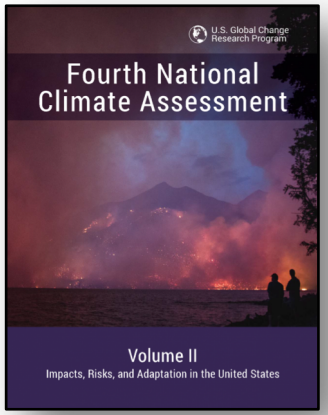
# What climate change means for Maine

*Shortened snowmobile and ski seasons*

*Lobster-shell disease*

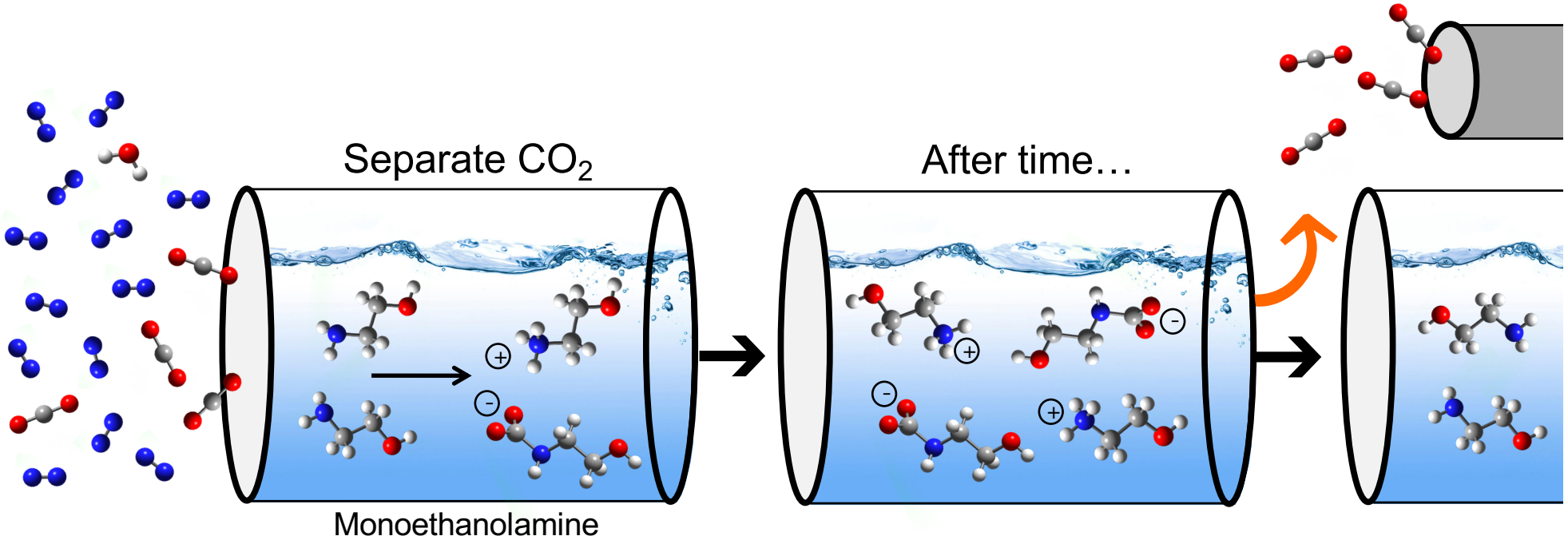
*Increased inland and coastal flooding*


*All hands on deck*

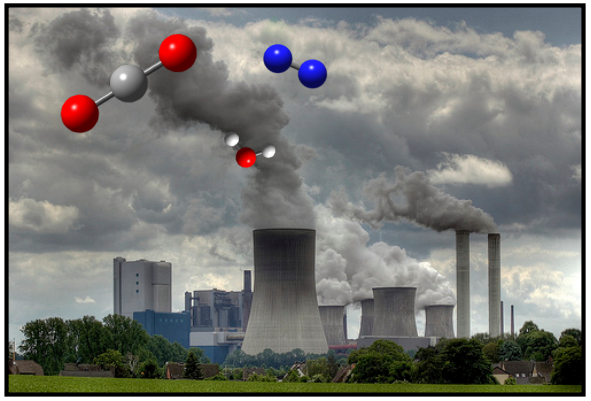
*Nov. 23rd (2018)*

# $CO_2$ capture via amine scrubbing



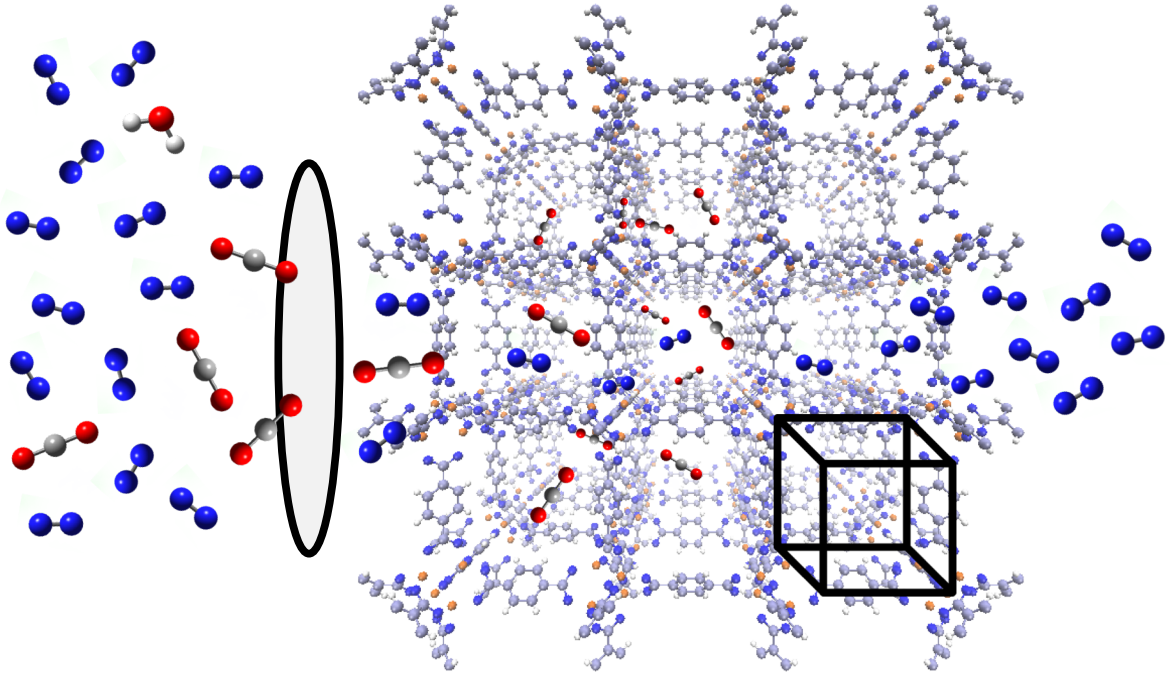

Solvent Regeneration

**13% $CO_2$ 77% $N_2$ 6% $H_2O$**

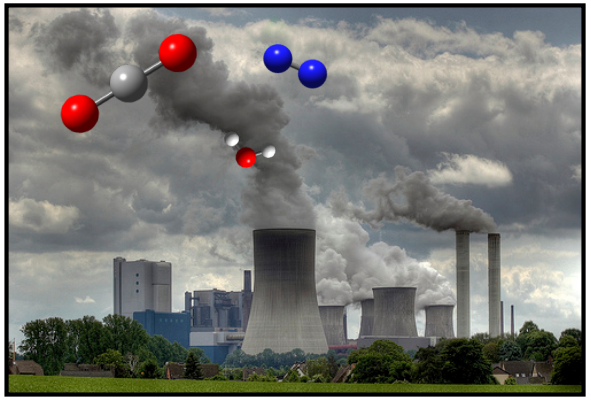


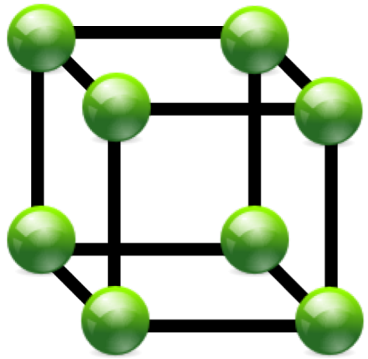
**Energy Penalty**

# How to reduce the cost of $CO_2$ capture?



13% $CO_2$ 77% $N_2$ 6% $H_2O$



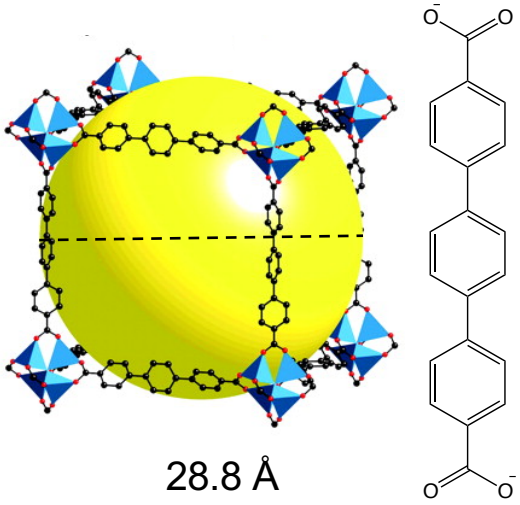


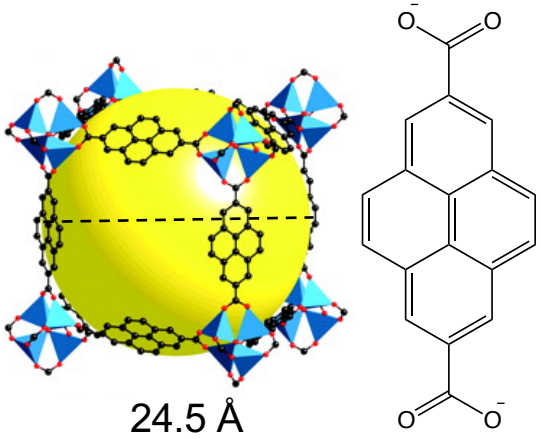
Linker (organic)

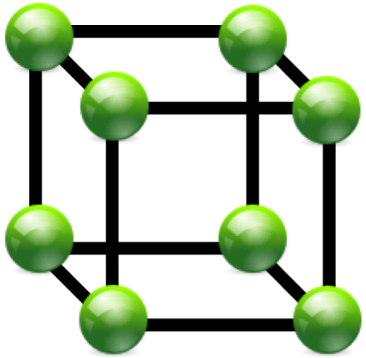
Node (metal)

Metal-Organic Frameworks
"MOFs"

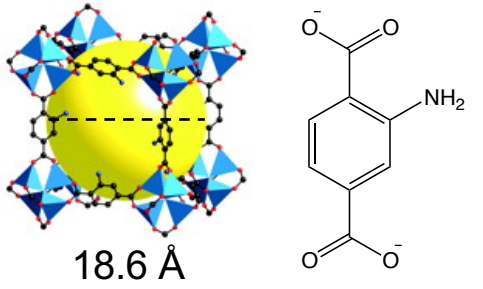
# Metal-organic frameworks

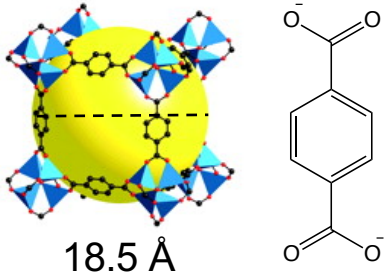


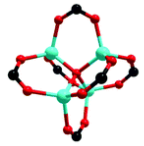
**Tailor-make a MOF**




Linker (organic)

