Ab Initio Molecular Dynamics

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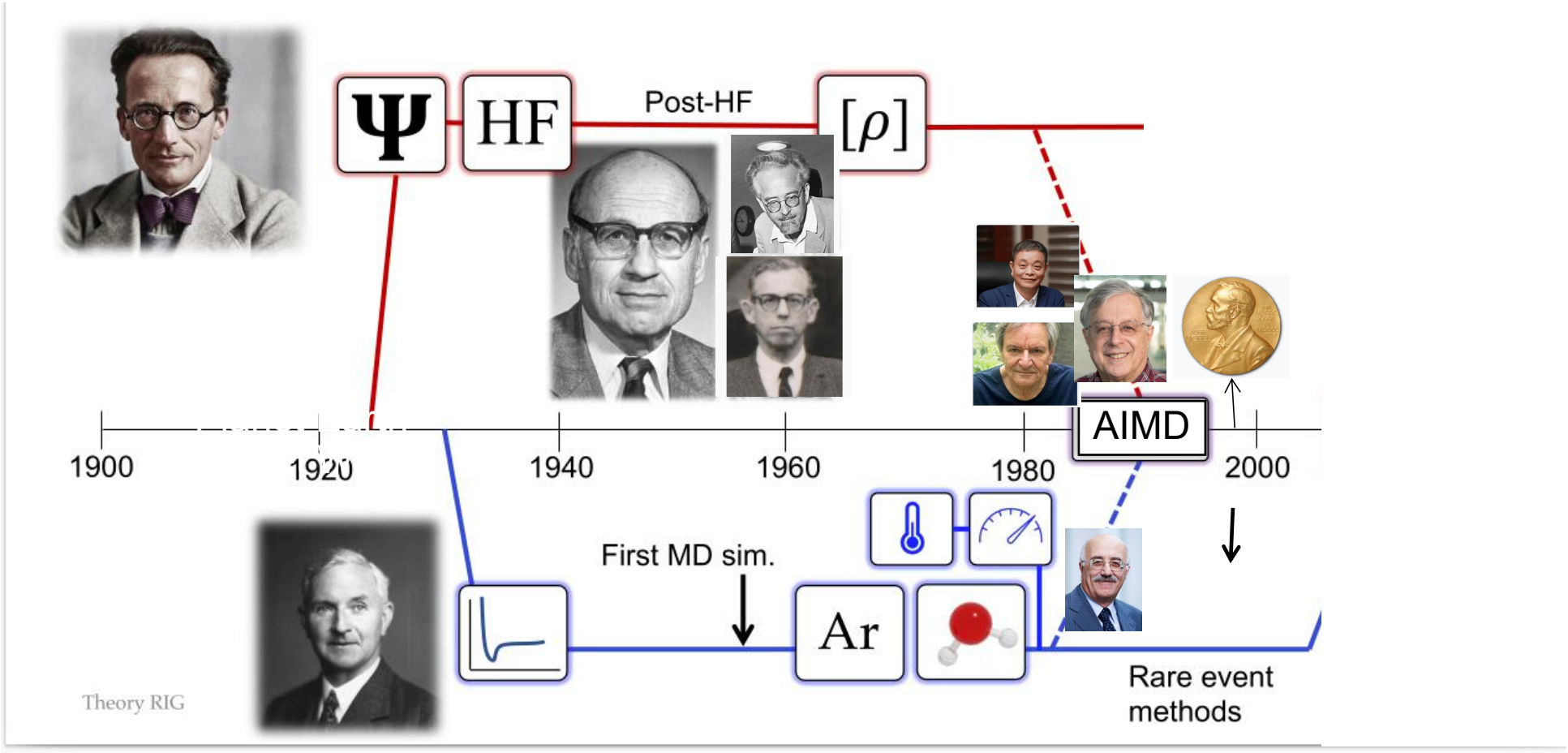
I’ve been in your place (many years ago)

Image of Neo being connected to the Matrix

Standing on the Shoulder of Giants

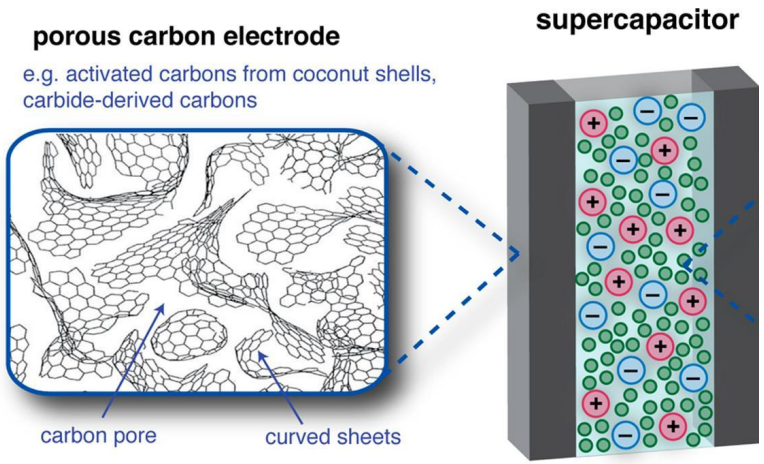


(Slide courtesy of Samuel Brookes@Cambridge)

Aqueous Electrochemical Devices

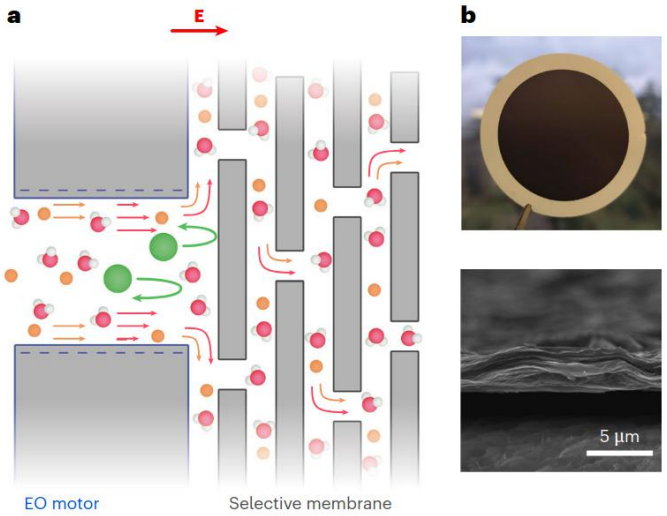
Aqueous electrochemical devices play a critical role in the green energy transition

Supercapacitors



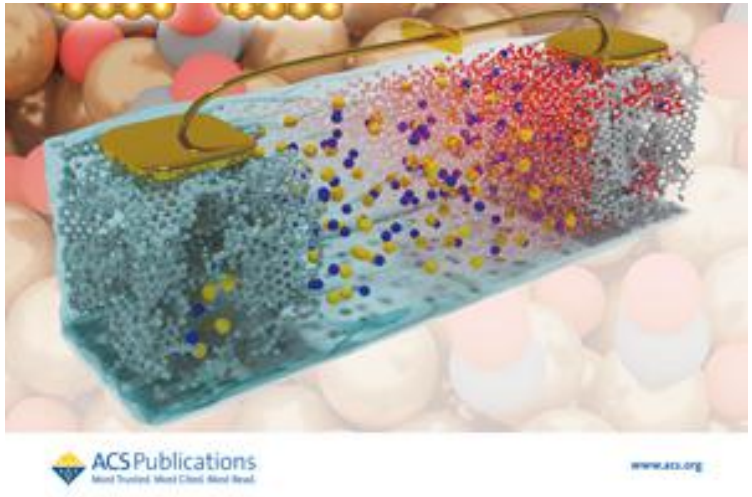
Forse, *et al. JACS*, **138**, 5731-5744 (2016)

Water desalination/purification



Abdelghani-Idrissi, et al. Nat. Mat. **24**, 1109-111 (2025)

Aqueous batteries



Koper, *et al. Chem. Rev*. **122**, 10579 (2022)

The Hamiltonian that Rules Everything

"The underlying physical laws necessary for the mathematical theory of large parts of physics and the whole of chemistry are thus completely known ..." (Dirac, 1929)

$$\hat{H} = \hat{T}_{\text{nuc}} + \hat{V}_{\text{nuc-nuc}} + \underbrace{\hat{T}_{\text{e}} + \hat{V}_{\text{nuc-e}} + \hat{V}_{\text{e-e}}}_{\hat{H}_{\text{e}}}$$

$$\hat{T}_{\text{nuc}} = -\sum_{I}^{N} \frac{\vec{\nabla}_I^2}{2M_I}$$

$$\hat{V}_{\text{nuc-nuc}} = \frac{1}{2}\sum_{I\neq J}^{N} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|}$$

$$\vec{V}_{\text{nuc-e}} = -\sum_{i}^{n}\sum_{I}^{N} \frac{Z_I}{|\vec{r}_i - \vec{R}_I|} \qquad \hat{V}_{\text{e-e}} = \frac{1}{2}\sum_{j\neq i}^{n} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

$$\hat{T}_{\text{e}} = -\sum_{i}^{n} \frac{\vec{\nabla}_i^2}{2}$$

"…. the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble"

Born-Huang Expansion

We want to solve the time-independent Schrödinger equation

$$\hat{H}\Psi = E\Psi$$

Assuming we could solve first the electronic problem at fixed nuclei, we would get

$$\hat{H}_{\mathrm{e}}\Phi_s(\mathbf{R},\mathbf{r}) = E_s(\mathbf{R})\Phi_s(\mathbf{R},\mathbf{r}),$$

for each nuclei position.

Then we use these solutions as a basis,

$$\Psi_\nu = \sum_s \Lambda_s^\nu(\mathbf{R})\Phi_s(\mathbf{R},\mathbf{r}),$$

So far we haven't made any additional approximation, so if we introduce the previous equation into the first one, we obtain ....

