An Introduction to *Ab initio* Molecular Dynamics Simulations

Computational Molecular Science Research Team

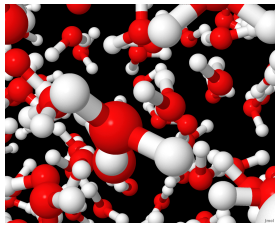
Y. Ootani

What is Theoretical Chemistry?

Theoretical Chemistry

- Explain chemical observation from physical theory
- Predict the chemical property

Atom, Molecule



the universe

1.0^{-10} m

1.0^{0} m

1.0^{10} m

Quantum mechanics

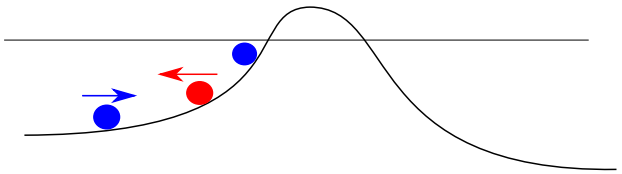
Classical mechanics

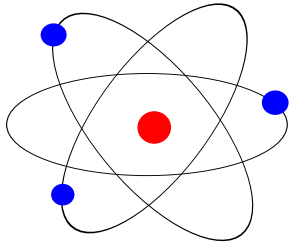
Classical mechanics and Quantum mechanics

Classical Mechanics

Newton's Equations of Motion

$$F = ma$$

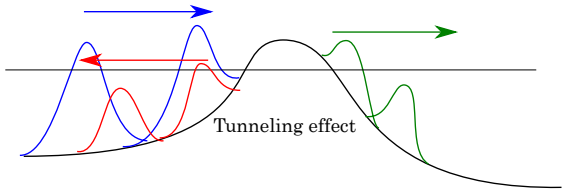




Quantum Mechanics

Schrödinger equation

$$H\Psi = E\Psi$$

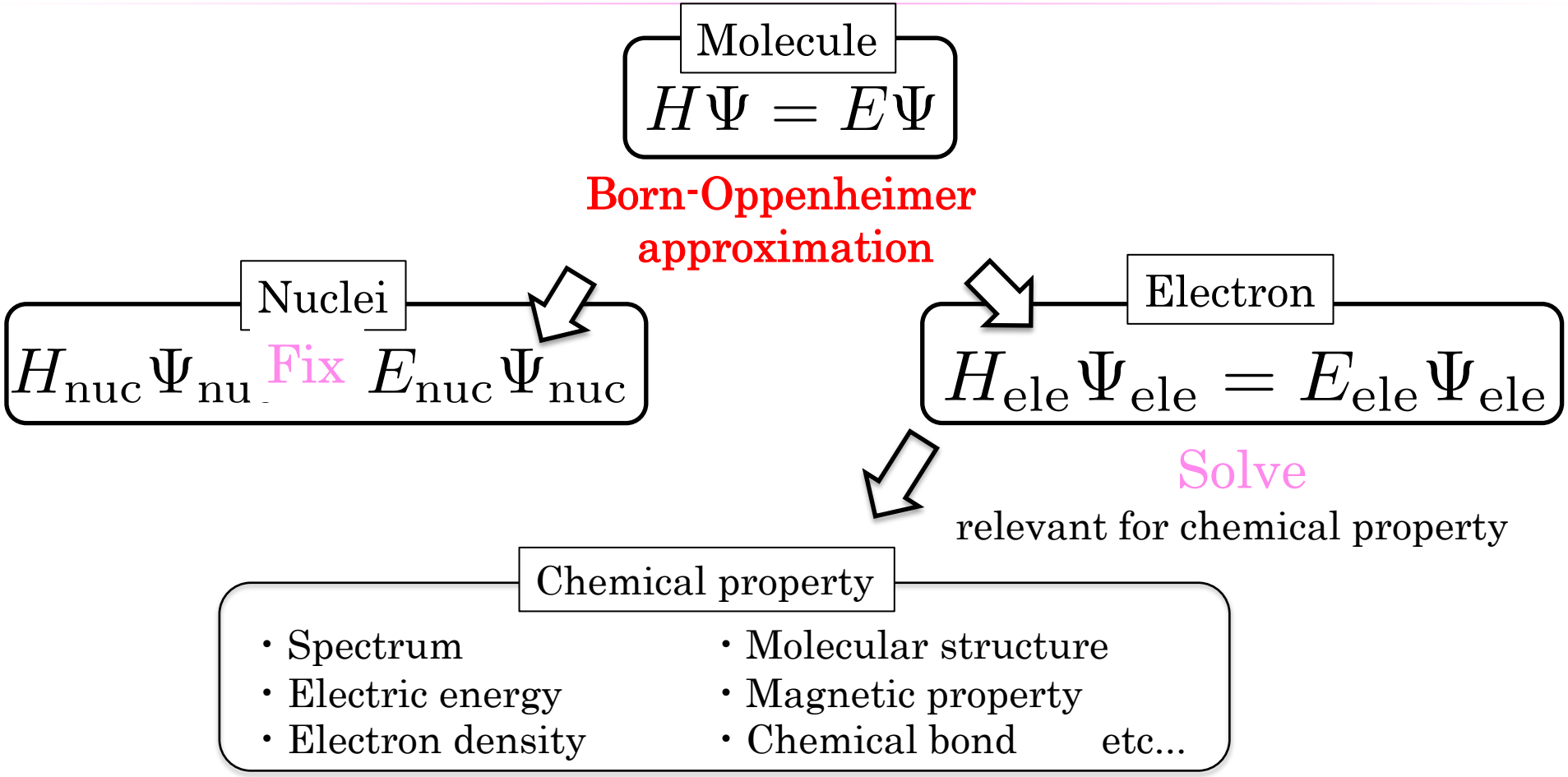


Schrödinger equation for molecule

$$\left[-\sum_{i}^{n}\frac{1}{2}\Delta_i - \sum_{a}^{m}\frac{1}{2}\Delta_a + \sum_{i<j}^{n}\frac{1}{r_{ij}} + \sum_{a<b}^{m}\frac{Z_a Z_b}{R_{ab}} - \sum_{i}^{n}\sum_{a}^{m}\frac{Z_a}{r_{ia}}\right]\Psi(x_1\cdots x_n X_1\cdots X_m) = E\Psi(x_1\cdots x_n X_1\cdots X_m)$$

⟶ No analytical solution!!