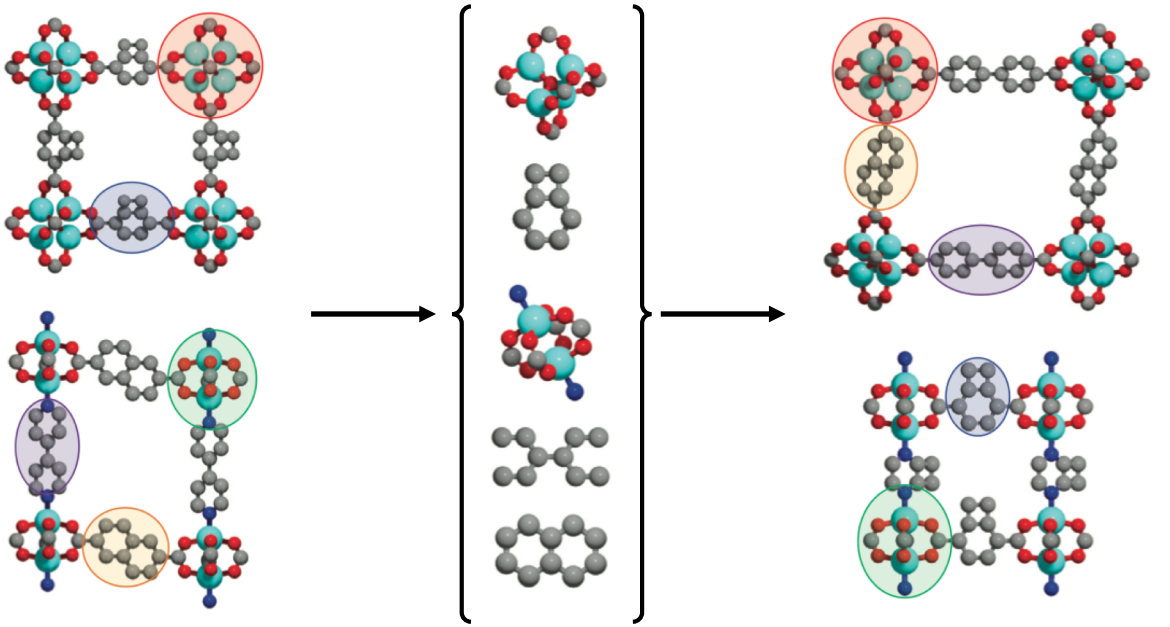
Node (metal)

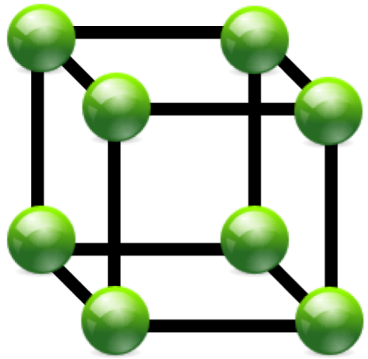


$Zn_4O^{6+}$

*M. Eddaoudi et al., Science (2002)*

# Computational design of hypothetical MOFs



Linker (organic)

Node (metal)

**137,000** Hypothetical MOFs

5 Nodes
42 Linkers
13 Functional Groups

*C. E. Wilmer et al., Nature Chem. (2012)*

# $CO_2$ adsorption in MOF-74

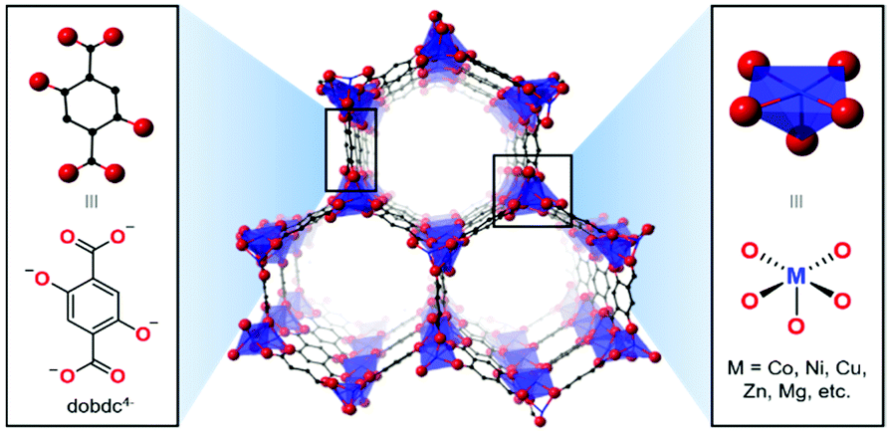
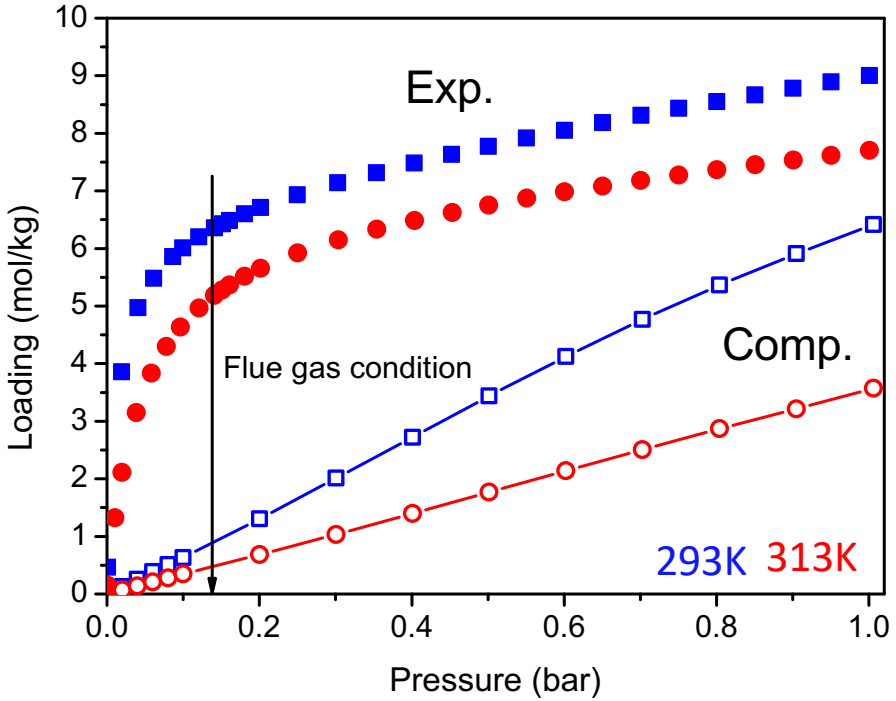
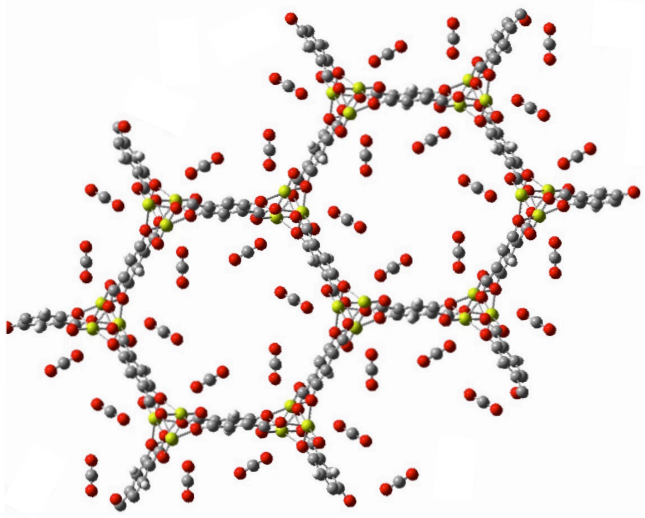
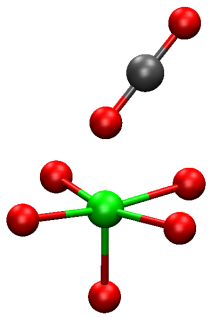



*Image from Liao et al., Chem. Commun. (2017)*



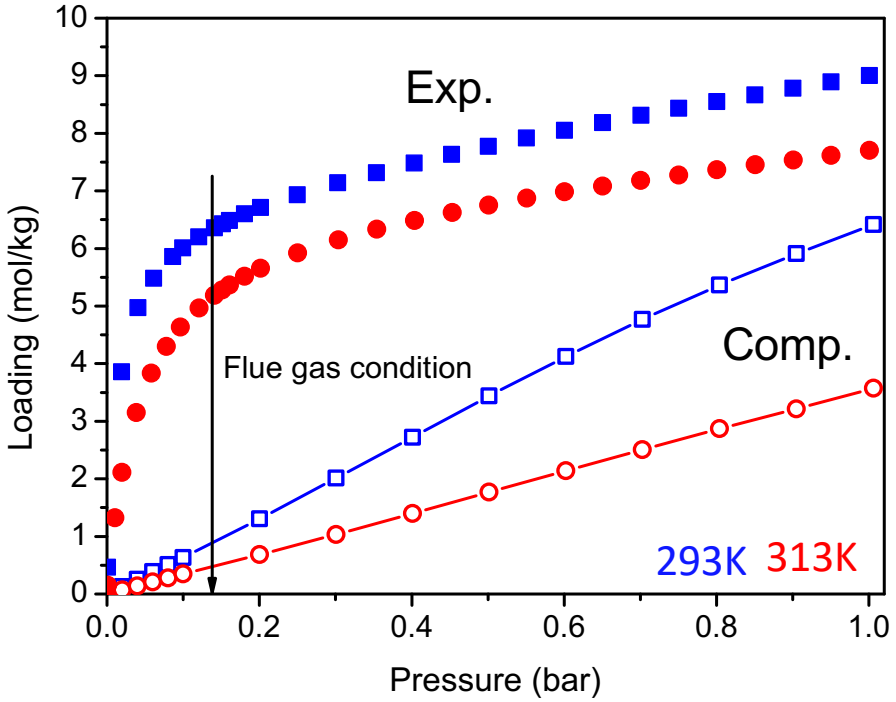



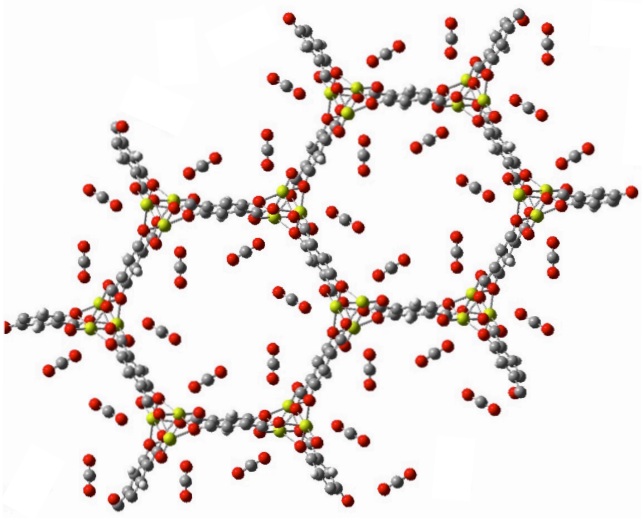


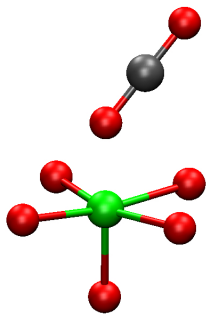
# $CO_2$ adsorption in MOF-74

Lennard-Jones + Charges

$$U(r_{ij}) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{1}{4\pi\epsilon_0}\left(\frac{q_i q_j}{r_{ij}}\right)$$



