

C7790 Introduction to Molecular Modelling

TSM Modelling Molecular Structures

Lesson 13 Potential Energy Surface I

PS/2021 Present Form of Teaching: Rev2

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Context

macroworld

states

(thermodynamic properties, G, T,...)

phenomenological thermodynamics

equilibrium (equilibrium constant)

kinetics (rate constant)

free energy
(Gibbs/Helmholtz)



partition function

statistical thermodynamics

microstates

(mechanical properties, E)

microstate \neq microworld

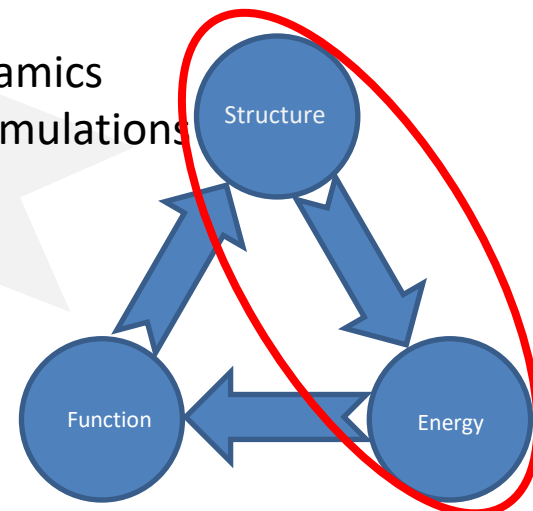
microworld

Description levels (model chemistry):

- quantum mechanics
 - semiempirical methods
 - ab initio methods
 - post-HF methods
 - DFT methods
- molecular mechanics
- coarse-grained mechanics

Simulations:

- molecular dynamics
- Monte Carlo simulations
- docking
- ...



Revision

$$\hat{H}\phi(\mathbf{x}, t) = i\hbar \frac{\partial \phi(\mathbf{x}, t)}{\partial t}$$

time dependent Schrödinger equation

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time dependent Schrödinger equation

$$\phi(\mathbf{x}, t) = \psi(\mathbf{x})f(t)$$

time independent Schrödinger equation

$$\hat{H}\psi_k(\mathbf{x}) = E_k\psi_k(\mathbf{x})$$

system can exist in several quantum states, each state is described by wavefunction ψ_k and has energy E_k

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time independent Schrödinger equation

Born- Oppenheim approximation

$$\psi(\mathbf{x}) = \Psi(\mathbf{r}, \mathbf{R})\chi(\mathbf{R})$$

$$\hat{H}\psi_k(\mathbf{x}) = E_k\psi_k(\mathbf{x})$$

$$\hat{H}_e\Psi_m(\mathbf{r}, \mathbf{R}) = E_m(\mathbf{R})\Psi_m(\mathbf{r}, \mathbf{R})$$

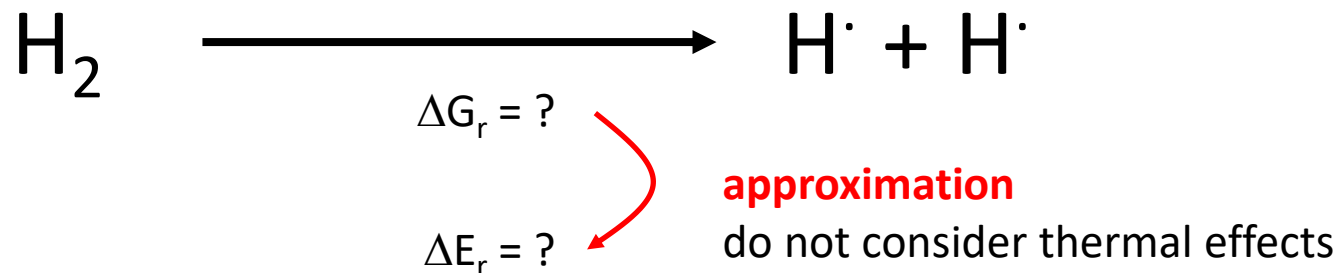
electron motion in the static field of nuclei
electronic properties

$$\hat{H}_R\chi_l(\mathbf{R}) = E_{VRT,l}\chi_l(\mathbf{R})$$

nuclei motion in effective field of electrons
vibration, rotation, translation

Hydrogen molecule

HW: What is the dissociation energy of H₂, D₂, and T₂?