Born-Oppenheimer Approximation

... this beauty

$$E_t\Lambda_t^\nu(\mathbf{R}) = \left[\hat{T}_{\text{nuc}} + \hat{V}_{\text{nuc-nuc}} + E_t(\mathbf{R})\right]\Lambda_t^\nu(\mathbf{R}) - \sum_s\sum_I \frac{1}{2M_I}[2\vec{A}_{ts,I}^{(1)}(\mathbf{R})\vec{\nabla}_I + A_{ts,I}^{(2)}(\mathbf{R})]\Lambda_s^\nu(\mathbf{R})$$

where

$$A_{ts,I}^{(2)}(\mathbf{R}) = \int d\mathbf{r}\Phi_t^*(\mathbf{R},\mathbf{r})\vec{\nabla}_I^2\Phi_s(\mathbf{R},\mathbf{r}) \qquad \vec{A}_{ts,I}(\mathbf{R}) = \int d\mathbf{r}\Phi_t^*(\mathbf{R},\mathbf{r})\vec{\nabla}_I\Phi_s(\mathbf{R},\mathbf{r})$$

If we neglect the last two terms, (i.e. movement of nuclei can't induce electronic excitations), we obtain

$$\hat{H}_{\text{nuc}}\Lambda_0^\nu(\mathbf{R}) = \left[\hat{T}_{\text{nuc}} + V_{\text{nuc},0}^{\text{BO}}(\mathbf{R})\right]\Lambda_0^\nu(\mathbf{R})$$

where

$$V_{nuc,s}^{\text{BO}}(\mathbf{R}) := E_s(\mathbf{R}) + V_{\text{nuc-nuc}}(\mathbf{R})$$

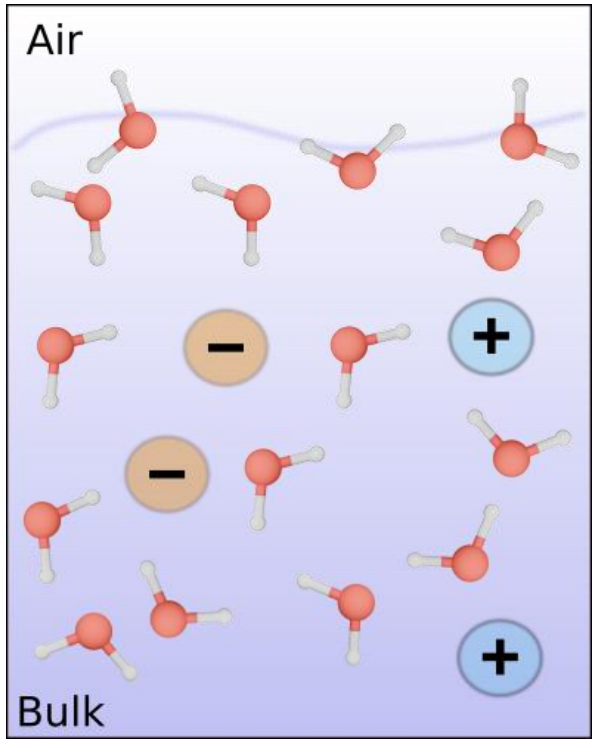
We effectively separated the nuclei and electronic problems!

Note that nuclei are still quantum particles!

Born, Huang, Dynamical Theory of Crystal Lattices, Oxford University Press, 1954

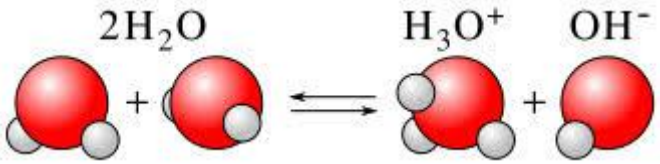
Chemistry/Physics doesn't Stop at the Minimum

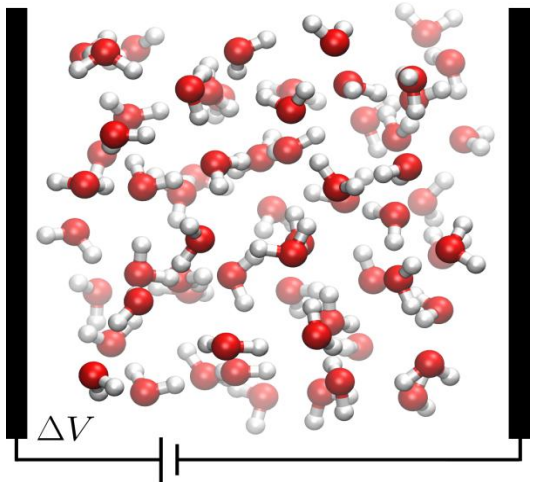
Interfacial structure of simple electrolyte at aqueous solutions



Litman, Chiang, Seki, Nagata, Bonn, Nat. Chem, **16,** 644 (2024)

Water dissociation under electric fields





Litman, Michaelides, J. Am. Chem. Soc. *in press* (2025)

Equilibrium Properties at Finite Temperature

We first consider the classical nuclei case. The canonical partition function is defined as

$$\beta = \frac{1}{k_{\mathrm{B}}T}$$

$$Q^{\mathrm{CL}}(\beta) = \frac{1}{(2\pi\hbar)^{3N}} \int d\mathbf{R} d\mathbf{P} e^{-\beta H_{\mathrm{nuc}}(\mathbf{R},\mathbf{P})}$$

$$k_{\mathrm{B}}T/\hbar\omega >> 1$$

Equilibrium averages are computed as

$$\langle A \rangle_{\mathrm{CL}} = \frac{1}{(2\pi\hbar)^{3N} Q^{\mathrm{CL}}(\beta)} \int d\mathbf{R} d\mathbf{P} A(\mathbf{R},\mathbf{P}) e^{-\beta H_{\mathrm{nuc}}(\mathbf{R},\mathbf{P})}$$

Evaluating the previous integral on a grid is a bad idea (why?), so we normally ‘sample’ it.

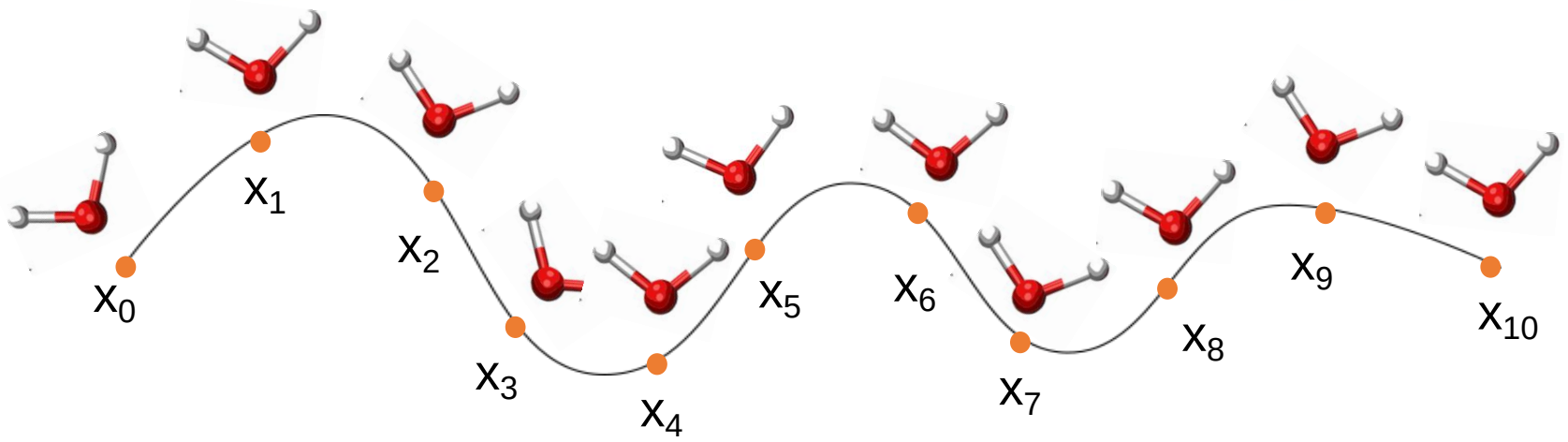
if we sample from the Boltzmann distribution, $e^{-\beta H_{\mathrm{nuc}}(\mathbf{R},\mathbf{P})}$, we can compute thermal averages as

$$\langle A(R) \rangle = \frac{1}{N} \sum_{i}^{\mathrm{N}} A(R^i)$$

Molecular Dynamics

Hamilton's equations of motion (EOM)

$$\dot{\vec{R}}_I = \frac{\partial H_{\text{nuc}}}{\partial \vec{P}_I} = \frac{P_I}{2M} \qquad \dot{\vec{P}}_I = -\frac{\partial H_{\text{nuc}}}{\partial \vec{R}_I} = -\nabla V_{\text{nuc}}^{\text{BO}}$$



Ergodic hypothesis: *The system will visit every accessible region of phase space, given enough time.*

$$\langle A \rangle = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^{\tau} dt A(t)$$

EOM in Practice

The integration of the equations of motion (EOM) is normally done using the velocity Verlet algorithm

velocity update

$$\dot{R}\left(t+\frac{\Delta t}{2}\right)=\dot{R}(t)+\frac{F(t)}{M}\frac{\Delta t}{2}$$

position update

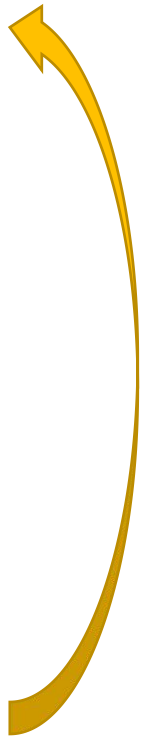
$$R(t+\Delta t)=R(t)+\dot{R}\left(t+\frac{\Delta t}{2}\right)\Delta t$$

force update

$$\text{Evaluate } F(t+\Delta t) \text{ from } R(t+\Delta t)$$

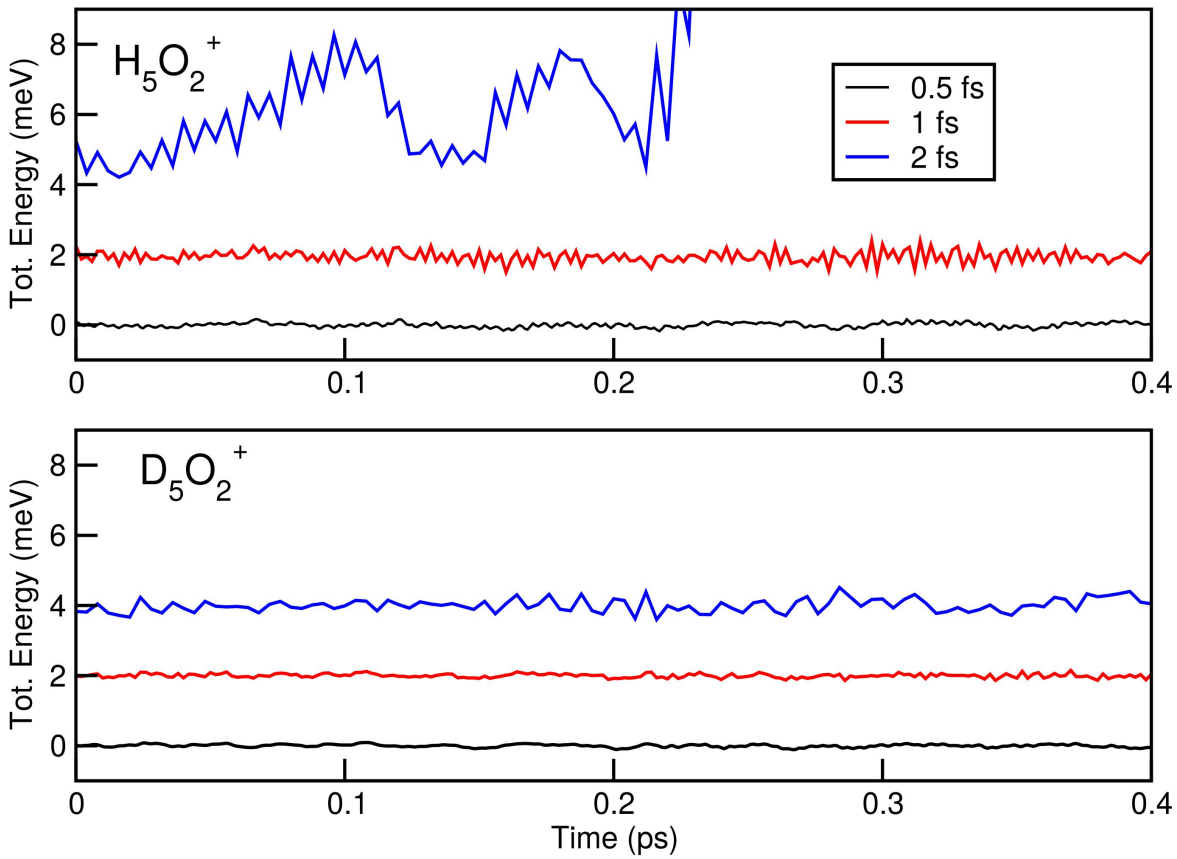
velocity update

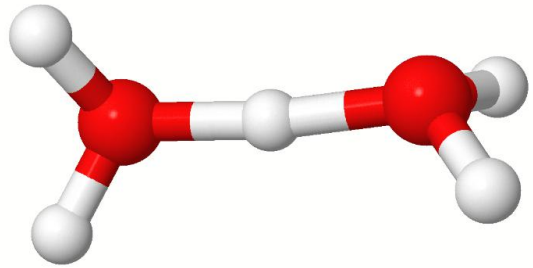
$$\dot{q}\left(t+\Delta t\right)=\dot{q}\left(t+\frac{\Delta t}{2}\right)+\frac{F(t+\Delta t)}{M}\frac{\Delta t}{2}$$