What is *"Ab initio"*



Ab initio calculation

Latin term "from the beginning"

Ab initio calculation

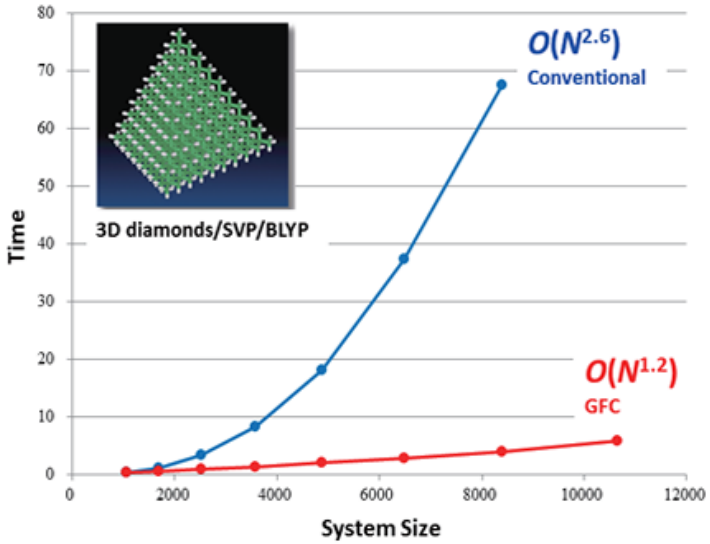
Ab initio quantum chemistry software

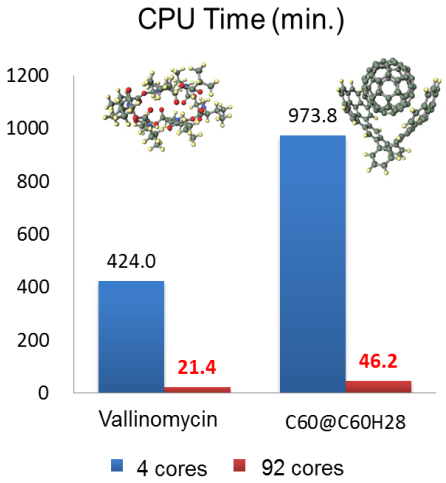
- Gaussian
- Gamess
- NWChem
- Molpro
- Molcas
- Turbomol
- Dirac

etc...