$$\hat{H}_e \Psi_m(\mathbf{r}, \mathbf{R}) = E_m(\mathbf{R}) \Psi_m(\mathbf{r}, \mathbf{R})$$

Energy is a function of nuclei positions.

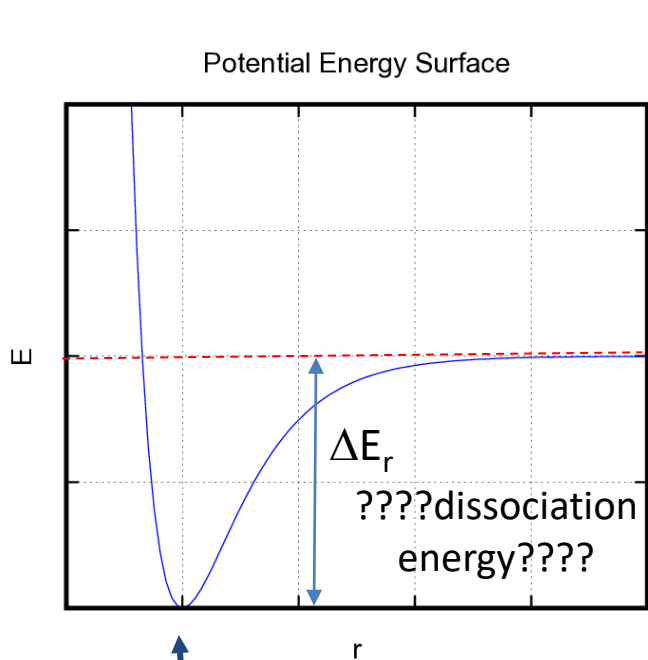
The function and its projections to lower dimensional configurational spaces are called potential energy surface.

What is the potential energy surface for H₂, D₂, and T₂?

Do they differ?

H₂ - Potential Energy Surface

$$\hat{H}_e \Psi_m(\mathbf{r}, \mathbf{R}) = E_m(\mathbf{R}) \Psi_m(\mathbf{r}, \mathbf{R})$$



dissociated state

2H·

What is the energy of dissociated state?
How is it related to reference states?

Two suitable reference states:

- **standard QM reference state** (infinite separation of electrons and nuclei, no kinetic energy) - negative energy
- **dissociated state** is considered as a reference with zero energy

REMEMBER:

- The **reference state** represents well defined state with well defined energy, usually zero.
- Its choice is arbitrary, but it must be consistent for all compounds and their states.

bound state H₂

Recall Hamiltonian of chemical system

Hamiltonian of chemical system consisting of N nuclei of mass M and charge Z and n electrons is given by:

kinetic energy operator (**ELECTRONS ONLY**)

potential energy

$$\hat{H} = -\frac{1}{2m} \sum_{i=1}^n \nabla_i^2 + \sum_{i=1}^N \sum_{j>i}^N \frac{Z_i Z_j}{r_{ij}} - \sum_{i=1}^N \sum_{j=1}^n \frac{Z_i}{r_{ij}} + \sum_{i=1}^n \sum_{j>i}^n \frac{1}{r_{ij}}$$