EOM in Practice

Selection of time step:

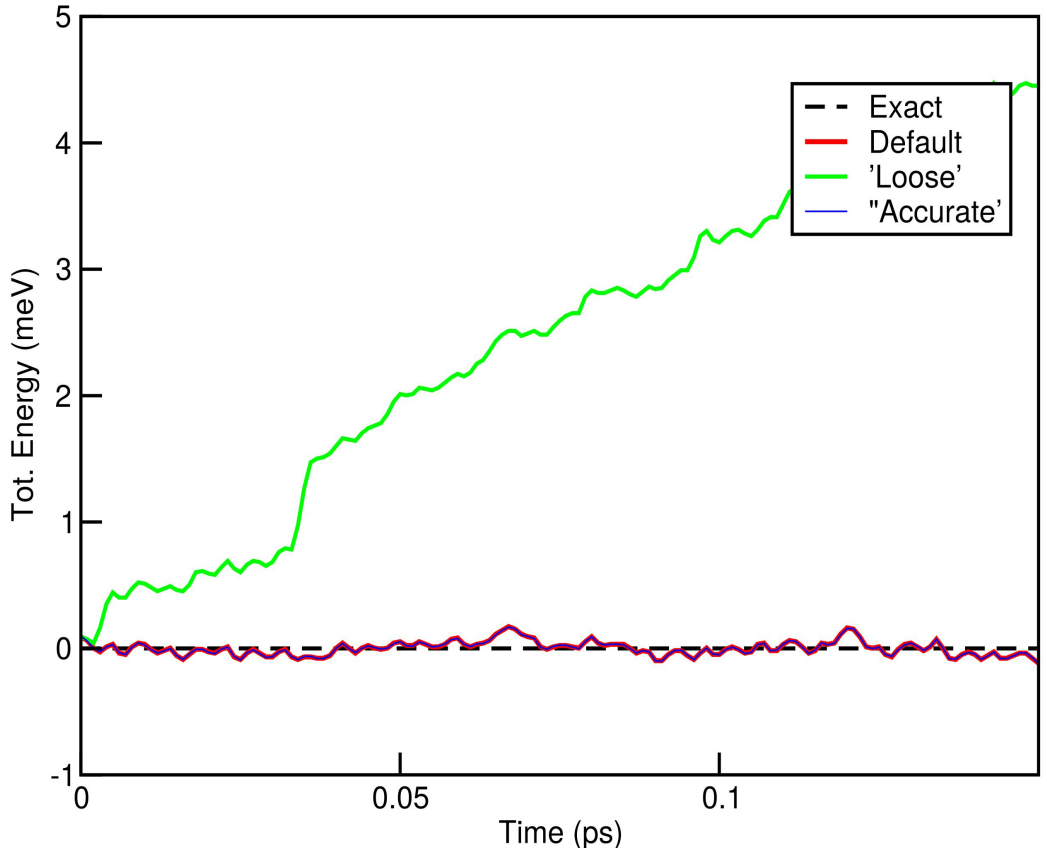




Rule of thumb: time step ≈ 1/10 of the maximum frequency

SCF Accuracy

Selection of SCF accuracy (in FHI-aims)



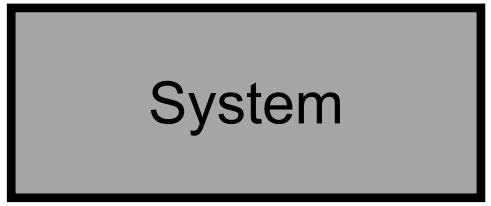
Stability of MD simulations depends critically on the accuracy of the forces

Ensembles

We can perform simulations on different ensembles. The most common are

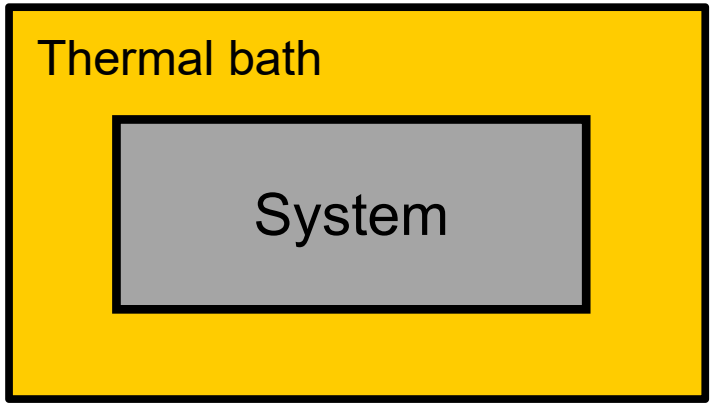
Microcanonical ensemble (NVE)

N,V,E = constant



Canonical ensemble (NVT)

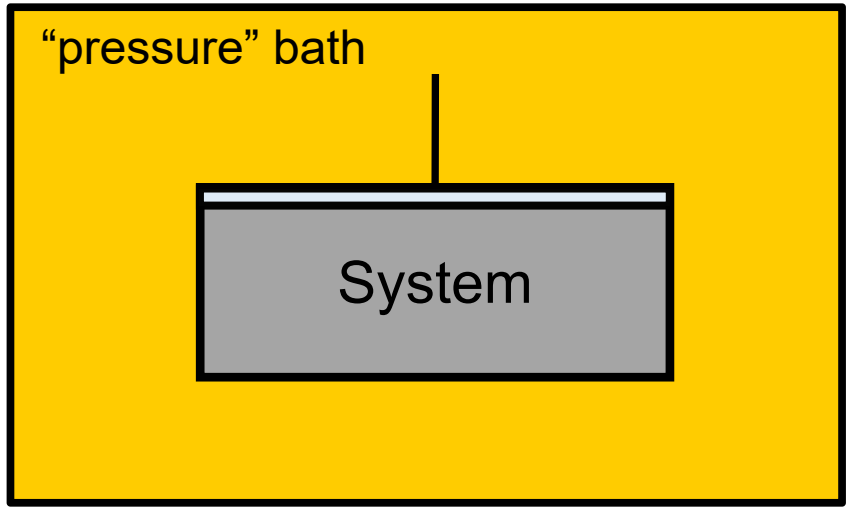
N,V,T = constant



Thermostat

Isothermal-Isobaric ensemble (NPT)

N,P,T = constant



Barostat and Thermostat (not shown)

Thermostat

Extended Lagrangian approach (deterministic):

Seminal idea from Nose

$$H^{\mathrm{Nose}} = H_{\mathrm{nuc}} + \frac{P_s^2}{2Q} + gkTln(s)$$

= additional degree of freedom

More complex and reliable implementations:

- Nose-Hoover
- Nose-Hoover chains

Nose, J. Chem. Phys. **81**, 511 (1984)

Hoover, Phys. Rev. A. **31,** 1695 (1985)

Martyna, Klein, Tuckerman, J. Chem. Phys. 97 2635 (1992)

Langevin Thermostats (stochastic):

Simplest formulation:

$$M_I \ddot{R} = F_I - \gamma_I \dot{R}_I + \xi(t)$$

Friction White noise

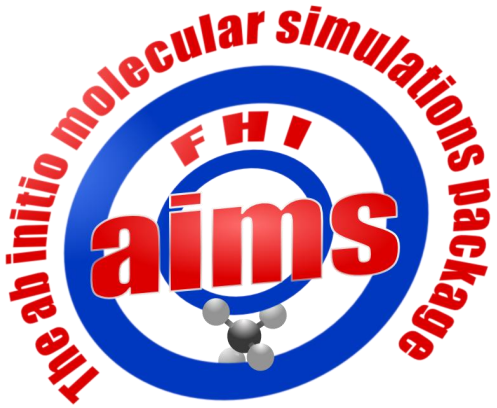
More complex and reliable implementations:

- Stochastic velocity rescaling
- Colored noise thermostat

Bussi, Donadio, Parrinello, J. Chem. Phys. **126**, 014101 (2007)

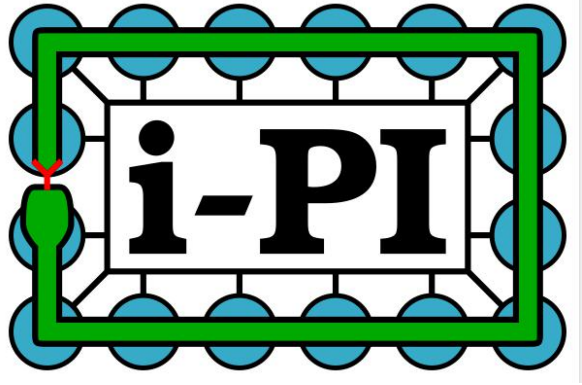
Ceriotti, Bussi, Parrinello, J. Chem. Theory Comput, 6, 1170 (2010)

A Universal Force Engine



Energy, forces and stress

Coordinates, cell



Compute forces and potential energy

Evolve atomic positions and velocities

Apply thermostat

Apply barostat

....