NTChem

- Scalable algorithm
- Highly parallelized ab initio calculation

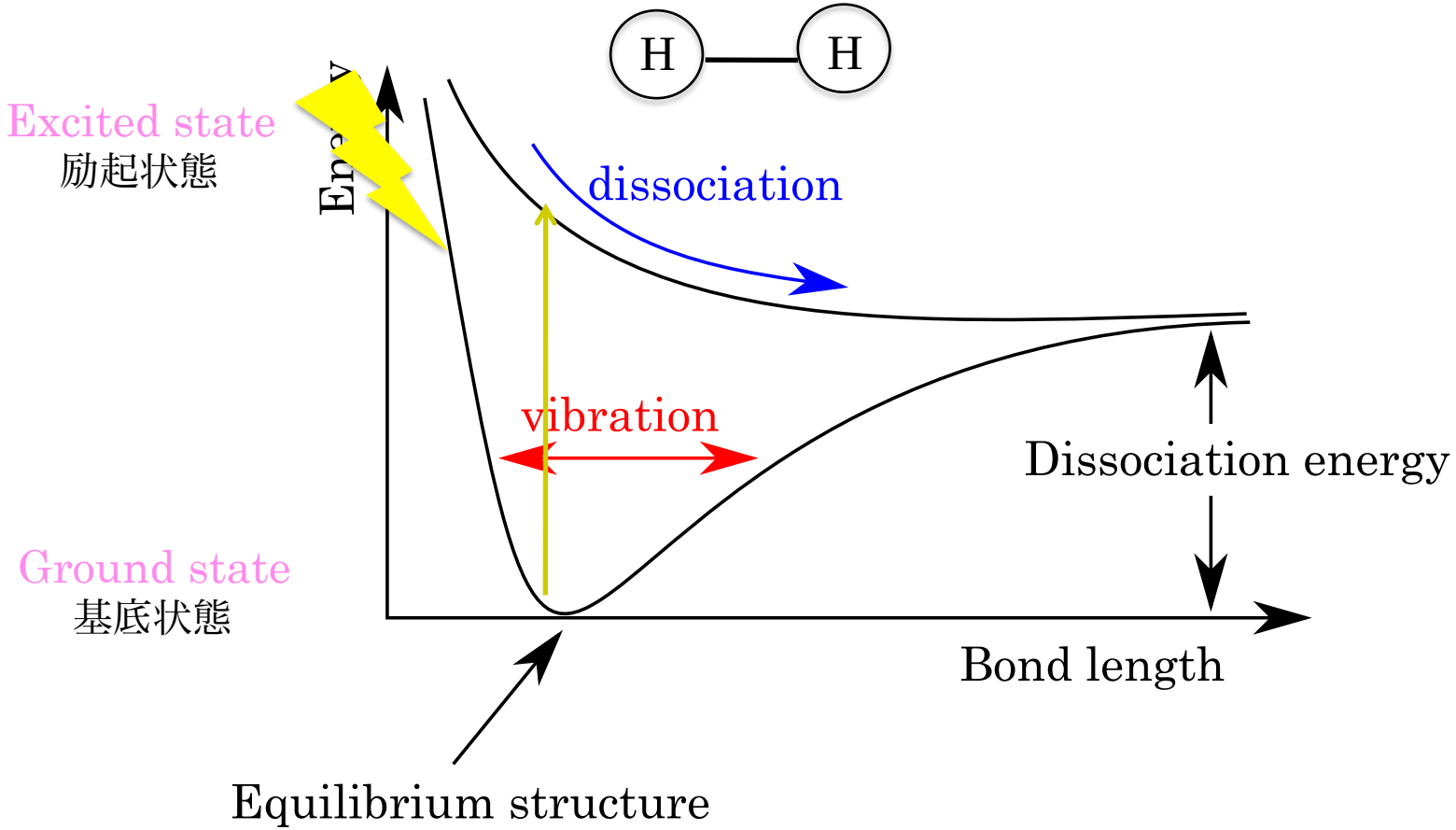




Potential energy surface

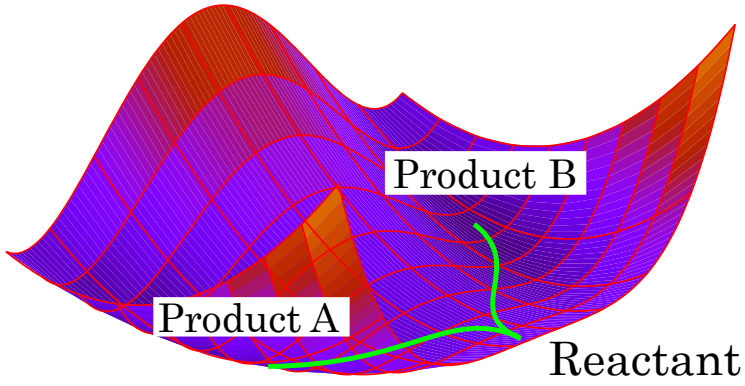
Potential Energy Surface : PES

ポテンシャルエネルギー曲面



How do nucleus move?

Potential energy surface



Reactant
反応物

Product A?

Product B?
生成物

Molecule

$$H\Psi = E\Psi$$

Born-Oppenheimer approximation

Nuclei

$$H_{\mathrm{nuc}}\Psi_{\mathrm{nu}} \text{ Fix } E_{\mathrm{nuc}}\Psi_{\mathrm{nuc}}$$

Solve

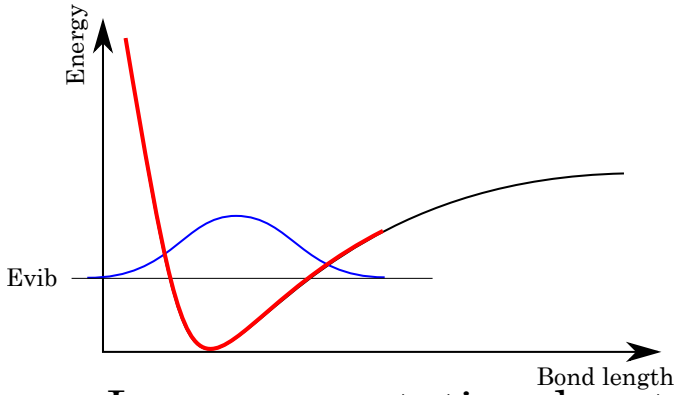
Electron

$$H_{\mathrm{ele}}\Psi_{\mathrm{ele}} = E_{\mathrm{ele}}\Psi_{\mathrm{ele}}$$

Solve