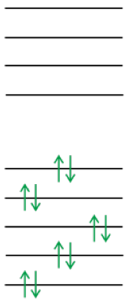





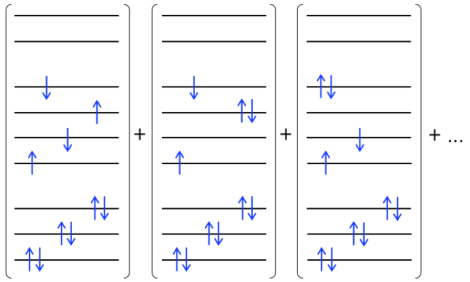
# Reference intermolecular interaction energies

## Wavefunctions $\psi$

single-configurational (single-reference)

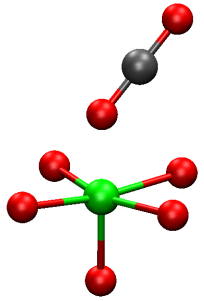


multi-configurational (multi-reference)


$$E_{int} = E_{elec} + E_{ind} + E_{disp} + E_{exrep}$$

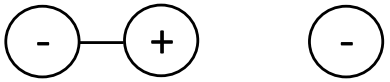
**Ab initio**



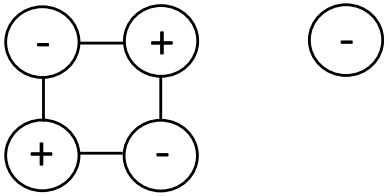
# Distributed multipole expansion

Charge – Charge

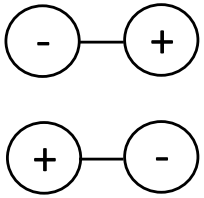

Dipole – Charge



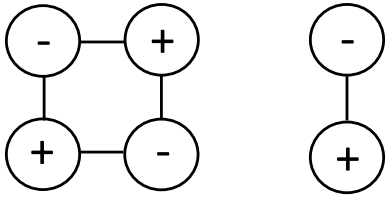

Quadrupole – Charge



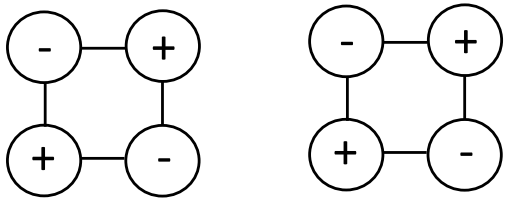

Dipole – Dipole




Quadrupole – Dipole

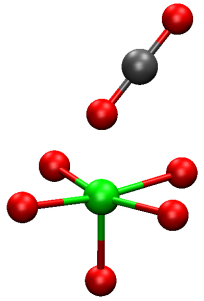



Quadrupole – Quadrupole



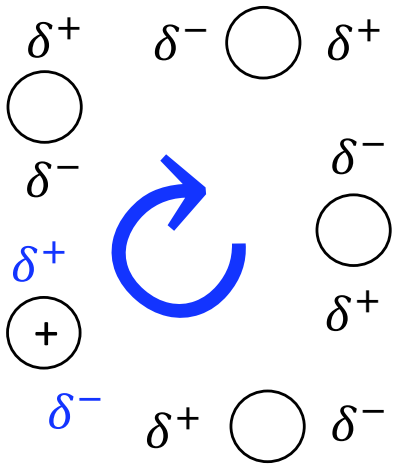

$$E_{int} = \boxed{E_{elec}} + E_{ind} + E_{disp} + E_{exrep}$$

$$\boxed{E_{elec} = \sum_{i}^{A} \sum_{j}^{B} E_{elec}^{AB}}$$



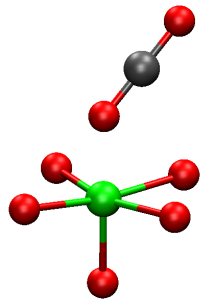
$$\begin{aligned} E_{elec}^{AB} = \; & T^{ij}\left(q^i q^j\right) + \\ & T_{\alpha}^{ij}\left(q^i \mu_{\alpha}^{j} - \mu_{\alpha}^{i} q^j\right) + \\ & T_{\alpha\beta}^{ij}\left(\frac{1}{3} q^i \Theta_{\alpha\beta}^{j} - \mu_{\alpha}^{i}\mu_{\beta}^{j} + \frac{1}{3}\Theta_{\alpha\beta}^{i} q^j\right) + \\ & T_{\alpha\beta\gamma}^{ij}\left(\frac{1}{3}\Theta_{\alpha\beta}^{i}\mu_{\gamma}^{j} - \frac{1}{3}\mu_{\alpha}^{i}\Theta_{\beta\gamma}^{j}\right) + \\ & T_{\alpha\beta\gamma\delta}^{ij}\left(\frac{1}{9}\Theta_{\alpha\beta}^{i}\Theta_{\gamma\delta}^{j} + \ldots\right) \end{aligned}$$

# Induced point dipole model




$$E_{int} = E_{elec} + \boxed{E_{ind}} + E_{disp} + E_{exrep}$$

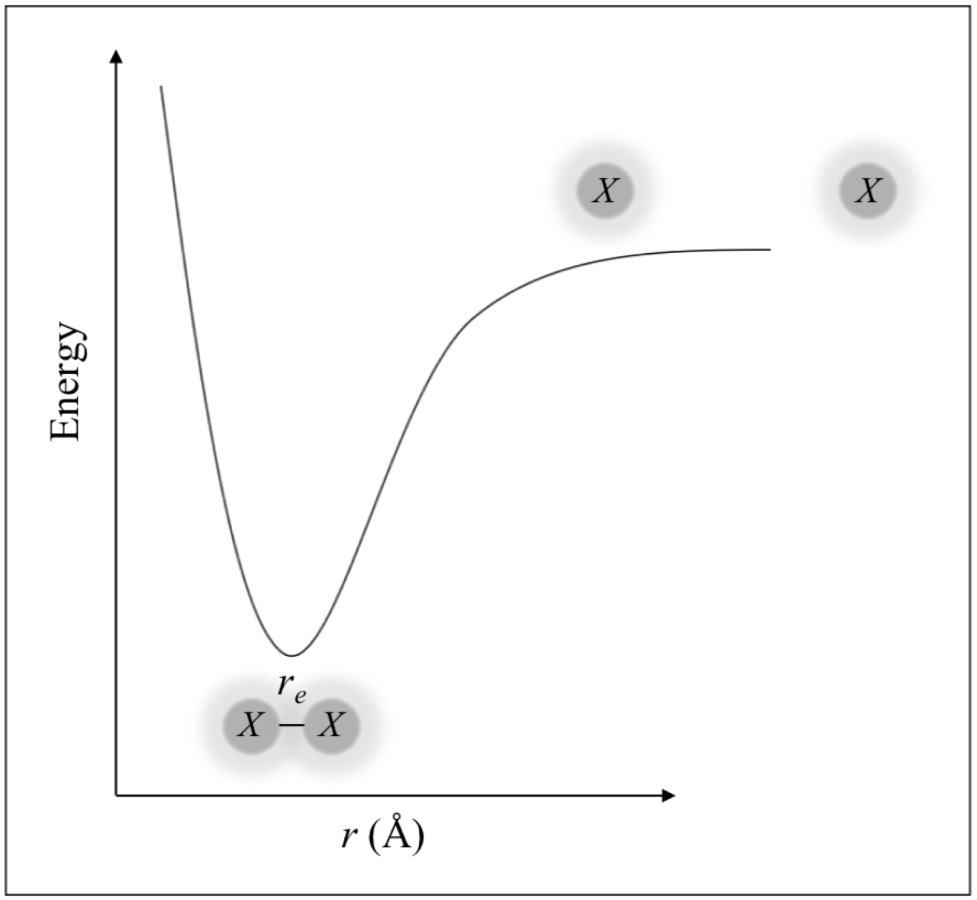
$$\boxed{E_{ind} = \sum_{i}^{A} E_{ind}^{A} + \sum_{j}^{B} E_{ind}^{B}}$$



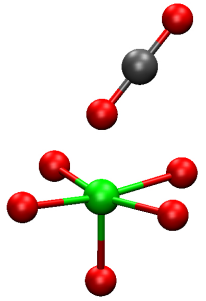
$$E_{ind}^{A} = -\left(\frac{1}{2}\mu_{\alpha}^{i,ind} F(A)_{\alpha}\right)$$

$$\mu_{\alpha}^{i,ind} = \alpha_{\alpha\beta}^{i} F(A)_{\beta}^{total}$$

# Dispersion and exchange-repulsion




$$E_{int} = E_{elec} + E_{ind} + \boxed{E_{disp} + E_{exrep}}$$



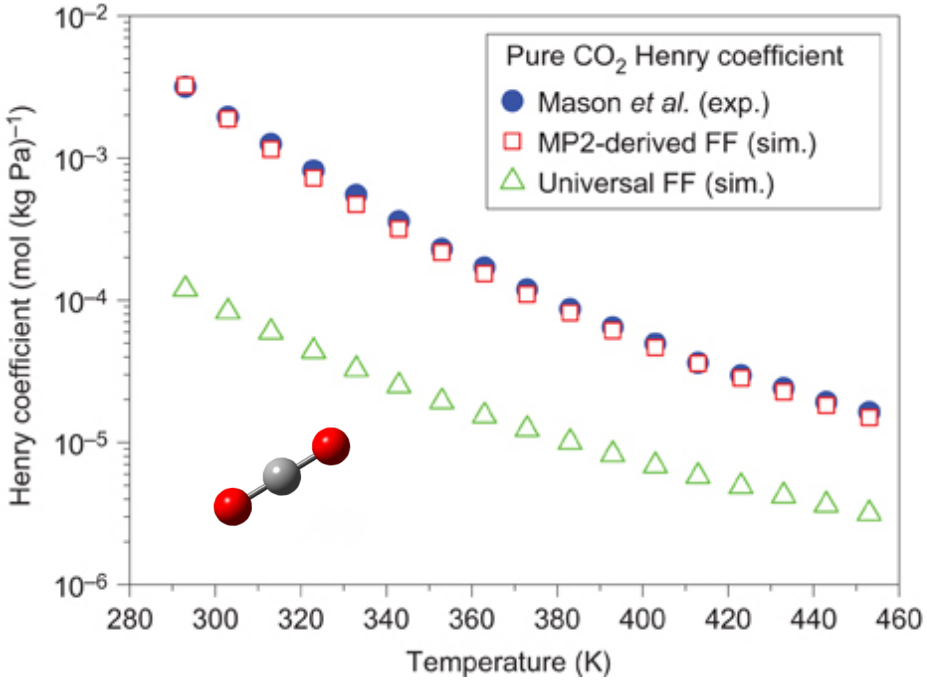
London-type

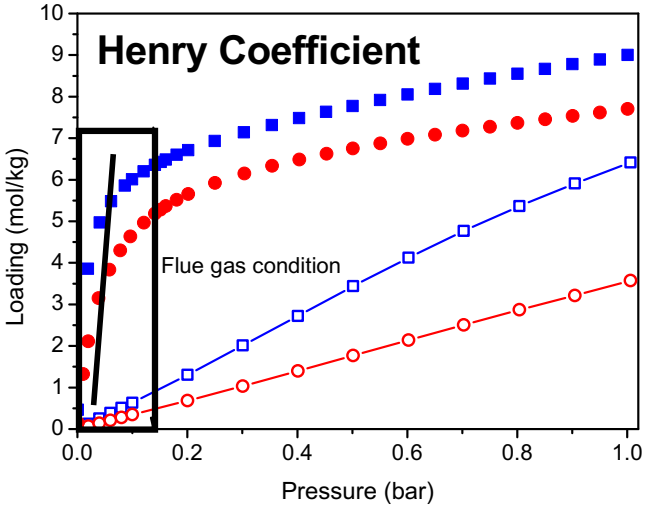
$$E_{disp} = -\sum_{i}^{A}\sum_{j}^{B} D^{ij}\frac{E_{ab}}{4}\alpha^{i}_{\alpha\beta}\alpha^{j}_{\gamma\delta}T^{ij}_{\alpha\gamma}T^{ij}_{\beta\delta}$$

