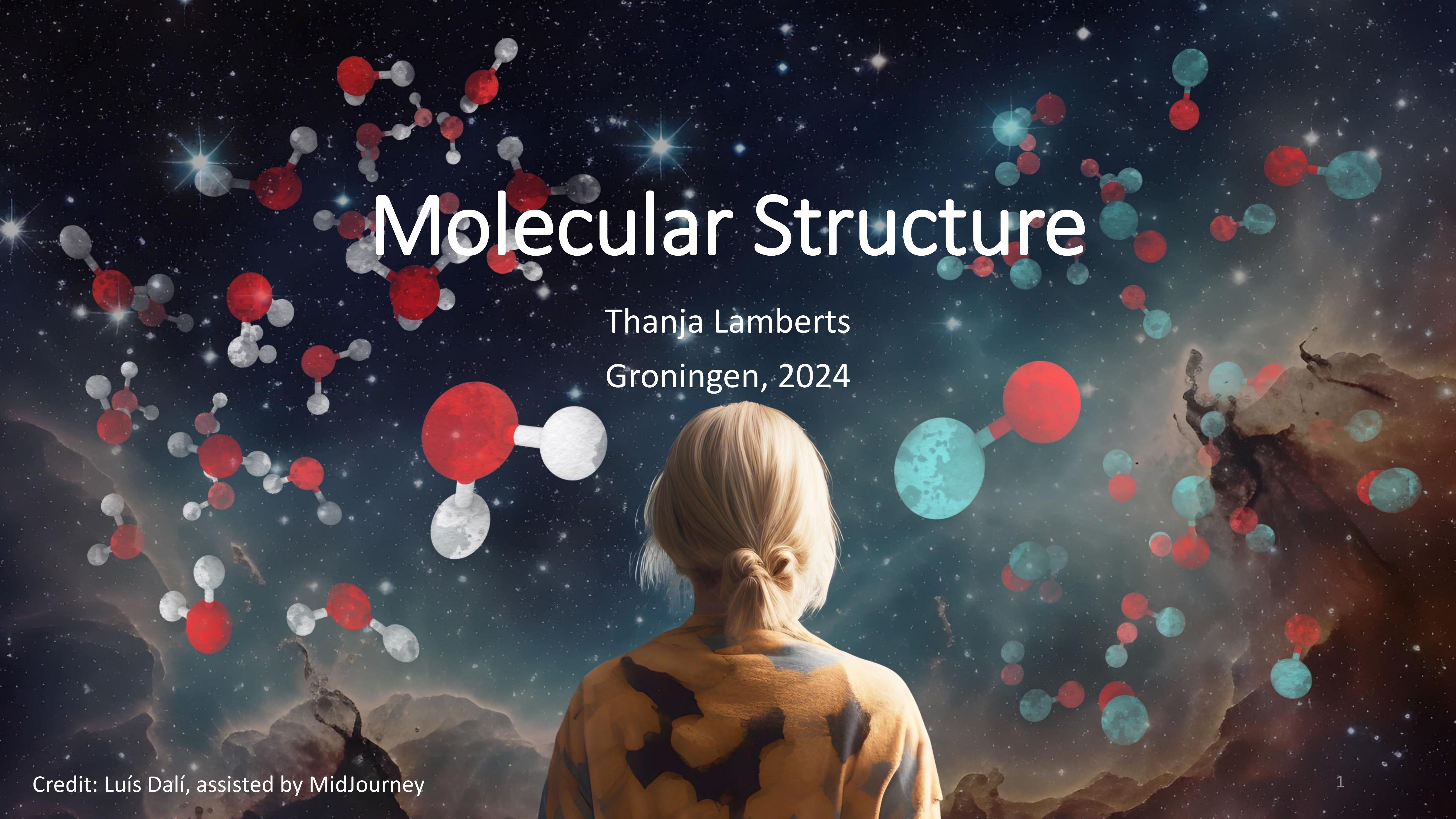


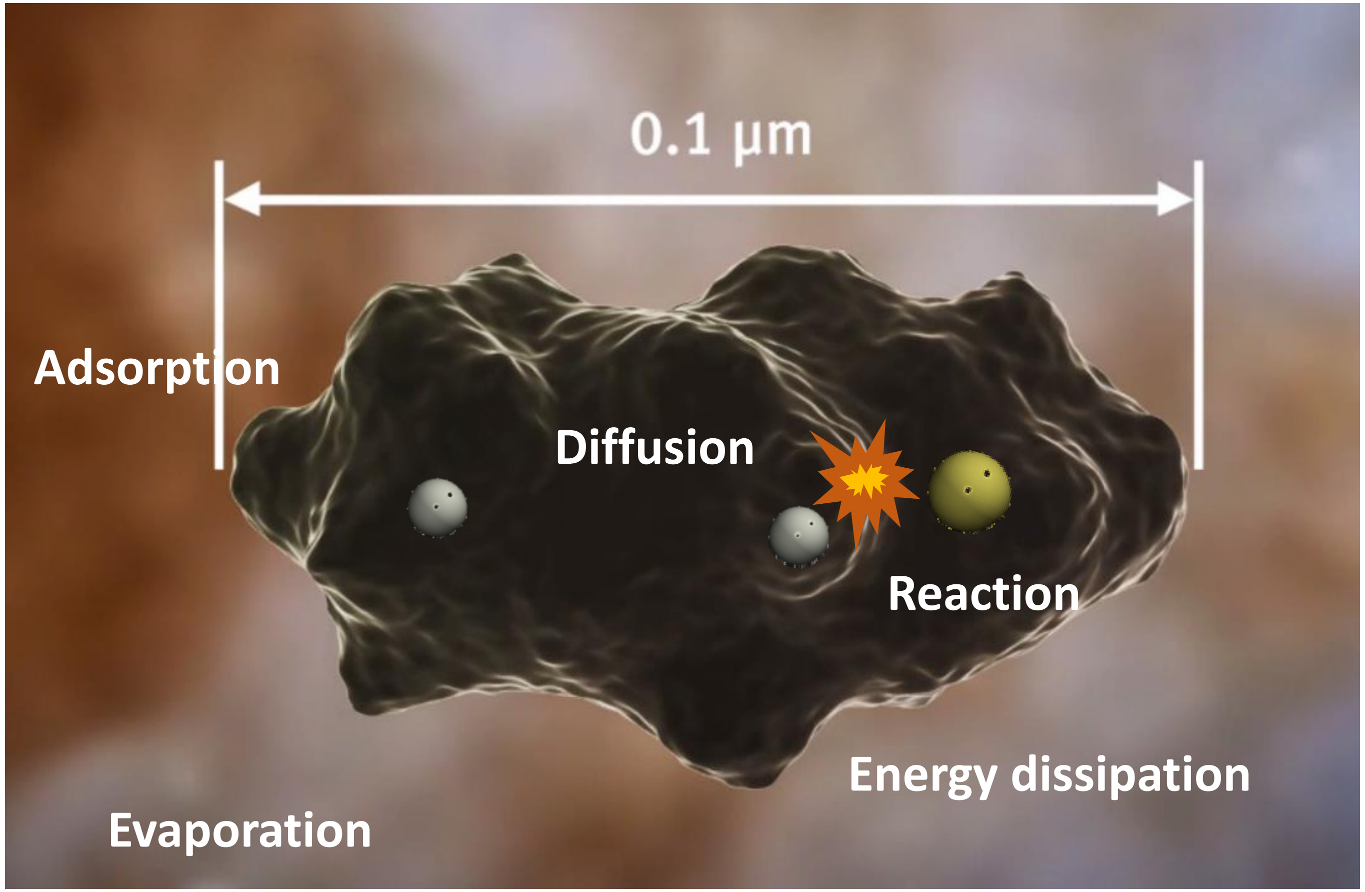
Molecular Structure

Thanja Lamberts

Groningen, 2024

Credit: Luís Dalí, assisted by MidJourney

Reminder


0.1 µm
Adsorption
Diffusion
Reaction
Energy dissipation
Evaporation

Similarities: diffusion, desorption, and reaction

$$\kappa_{react} = \frac{k_{react}}{k_{react} + k_{diff} + k_{des}}$$

$$k_{react,\,thermal} = \nu \cdot e^{-\boxed{E_{act}}/k_B T}$$

$$k_{react,\,tunneling} = \text{not trivial}$$

$$k_{des} = \nu \cdot e^{-\boxed{E_{bind}}/k_B T}$$

$$k_{diff} = \nu \cdot e^{-\boxed{E_{diff}}/k_B T}$$

Outline

1. Intermolecular interactions
2. Potential Energy Surface

Math intermezzo

3. Minima and “maxima”

Intermezzo

4. Example

Disclaimers

Assuming electronic motion and nuclear motion can be separated

The electronic wavefunction depends on the nuclear positions, but not on their velocities: nuclear motion is so much slower than electron motion that they can be considered to be fixed: elephant and a fly analogy

In any of the methods described, temperature is not included

In the Gibbs free energy definition $\Delta \mathrm{G} = \Delta U - T\Delta S + P\Delta V$ the second term becomes more important with increasing temperature. What I will discuss deals with the calculation of the first term, the internal energy U.

1. Intermolecular interactions

“Weak”

Van der Waals

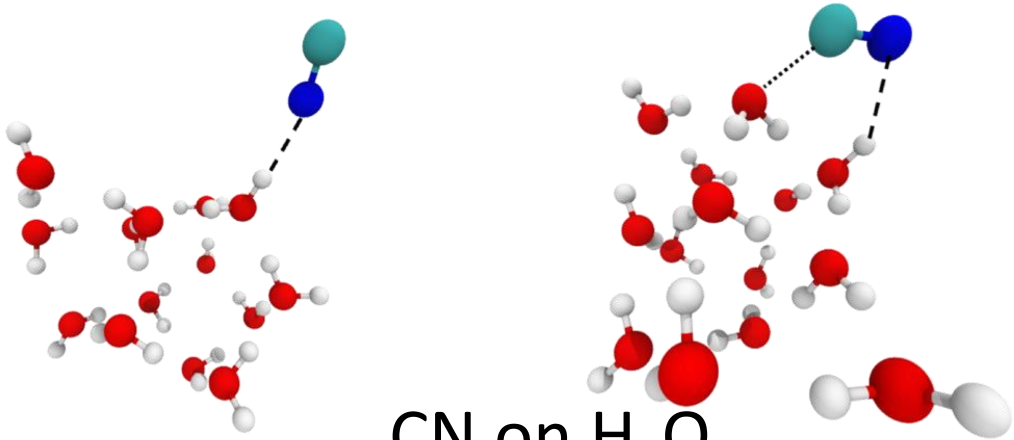
Hydrogen bonded

Ionic?

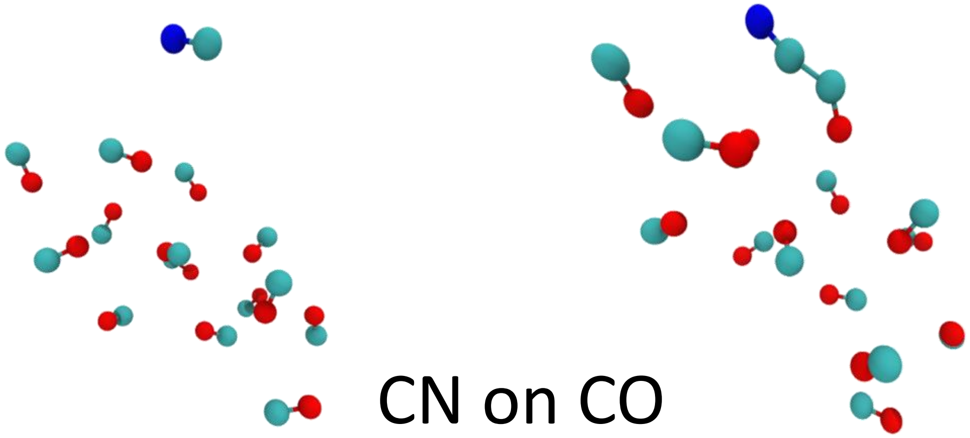
Hemibonded

“Strong”

Covalently bonded



CN on H_2O



CN on CO

2. Potential energy surface

The energetic landscape determines whether a process is likely to take place or not.