↑
electrons

↑
nucleus-nucleus

↑
electron-nucleus

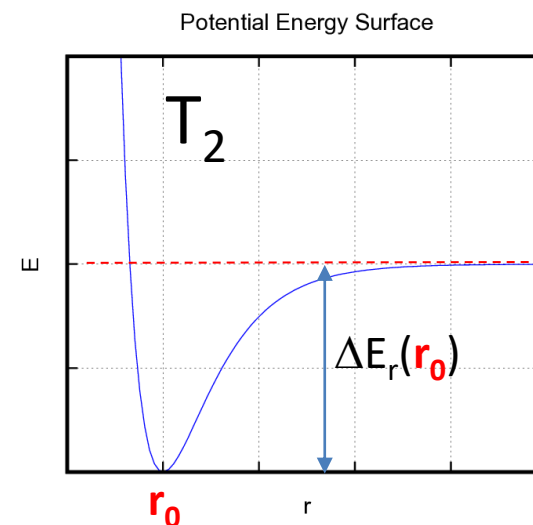
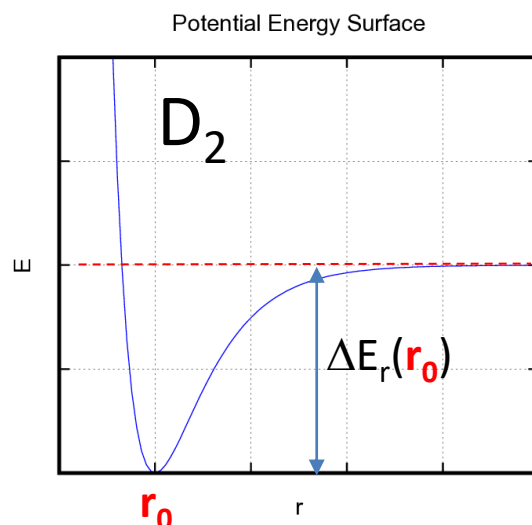
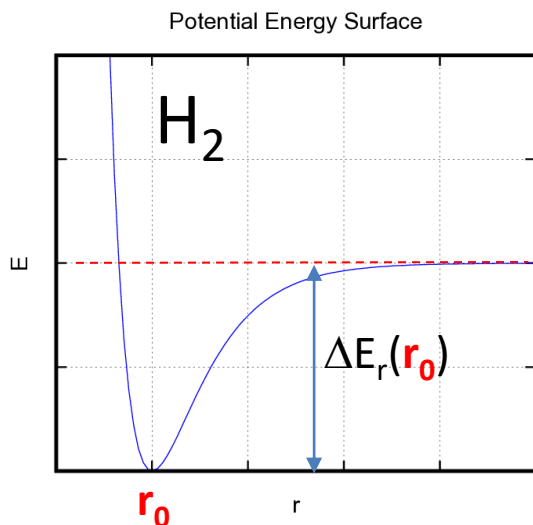
↑
electron-electron

Schrödinger equation:

$$\hat{H} \psi_k(\mathbf{r}, \mathbf{R}) = E_k(\mathbf{R}) \psi_k(\mathbf{r}, \mathbf{R})$$

Nuclei motion (nuclei mass) is not considered in the BO approximation.