Buckingham-type

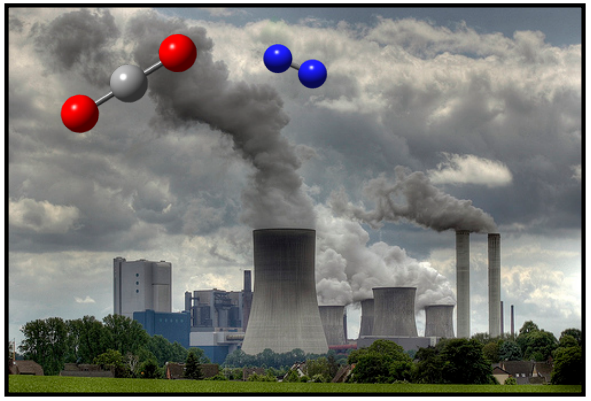
$$E_{exrep} = \sum_{i}^{A}\sum_{j}^{B} K_{ij}e^{(-\sigma_{ij}R)}$$

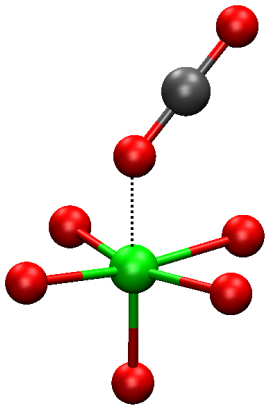
# $CO_2$ adsorption in MOF-74



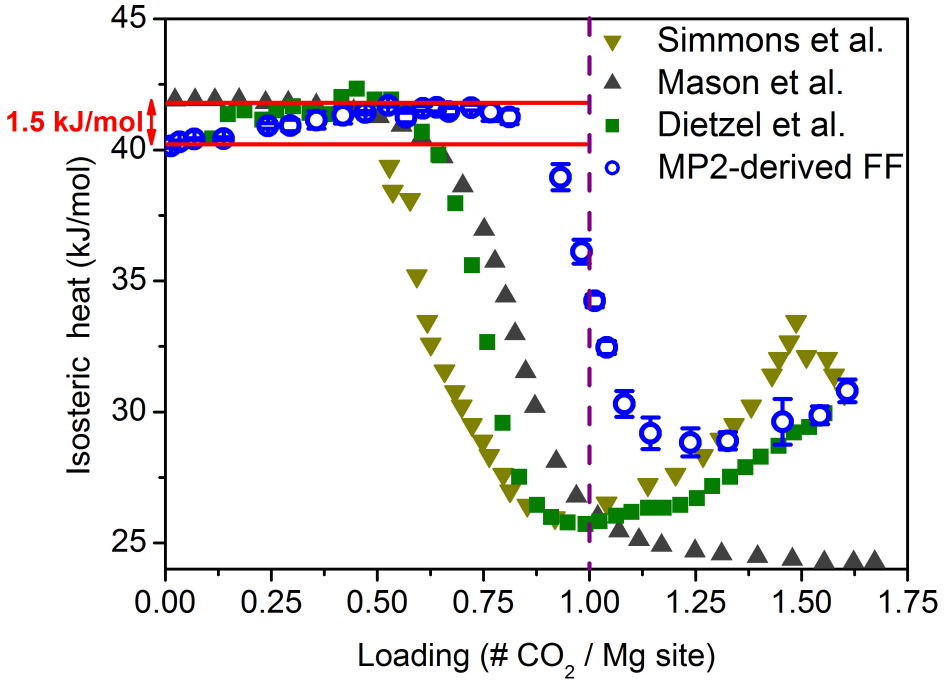




*A. L. Dzubak et al., Nature Chem. (2012)*



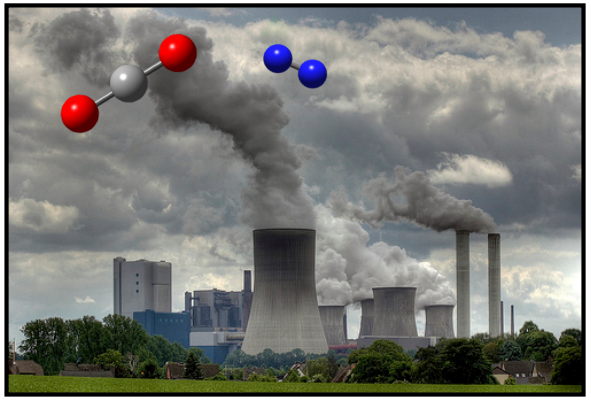


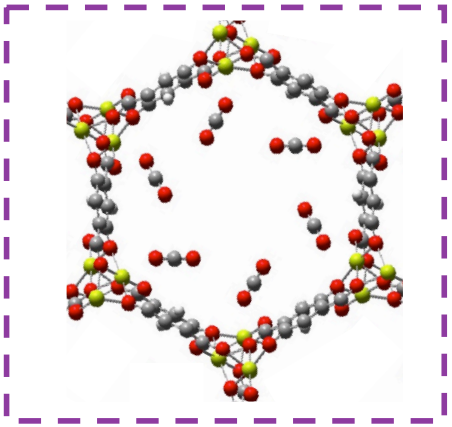
# Provides physical insight

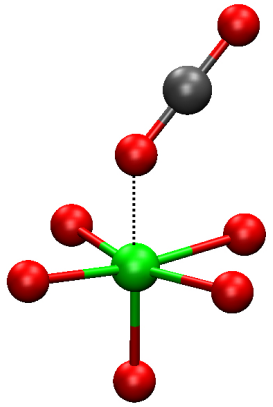



**Our Constraints:**

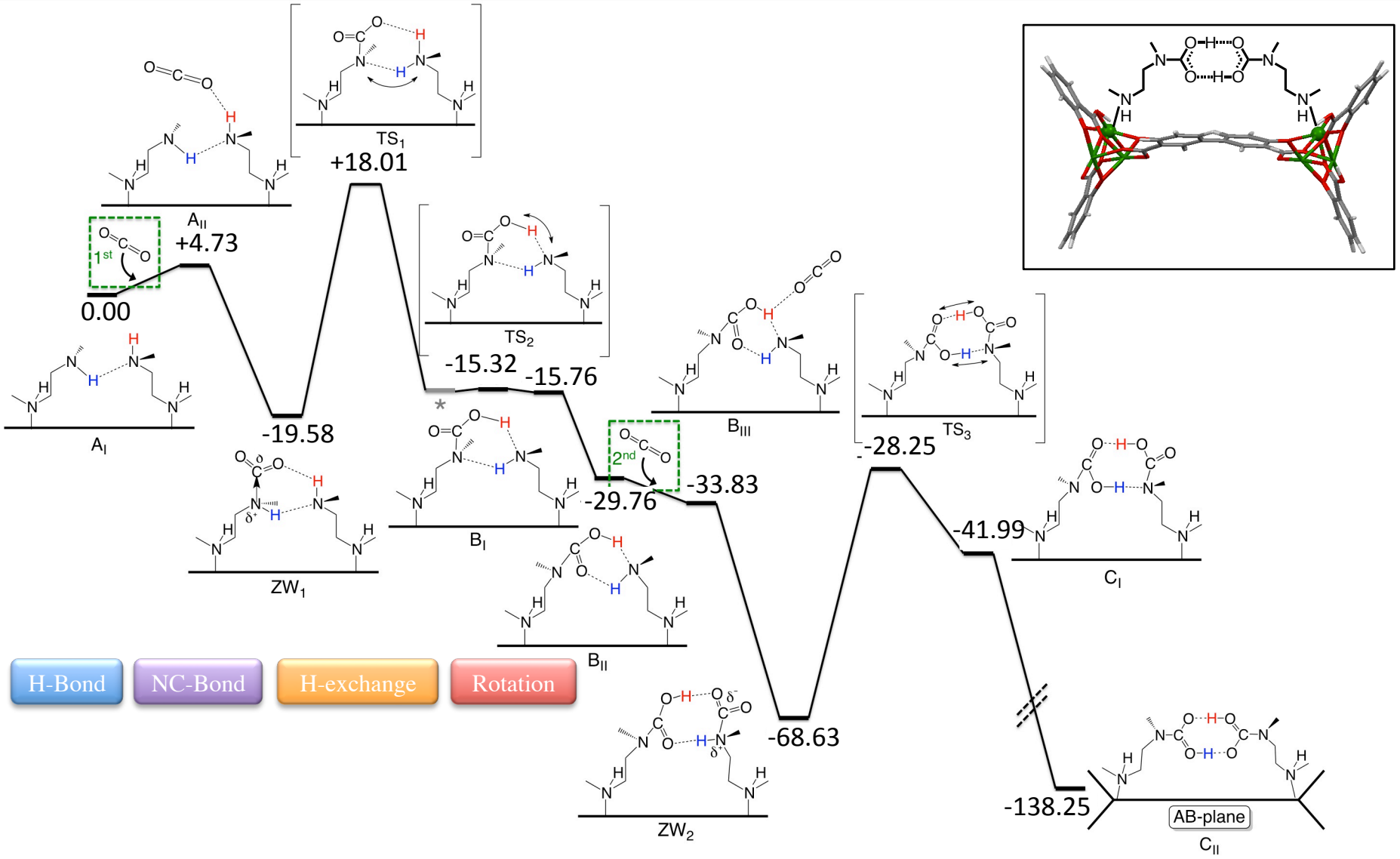
- No empirical parameters ✓
- Systematic Improvement ✓
- Transition metal accuracy ✓
- Transferrable procedure ✓
- Provides physical insight