Simple case is H_2

E depends on the distance r reducing the "surface" to a 1-D potential energy curve

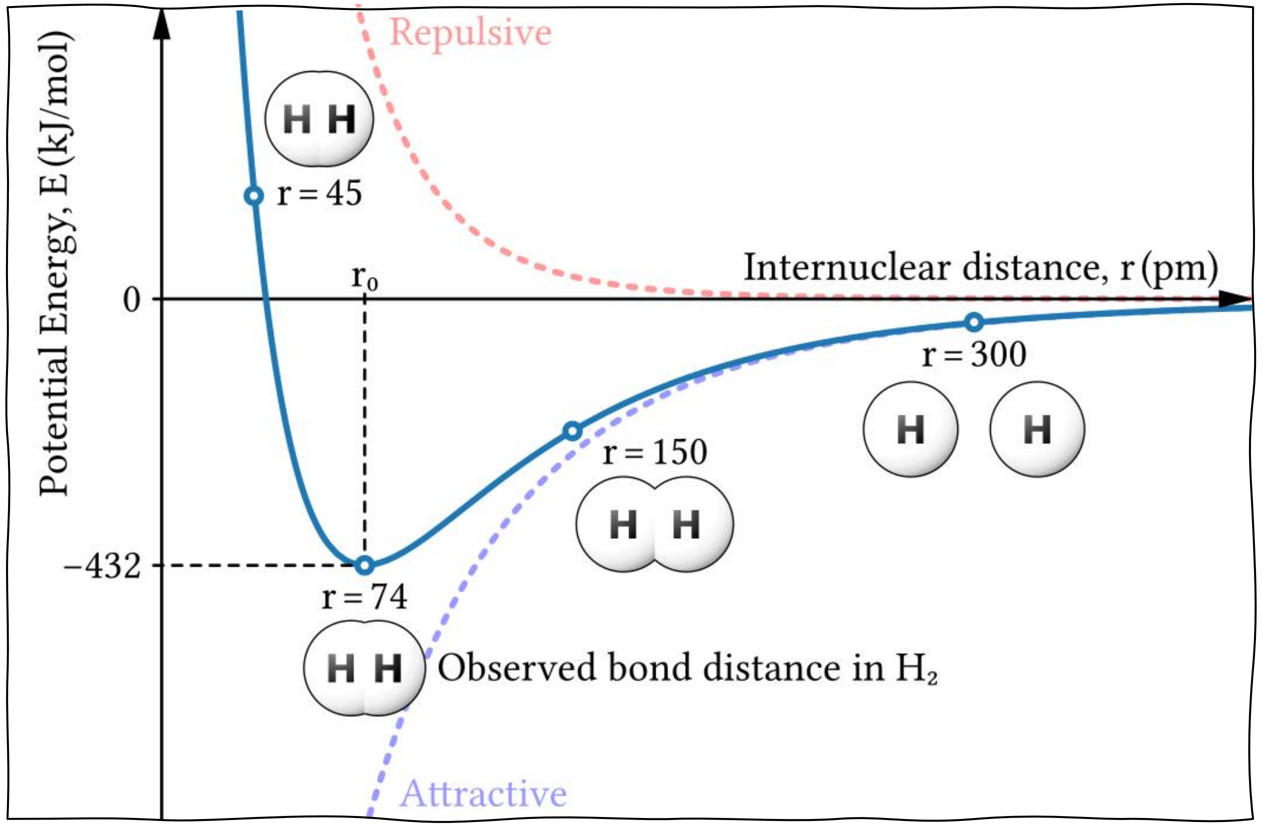
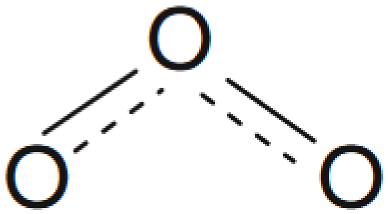


Figure courtesy: Wikimedia Commons

2. Potential energy surface

O_3 : $E_{molecule}$ depends on two bond lengths and one angle

3-D surface, i.e., how to plot?



ozone

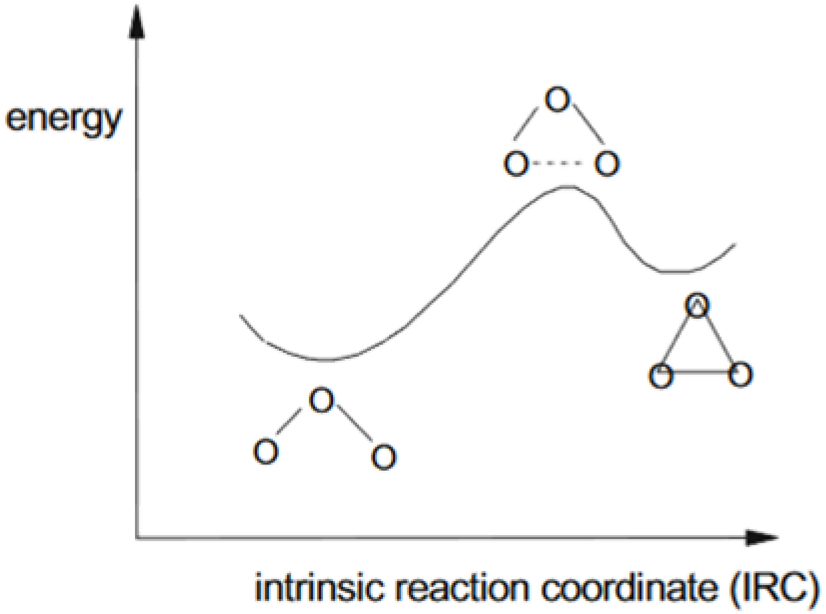
Pick two suitable descriptors and fix the third

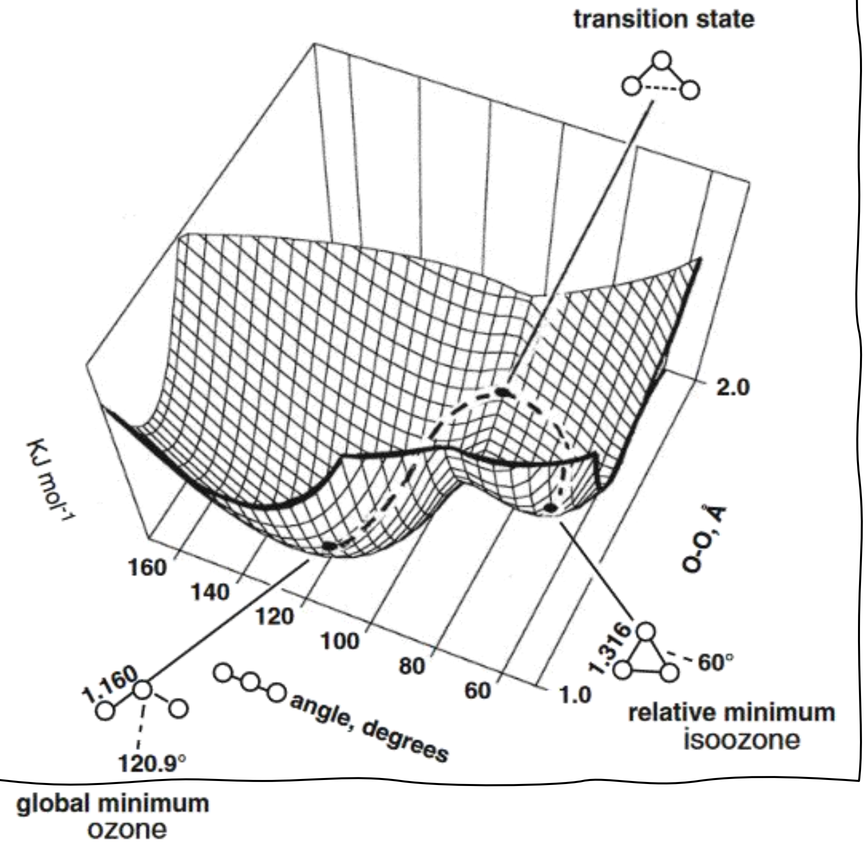
- O1-O2-O3 angle
- O1-O2 distance
- O2-O3 ‘fixed’ by symmetry

2. Potential energy surface

O_3 : $E_{molecule}$ depends on two bond lengths and one angle

3-D surface, i.e., how to plot?





E. Lewars, *The Concept of the Potential Energy Surface* Computational Chemistry, Chapter 1, Springer (2016)

2. Potential energy surface

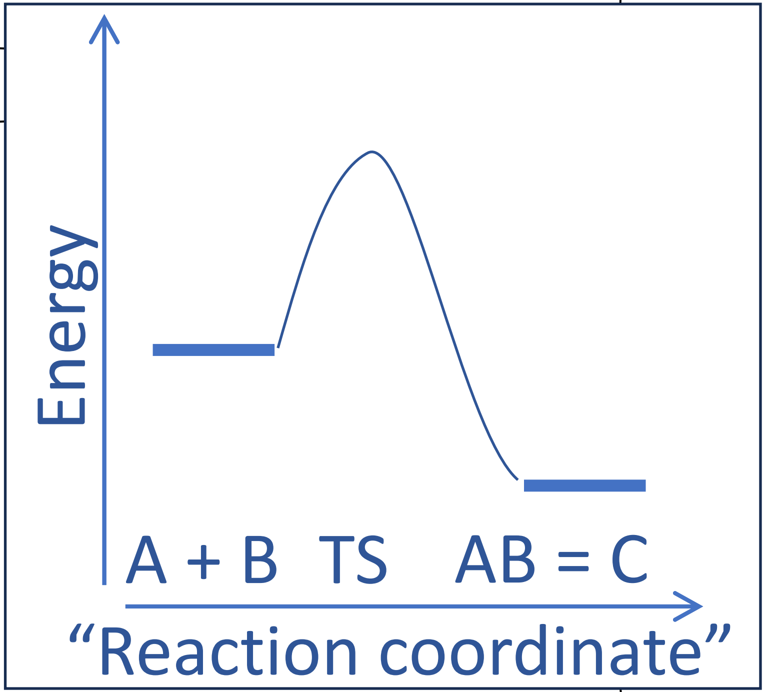
For a given molecule with N atoms, what is the dimension of the PES?

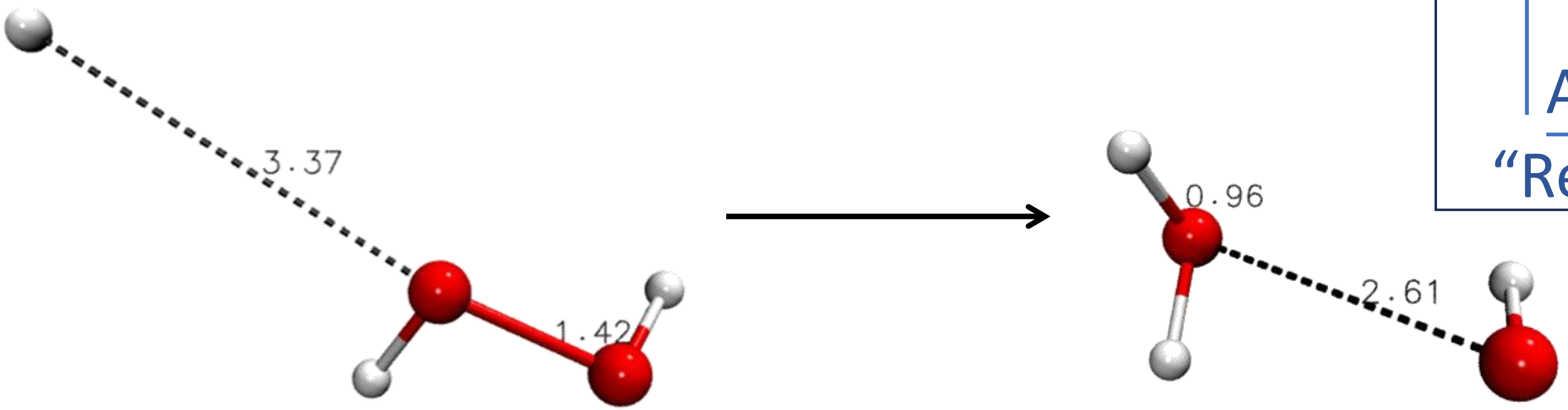
A. 3 dimensional
B. 3N dimensional
C. 3N-5 dimensional
D. 3N-6 dimensional

NB: In astrochemical models there is no PES, only input parameters

Example: H + $H_2O_2 \longrightarrow H_2O$ + OH

$3 * (N = 5) - 6 =$ 9D PES

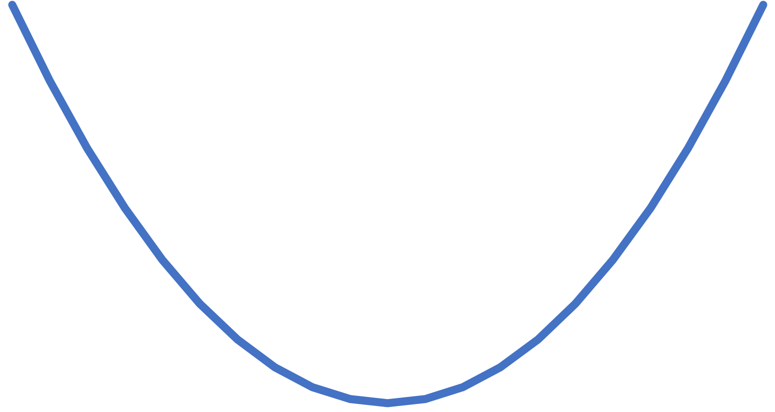




Math intermezzo: harmonic "oscillator"