Litman, et al. J. Chem. Phys. **161**, 062504 (2024)

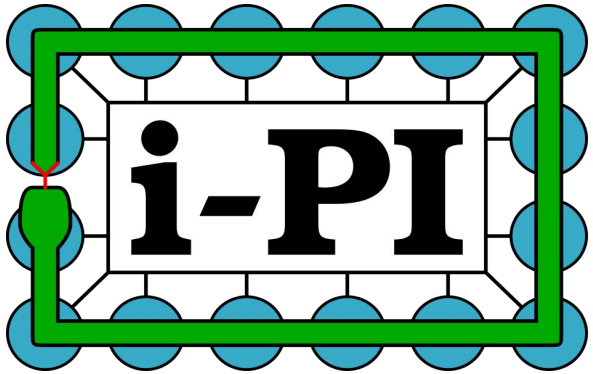
A Universal Force Engine

Molecular Dynamics

Geometry Optimization

Phonons

Nudge Elastic Band



Path Integral Molecular Dynamics

Ring Polymer Molecular Dynamics

Centroid Molecular Dynamics

Ring Polymer Instantons

Replica Exchange Molecular Dynamics

Metadynamics

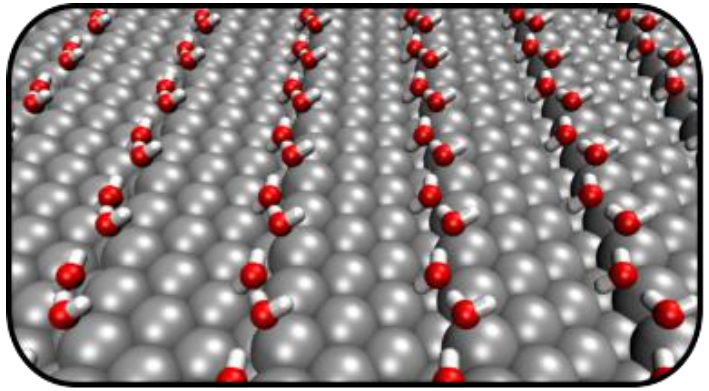
Committee Models

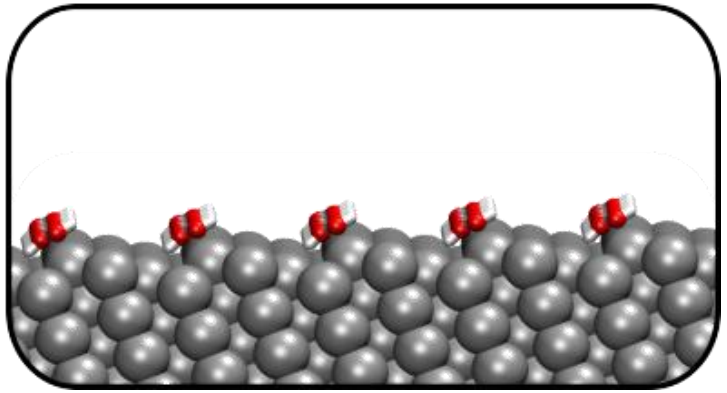
See full list of features at: https://docs.ipi-code.org/features.html

Litman, et al. J. Chem. Phys. **161**, 062504 (2024)

Water Dissociation in Pt(221)

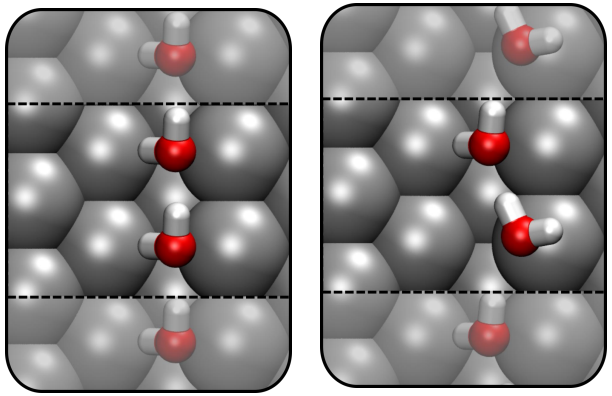
Model system to study water dissociation at metallic interfaces.



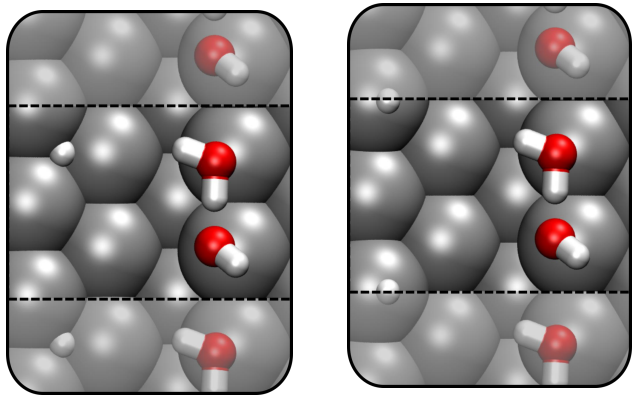


Geometry optimization leads to:

Intact



Dissociated

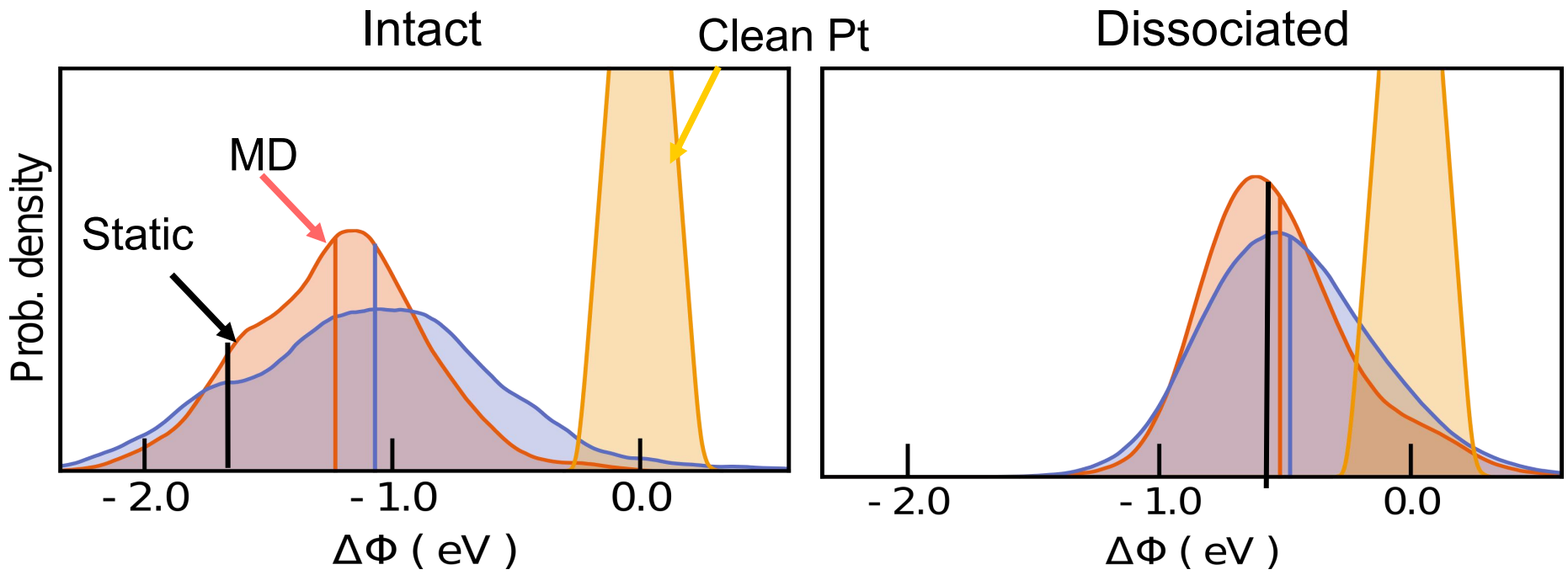


Y. Litman, et al. J. Chem. Phys. **148**, 102320 (2018)

Water Dissociation in Pt(221)

PBE+TS, 300K

Work function change: $\Delta\Phi = \Phi_{\mathrm{FullSystem}} - \Phi_{\mathrm{CleanPt}}$



Temperature effects change work function by more than 0.5 eV!

But, sometimes static estimates are really good!

Litman, et al. J. Chem. Phys. **148**, 102320 (2018)

Water Dissociation in Pt(221)

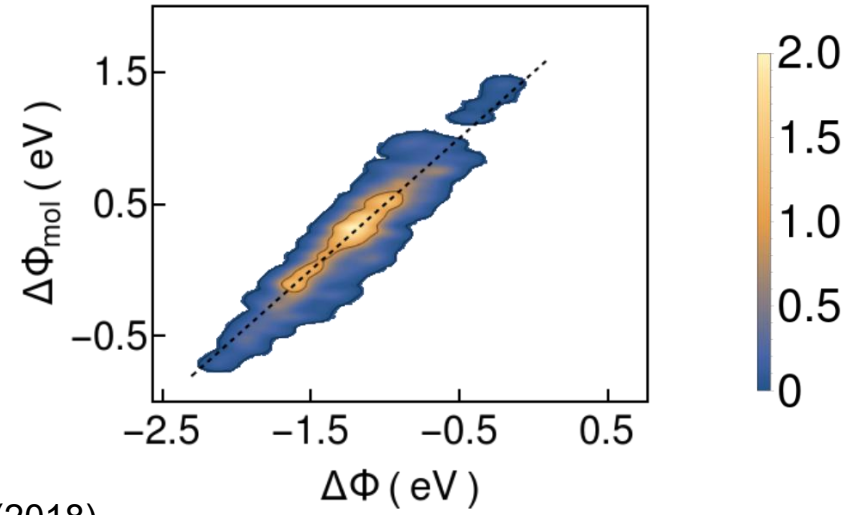
Work function change decomposition:

$$\Delta\Phi = \Delta\Phi_{\mathrm{BD}} + \Delta\Phi_{\mathrm{mol}}$$

Total work function change

Caused by charge rearrangement on the interface (“Bond dipole”)

Caused by molecular dipole perpendicular to the surface

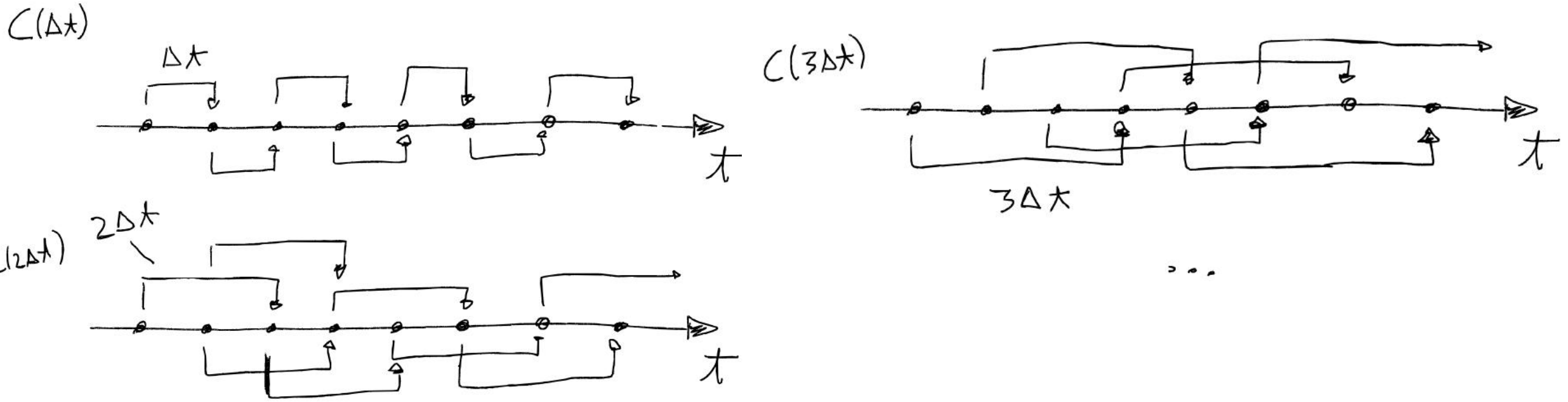


Litman, et al. J. Chem. Phys. **148**, 102320 (2018)

Dynamical Properties

Molecular dynamics simulations enable the calculation of time correlations functions (TCF)

$$c_{\mathrm{AB}}^{\mathrm{CL}}(t) = \frac{1}{2\pi\hbar Q^{\mathrm{CL}}(\beta)} \int dRdPA(0)B(t)e^{-\beta H(R,P)} = \langle A(0)B(t)\rangle$$



Time Correlation Functions

$$c_{\mathrm{AB}}^{\mathrm{CL}}(t) = \frac{1}{2\pi\hbar Q^{\mathrm{CL}}(\beta)} \int dR dP A(0) B(t) e^{-\beta H(R,P)}$$