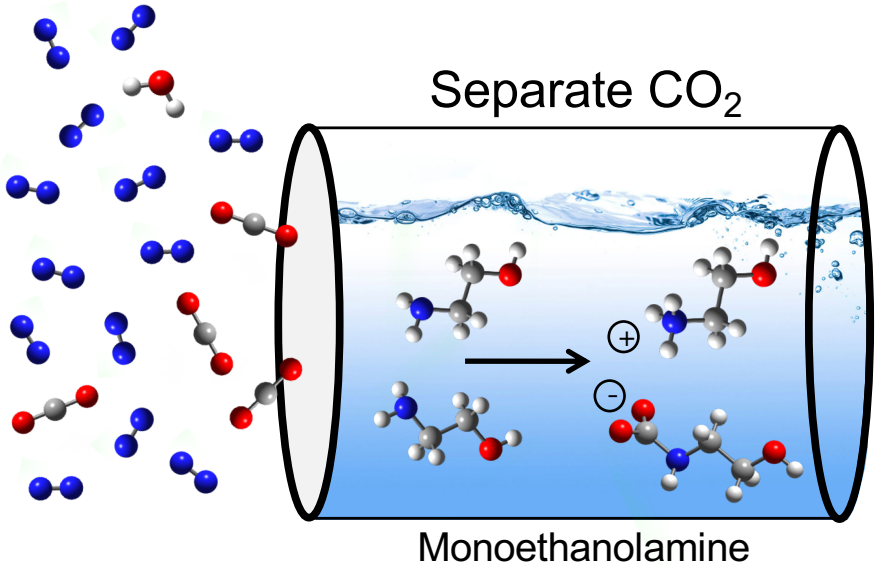


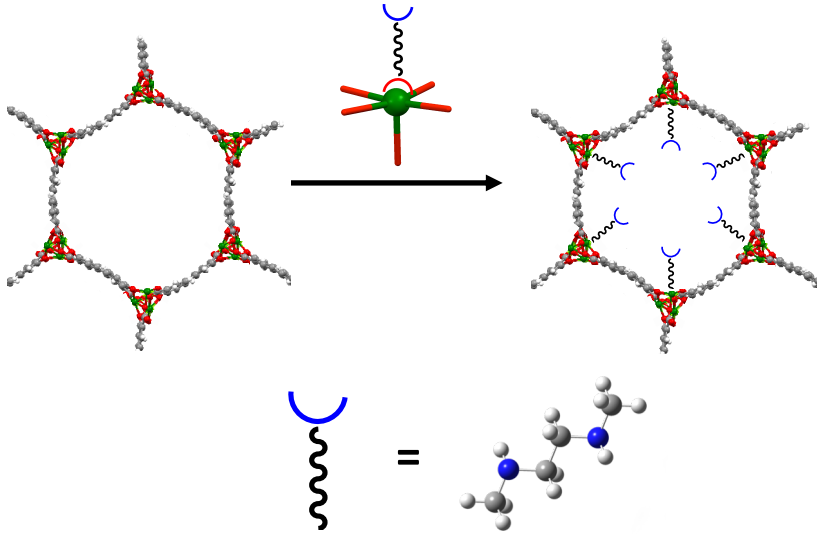
# Cluster models predict carbamic acid adducts