H₂, D₂, T₂ - Potential Energy Surface

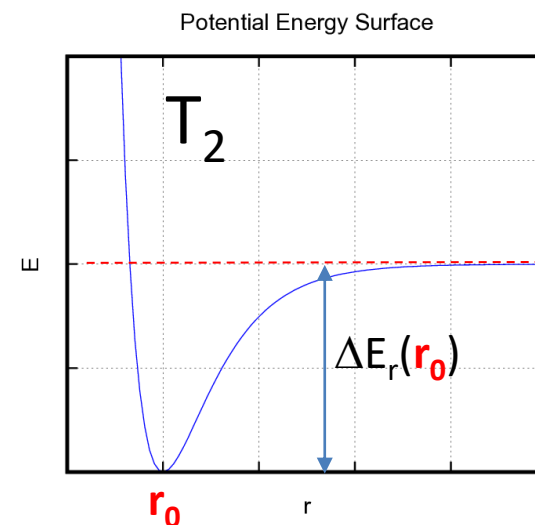
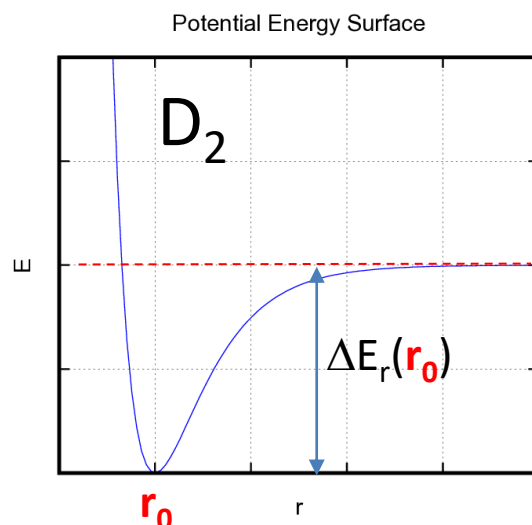
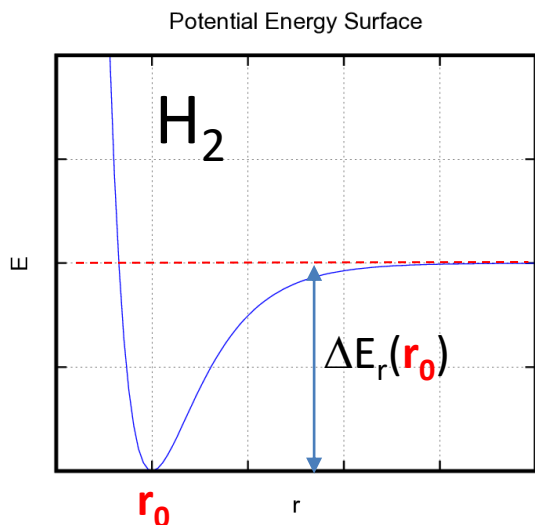


**Potential energy surfaces are the same!
 r_0 is the same as well.**

Reason:

All three systems are chemically identical
(two electrons and two +1 charged nuclei).

H₂, D₂, T₂ - Potential Energy Surface



What about vibrations? Do they contribute and how?

Consider harmonic oscillator (approximation):

$$E_V = \left(v + \frac{1}{2} \right) h\nu$$

characteristic frequency ν (indicated by an arrow pointing to ν)

non-zero energy even in the ground vibration state!!!

$$v = 0, 1, 2, \dots$$

H₂, D₂, T₂ - Vibrations

Harmonic oscillator:

$$E_V = \left(v + \frac{1}{2} \right) h\nu \quad v = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}}$$

$v = 0, 1, 2, \dots$

characteristic frequency

force constant; does it differ?

reduced mass (clearly this differs among H₂, D₂, and T₂)

H₂, D₂, T₂ - Vibrations

Harmonic oscillator:

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What about the force constant?

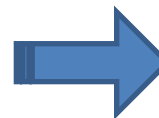
Harmonic potential:

$$V(r) = \frac{1}{2} K(r - r_0)^2 \quad \xrightarrow{\text{tangent}} \quad \frac{\partial V(r)}{\partial r} = K(r - r_0) \quad \xrightarrow{\text{curvature}} \quad \frac{\partial^2 V(r)}{\partial r^2} = K$$