Classical approximation

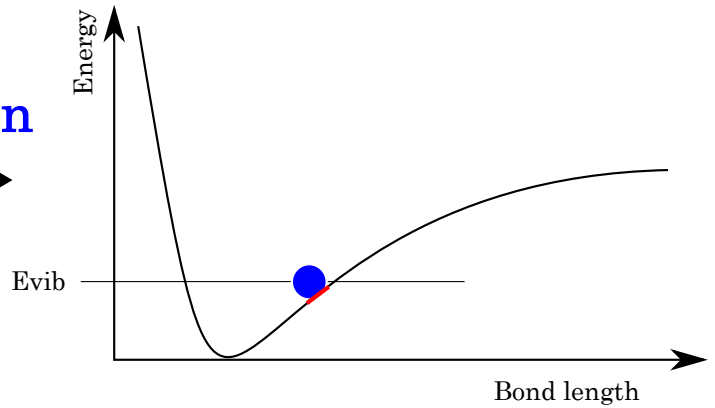
Quantum mechanics



Large computational cost

Classical approximation

Classical mechanics



Molecule

$$H\Psi = E\Psi$$

Born-Oppenheimer approximation

Nuclei

$$H_{\mathrm{nuc}}\Psi_{\mathrm{nuc}} = E_{\mathrm{nuc}}\Psi_{\mathrm{nuc}}$$

Solve $F = ma$

Classical approximation

Electron

$$H_{\mathrm{ele}}\Psi_{\mathrm{ele}} = E_{\mathrm{ele}}\Psi_{\mathrm{ele}}$$

Solve

Ab initio Molecular Dynamics

Ab initio Molecular Dynamics

Electron

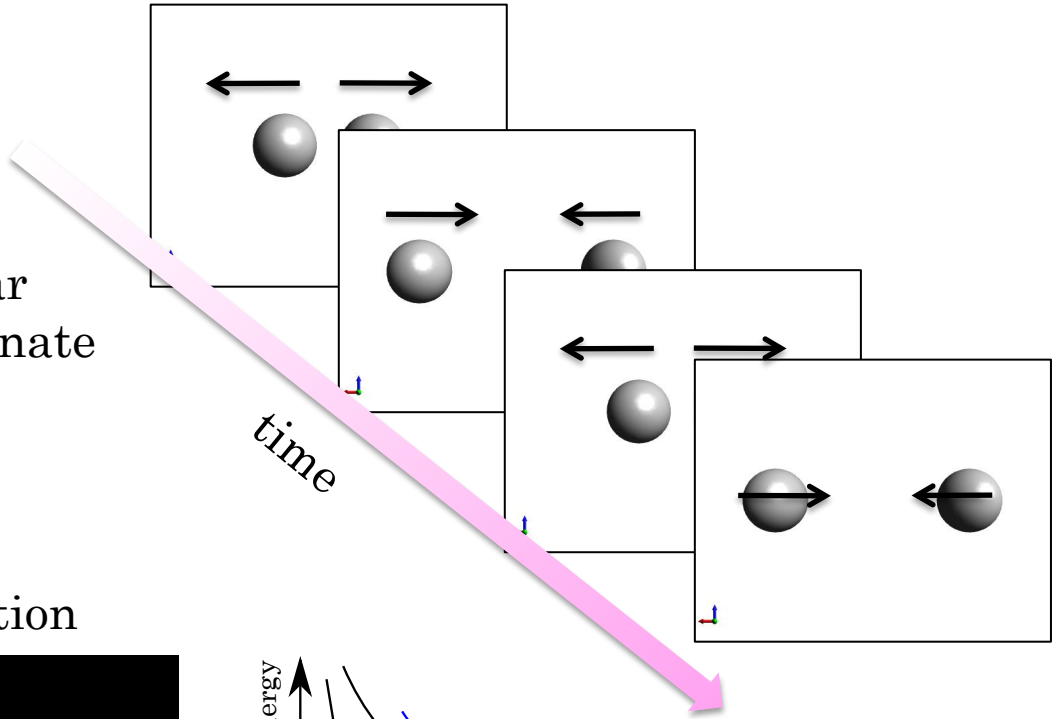
$H_{\mathrm{ele}}\Psi_{\mathrm{ele}} = E_{\mathrm{ele}}\Psi_{\mathrm{ele}}$