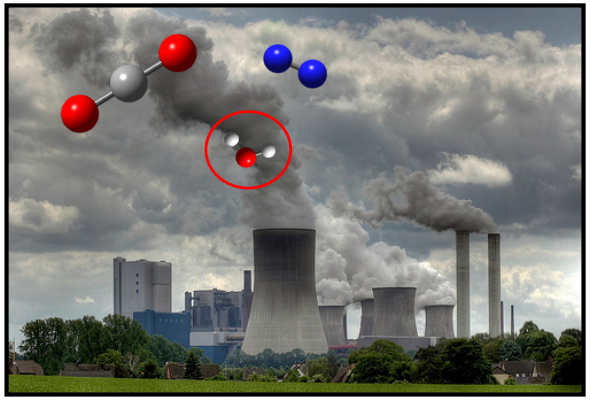


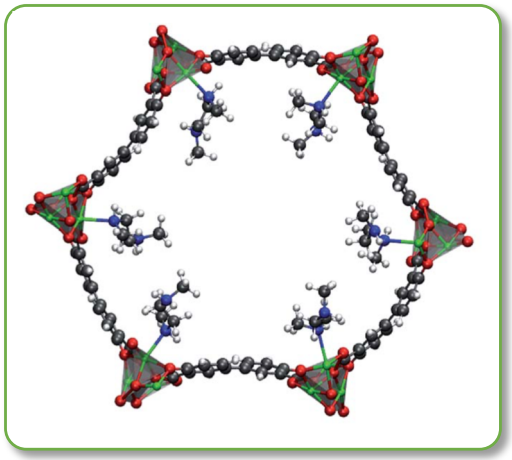

*N. Planas, A. L. Dzubak et al., J. Am. Chem. Soc. (2013)*

# Amine-functionalized MOF-74



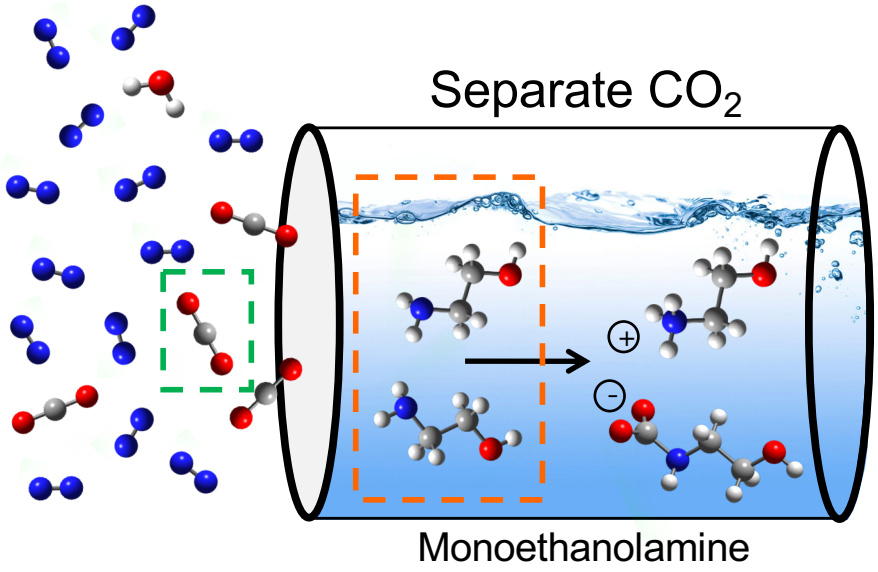





*T. M. McDonald et al., J. Am. Chem. Soc. (2012)*

# Amine-functionalized MOF-74

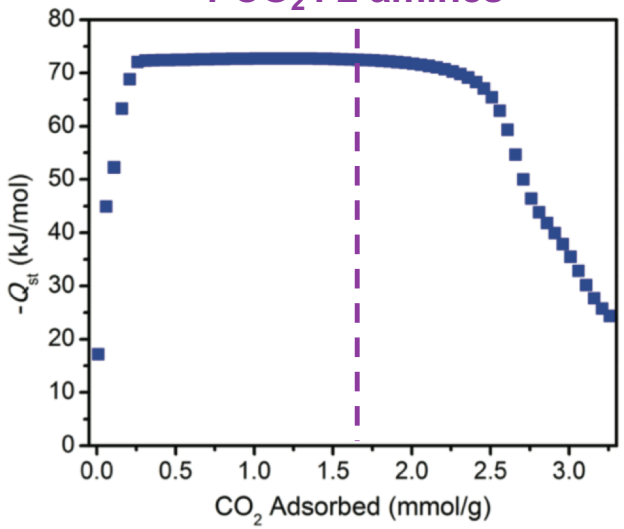


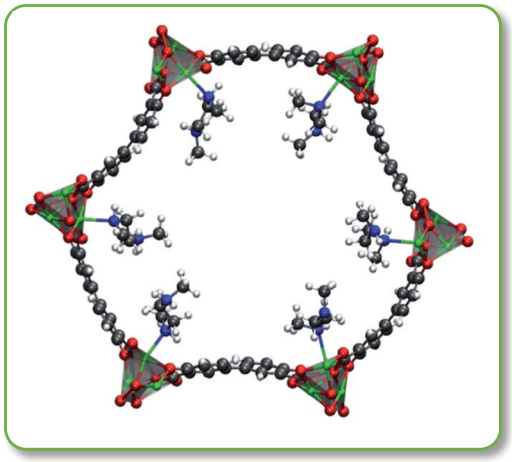

**1** $CO_2$ + **2** $NH_2(CH_2)_2OH$

It takes 2 amines to capture 1 $CO_2$

**Can theory explain the unexpected experimental stoichiometry?**

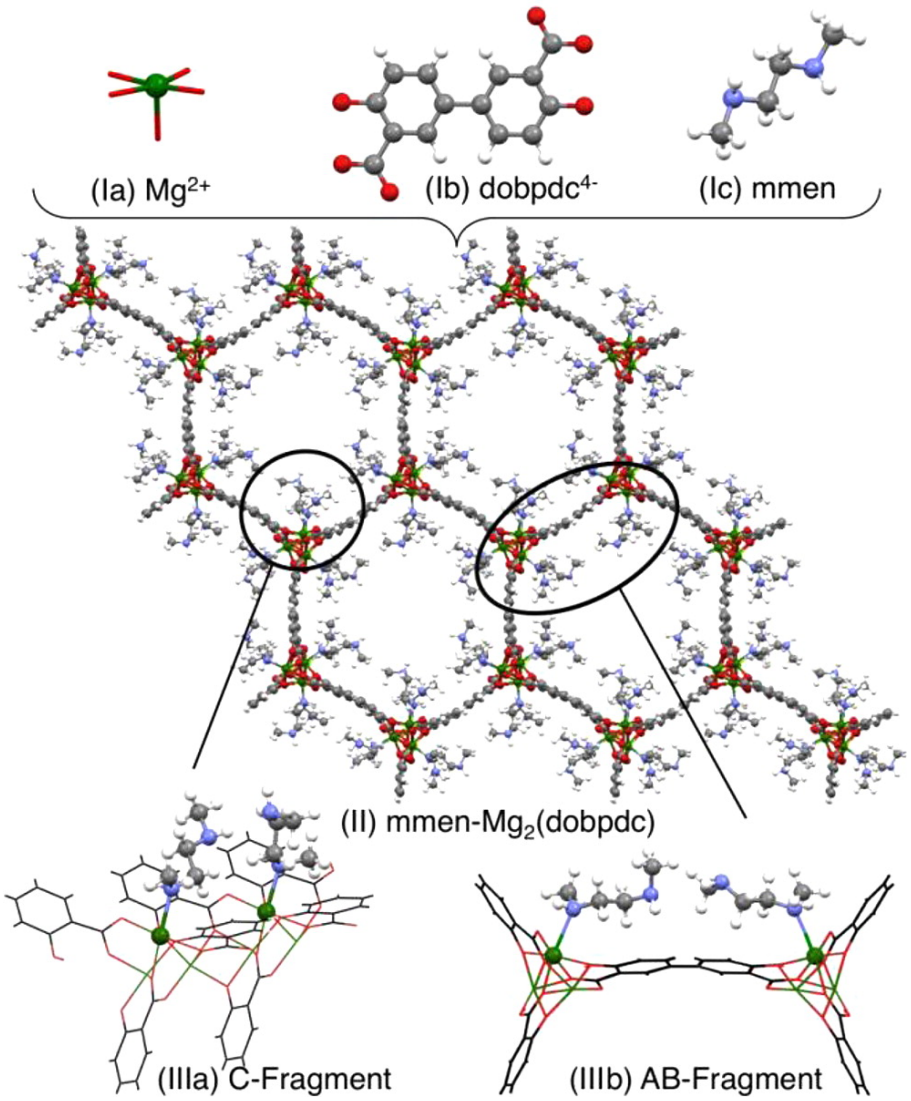
**1 $CO_2$ : 2 amines**



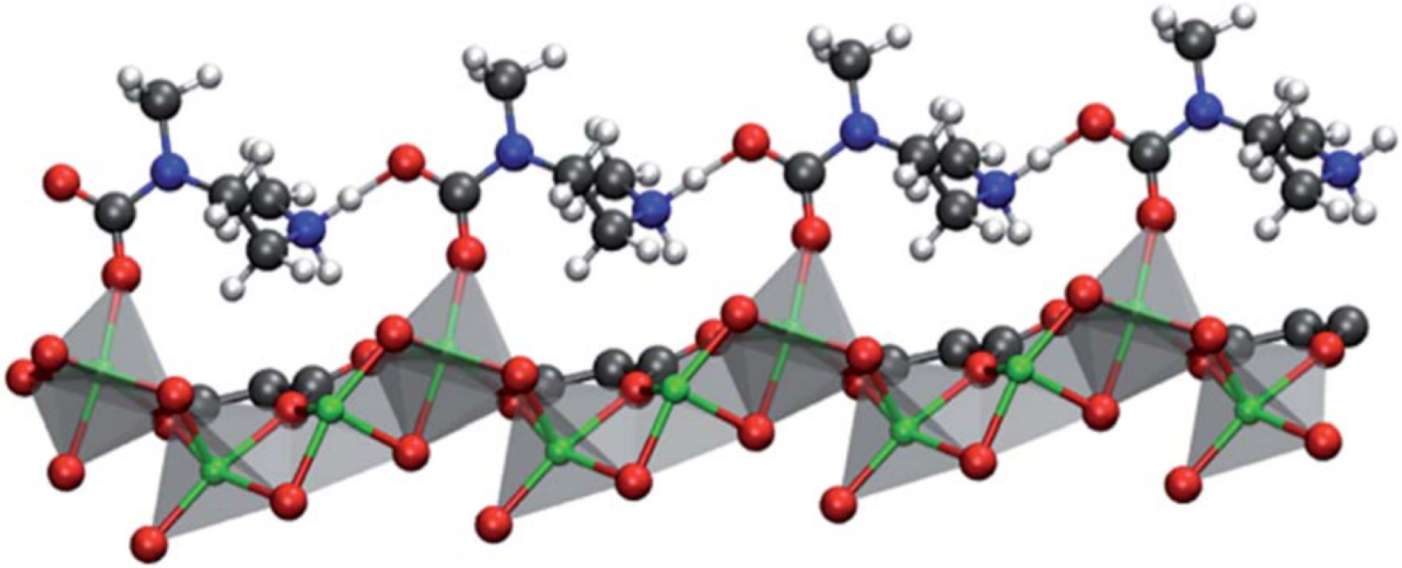



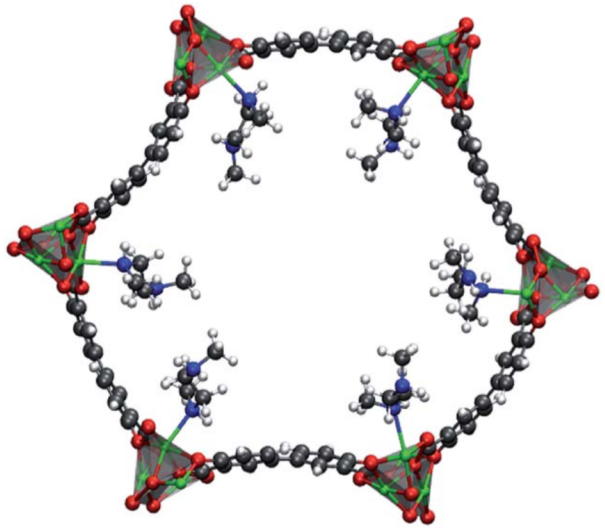
*T. M. McDonald et al., J. Am. Chem. Soc. (2012)*

# What is the mechanism of $CO_2$ adsorption?



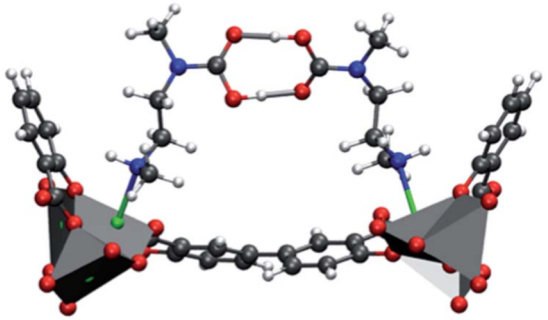
# Periodic models predict ammonium carbamate chains



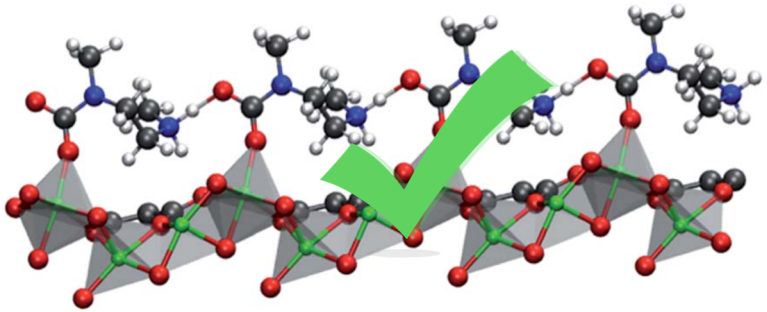


*B. Vlaisavljevich,…A. L. Dzubak et al., Chem. Sci. (2015)*

# What is the mechanism of $CO_2$ adsorption?



*N. Planas, A. L. Dzubak et al., J. Am. Chem. Soc. (2013)*



*B. Vlaisavljevich,…A. L. Dzubak et al., Chem. Sci. (2015)*
*T. M. McDonald,…A. L. Dzubak et al., Nature (2015)*

**Change the linker?**

Would affect mechanism

Would NOT affect mechanism

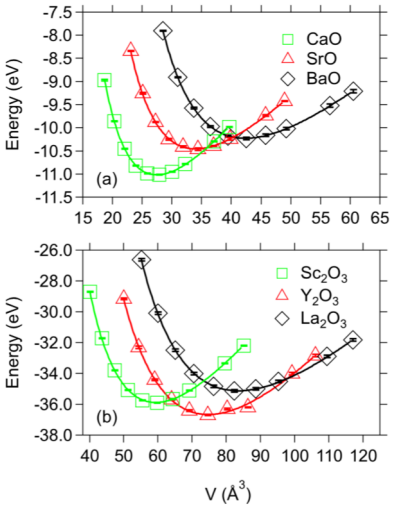
**Change the metal?**

Would NOT affect mechanism

Would affect mechanism

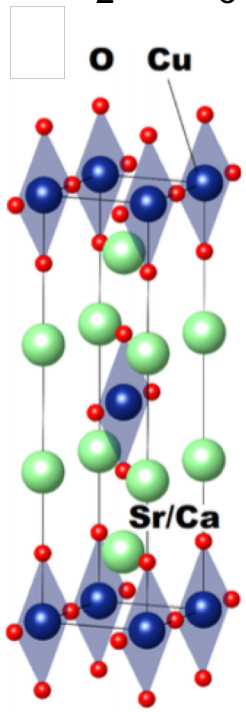
# Diffusion quantum Monte Carlo (DMC)