first derivative
with respect to r

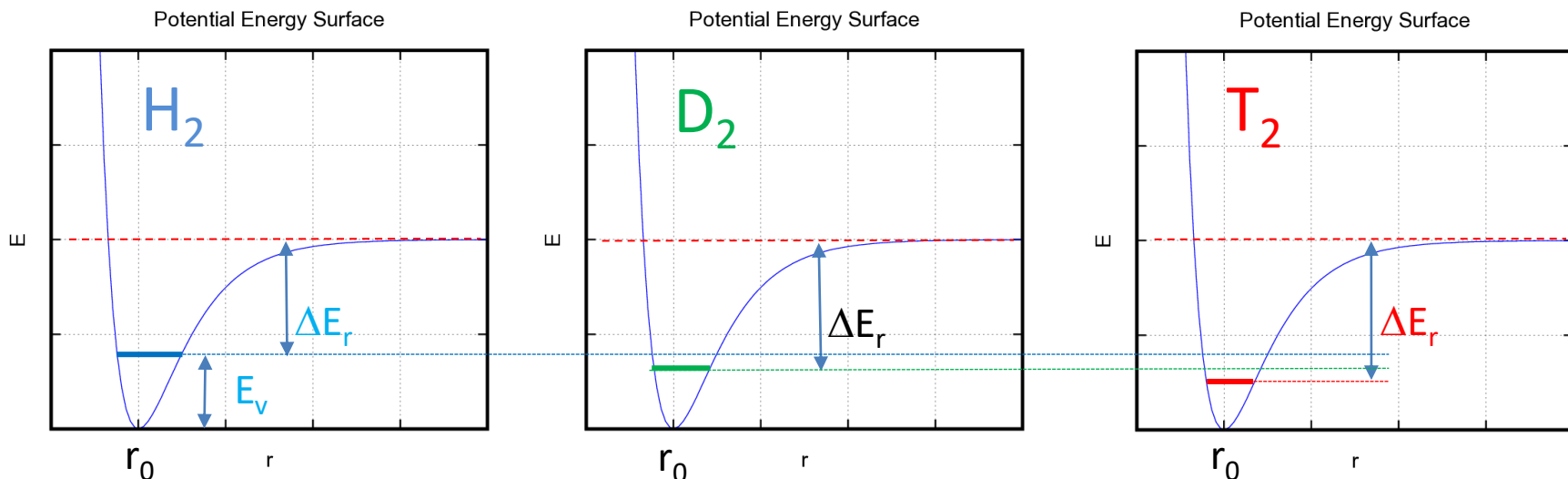
second derivative
with respect to r

The force constant can be determined from the PES curvature at equilibrium distance (r_0) in harmonic approximation.



All three systems have the same PES and thus the same K as well .

H₂, D₂, T₂ - PES + Vibrations



!! not in scale !!

$$|\Delta E_r| < |\Delta E_r| < |\Delta E_r|$$

$$r_0 = r_0 = r_0$$

$r_e \sim r_e \sim r_e$ observable equilibrium bond lengths
 impact of anharmonicity and QM
 character of vibrations

bigger mass \rightarrow smaller frequency \rightarrow lower energy

$$E_V = \left(v + \frac{1}{2} \right) h\nu$$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}}$$

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electron motion in the static field of nuclei
electronic properties

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nuclei motion in effective field of electrons
vibration, rotation, translation