Spectroscopy:

IR

$$I_{\mathrm{IR}}(\omega) \propto \int_0^\infty dt e^{-i\omega t} \langle \mu(t)\mu(0) \rangle$$

Raman

$$I_{\mathrm{Raman}}(\omega) \propto \int_0^\infty dt e^{-i\omega t} \langle \alpha(t)\alpha(0) \rangle$$

Sum Frequency Generation

$$\chi^{(2)}(\omega) \propto i \int_0^\infty dt e^{-i\omega t} \langle \alpha(t)\mu(0) \rangle$$

Reaction rates:

$$k_{\mathrm{Q}}(T) = c_{\mathrm{fs}}(t)\Big|_{t>\tau} = \frac{1}{(2\pi\hbar)^F} \int \mathrm{d}p \int \mathrm{d}q \, \mathrm{e}^{-\beta H} \delta[s(R))] v_{\mathrm{s}}(R) h[s(R(t))]$$

Transport properties:

$$D = \frac{1}{6N} \lim_{t\to\infty} \frac{d}{dt} \sum_{i=1}^{N} \langle [R_i(t) - R_i(0)]^2 \rangle$$

$$\kappa \propto \int_0^\infty dt \langle J(t) J(0) \rangle$$

Harmonic Approximation

A very powerful (first) approximation to the potential energy surface can be obtained by Taylor expanding the energy:

Harmonic approximation

$$V^{\mathrm{BO}} = V(R_{\mathrm{min}}) + \sum_I \left.\frac{\partial V}{\partial R_I}\right|_{R_{\mathrm{min}}} \Delta R_I + \frac{1}{2}\sum_{I,J} \left.\frac{\partial^2 V}{\partial R_I \partial R_J}\right|_{R_{\mathrm{min}}} \Delta R_I \Delta R_J$$

Static Equilibrium Energy from DFT

Hessian matrix

It is convenient to define the mass-weighted Hessian

$$H_{IJ} = \frac{1}{\sqrt{M_I M_J}} \left.\frac{\partial^2 V}{\partial R_I \partial R_J}\right|_{R_{\mathrm{min}}}$$

which leads to the eigenvalue problem

$$HQ = \omega^2 Q$$

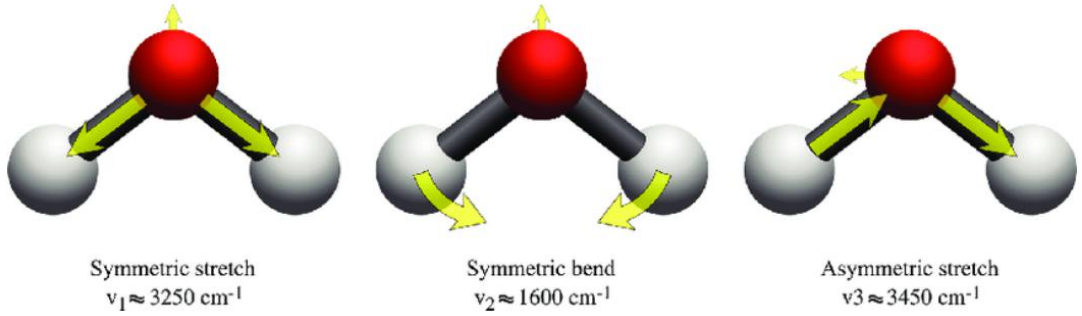
Normal modes

Normal mode frequencies

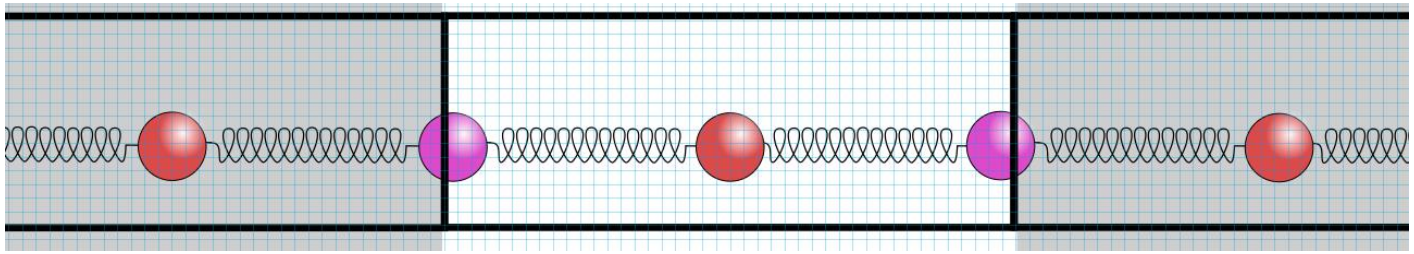
Harmonic Approximation

In (non-linear) molecules we have 3N-6 vibrations

Example water molecule



However in periodic solids we have infinitely many atoms,



So, we have to go to reciprocal space and define the dynamical matrix as

$$D_{IJ}(q) = e^{i\mathbf{q}(R_I^0 - R_J^0)} H_{IJ}$$

Vibrations in Extended Systems

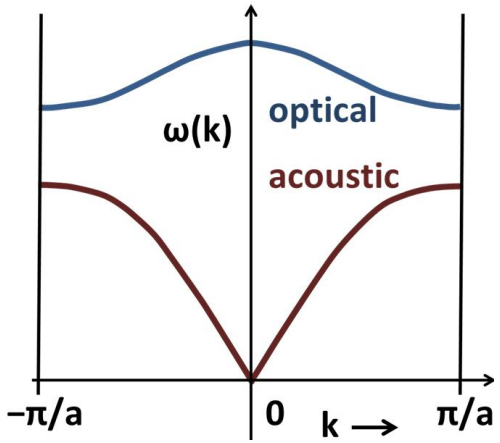
$$D_{IJ}(q) = e^{i\mathbf{q}(R_I^0 - R_J^0)} H_{IJ}$$

Now, we have to solve an eigenvalue problem for each value of wave vector, q

$$D(q)\nu(q) = \omega^2(q)\nu(q)$$

→ phonon modes

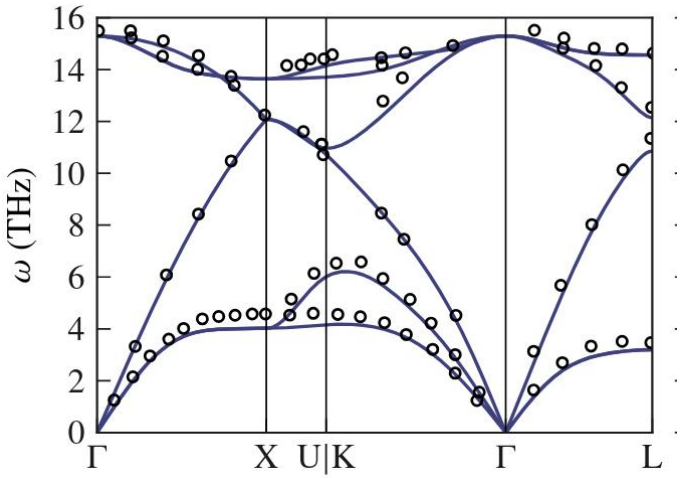
↓ phonon frequencies



3 acoustic modes (vanish at Γ)

$3N_p$-3 optical modes (for a primitive cell with N_p atoms)

Example Silicon (diamond)



DFT

○ inelastic neutron scattering

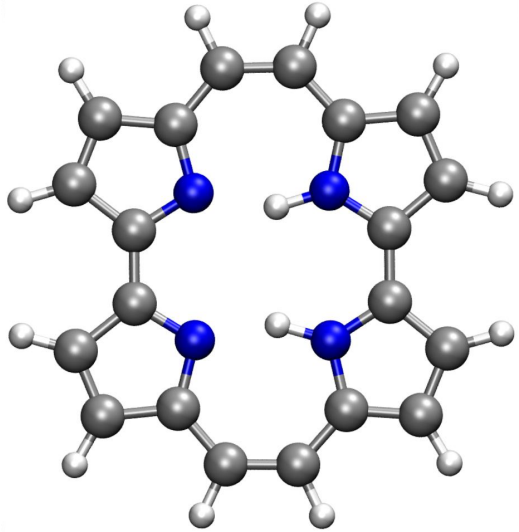
F. Knoop, PhD Thesis (2022)

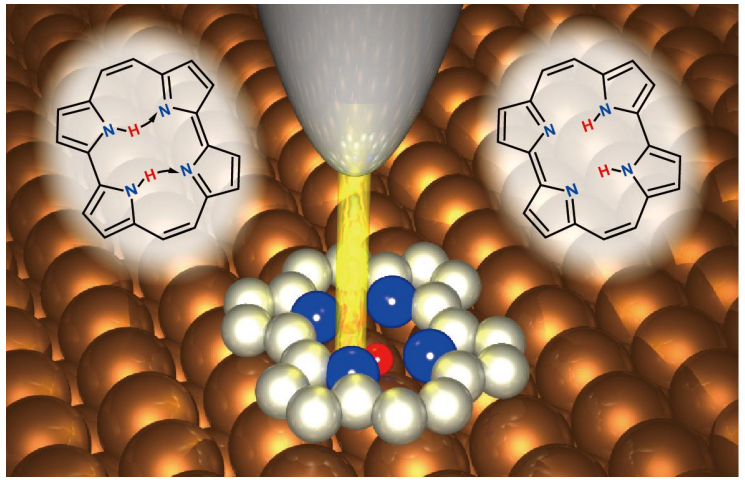
Test case: Porphycene Molecule

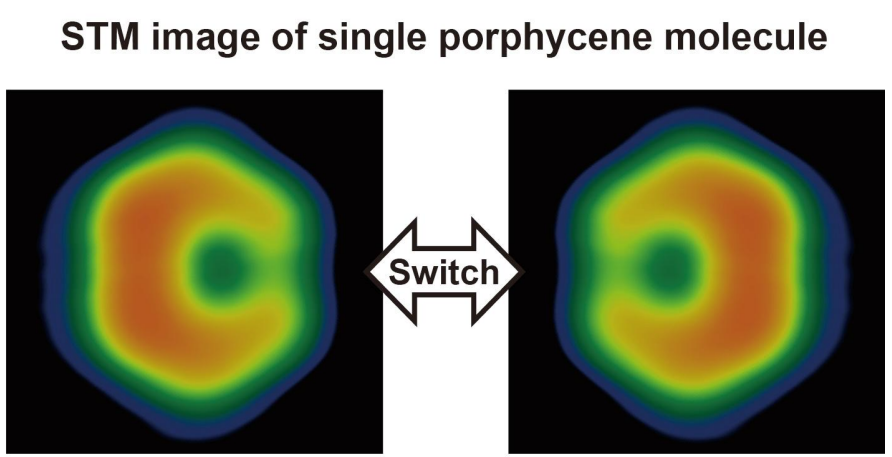
Well studied model of intramolecular hydrogen transfer processes in both ground and excited electronic states