## Binary Oxides



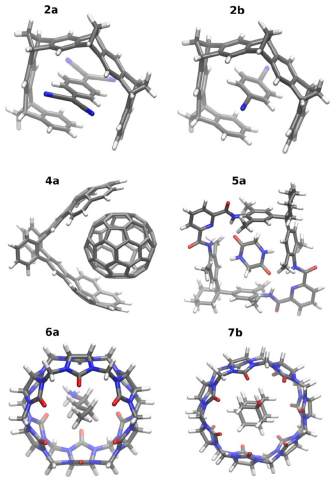

*Santana et al.*
*J. Chem. Phys. (2016)*

## $Ca_2CuO_3$



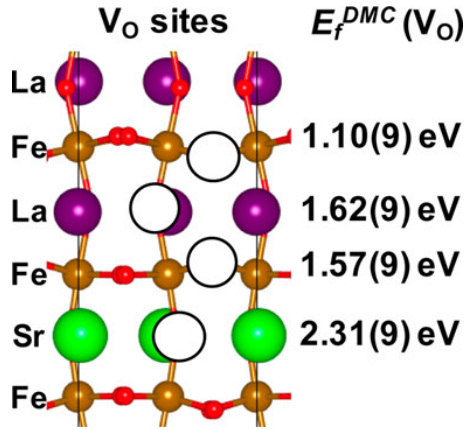

*Foyevtsova et al.*
*Phys. Rev. X (2014)*

## Host / Guest



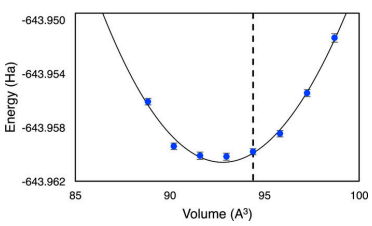

*Ambrosetti et al.*
*J. Phys. Chem. Lett. (2014)*

## $(LaFeO_3)_2$ / $SrFeO_3$




*Santana et al.*
*J. Chem. Theory Comp. (2017)*

## $MnNiO_3$




*Dzubak et al.,*
*J. Chem. Phys. (2017)*

## QMCPACK

*Kim et al.,*
*J. Phys.: Condens. Matter (2018)*

Active Development:
ORNL
ANL
LLNL
SNL
UC Berkeley

# Diffusion quantum Monte Carlo (DMC)

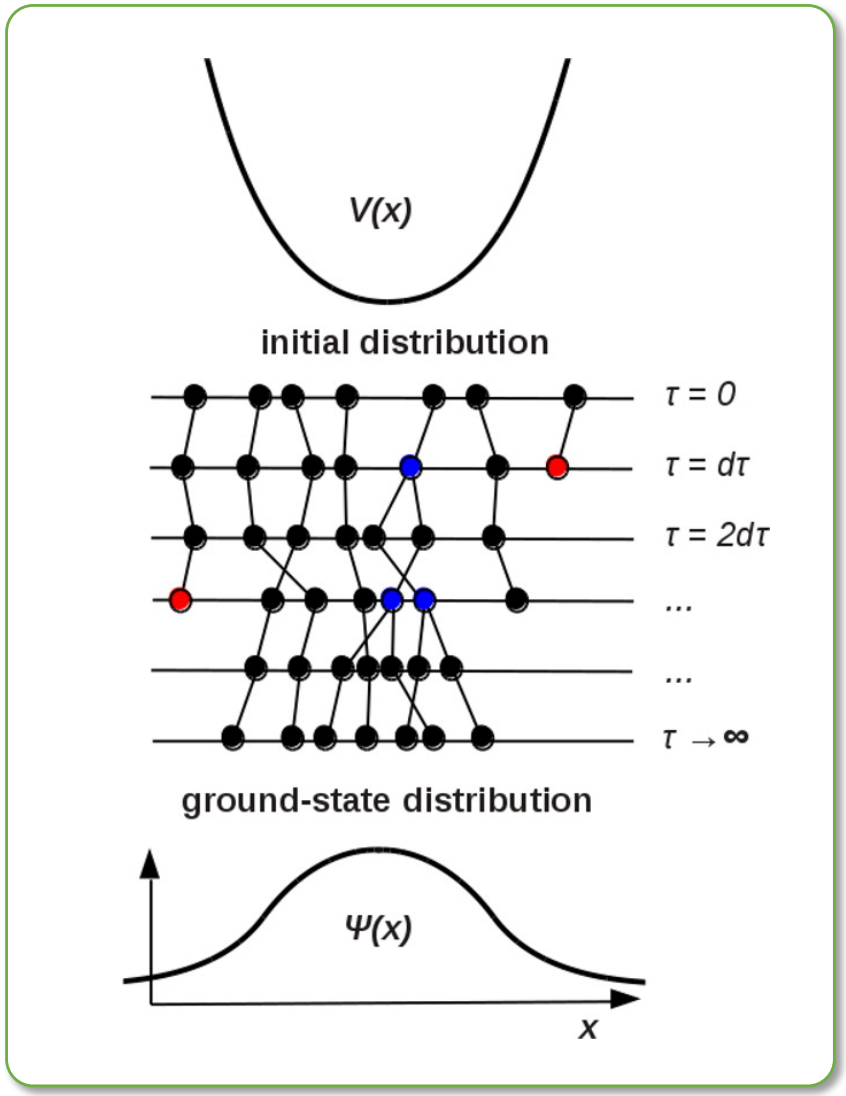
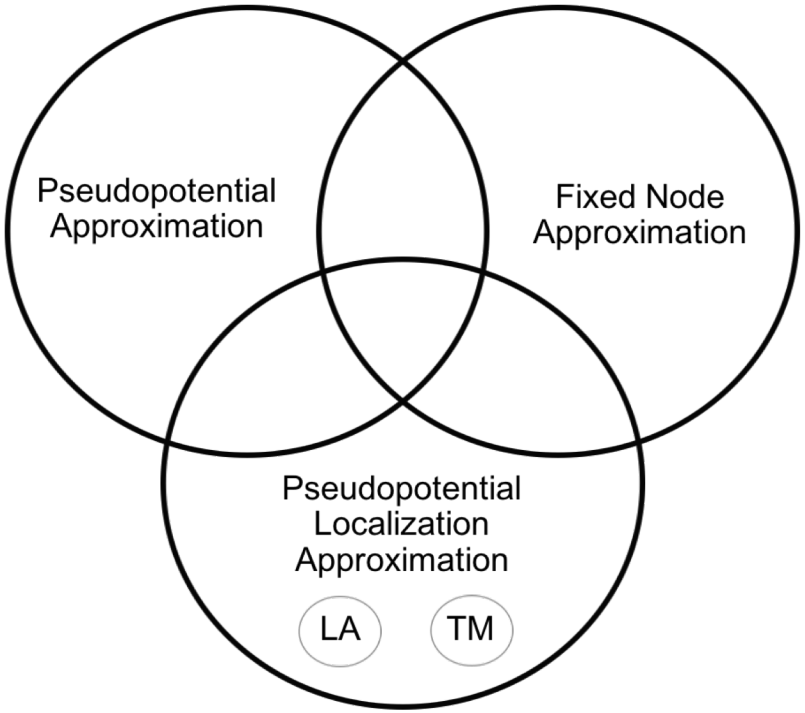
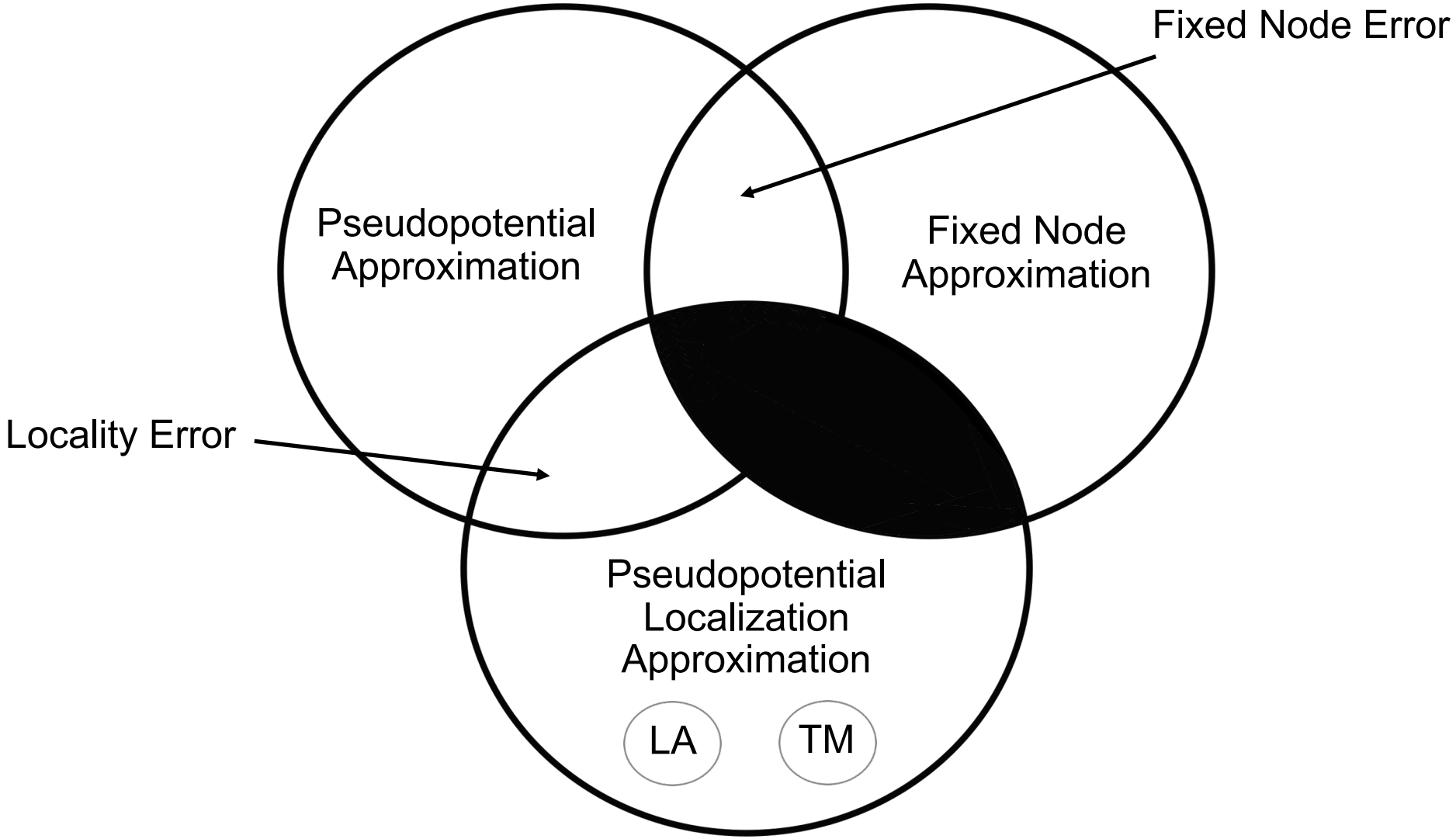