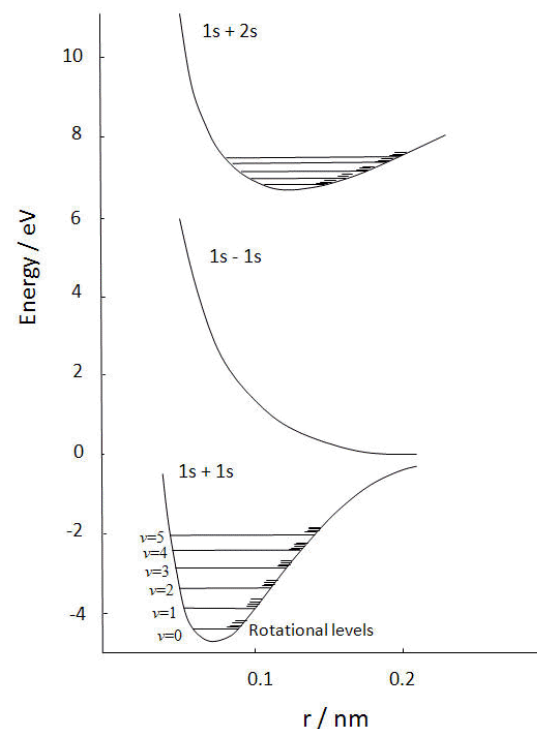
electronic energy part

vibration, rotation,
translation energy part

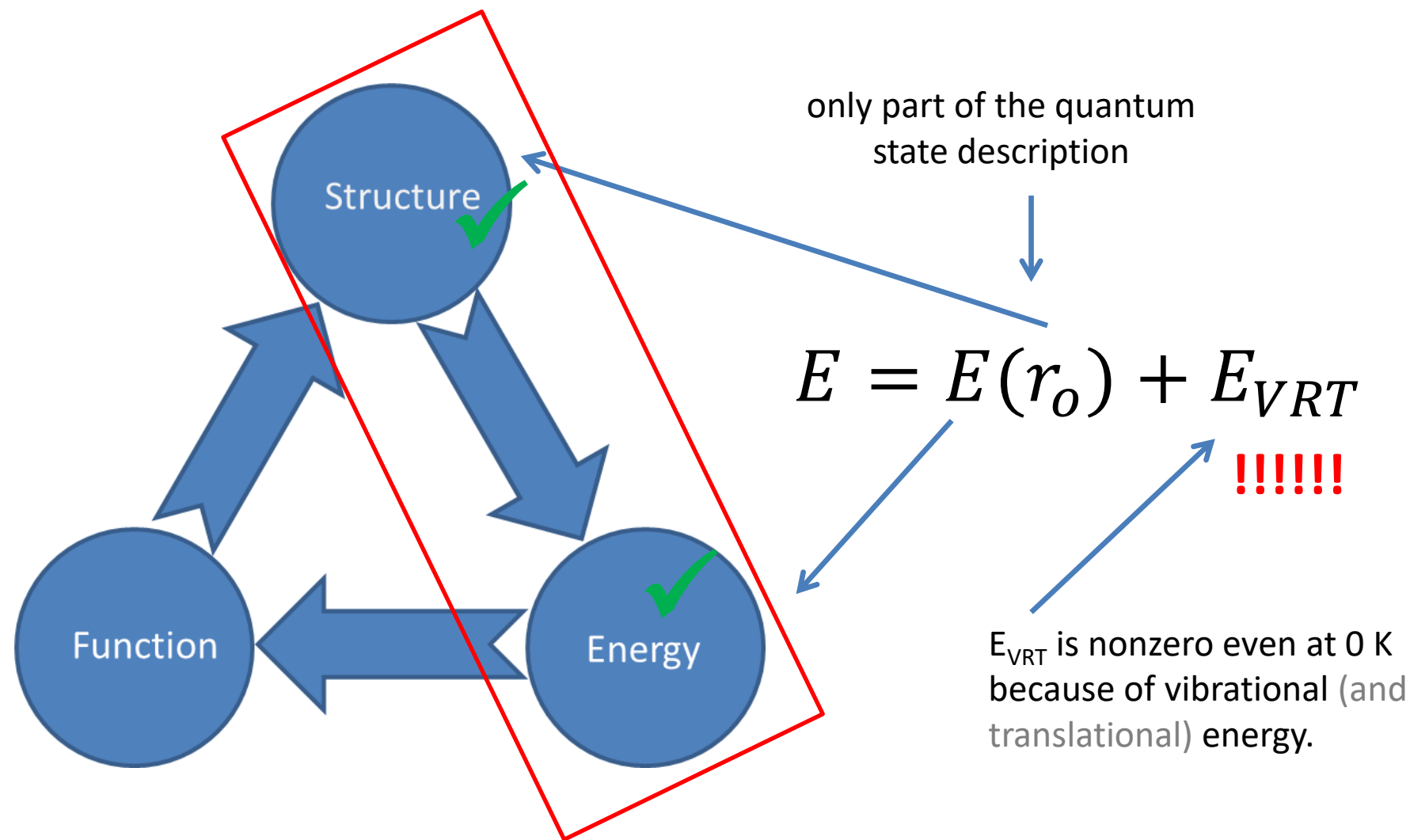
$$E_k = E_m(R_{opt,m}) + E_{VRT,l}$$

total energy of the state

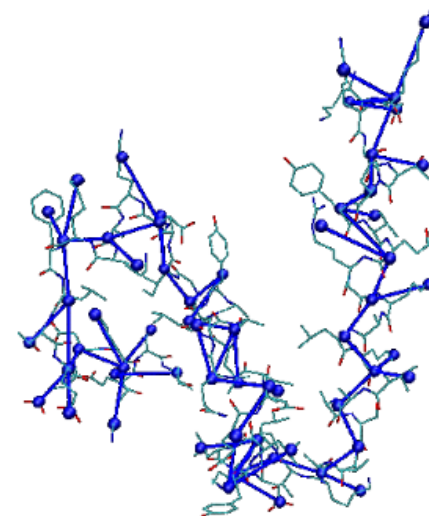