Serves as a playground to test methods

Prototype of a molecular switch



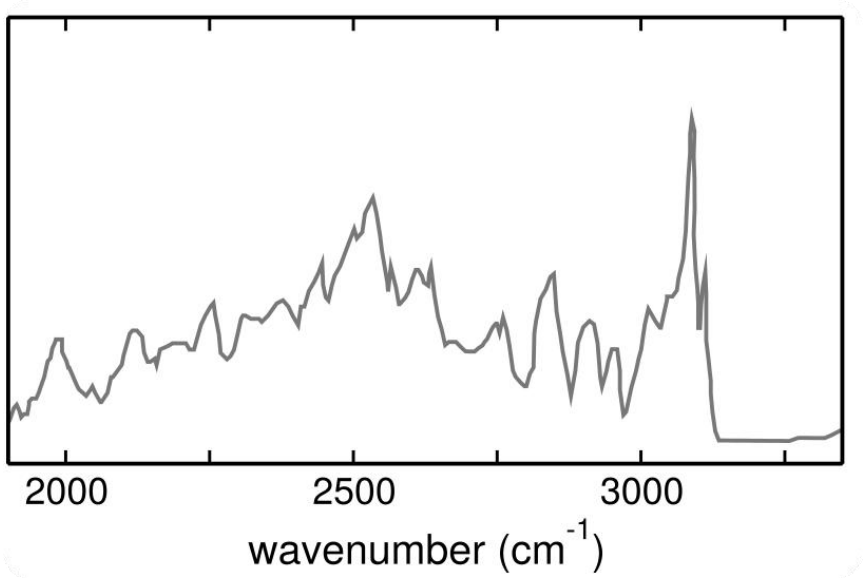




Pictures taken from http://www.fhi-berlin.mpg.de/pc/kumagai/nsc_research.html

Anharmonic Vibrational Dynamics

Experiment
(KBr matrix, 290K)



Gawinkowski, et al. Phys. Chem. Chem. Phys., 14, 5489 (2012)

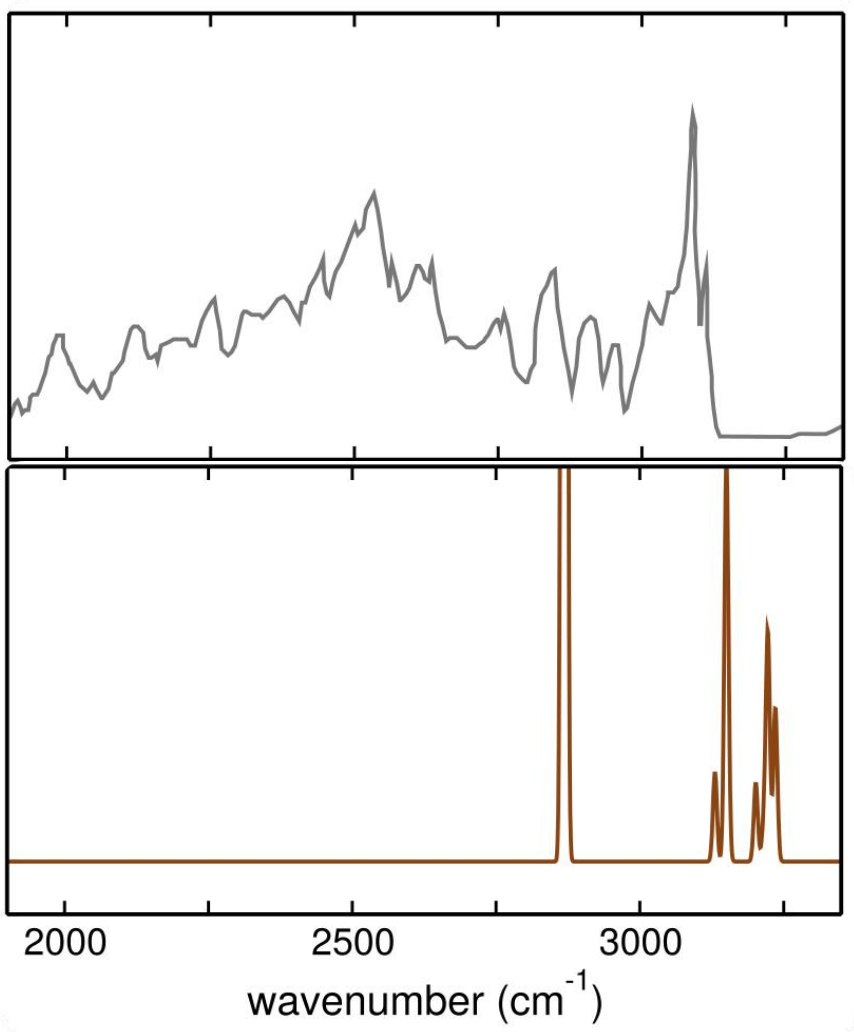
Litman et al. J. Am. Chem. Soc. **141**, 2526 (2019)

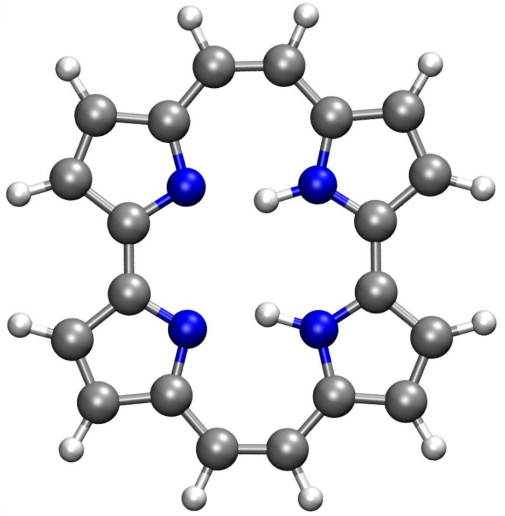
Anharmonic Vibrational Dynamics

$$I_{\mathrm{IR}}(\omega) \propto \int_0^\infty dt e^{-i\omega t}\langle \mu(t)\mu(0)\rangle$$

Experiment
(KBr matrix, 290K)

Harmonic





Gawinkowski, et al. Phys. Chem. Chem. Phys., 14, 5489 (2012)

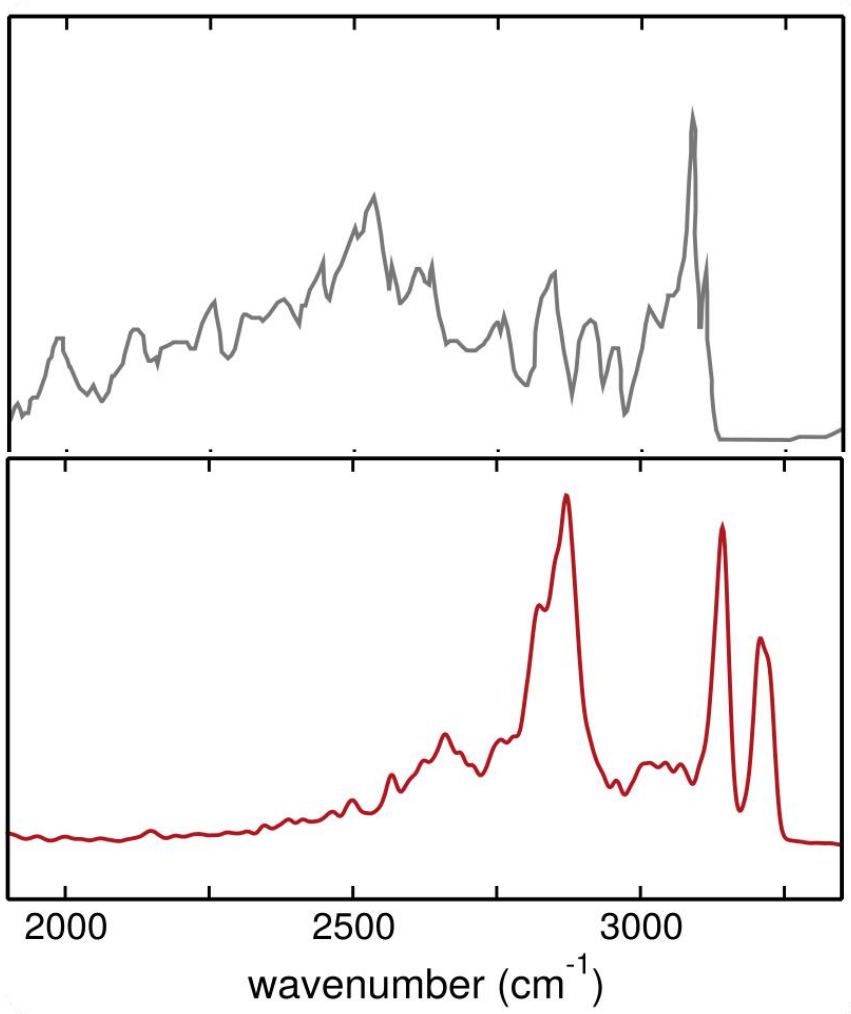
Litman et al. J. Am. Chem. Soc. **141**, 2526 (2019)

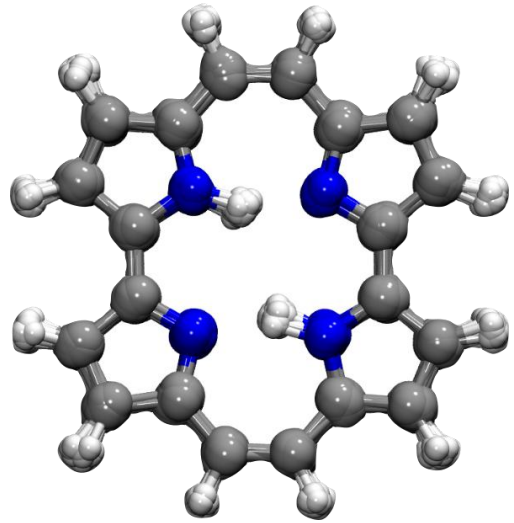
Anharmonic vibrational dynamics

$$I_{\mathrm{IR}}(\omega) \propto \int_0^{\infty} dt e^{-i\omega t} \langle \mu(t)\mu(0) \rangle$$

Experiment
(KBr matrix, 290K)

MD
(290K, 4 x 10ps)



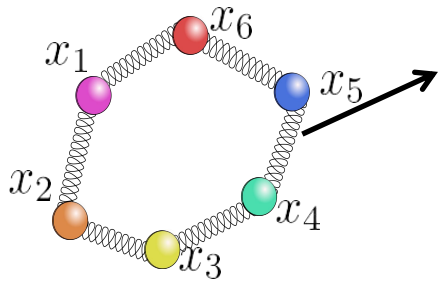


Gawinkowski, et al. Phys. Chem. Chem. Phys., 14, 5489 (2012)
Litman et al. J. Am. Chem. Soc. **141**, 2526 (2019)

Path Integral Isomorphism

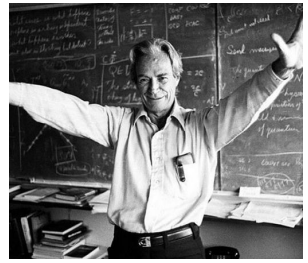
Path integral formulation of quantum mechanics

***Quantum** particle*



$$\omega_N = \frac{N k_B T}{\hbar}$$

Ring Polymer (RP) made of **classical** particles



Feynman

$$\hat{H} = \frac{\hat{P}}{2M} + \hat{V}(R)$$

Sum over replicas

$$H_N = \sum_{k=1}^{N} \left[\frac{P^{(k)}}{2M} + V(R^{(k)}) + \frac{1}{2} m \omega_N^2 (R^{(k+1)} - R^{(k)})^2 \right]$$

classical Hamiltonian

This mapping is known as the *path integral isomorphism*

Algorithm: path integral molecular dynamics (PIMD)