Finding a minimum = going downhill

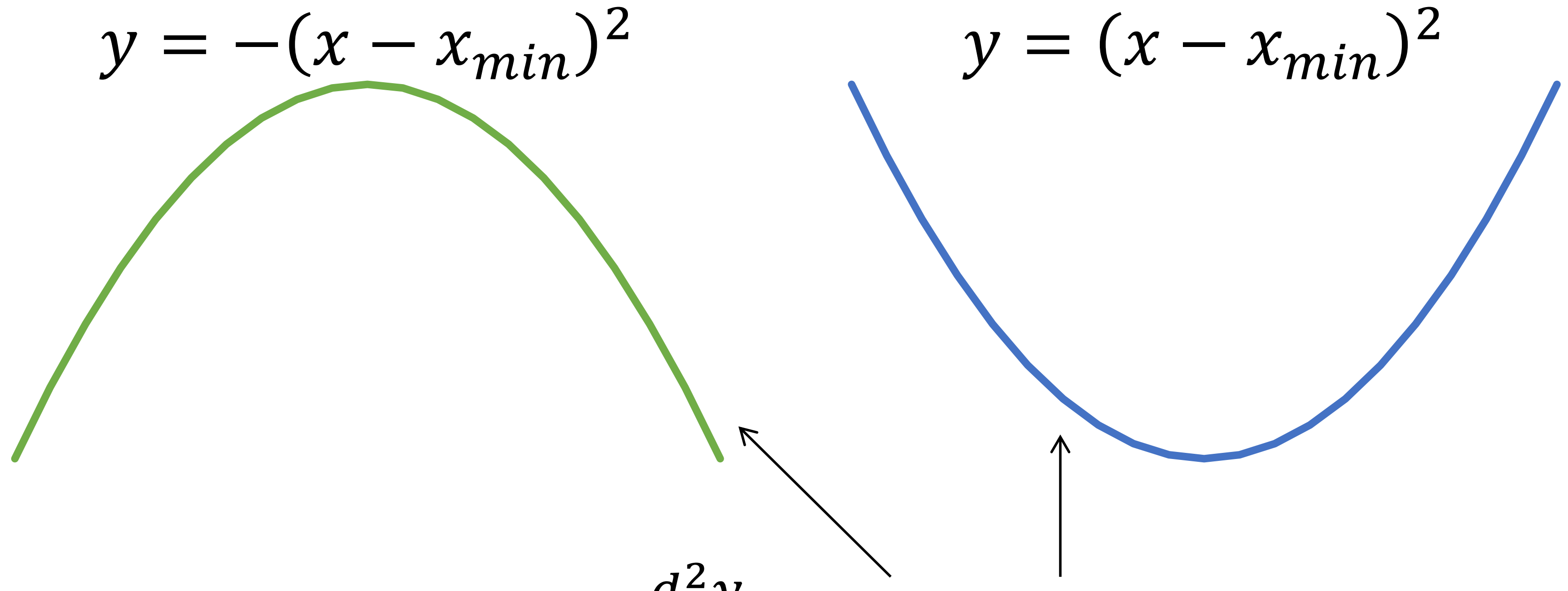
$$y = (x - x_{min})^2$$



First derivative has to be zero

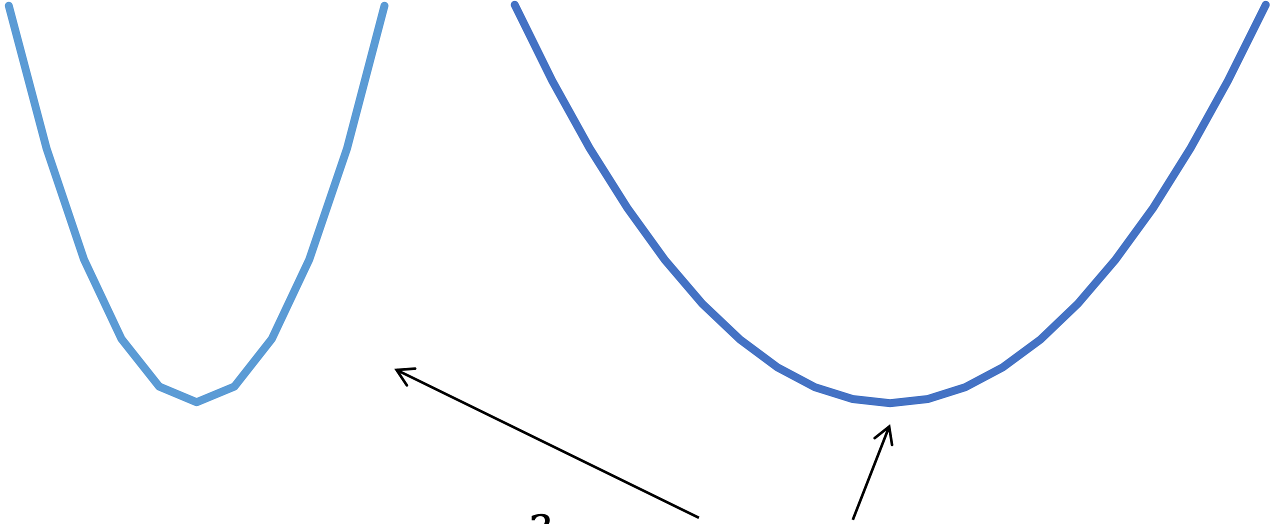
$$\frac{dy}{dx} = 2(x - x_{min}) \xrightarrow{x_{min}} 0$$

Math intermezzo



Second derivative has to be positive $\frac{d^2y}{dx^2} = -2$ or 2

Math intermezzo



$$y = 4 \cdot (x - x_{min})^2 \qquad y = (x - x_{min})^2$$

Second derivative indicates the steepness $\frac{d^2y}{dx^2} = 8 \text{ or } 2$

Math intermezzo

First derivative = gradient

$$\nabla y = \begin{bmatrix} \frac{\partial y}{\partial x_1} \\ \vdots \\ \frac{\partial y}{\partial x_N} \end{bmatrix}$$

Second derivative = Hessian

$$\mathrm{H}_{\mathrm{i,j}} = \frac{\partial^2 y}{\partial x_i x_j} \rightarrow \mathrm{H} = \begin{bmatrix} \frac{\partial^2 y}{\partial x_1^2} & \cdots & \frac{\partial^2 y}{\partial x_1 x_N} \\ \vdots & \ddots & \vdots \\ \frac{\partial^2 y}{\partial x_N x_1} & \cdots & \frac{\partial^2 y}{\partial x_N^2} \end{bmatrix}$$

Math intermezzo

Hessian $$\mathrm{H} = \begin{bmatrix} \frac{\partial^2 y}{\partial x_1^2} & \cdots & \frac{\partial^2 y}{\partial x_1 x_N} \\ \vdots & \ddots & \vdots \\ \frac{\partial^2 y}{\partial x_N x_1} & \cdots & \frac{\partial^2 y}{\partial x_N^2} \end{bmatrix}$$

Eigenvector = direction where curvature is independent of other directions

Eigenvalue = determines the curvature in the direction of the eigenvector

Vibrational spectrum!

3. Geometry optimization: steepest descent

Making use of the gradient

$$\boldsymbol{r}_{n+1} = \boldsymbol{r}_n - \alpha \cdot \nabla E(\boldsymbol{r})$$

$\boldsymbol{r}_i$	coordinates of geometry i
$-$	ensures going downhill
α	step size
∇E	gradient of the energy