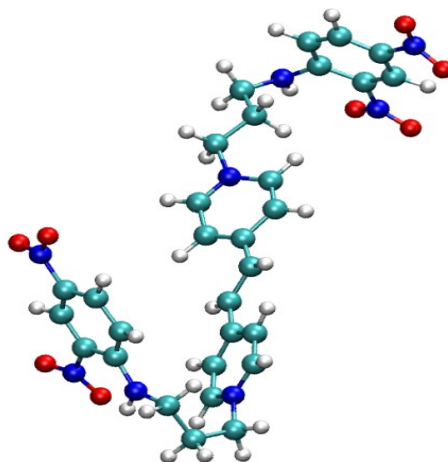
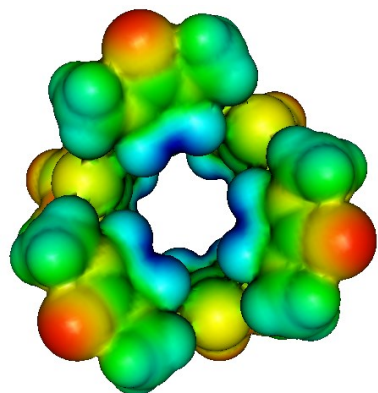
optimal geometry, at
which E_m is minimal



Structure vs system state



Method overview (model chemistry)



QM (Quantum mechanics)

MM (Molecular mechanics)

CGM (Coarse-grained mechanics)