(Ab initio calculation)

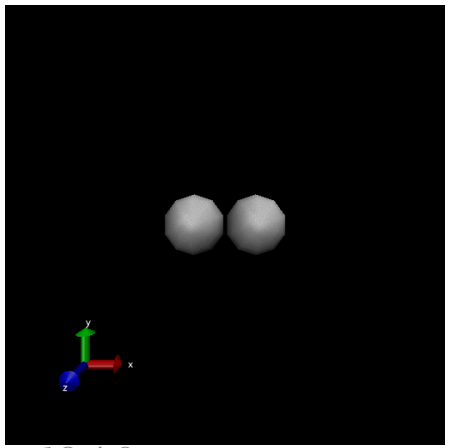
Force ⇩ ⇧ Nuclear Coordinate

Nuclei

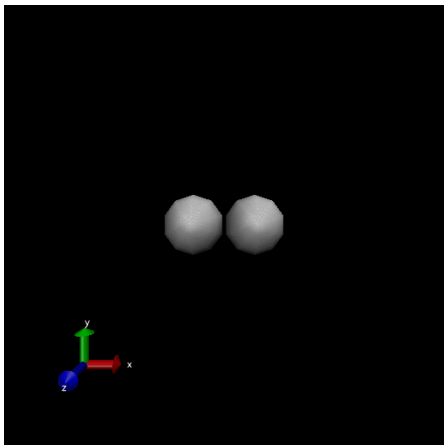
$F = ma$

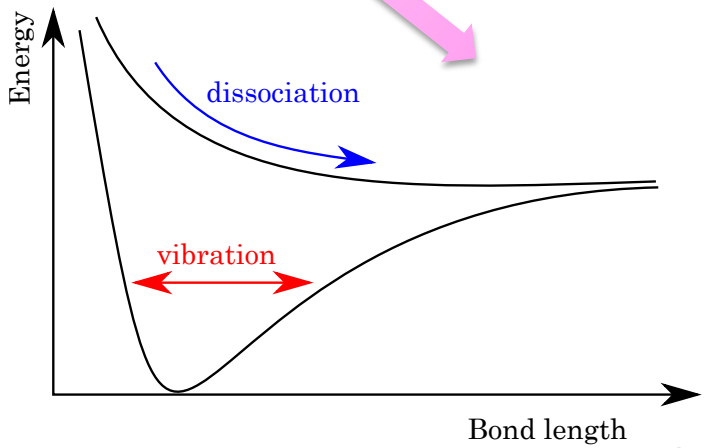


vibration



dissociation





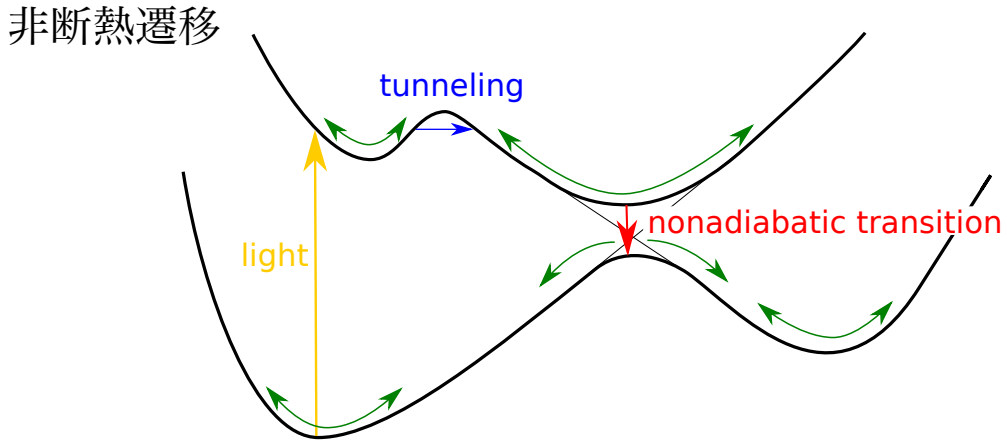
Beyond the Ab initio Molecular Dynamics

Two approximations

- Born-Oppenheimer approximation
- Classical approximation

Can not reproduce

- Nonadiabatic transition
- Tunneling effect



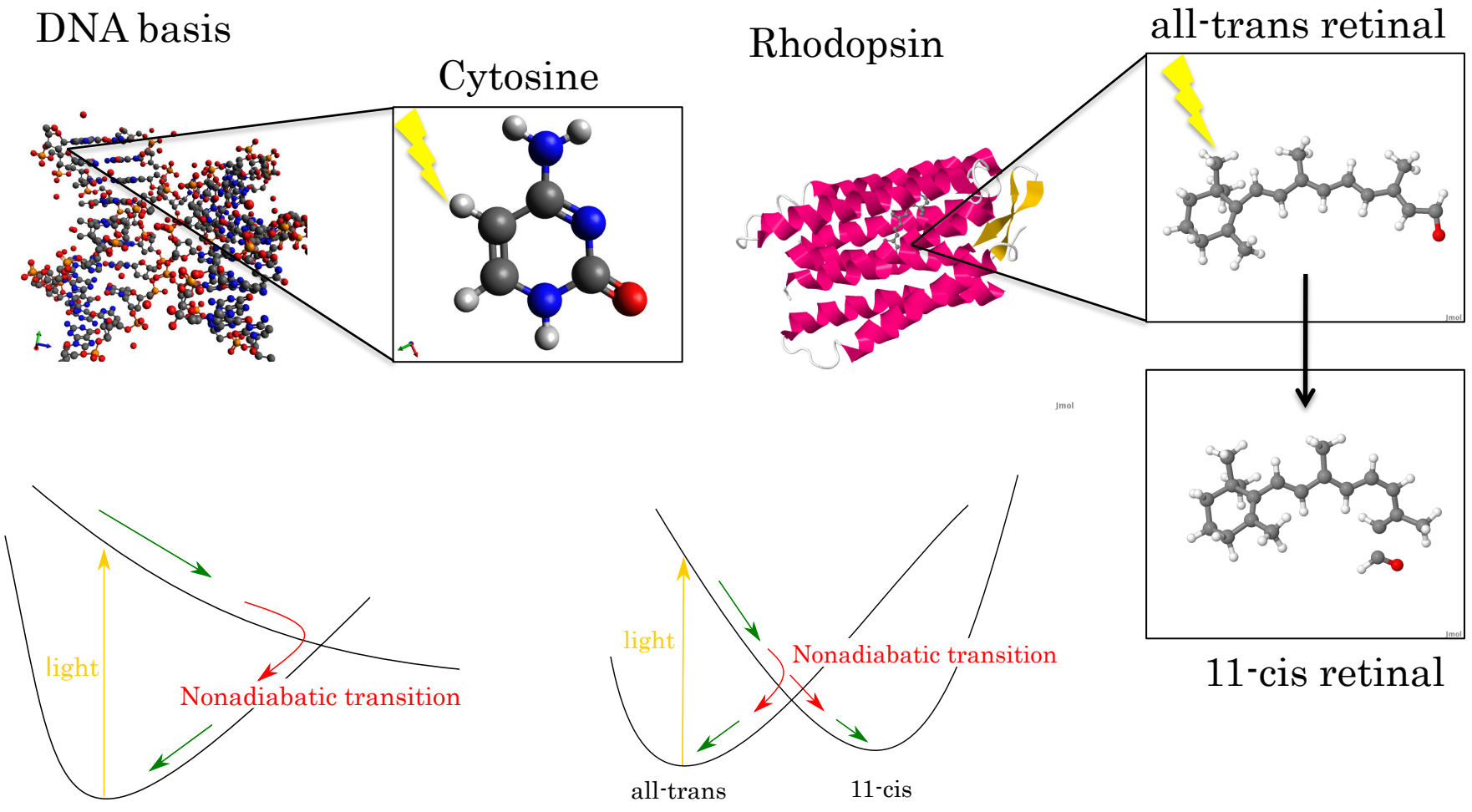
Efficient schemes are required to reproduce these phenomena.