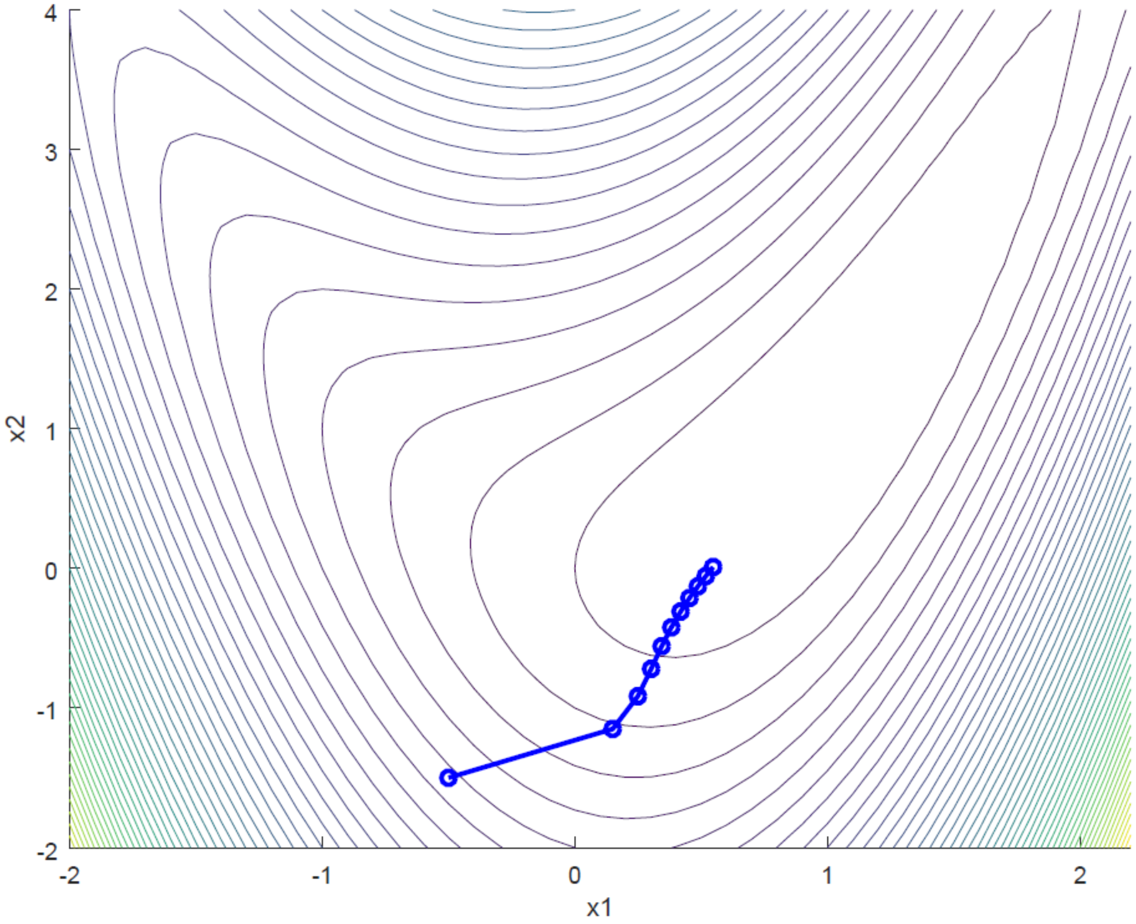


Figure courtesy: based the Matlab code by John D. Hedengren

3. Geometry optimization: steepest descent

Making use of the gradient

Large step size α

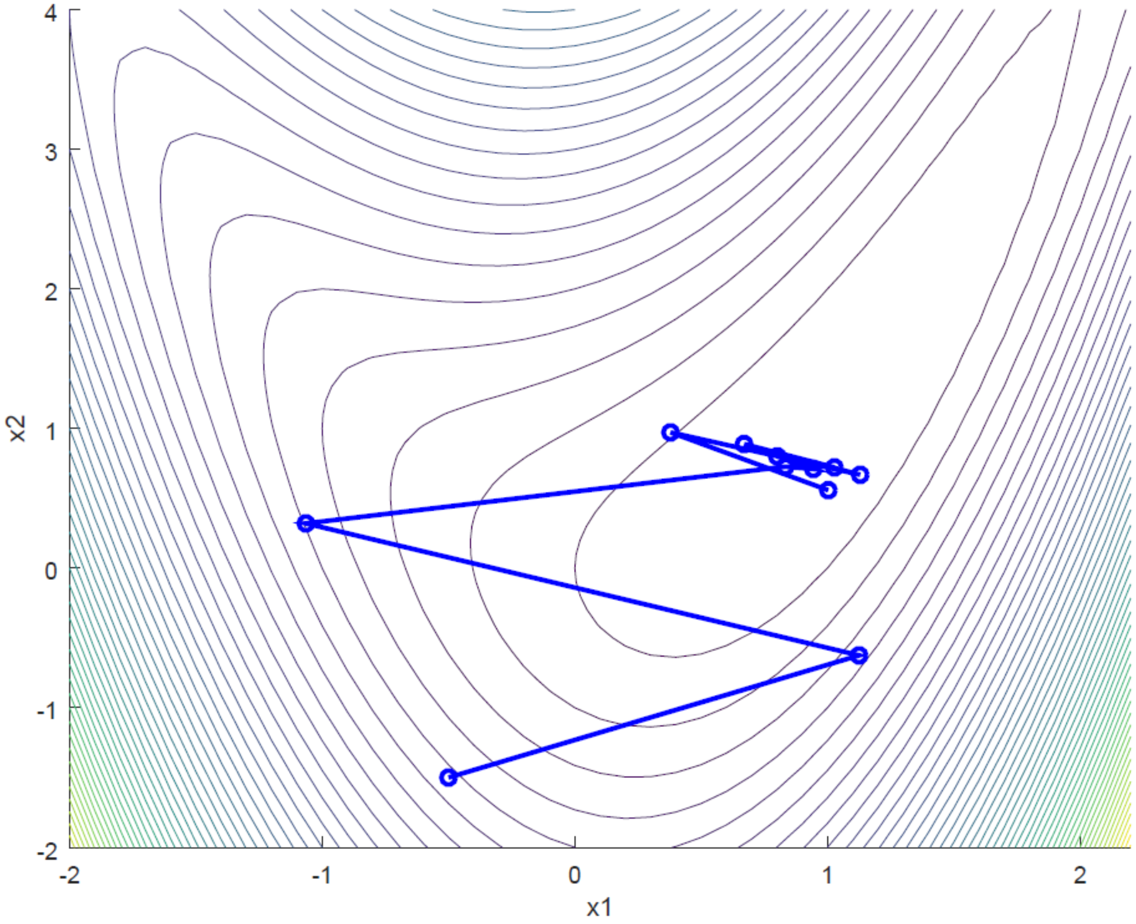


Figure courtesy: based the Matlab code by John D. Hedengren

3. Geometry optimization: steepest descent

Making use of the gradient

Small step size α

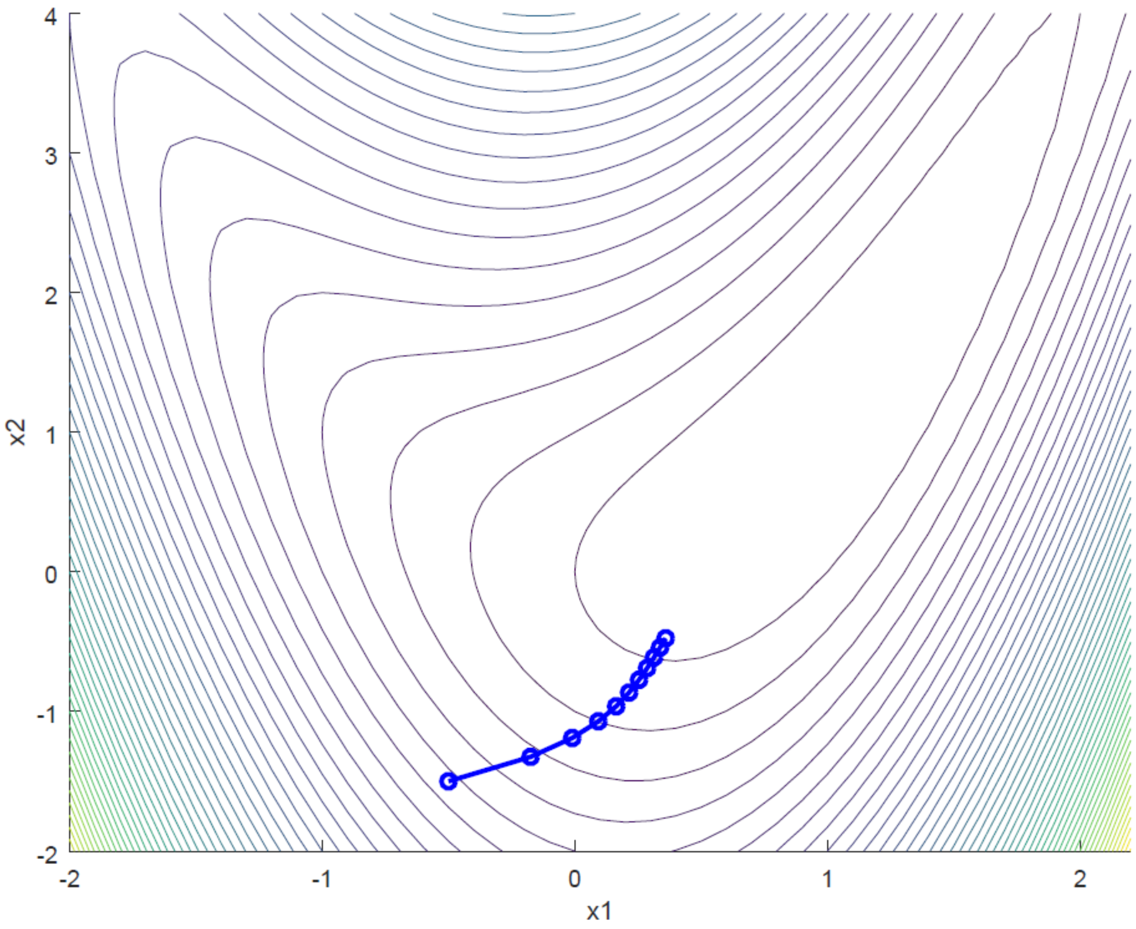


Figure courtesy: based the Matlab code by John D. Hedengren

3. Geometry optimization: steepest descent

Making use of the gradient

“foggy mountain paths”

Inefficient for shallow potentials

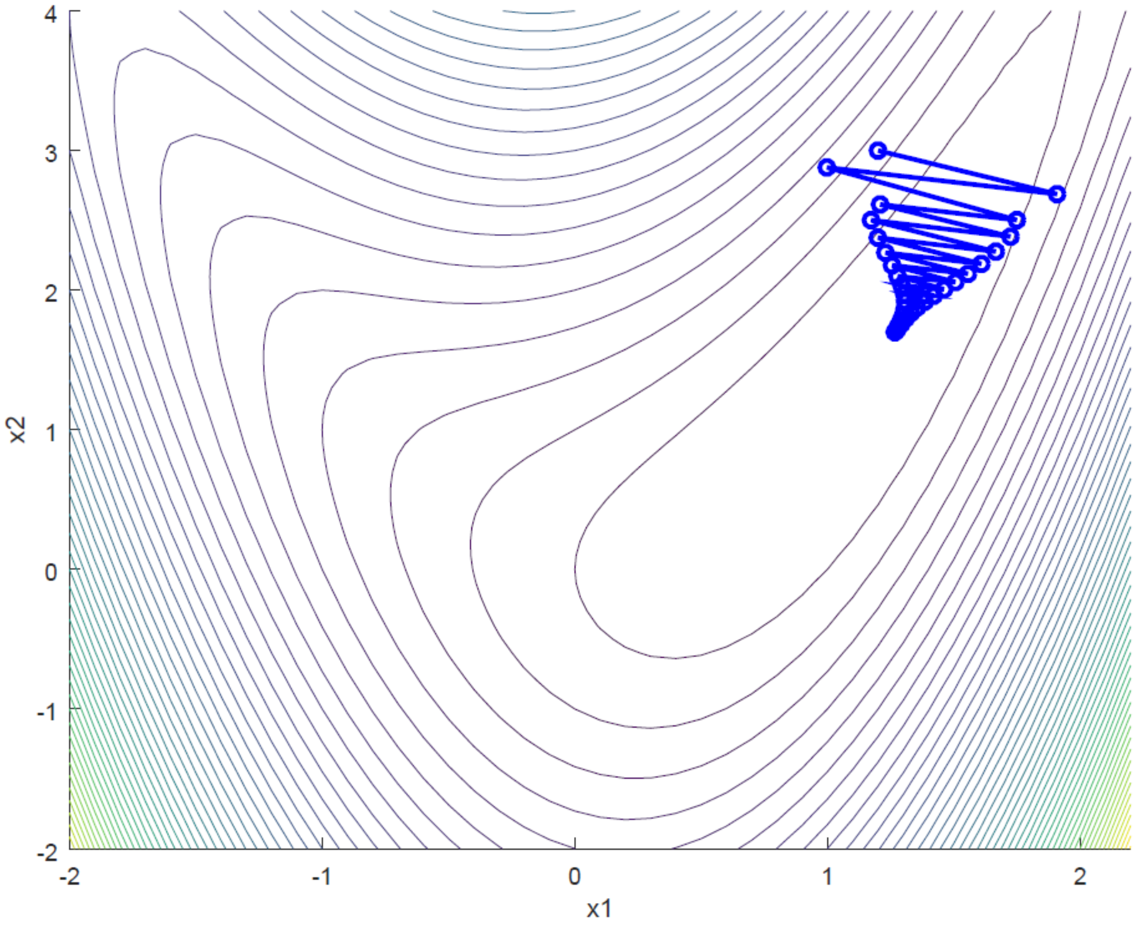


Figure courtesy: based the Matlab code by John D. Hedengren

3. Geometry optimization: Newton-Raphson method

Including the Hessian

$$r_{n+1} = r_n - \frac{\nabla E(r)}{\nabla^2 E(r)}$$

Computationally expensive

(and it can diverge)

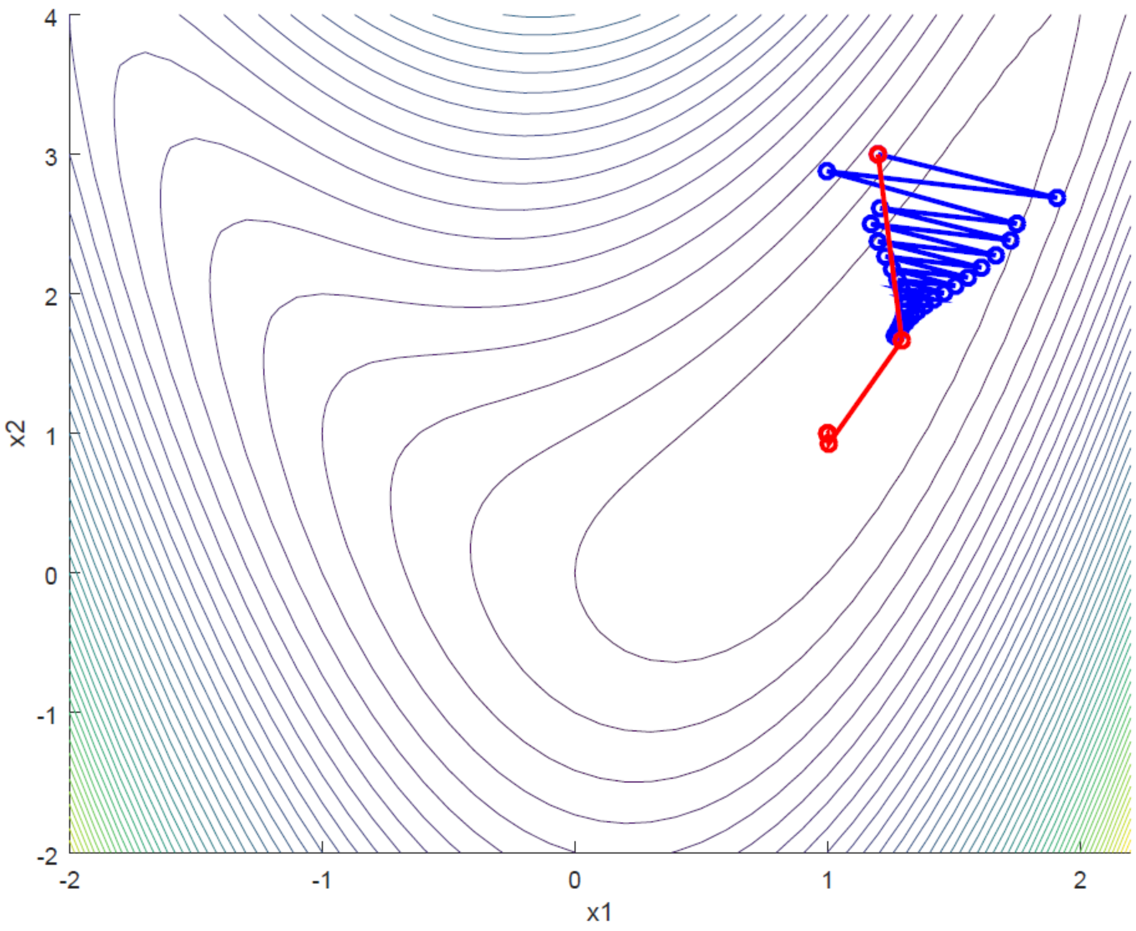


Figure courtesy: based the Matlab code by John D. Hedengren

3. Geometry optimization: quasi-Newton method

Approximate the Hessian

First step = steepest descent
$r_1 = r_0 - \alpha_0 \nabla E(r)$

Use ratio of $\nabla E(r_{n+1}) - \nabla E(r_n)$ to $r_{n+1} - r_n$ to estimate H

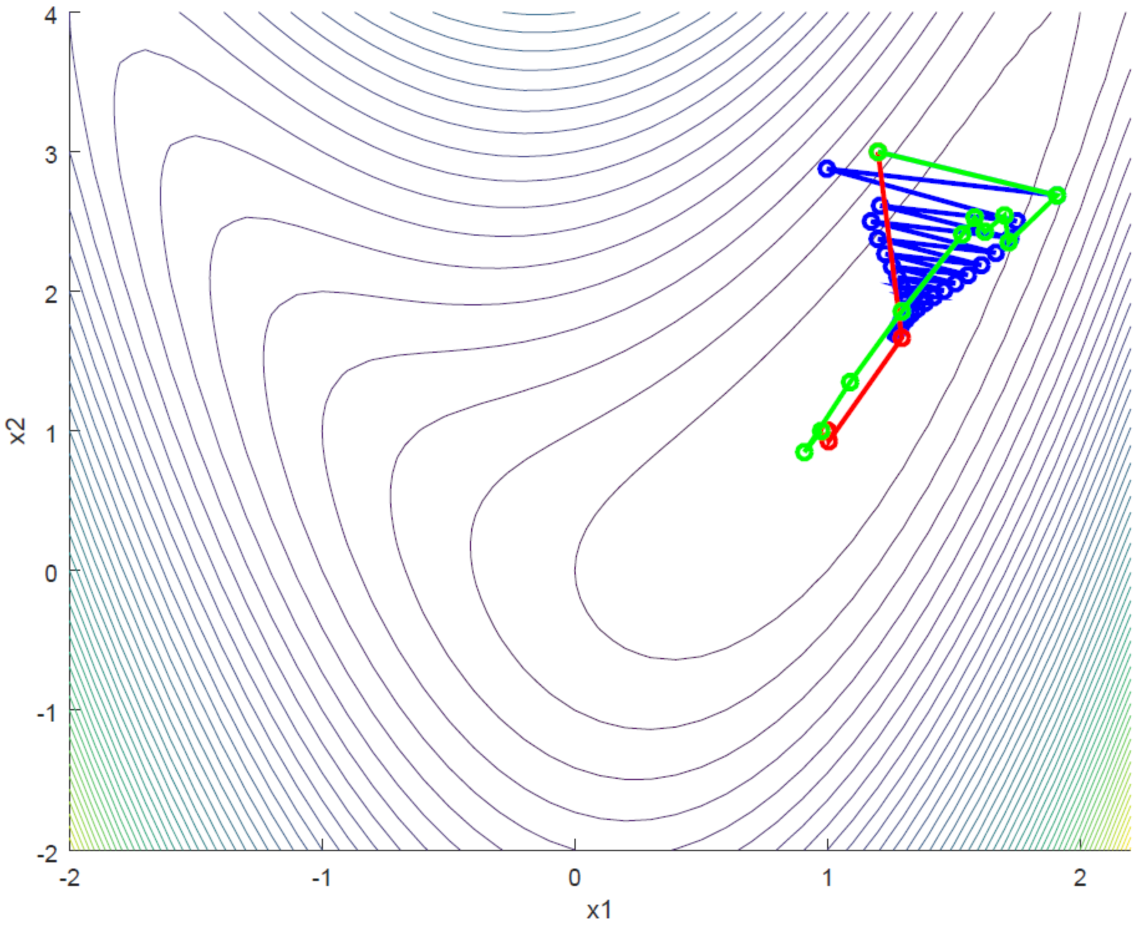
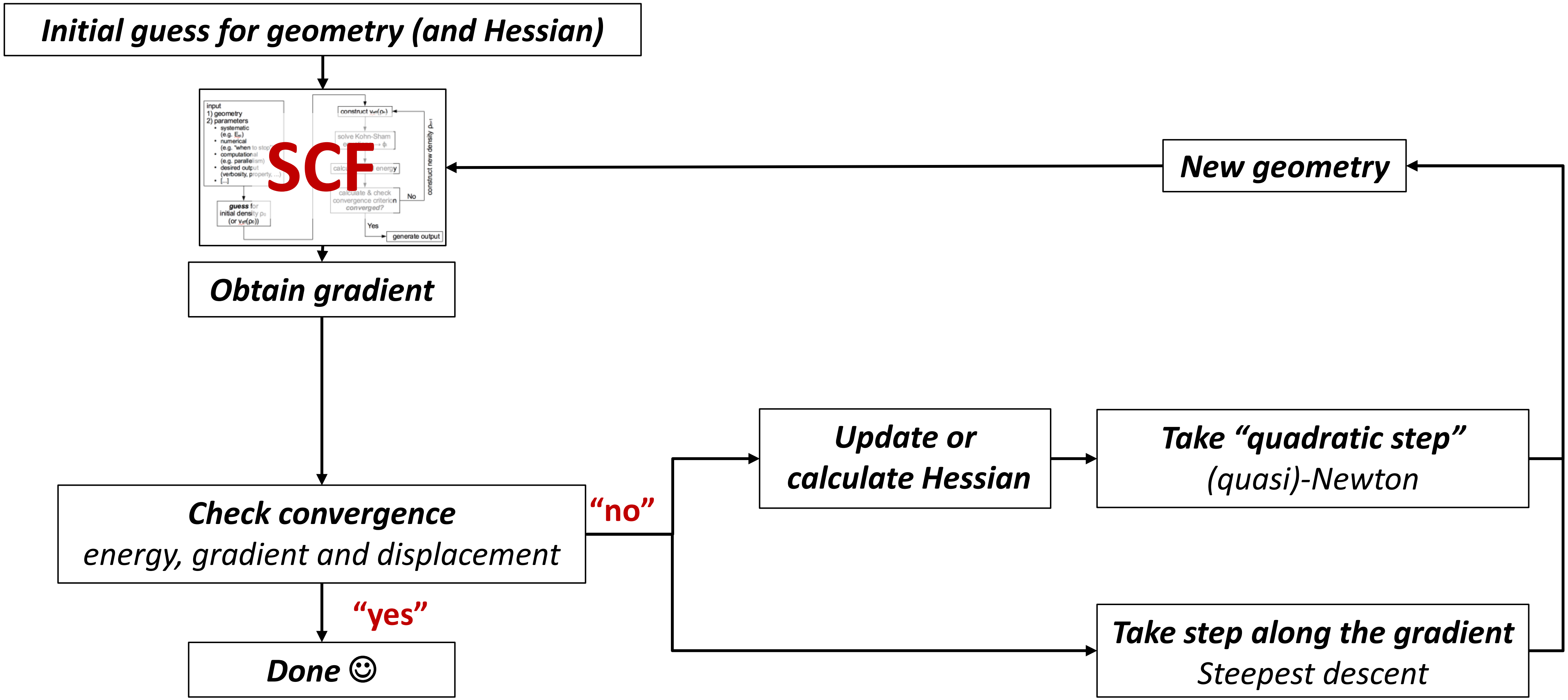