Exact results for time-independent equilibrium properties

Chandler, Wolynes, J. Chem. Phys. **74**, 4078 (1981)

Parrinello, Rahman, J. Chem. Phys. **80**, 860 (1984)

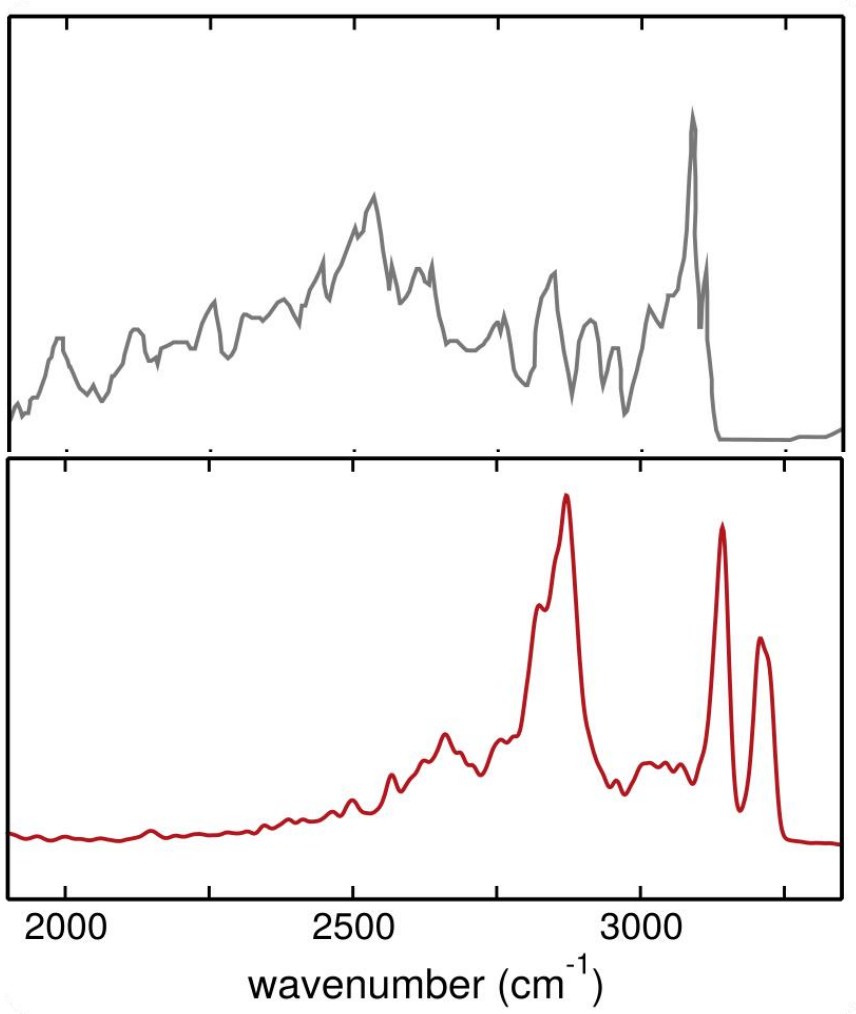
Want to become an expert in modeling nuclear quantum effects?

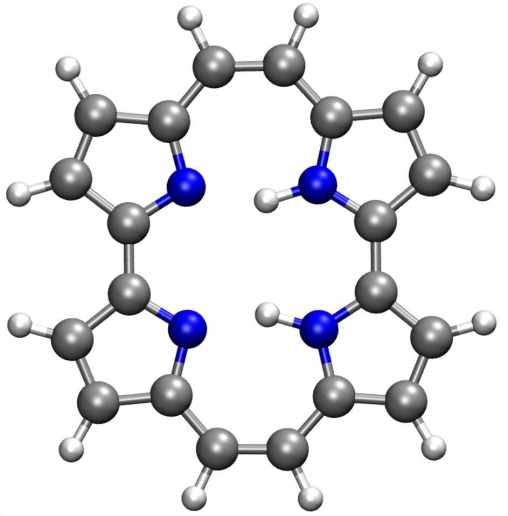
Anharmonic vibrational dynamics

$$I_{\mathrm{IR}}(\omega) \propto \int_0^{\infty} dt e^{-i\omega t} \langle \mu(t)\mu(0) \rangle$$

Experiment
(KBr matrix, 290K)

MD
(290K, 4 x 10ps)





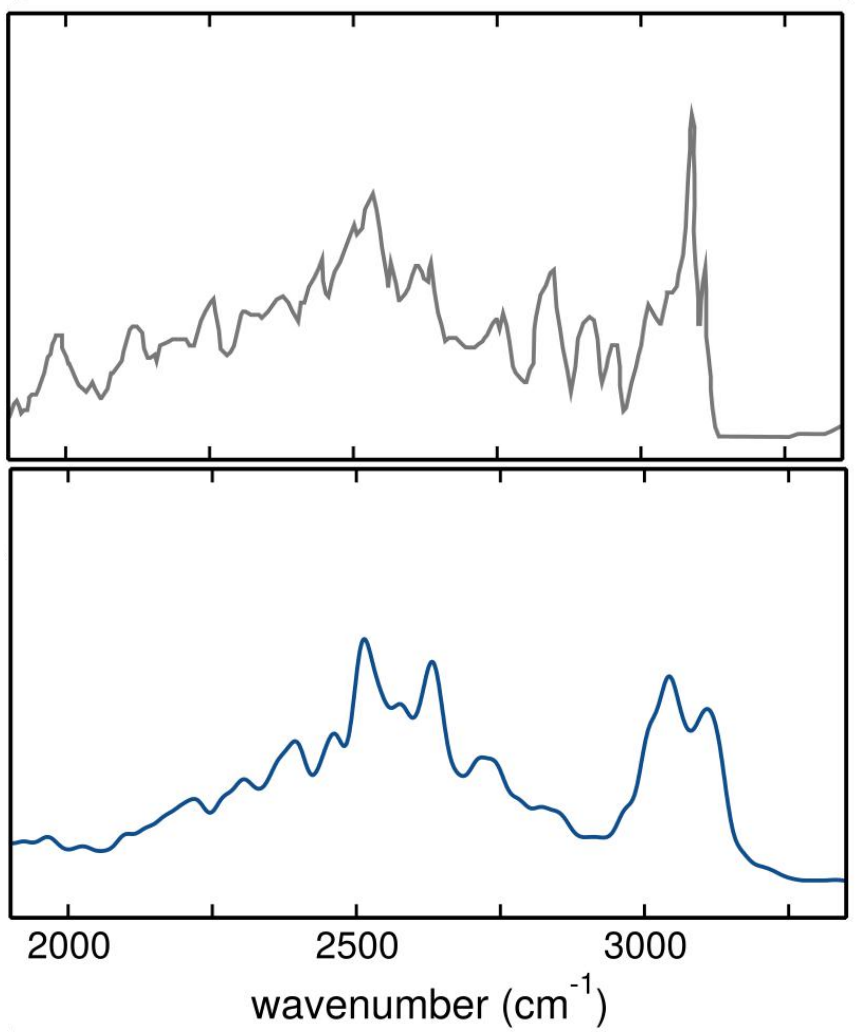
Gawinkowski, et al. Phys. Chem. Chem. Phys., 14, 5489 (2012)
Litman; et al. J. Am. Chem. Soc. **141**, 2526 (2019)

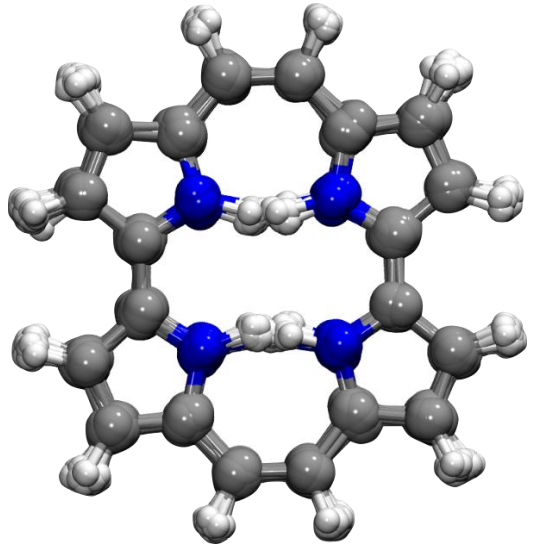
Anharmonic vibrational dynamics

$$I_{\mathrm{IR}}(\omega) \propto \int_0^\infty dt e^{-i\omega t}\langle \mu(t)\mu(0)\rangle$$

Experiment
(KBr matrix, 290K)

TRPMD,
(290K,7 x 10ps,
16 beads)

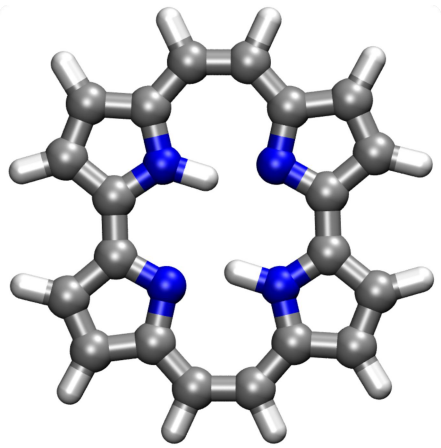




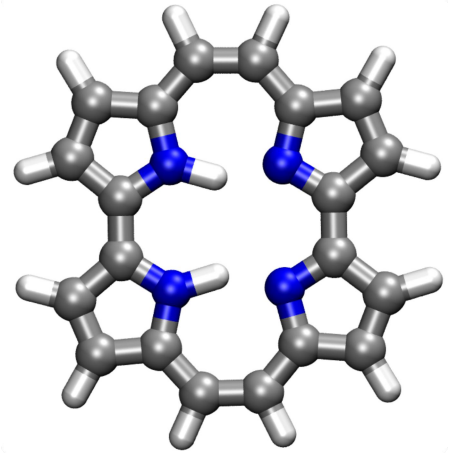
Gawinkowski, et al. Phys. Chem. Chem. Phys., 14, 5489 (2012)
Litman; et al. J. Am. Chem. Soc. **141**, 2526 (2019)

Mind the XC Functional!