- Surface Hopping
  - –Intuitive method
- Ehrenfest

- Semi-classical method
  - –Mathematically complex
  - –No practical scheme

Nonadiabatic transition

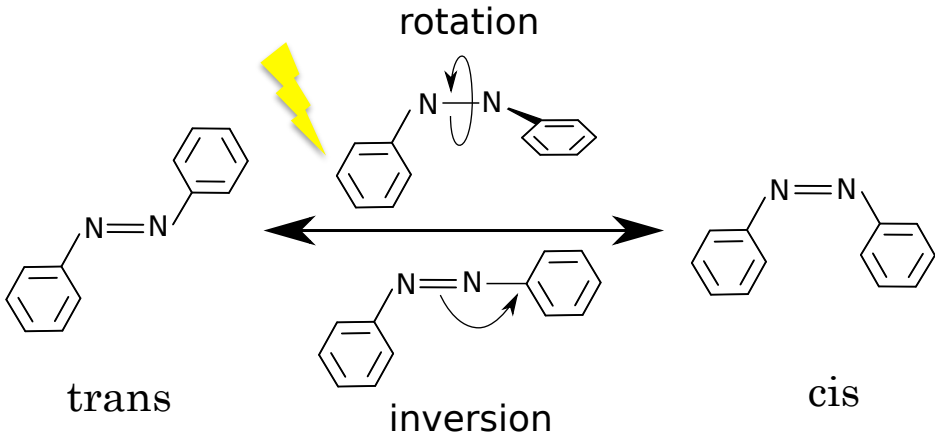
Nonadiabatic transition

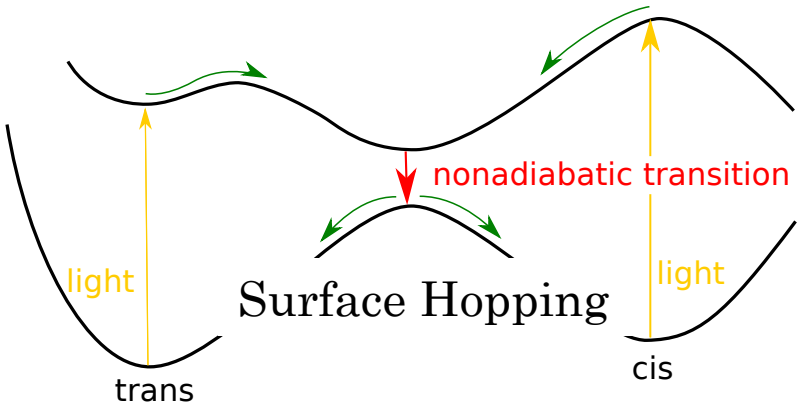


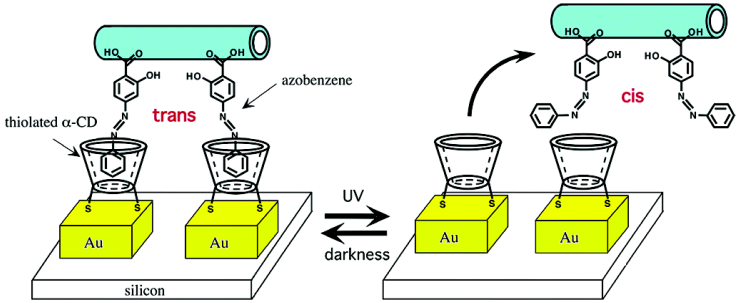
Photoisomerization of azabenzene

アゾベンゼンの光異性化

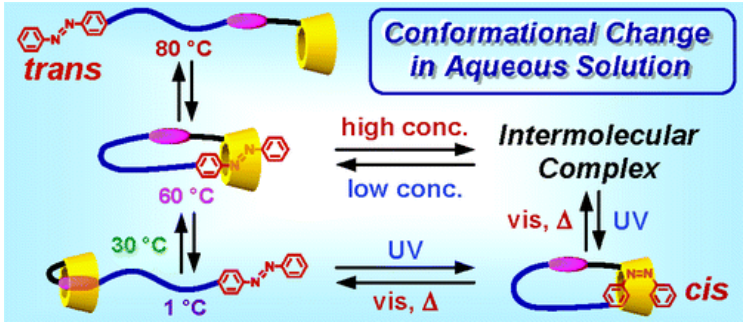
Azobenzene



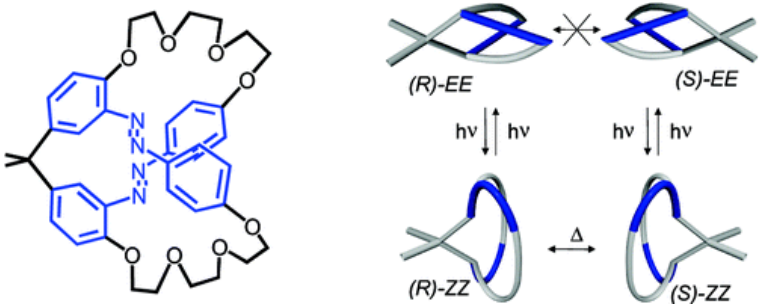




J.Am.Chem.Soc. 125, 9542 (2003)



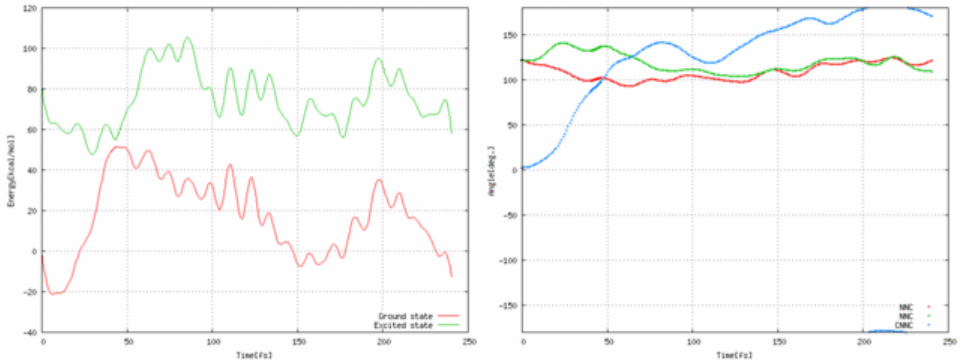
J.Am.Chem.Soc. 129, 6396 (2007)

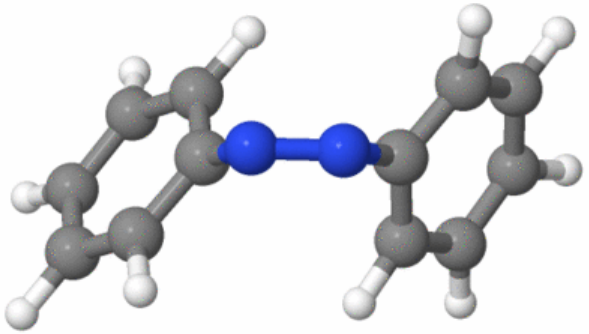


J.Am.Chem.Soc. 128, 6284 (2006)