*Image from Dubecky et al., Chem. Rev. (2016)*

## Main approximations

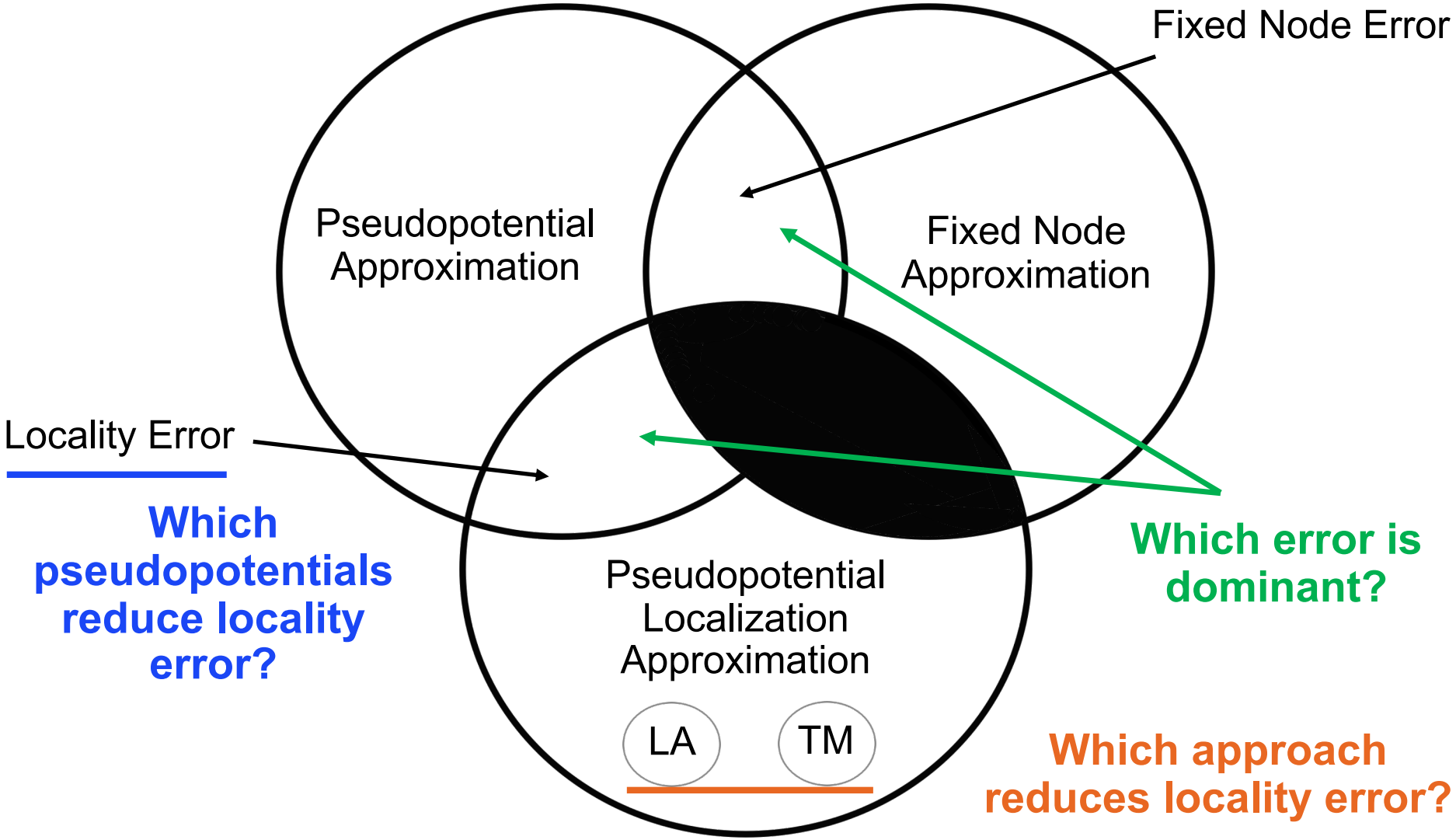


# Main approximations in DMC



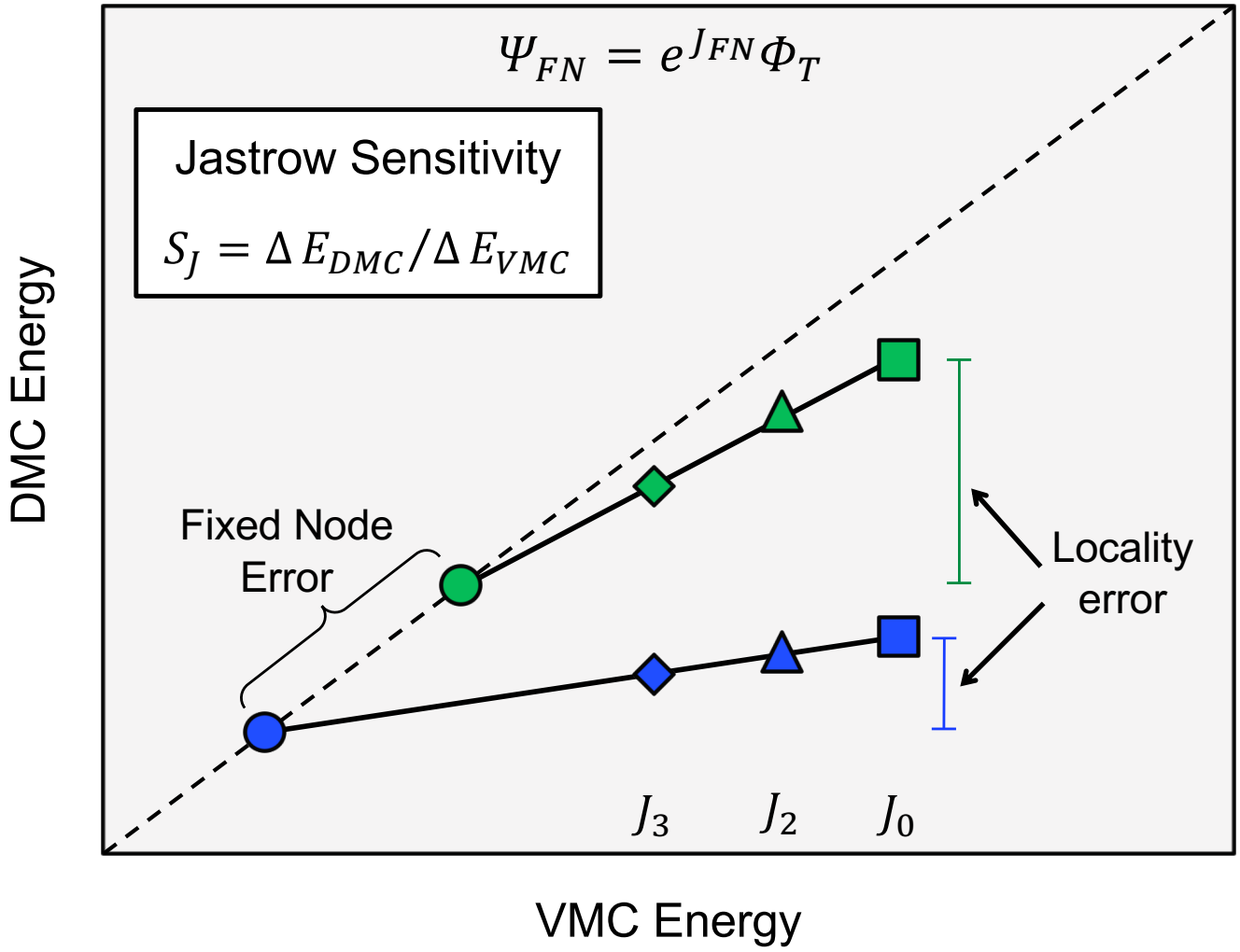

**LA:** M. M. Hurley et al., J. Chem. Phys. (1987), L. Mitas et al., J. Chem. Phys. (1991)
**TM:** M. Casula et al., Phys. Rev. Lett. (2005), M. Casula, Phys. Rev. B (2006)

# Main approximations in DMC



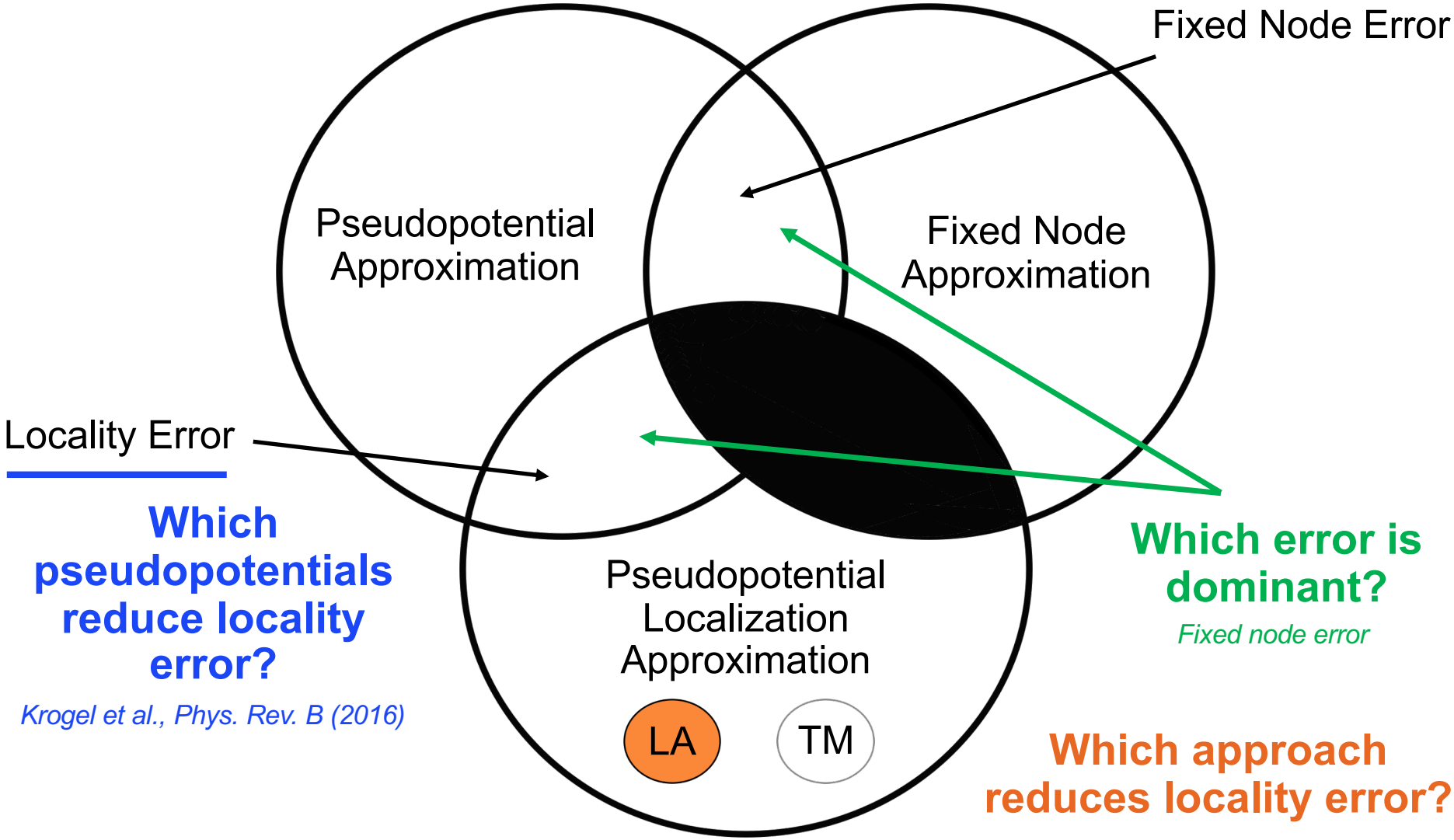

**LA:** M. M. Hurley et al., J. Chem. Phys. (1987), L. Mitas et al., J. Chem. Phys. (1991)
**TM:** M. Casula et al., Phys. Rev. Lett. (2005), M. Casula, Phys. Rev. B (2006)

# Extrapolation schematic




*A. L. Dzubak et al., J. Chem. Phys. (2017)*

# Main approximations in DMC




**Which pseudopotentials reduce locality error?**

*Krogel et al., Phys. Rev. B (2016)*

**Which error is dominant?**

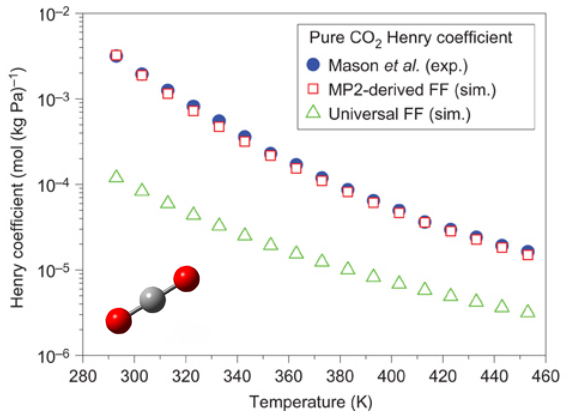
*Fixed node error*

**Which approach reduces locality error?**

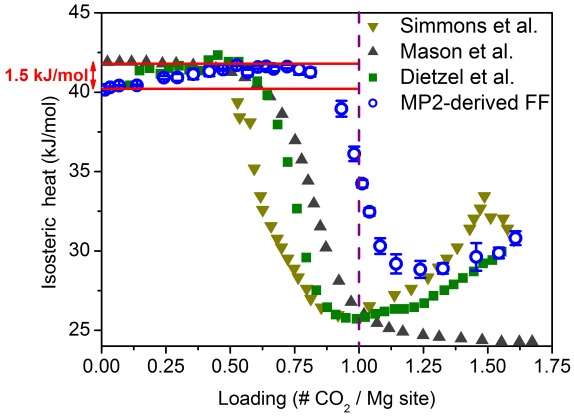
*A. L. Dzubak et al., J. Chem. Phys. (2017)*

# Summary

## Performance of *ab initio* force fields




## Insight from theory and computation



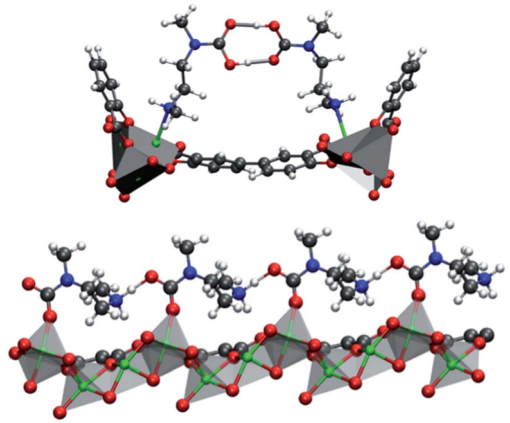

Materials Science

Physical Chemistry

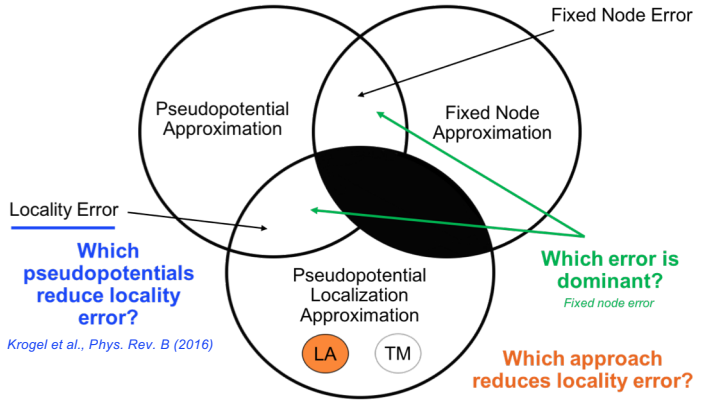
Chemical Engineering

Solid State Physics

## Cooperativity in Functionalized MOFs



## Systematic Reduction of DMC Errors




Environmental Chemistry

Inorganic Chemistry

Computer Science

Applied Mathematics