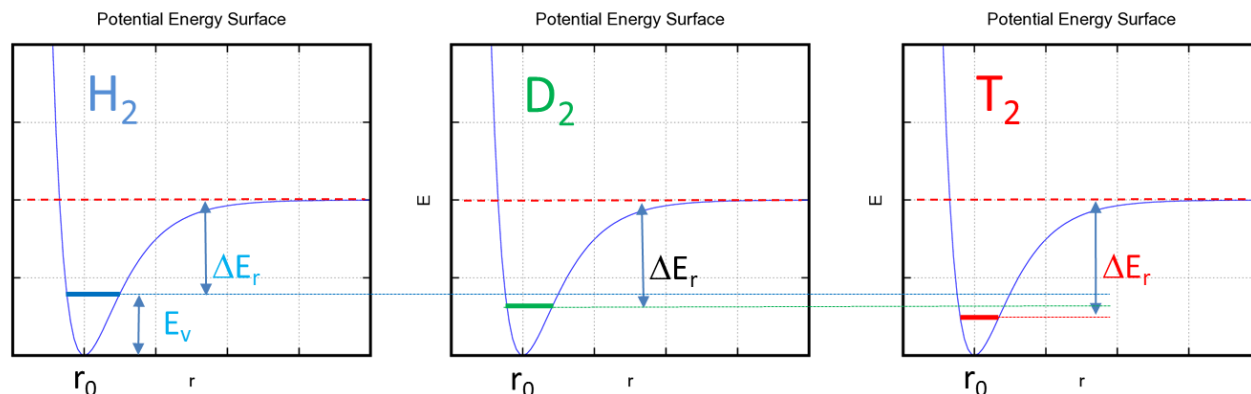
R - position of atom nuclei

R - position of atoms

R - position of beads

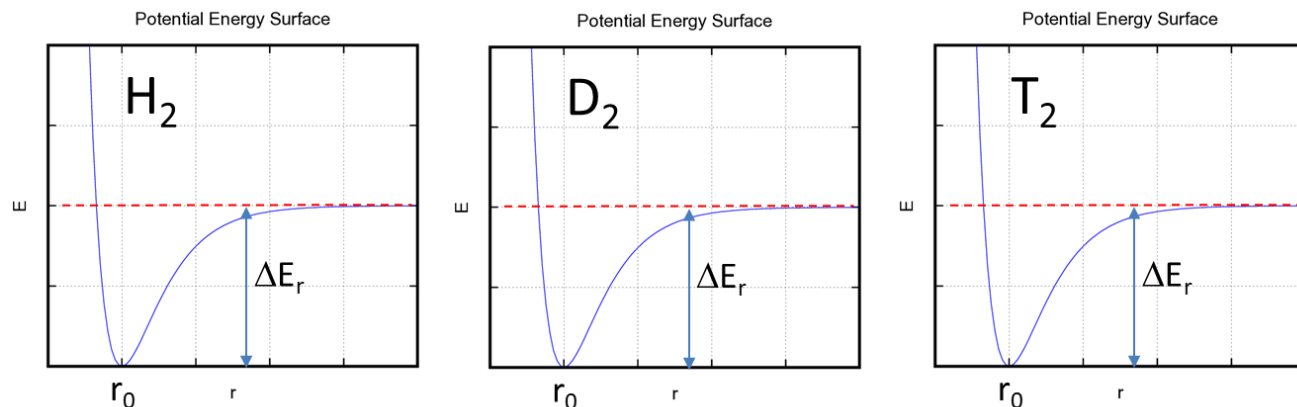
Quantum vs Classical description

- **Fully QM**
- QM, MM + **QM harmonic approximation**, or similar ω
- QM, MM + **path integral molecular dynamics**



thermal energy not shown in graphs is $1/2k_B T$ (equipartition principle) in all cases (fully quantum/classical)

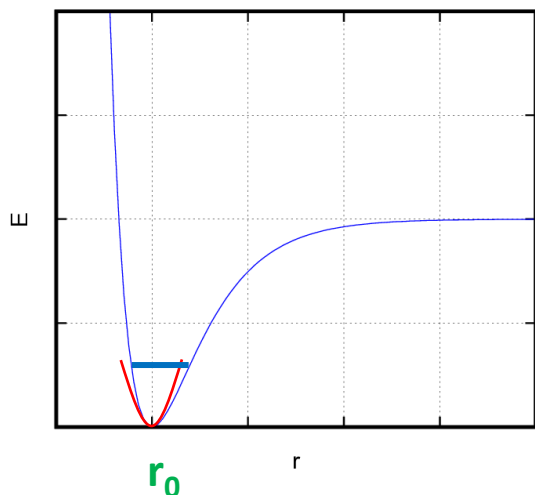
- QM, MM, CG + classical nuclei/atom motions, molecular dynamics (MD)



NO DIFFERENCE

Summary

Potential Energy Surface



To characterize a quantum state:

$$E = E(r_0) + E_{VRT}$$

a) we need to find
a potential energy minimum

b) we can further evaluate vibrations
from the PES curvature at the minimum



(too difficult to calculate, thus it is usually neglected)

- PES cannot describe mass effect of nuclei; it only describes electronic effects.
- Isotope effects can be measured experimentally
 - Primary Isotope Effect (kinetics)
 - Secondary Isotope Effect (kinetics)
 - It can be even tasted by your tongue, see:

Ben Abu, N.; Mason, P. E.; Klein, H.; Dubovski, N.; Ben Shoshan-Galeczki, Y.; Malach, E.; Pražienková, V.; Maletínská, L.; Tempra, C.; Chamorro, V. C.; Cvačka, J.; Behrens, M.; Niv, M. Y.; Jungwirth, P. Sweet Taste of Heavy Water. *Communications Biology* **2021**, 4 (1), 1–10. <https://doi.org/10.1038/s42003-021-01964-y>.