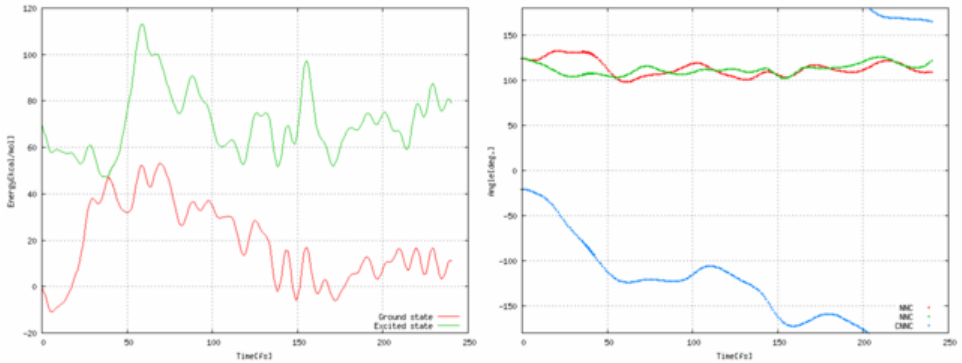
Photoisomerization of azobenzene

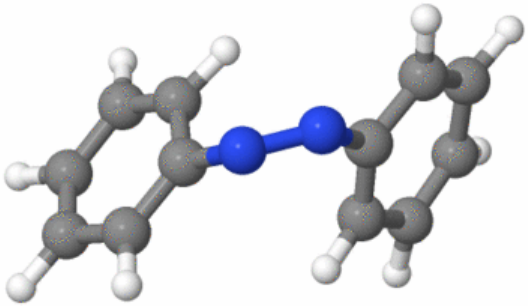
cis → trans





Jmol

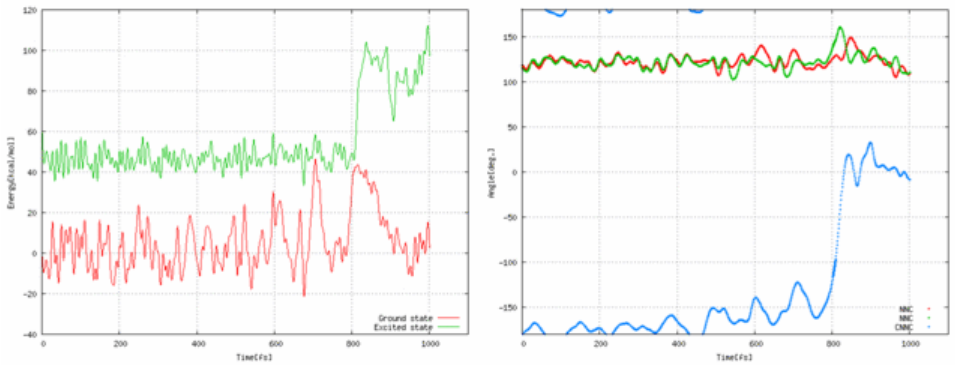


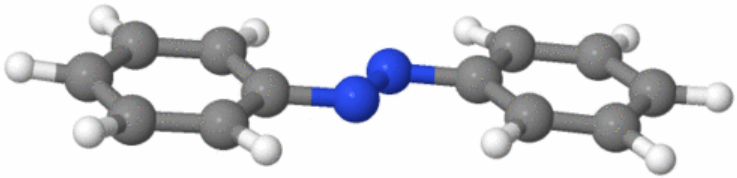


- Isomerization occurs via rotation pathway.
- Two pathways are found.

Photoisomerization of azobenzene

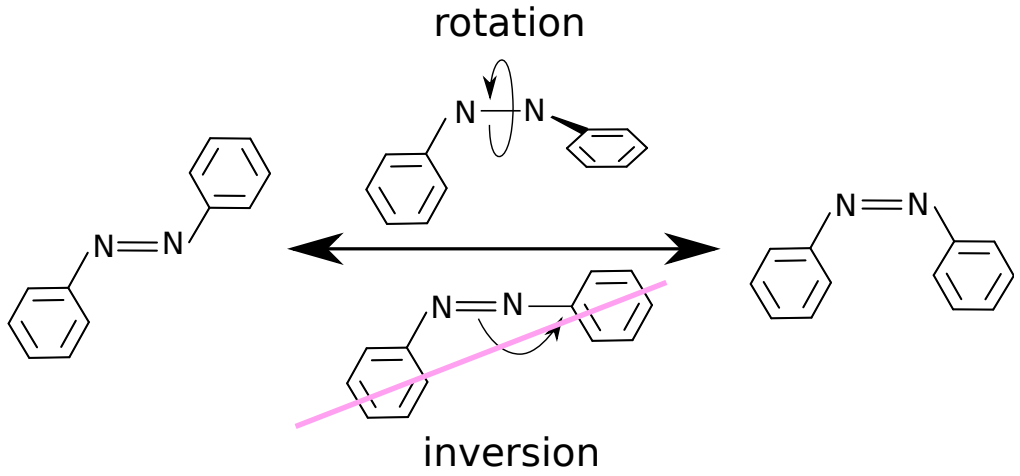
trans→ cis

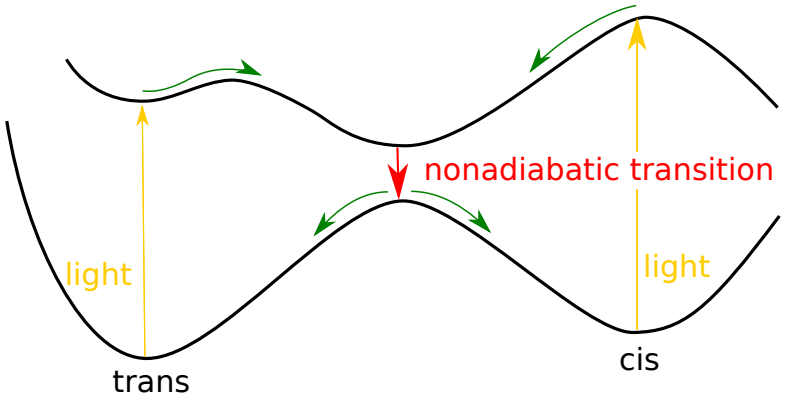




- Trans-azobenzene has longer lifetime than cis-azobenzene.
- Isomerization occurs via rotation pathway.

Photoisomerization of azobenzene



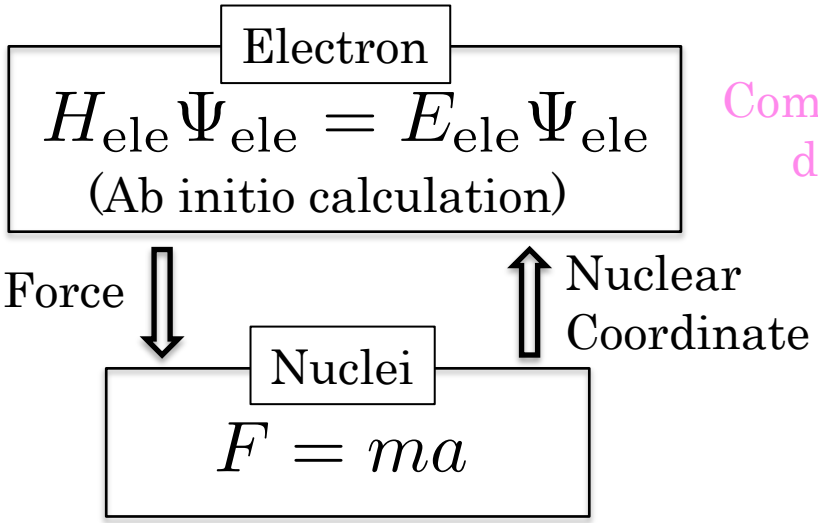


Blanching ratio

	Our results	Exp.
cis → trans	0.45	0.4 – 0.56
trans → cis	0.28±0.14	0.23 – 0.25

- Calculated blanching ratio are in good agreement with experimental results.