Figure courtesy: based the Matlab code by John D. Hedengren

3. Geometry optimization flow chart



Initial guess for geometry (and Hessian)

SCF

Obtain gradient

Check convergence
energy, gradient and displacement

"no"

Update or calculate Hessian

Take "quadratic step"
(quasi)-Newton

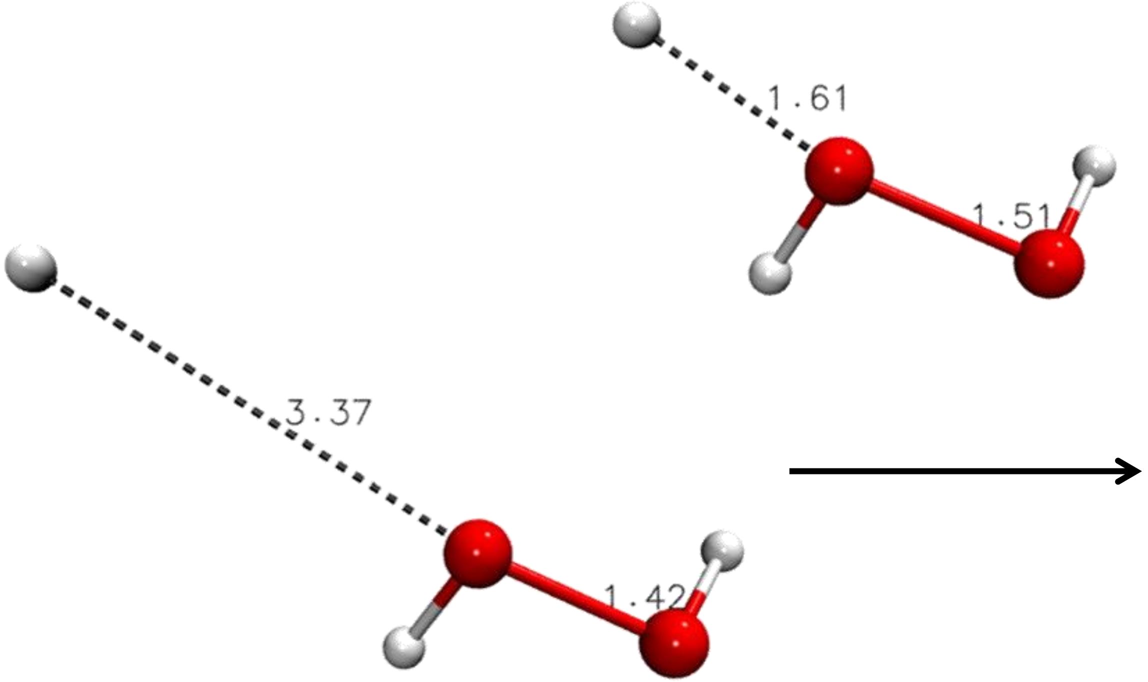
Take step along the gradient
Steepest descent

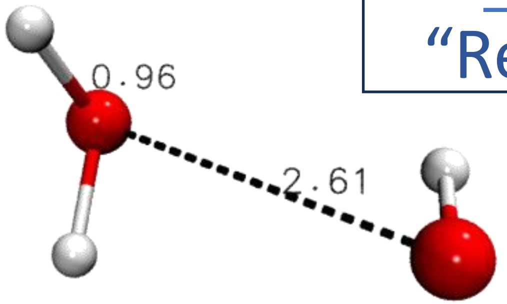
New geometry

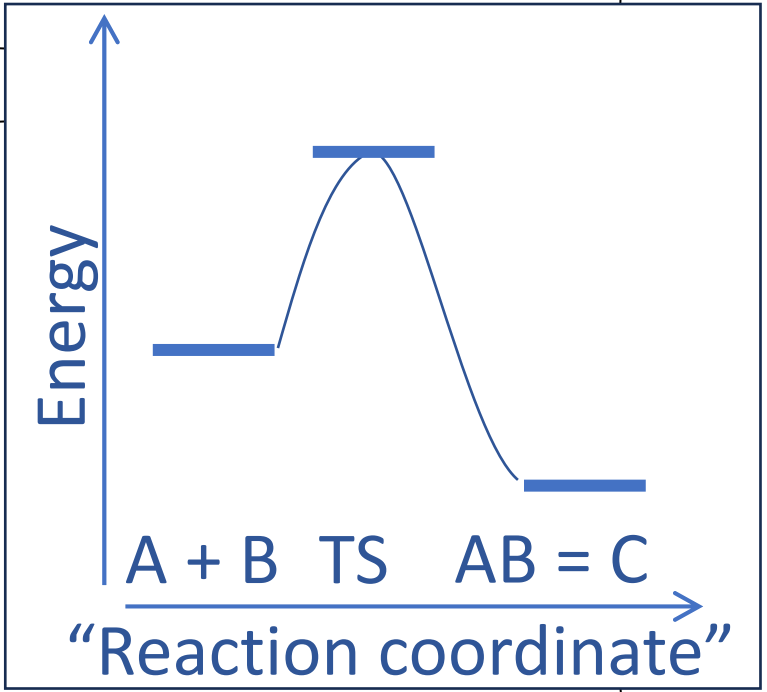
"yes"

Done ☺

Example: $H + H_2O_2 \longrightarrow H_2O + OH$







3. Finding saddle points: Nudged-elastic band

Two connecting minima

Finding the minimum energy path

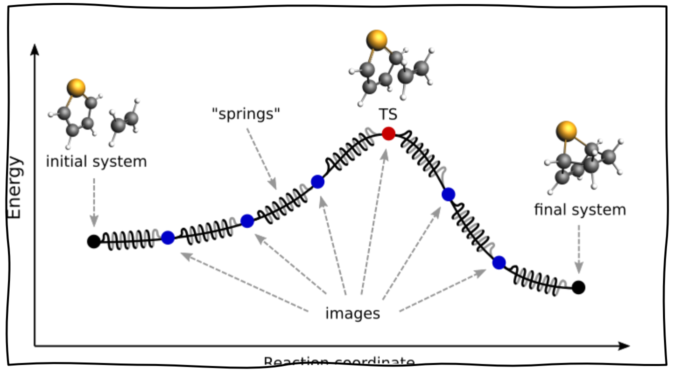


Figure courtesy: SCM website

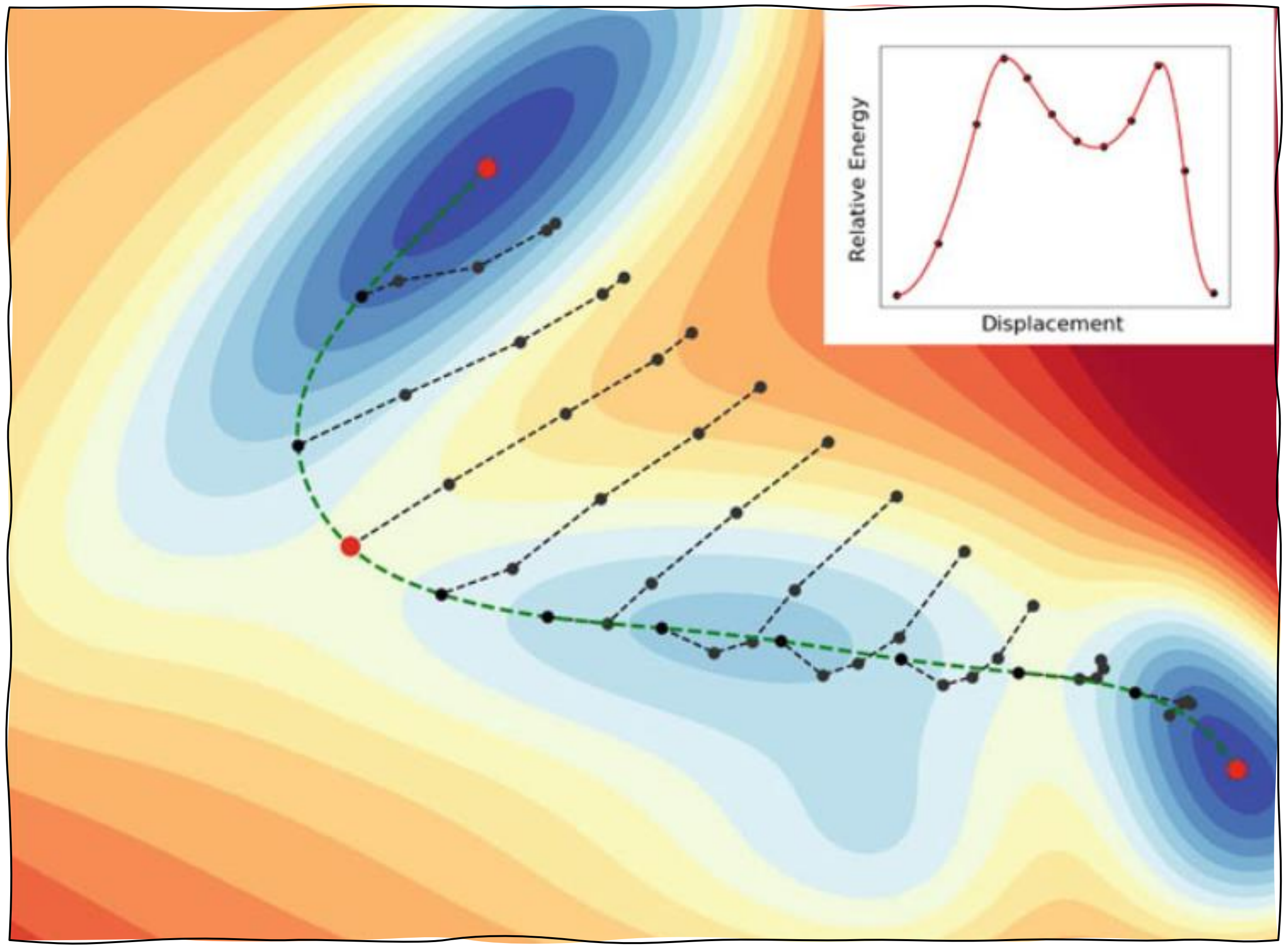


Figure courtesy: Ásgeirsson & Jónsson, Handbook of Materials Modelling

3. Finding saddle points: Dimer method

Two connected points/weights

Finding the steepest slope of the potential by rotating the dimer and moving uphill

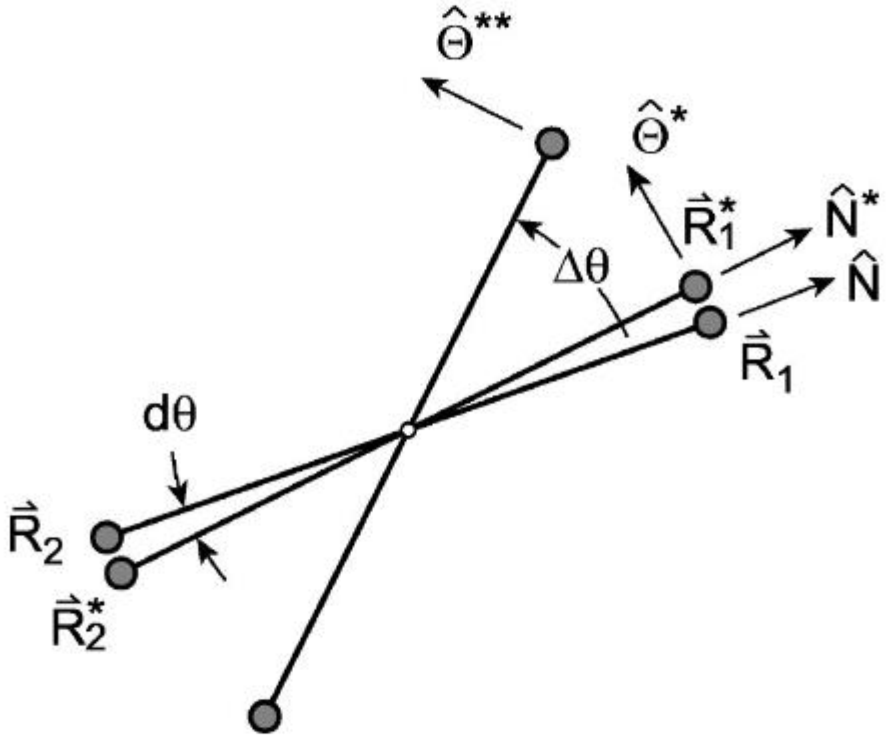


FIG. 1. Definition of the various position and force vectors of the dimer. The rotational force on the dimer, $\mathbf{F}^{\perp}$, is the net force acting on image 1 perpendicular to the direction of the dimer.

