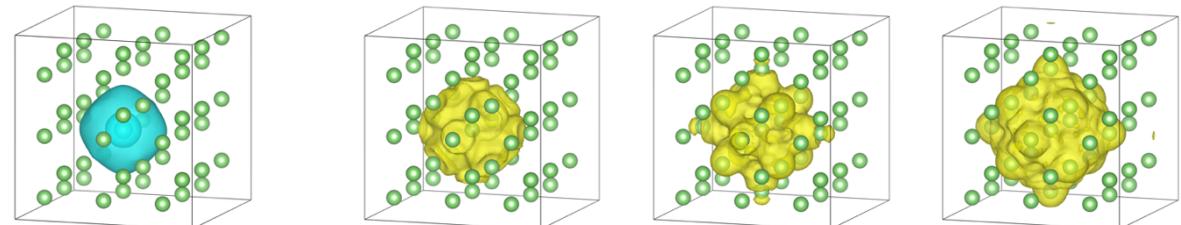
BCC lithium



Can local theory reduce the cost of CCSD?

Localized orbitals
(1s & 2s IAOs)

Local subspace of increasing size



	Ecoh eV	Lat. const. Angstrom	Cost CPUh
HF	0.6	3.67	
Full CCSD	1.5	3.48	5000
L-CCSD	1.5	3.48	20
Expt	1.7	3.45	

See also Shepard, Grüneis, et al. *Nat. Comput. Sci.* 2021

HY and TCB, submitted

Towards CCSD(T)-accuracy ML potential

CCSD(T)-accuracy ML potential for water from transfer learning

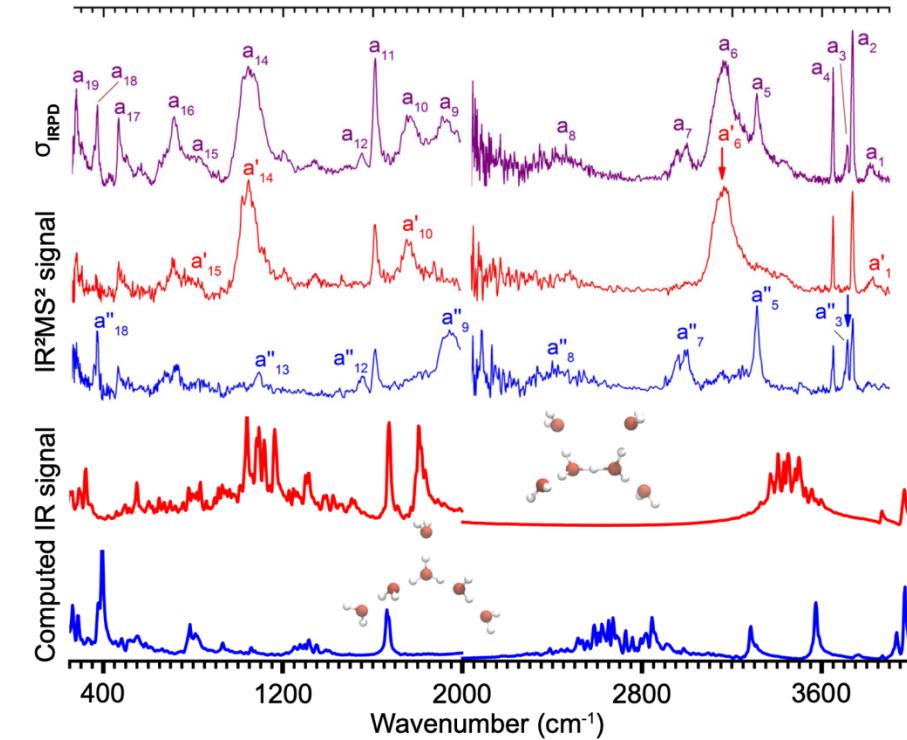
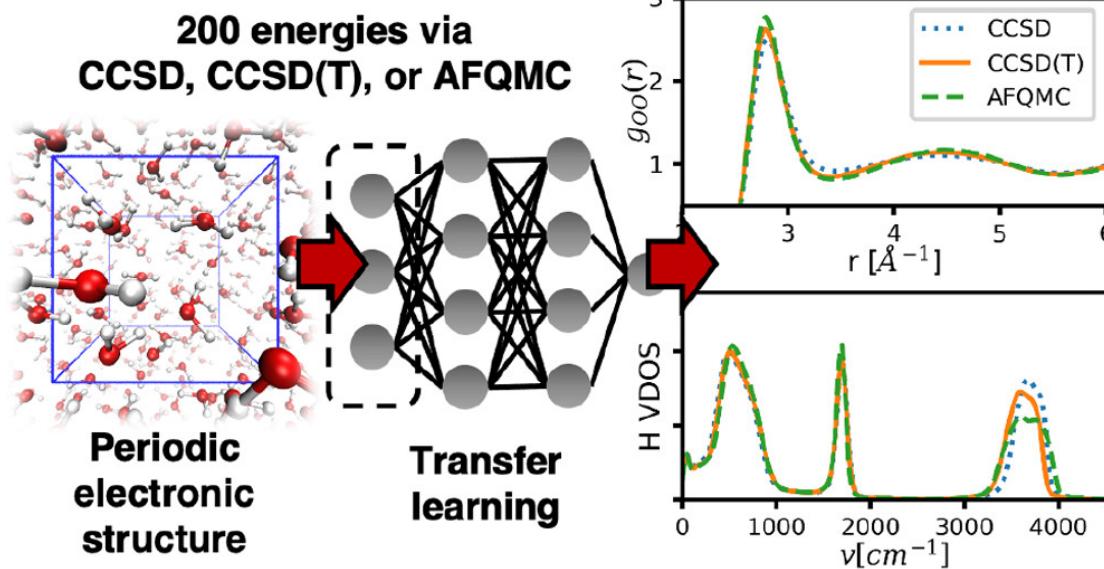