Computational cost



Computationally demanding

Example

cis → trans

- Ab initio calculation : 3 min
- Simulation time : 240fs
- Time step : 1.0 fs

3min × (240÷1.0) = <u>12h</u>

200 trajectories

trans → cis

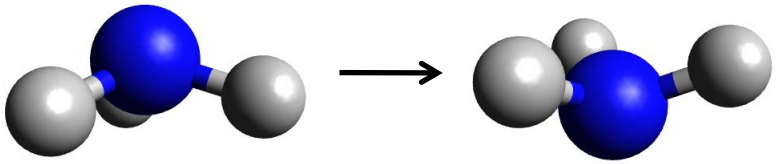
- Ab initio calculation : 3 min
- Simulation time : 1000 ～ 3000fs
- Time step : 1.0 fs

3min × (1000～3000÷1.0) = <u>50～150h</u>

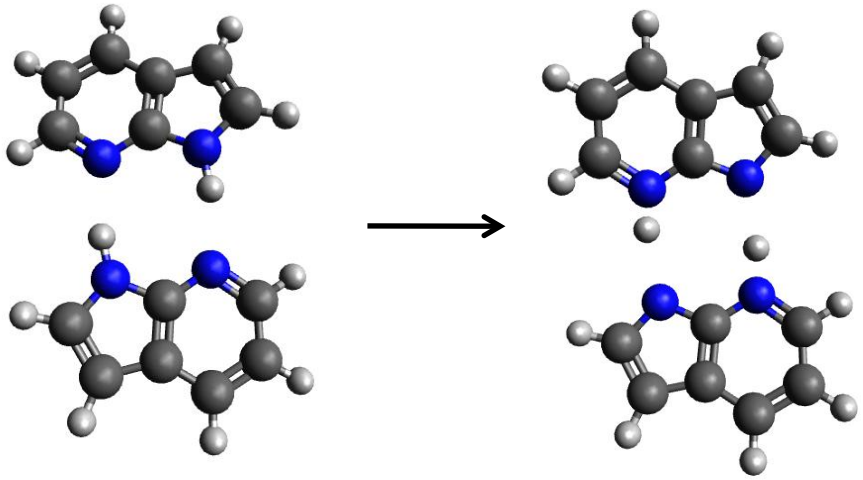
100 trajectories

Nuclear Quantum Effect

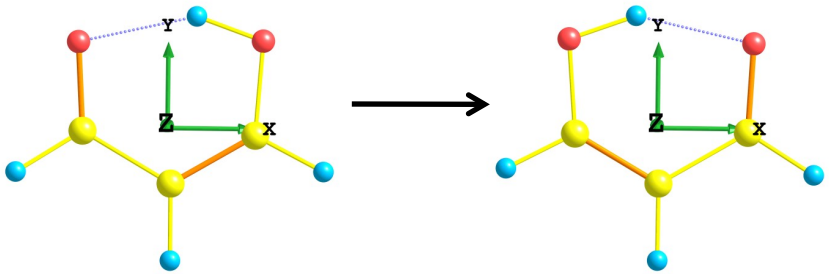
Tunneling Effect



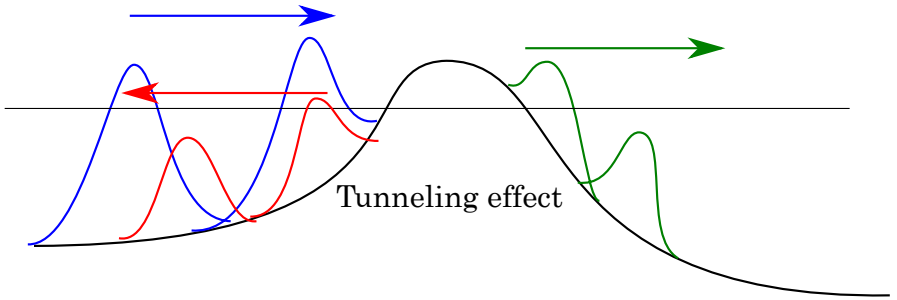
Umbrella inversion of ammonia



Proton transfer in 7-azaindole dimer

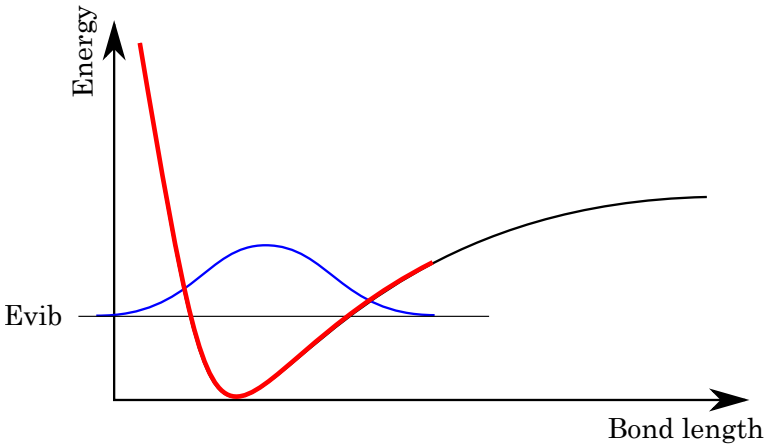


Intramolecular hydrogen transfer
in malonaldehyde



Nuclear quantum effect

Computational costs of quantum mechanical dynamics



- Ab initio calculation : 3 min
- Number of atoms : 9
  - 21 degrees of freedom
- Number of grids : 5
- Time step : 0.2fs
- Simulation time : 500fs

$3\text{min} \times 5^{21} \times (500 \div 0.2) \fallingdotseq 7 \times 10^{12}$ year!

- Quantum mechanical dynamics
- Semiclassical method
  - Makri-Miller method
  - Instanton theory
  - Classical S-Matrix method

Have not been developed...

Summary

Future work

- Electron correlation
- Relativistic effect
- Solvent
- Nuclear Quantum effect

Can computer be a test tube ?