Figure courtesy: Henkelman & Jónsson, JCP, 111 (15) 1999

4. Obtaining a PES

“Level of theory” for **energetics**

- Coupled cluster theory
  - Local
- Multi-reference methods
- Density functional theory
- Force field
- Neural network / machine learned

Abbreviation

- CCSD(T) -F12
  - DLPNO
- CASSCF, CASPT2, MRCI
- DFT
- FF
- NN / ML

CCSD(T): gold standard

$$\hat{\mathrm{H}}\,\boldsymbol{\Psi}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots) = \mathbf{E}\,\boldsymbol{\Psi}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots)$$

$$\boldsymbol{\Psi}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots) = \boldsymbol{e}^{\hat{\boldsymbol{T}}}\,\boldsymbol{\psi}_0(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots)$$

1. Hartree-Fock calculation obtains Slater determinant: $\boldsymbol{\psi}_0(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots)$
2. Creation of linear combination of excited determinants via: $\boldsymbol{e}^{\hat{\boldsymbol{T}}}$

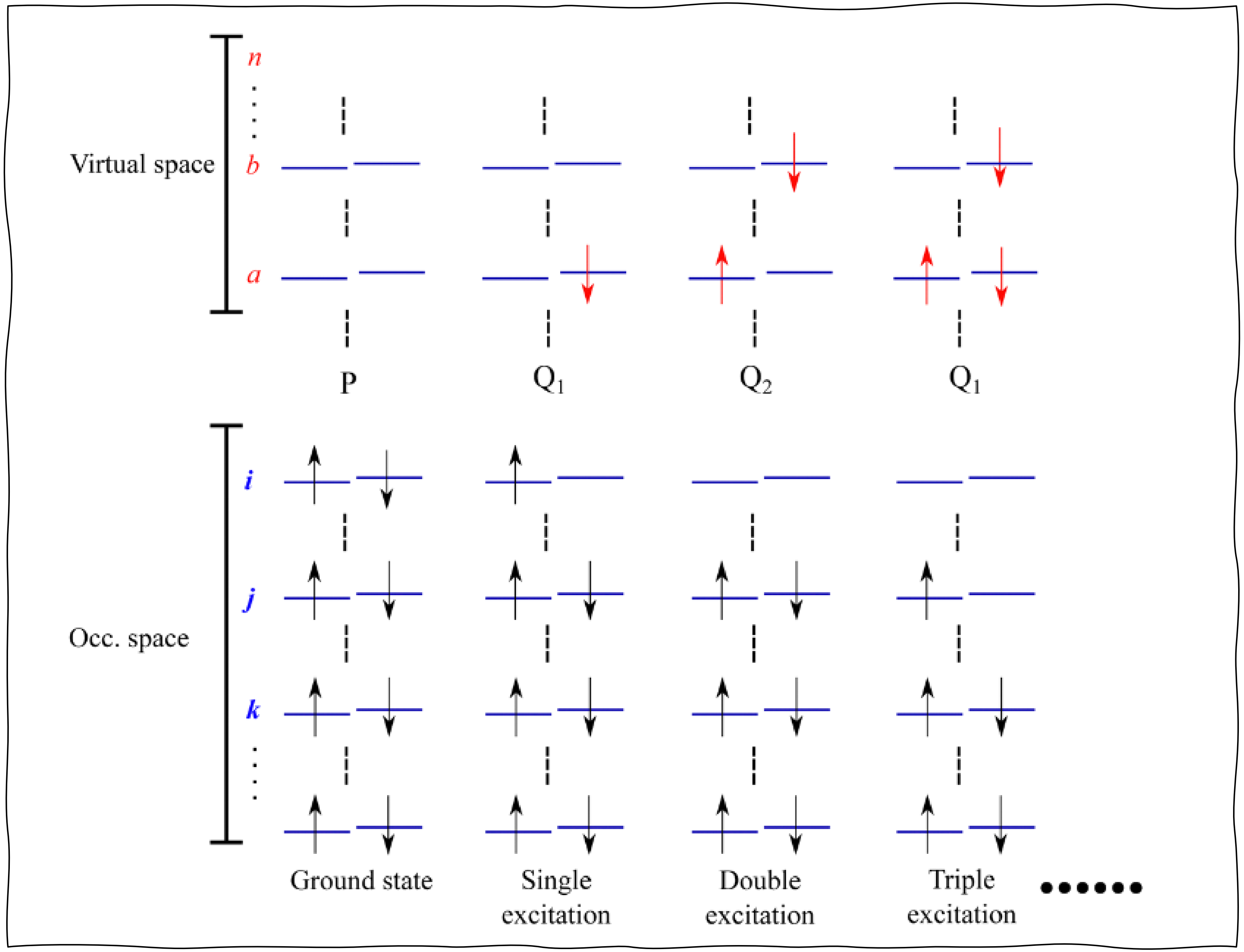


Figure courtesy: Bartlett Phys Chem Chem Phys 24, 8013 (2024)

CCSD(T): Pitfalls

- Single reference: T1 and D1 diagnostics
- Basis sets: high accuracy requires triple ζ basis sets
- Missing correlation: F12 accounts for some dynamic correlation
- Expensive: DLPNO can partially mitigate that

MR: beyond a single reference wavefunction

Relevant whenever a single Slater determinant is not a good reference:

- Transition metal chemistry
- Excited state chemistry
- Breaking of chemical bonds: radical-radical reactions
- Biradical species

DFT: workhorse of computational chemistry

$$\hat{\mathrm{H}}\,\Psi(r_1, r_2, \dots) = \mathrm{E}\,\Psi(r_1, r_2, \dots)$$

$$\Psi(r_1, \mathrm{r}_2, \dots) \rightarrow \Psi[\rho(r)]$$

Lower rung: useful for obtaining geometries

Higher rung: necessary for obtaining barriers

NB: Kohn-Sham DFT

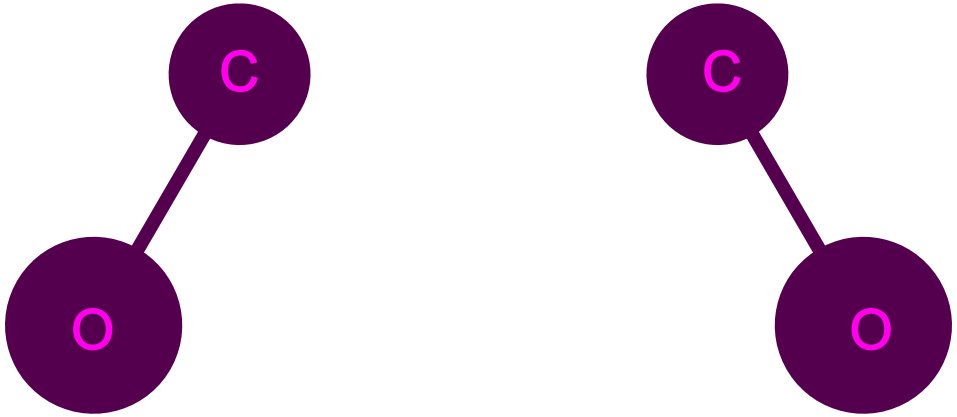
DFT: Pitfalls

- Highly functional dependent: Benchmarks necessary
- Single reference method: MR DFT is upcoming
- Delocalization error
- Basis set dependence: Basis set superposition error
- Radical-radical reactions: Broken-symmetry calculations

- Periodic boundary conditions versus cluster models

Force field potentials

Parametrizing a potential to a few approximate expressions, e.g.,



$$V_{exch} = A_{ij}e^{-B_{ij}r_{ij}}$$

$$V_{Coul} = \frac{Q_iQ_j}{r_{ij}}$$

$$V_{disp} = \frac{C_{ij}}{r_{ij}^6}$$

The force is $F = -\nabla\left(V_{Morse} + V_{exch} + V_{Coul} + V_{disp}\right)$

Force field potentials

• Usually non-reactive:	Though reactive versions exist
• Underlying level of theory matters	E.g., DFT or CCSD
• Parametrized for a purpose	Often cannot extrapolate

QM/MM: the best of both worlds

Small QM region at the DFT or DLPNO-CCSD(T) level

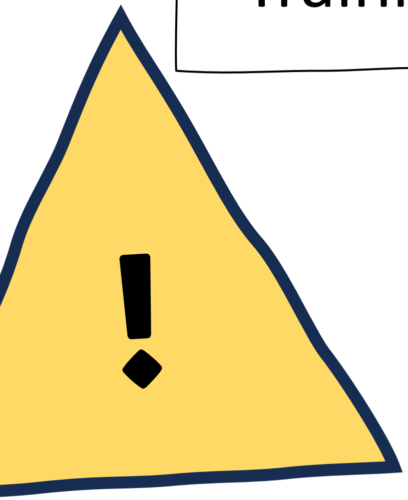
Large MM region at the FF level

NB: QM/QM methods also available

with the lower level being usually a computationally cheap density functional

Machine learned potentials

- At most as good as the underlying level of theory
- Training set is crucial: extrapolation is not trivial / possible



Intermezzo

Timescale of molecular vibrations: 2000 cm^{-1} = 6 x 10^{13} s^{-1}

Timescale of a 400 K diffusion step at 15 K: ~2 s^{-1}

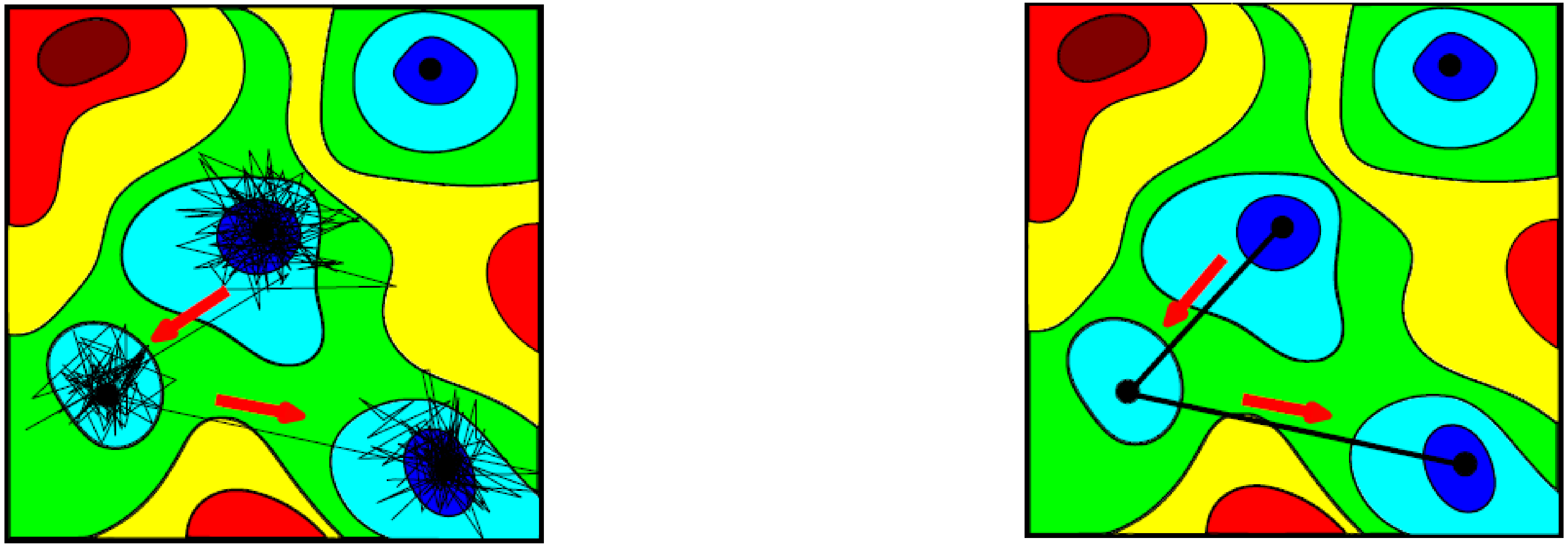


Figure courtesy: Herma Cuppen

What is a big difference between astrochemistry and surface chemistry ?