Chen, Lee, HY, TCB, Reichman, Markland, *JCTC*, **19** (2023)

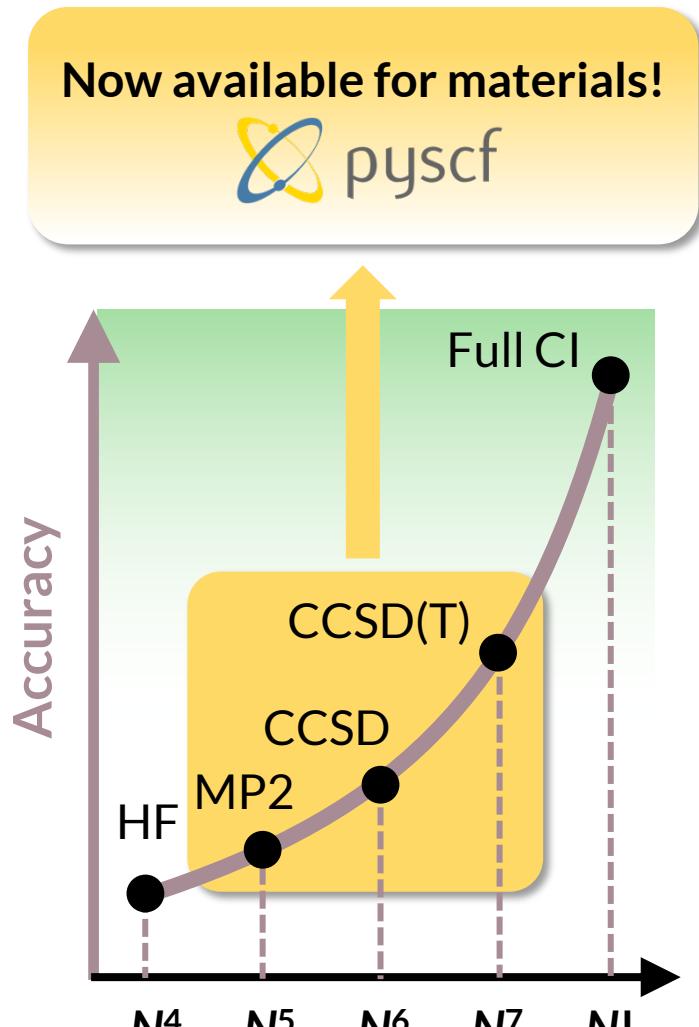
Atomic forces and *ab initio* MD from AD-local CCSD(T)