Trans



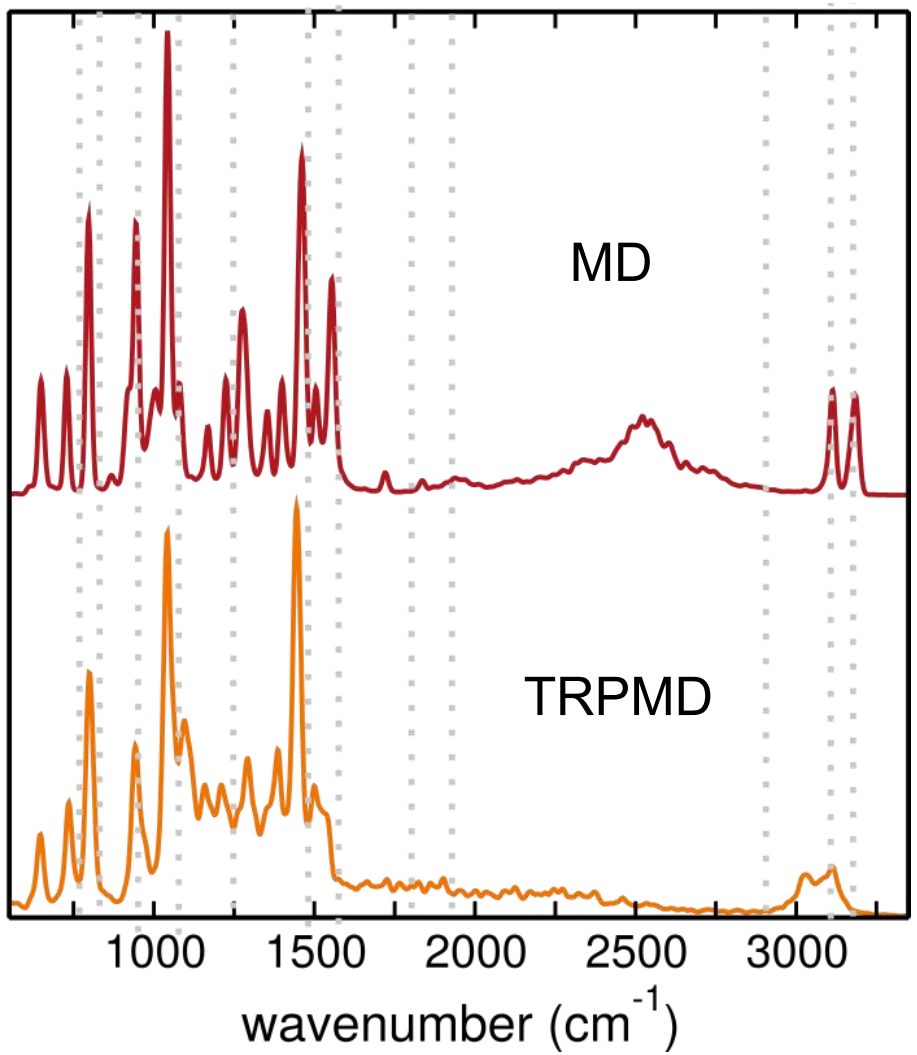
Cis



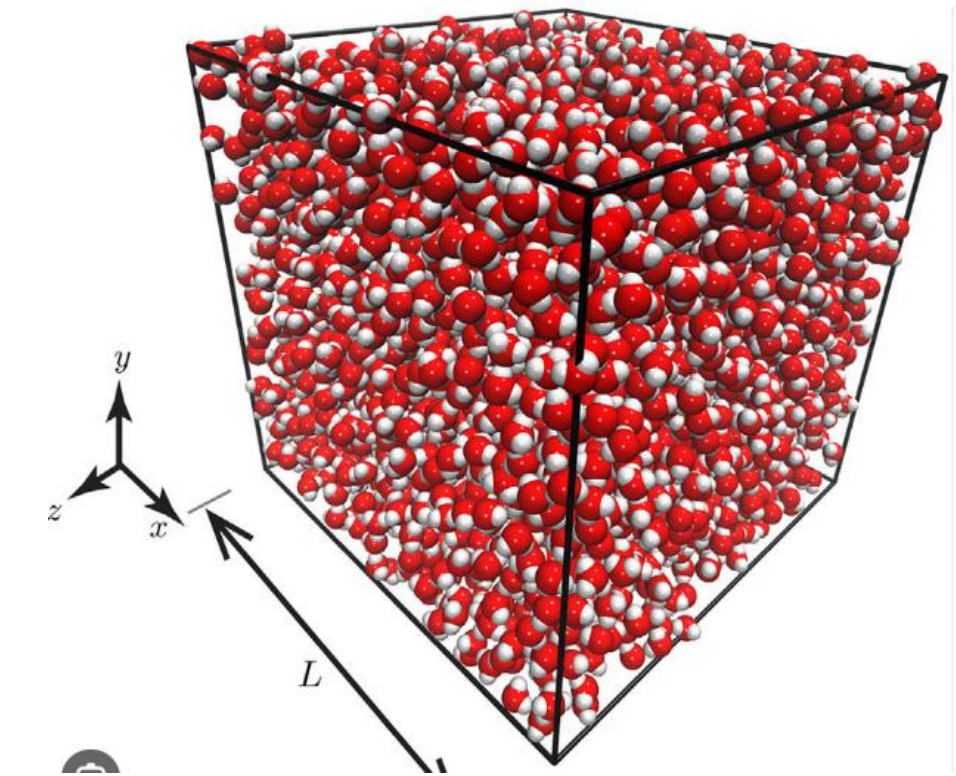
Energy in meV

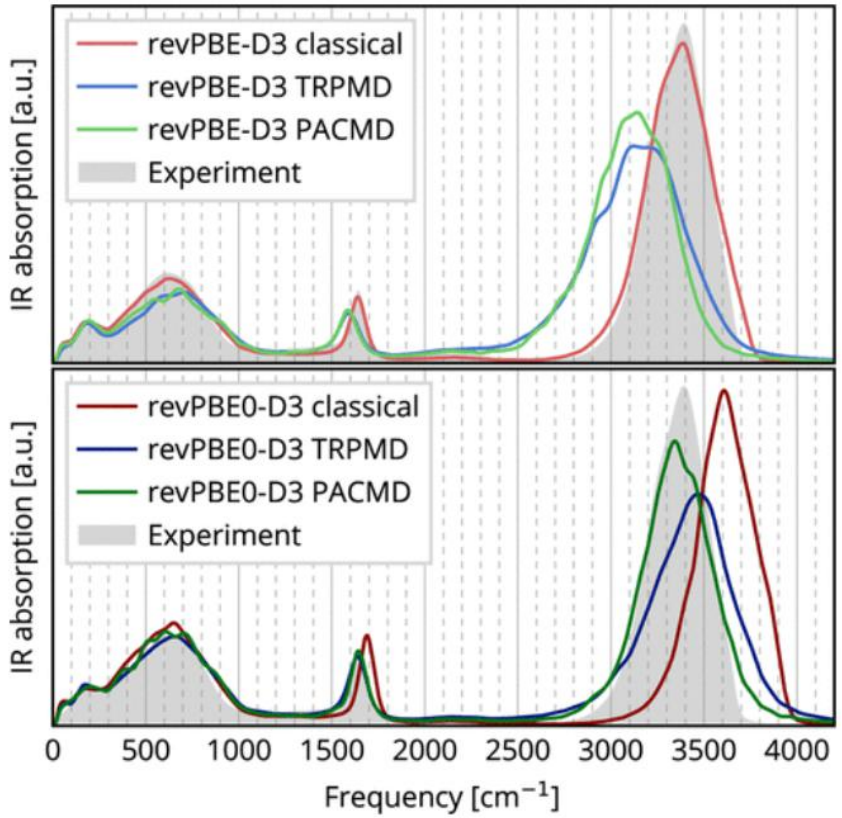
	PBE+TS	PBE0+TS	**B3LYP+TS**	MP2	CCSD(T)
cis	72 (35)	89 (60)	**93 (72)**	104	160
SP1	106 (-14)	155 (29)	**189 (62)**	144	218
SP2	150 (-61)	228 (-1)	**290 (56)**	194	322

TS: Tkatchenko.; Scheffler, Phys. Rev. Lett. 102, 073005 (2009)



Mind the XC Functional!



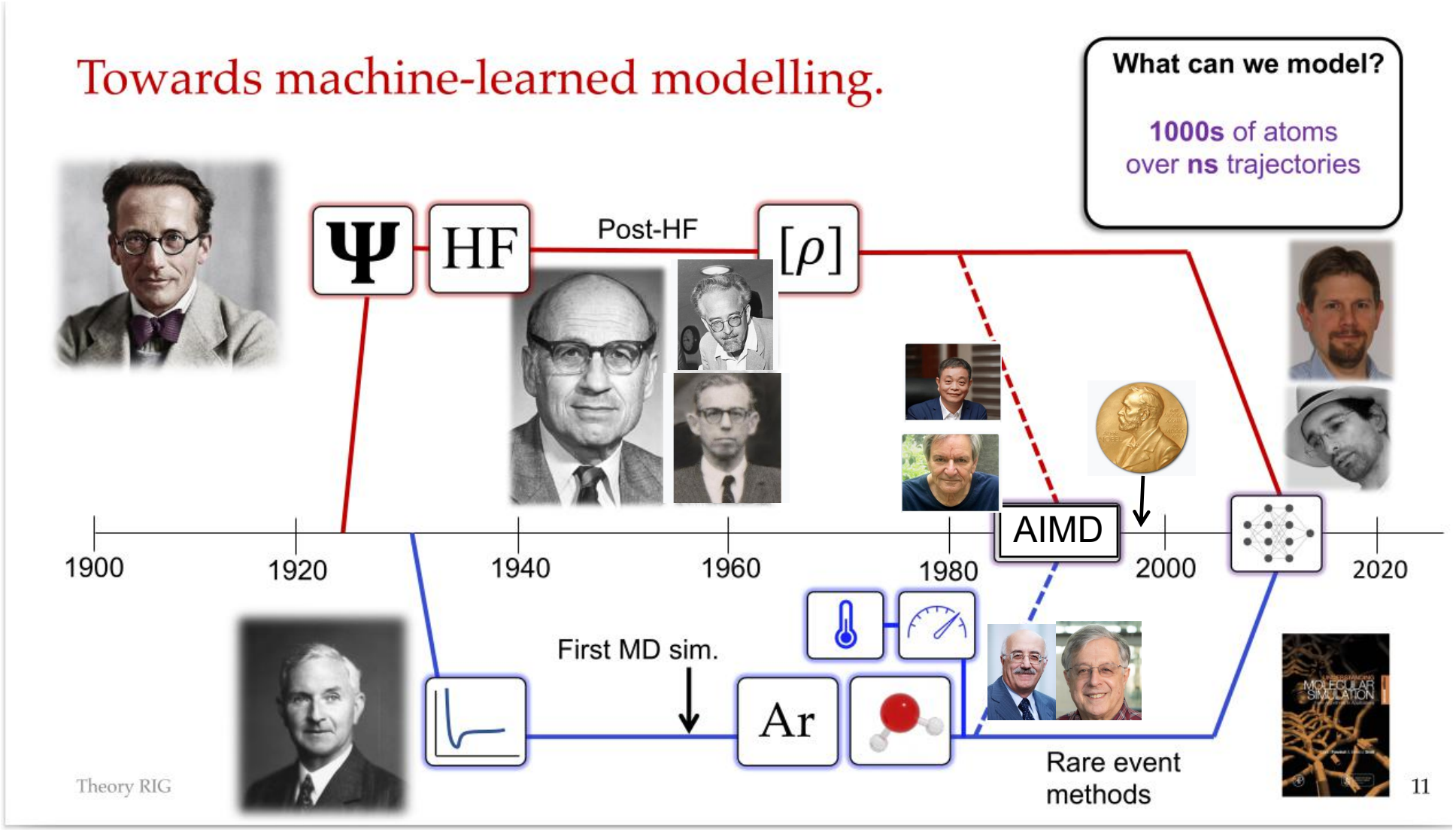


GGA XC functionals tend to over estimate the strength of hydrogen-bonds

DFT can predict the right results for the wrong reasons

Marsalek, Markland, J. Phys Chem. Lett. **8**, 1545 (2017)

The Future is Here



(Slide courtesy of Samuel Brookes@Cambridge)


THANK YOU