Example: energetics of binding sites

Method of choice: DFT + NN or ONIOM

- Generation of the ice
    - Periodic Boundary Conditions vs. cluster
    - Pure ices vs. mixtures
- Reorganisation of the ice
- Dual-level approach
- Benchmark!
- Corrections:
    - BSSE
    - Zero Point Energy
    - Dispersion

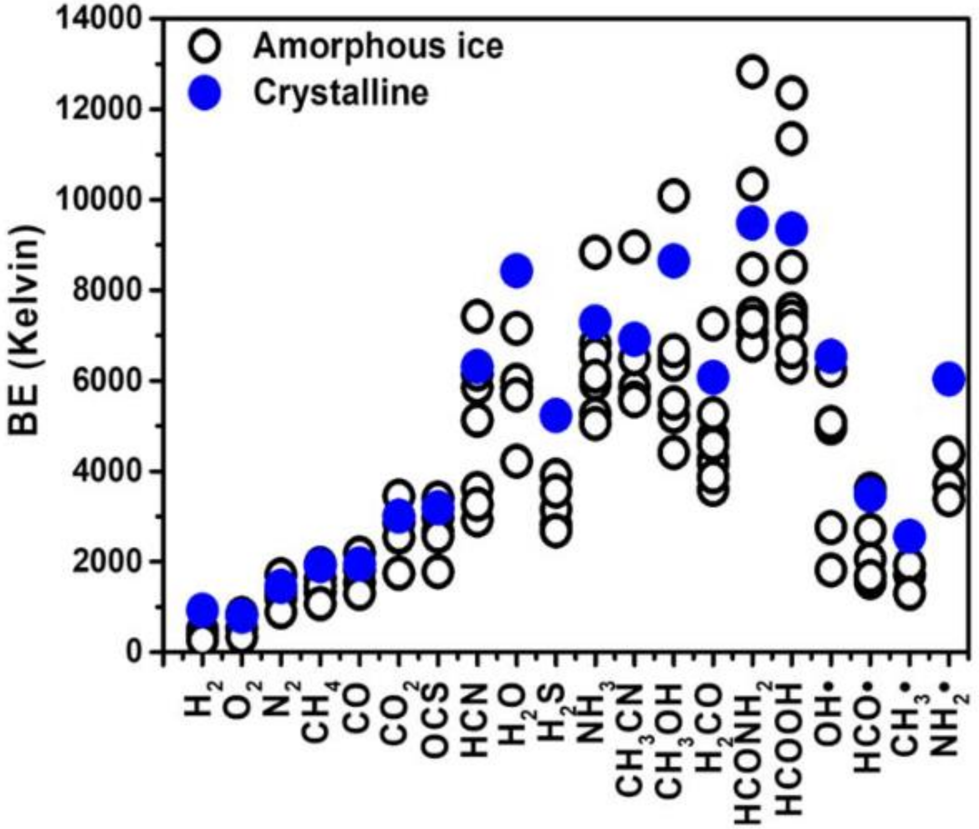


Figure 9. Comparison between the DFT//HF-3c BEs (in kelvin) computed on the crystalline ice (filled blue circles) and ASW (open circles), respectively, for 20 species studied here: HCl is missing as it dissociates on the ASW (see text).

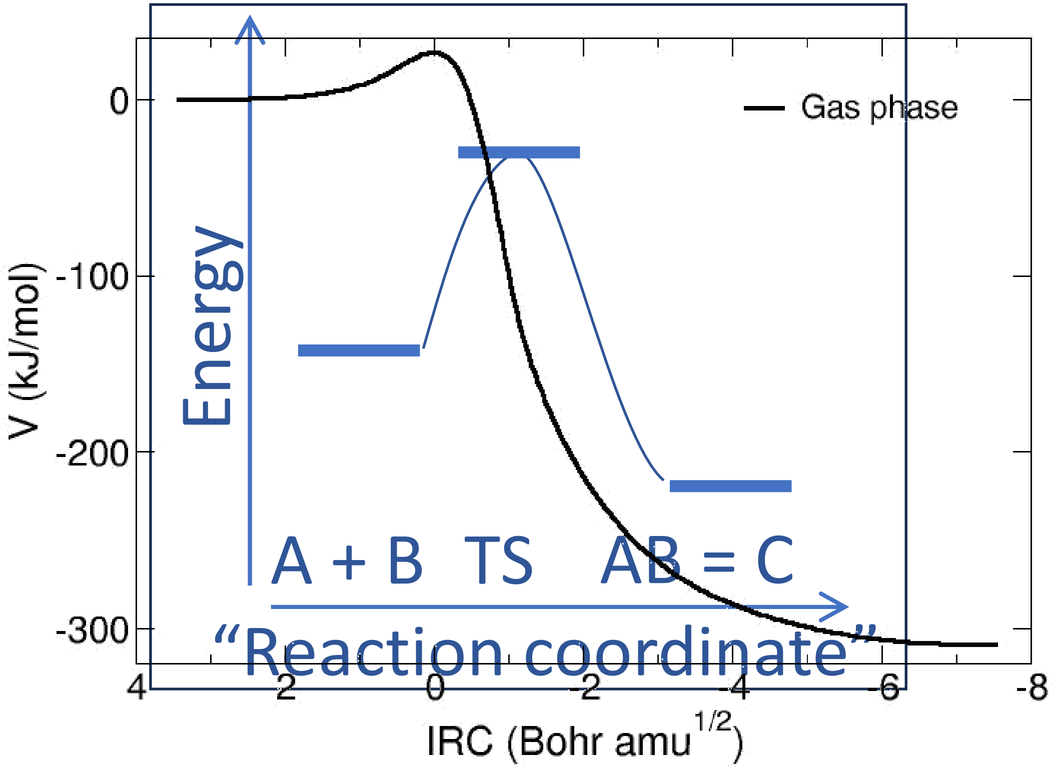
Ferrero *et al.* ApJ 904 (2018) 11

Example: H + H_2O_2 again

$$k_{react,\,thermal} = \nu \cdot e^{-E_{act}/k\_BT}$$

Higher E_{act} : a lower rate constant

Ideally the barrier should be determined accurately, why?



Example: H + H_2O_2 benchmark

Benchmark “high-level”

Functional / basis set combinations

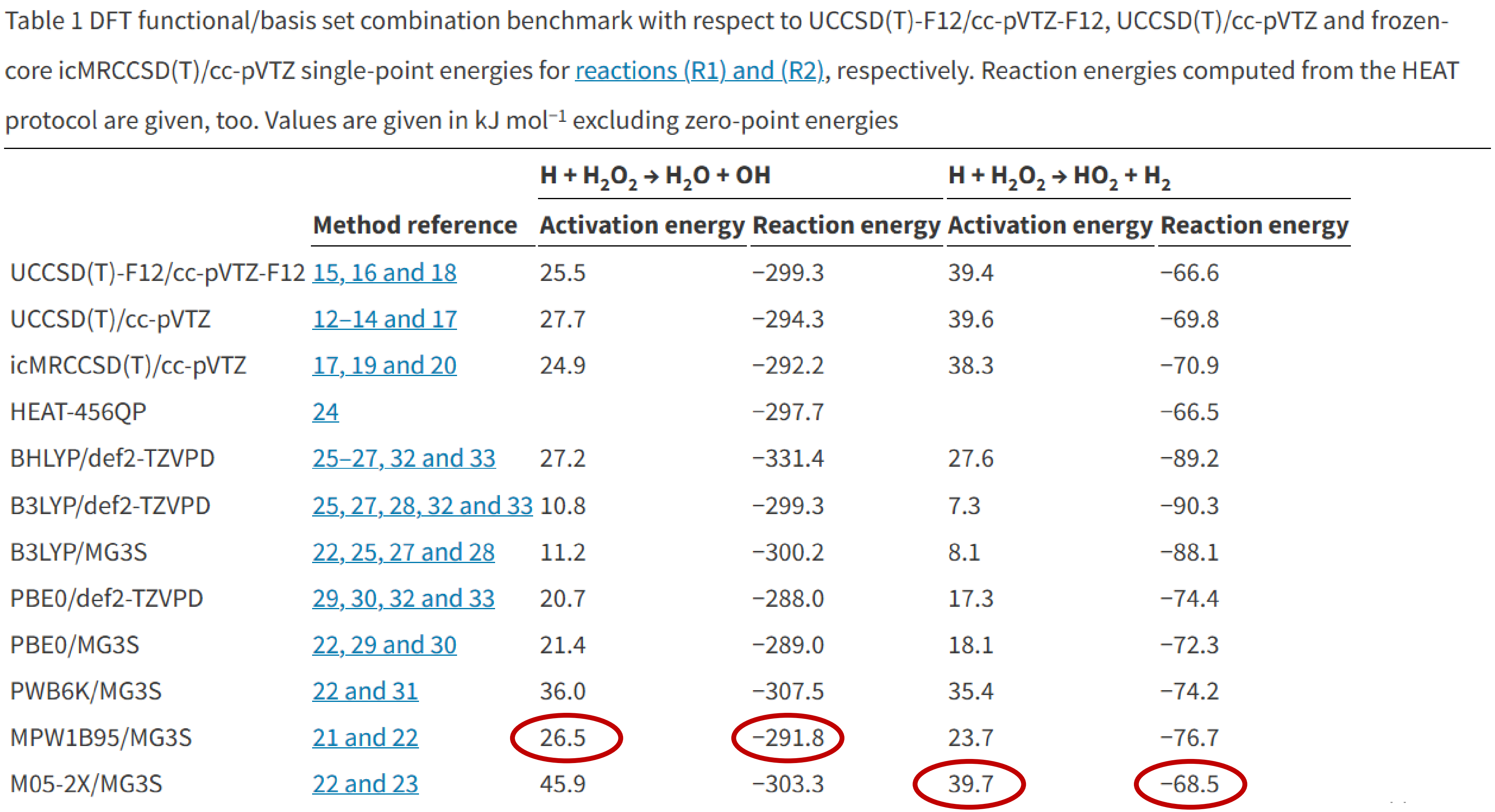
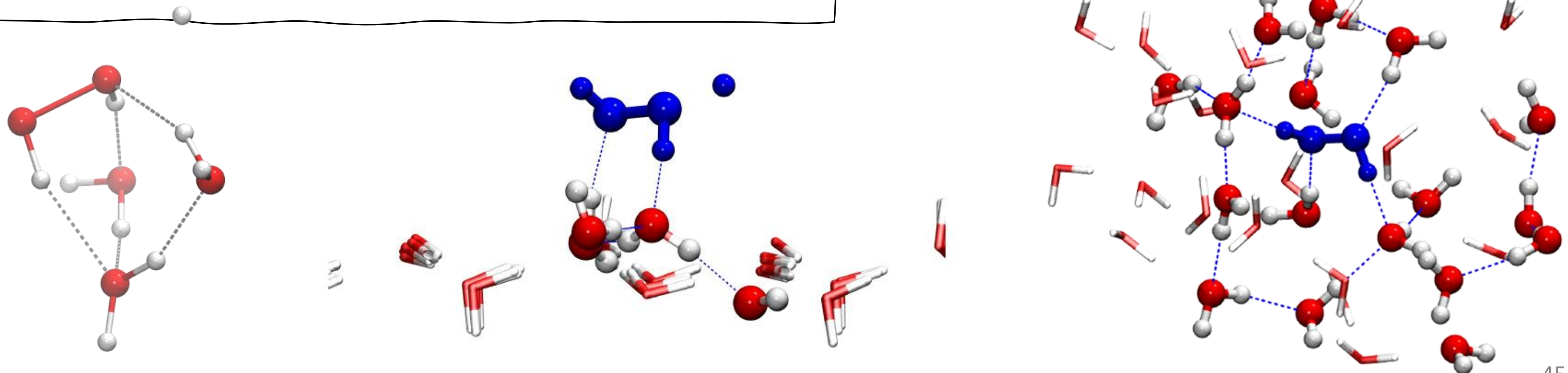


Table 1 DFT functional/basis set combination benchmark with respect to UCCSD(T)-F12/cc-pVTZ-F12, UCCSD(T)/cc-pVTZ and frozen-core icMRCCSD(T)/cc-pVTZ single-point energies for reactions (R1) and (R2), respectively. Reaction energies computed from the HEAT protocol are given, too. Values are given in kJ mol^{-1} excluding zero-point energies

		$H + H_2O_2 \rightarrow H_2O + OH$		$H + H_2O_2 \rightarrow HO_2 + H_2$	
	Method reference	**Activation energy**	**Reaction energy**	**Activation energy**	**Reaction energy**
UCCSD(T)-F12/cc-pVTZ-F12	15, 16 and 18	25.5	−299.3	39.4	−66.6
UCCSD(T)/cc-pVTZ	12–14 and 17	27.7	−294.3	39.6	−69.8
icMRCCSD(T)/cc-pVTZ	17, 19 and 20	24.9	−292.2	38.3	−70.9
HEAT-456QP	24		−297.7		−66.5
BHLYP/def2-TZVPD	25–27, 32 and 33	27.2	−331.4	27.6	−89.2
B3LYP/def2-TZVPD	25, 27, 28, 32 and 33	10.8	−299.3	7.3	−90.3
B3LYP/MG3S	22, 25, 27 and 28	11.2	−300.2	8.1	−88.1
PBE0/def2-TZVPD	29, 30, 32 and 33	20.7	−288.0	17.3	−74.4
PBE0/MG3S	22, 29 and 30	21.4	−289.0	18.1	−72.3
PWB6K/MG3S	22 and 31	36.0	−307.5	35.4	−74.2
MPW1B95/MG3S	21 and 22	26.5	−291.8	23.7	−76.7
M05-2X/MG3S	22 and 23	45.9	−303.3	39.7	−68.5