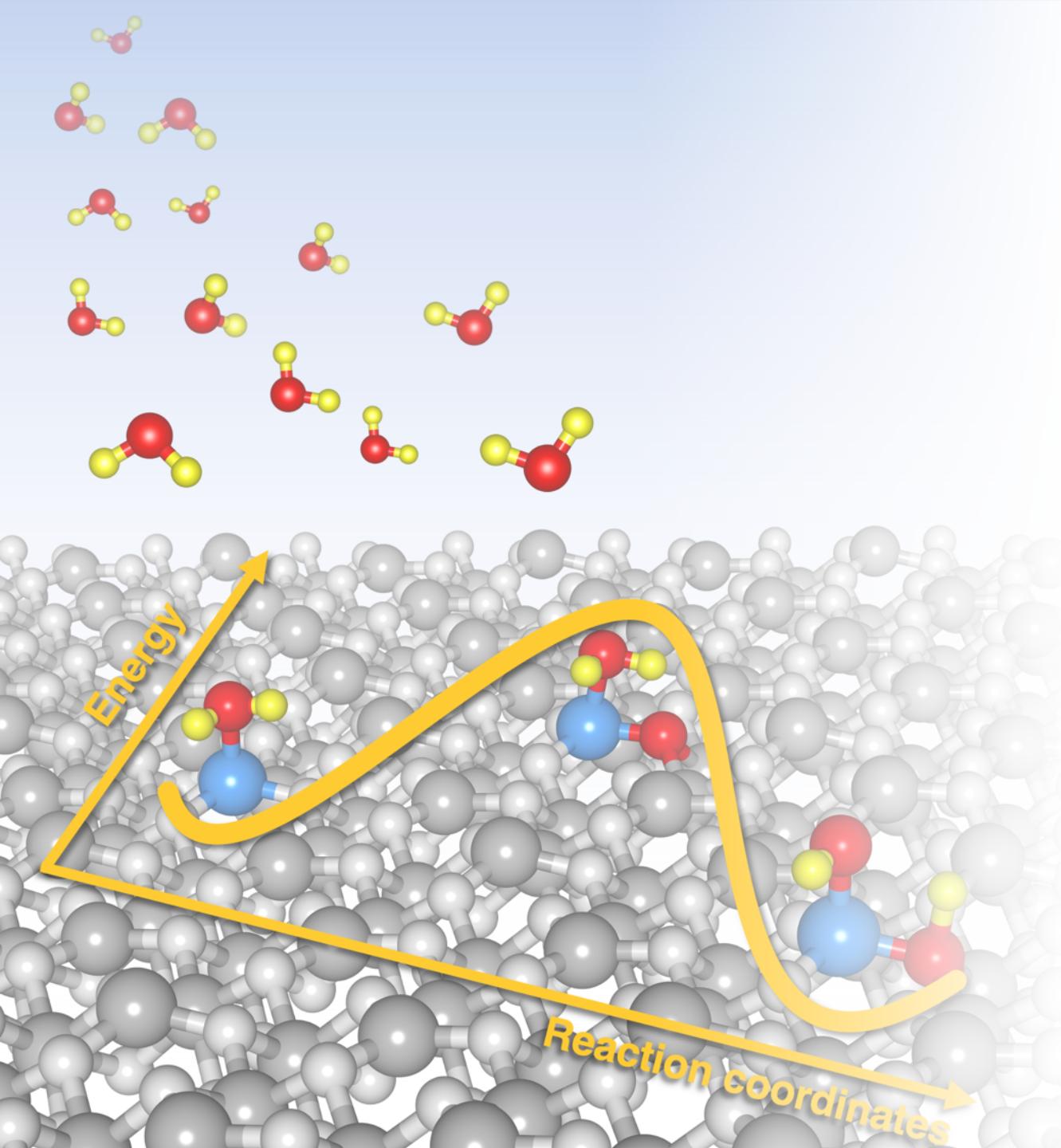
Zhang*, Li*, HY, TCB, Chan,, *arXiv:2404.03129*



Conclusion



- New infrastructure for periodic quantum chemistry
 - Fast periodic density fitting, integral screening and integral-direct
[HY](#) and TCB, JCP, **154** (2021); [HY](#) and TCB, JCP, **155** (2022); Bintrim, TCB and [HY](#) JCTC, **18** (2022)
- Correlation consistent Gaussian basis sets for solids
[HY](#) and TCB, JCTC, **18** (2022)
- “Gold standard” for materials from local CCSD(T)
 - Methodology & application to bulk diamond and BCC lithium
[HY](#) and TCB, submitted (to appear on arXiv soon)
 - Application to surface chemistry Water on Al_2O_3 and CO on MgO
[HY](#) and TCB, arXiv:2309.14640
[HY](#) and TCB, Faraday Discuss. (2024)
- Towards *ab initio* molecular dynamics at CCSD(T) level
 - Transfer learning from DFT-based neural-network potential
Chen, Lee, [HY](#), TCB, Reichman, Markland, JCTC, **19** (2023)
 - Automatic differentiation-based local CCSD(T)
Zhang*, Li*, [HY](#), TCB, Chan, arXiv:2404.03129



*Thank you all for
your attention!*

Prof. Timothy
C. Berkelbach