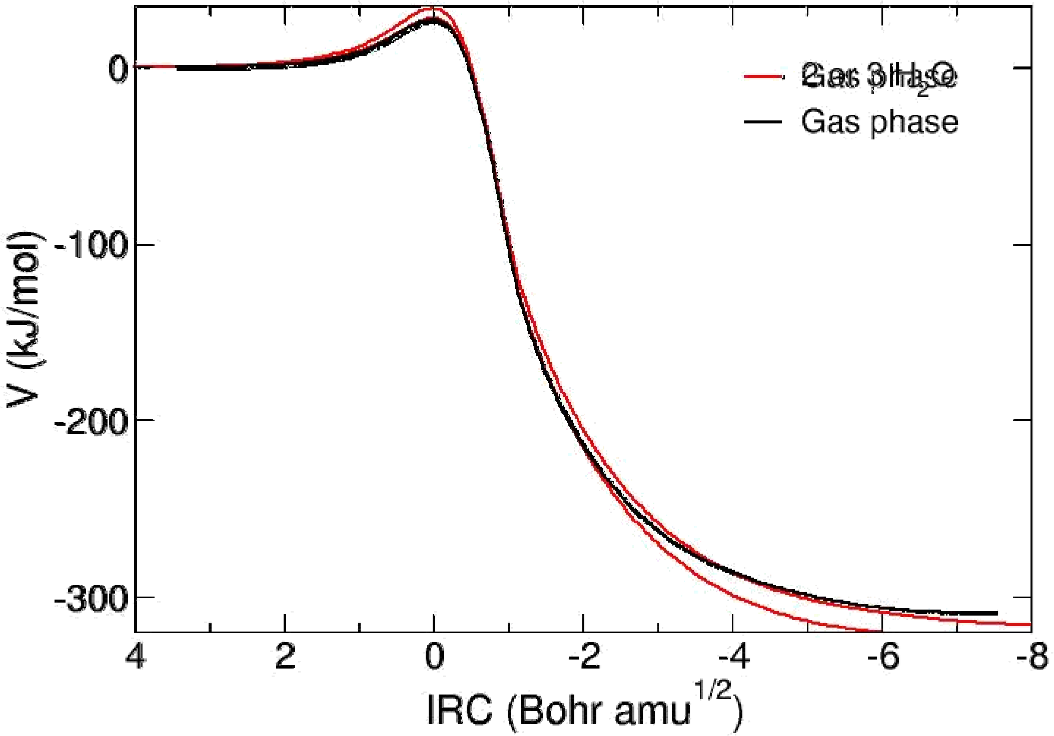
Example: H + H_2O_2 again

Including “surface molecules” as small clusters first to test influence on the potential energy

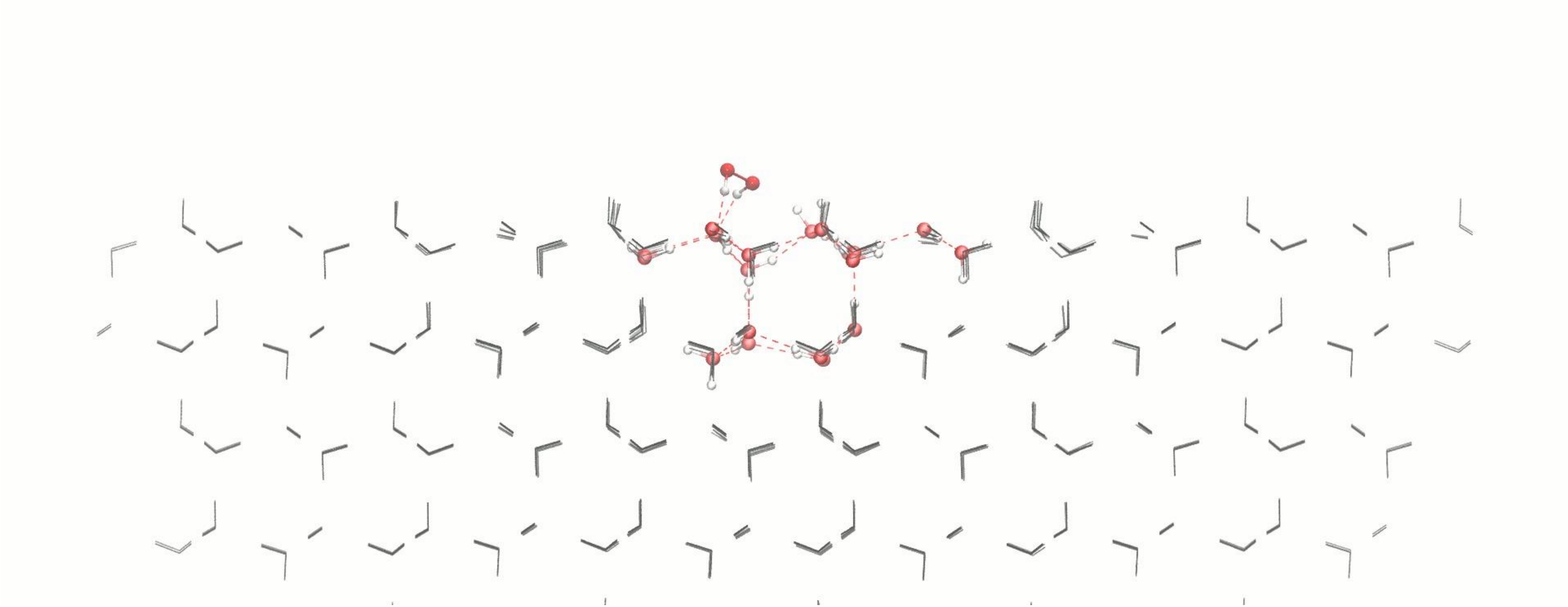


Example: H + H_2O_2 again

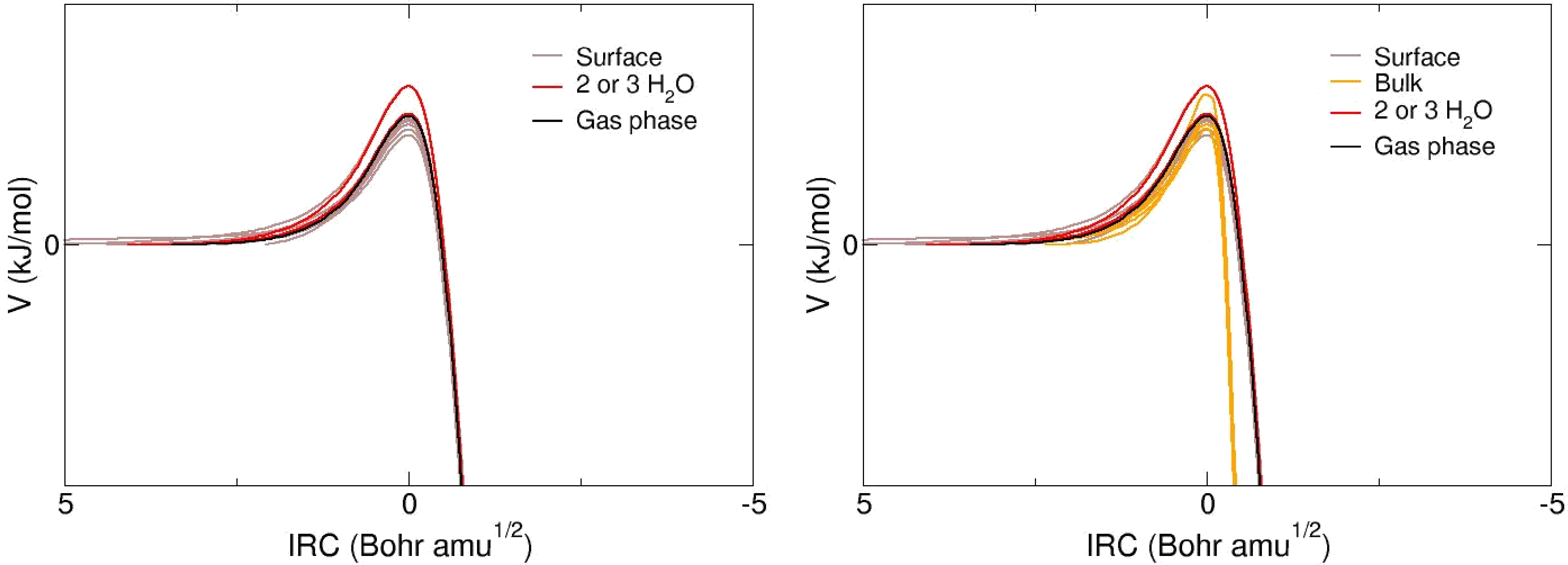
Including “surface molecules” as small clusters first to test influence on the potential energy



Example: H + H_2O_2 on a surface

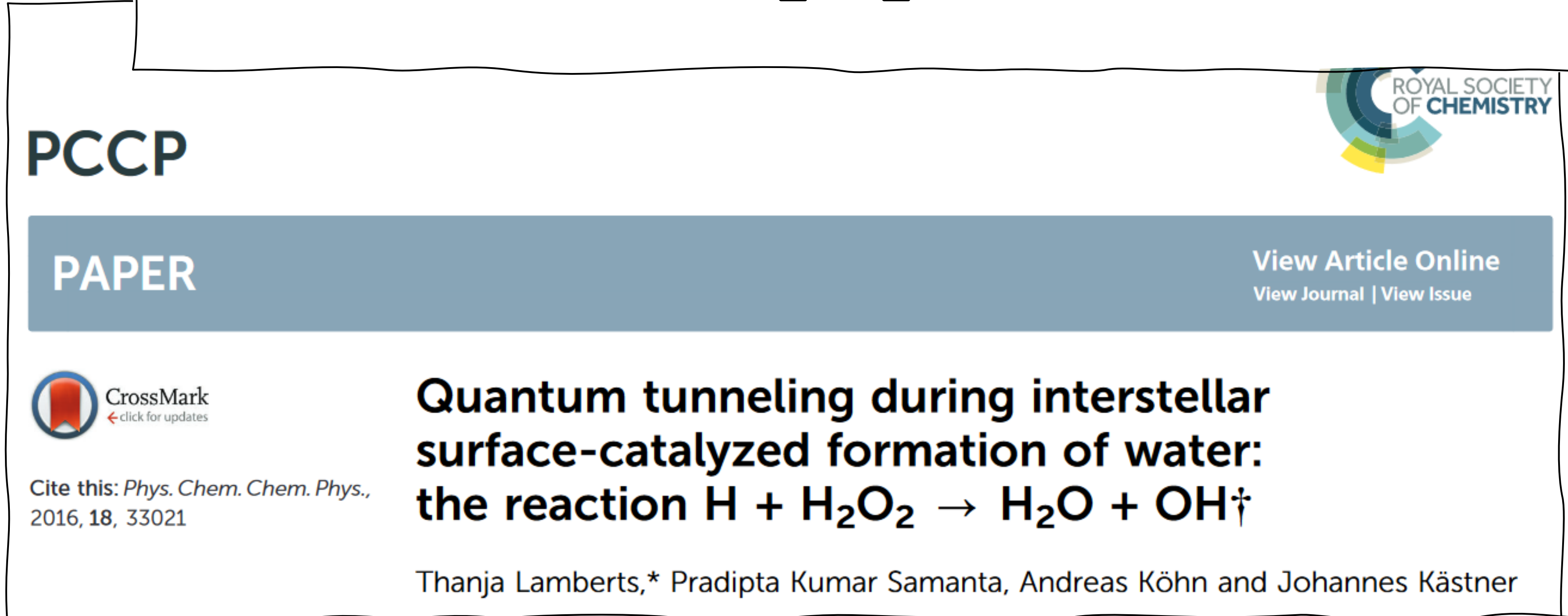


Example: H + H_2O_2 on a surface



Barrier height determines the rate constant: ice surface is catalytic

Example: $H + H_2O_2$ literature



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Quantum tunneling during interstellar surface-catalyzed formation of water: the reaction $H + H_2O_2 \rightarrow H_2O + OH$†

Thanja Lamberts,* Pradipta Kumar Samanta, Andreas Köhn and Johannes Kästner

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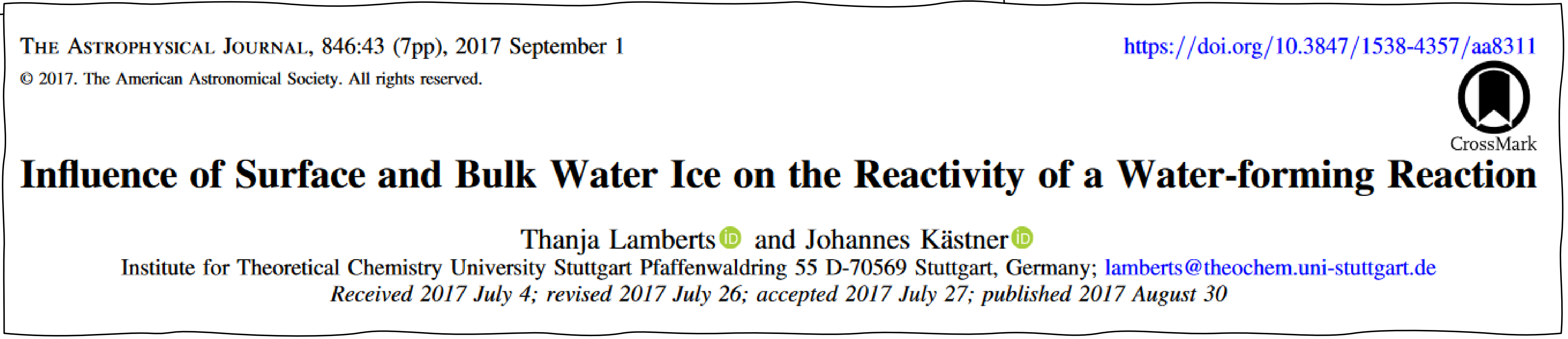

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Influence of Surface and Bulk Water Ice on the Reactivity of a Water-forming Reaction

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Take home messages

- Intermolecular interactions determine the so-called Potential Energy Surface (PES): a function of atom positions or bond lengths
- Geometry optimization = iterative procedure to find PES minima
- Saddle point search = iterative procedure to find a PES saddle point
- Intrinsic Reaction Coordinate = plotted as E_{system} vs a ‘suitable’ reaction coordinate

- Many different computational techniques exist to calculate the energies and it is key to find the right one for the system at hands

Theoretical Methods