

# Ab initio simulation of complex chemical systems: achievements and challenges

**Nikos L. Doltsinis**

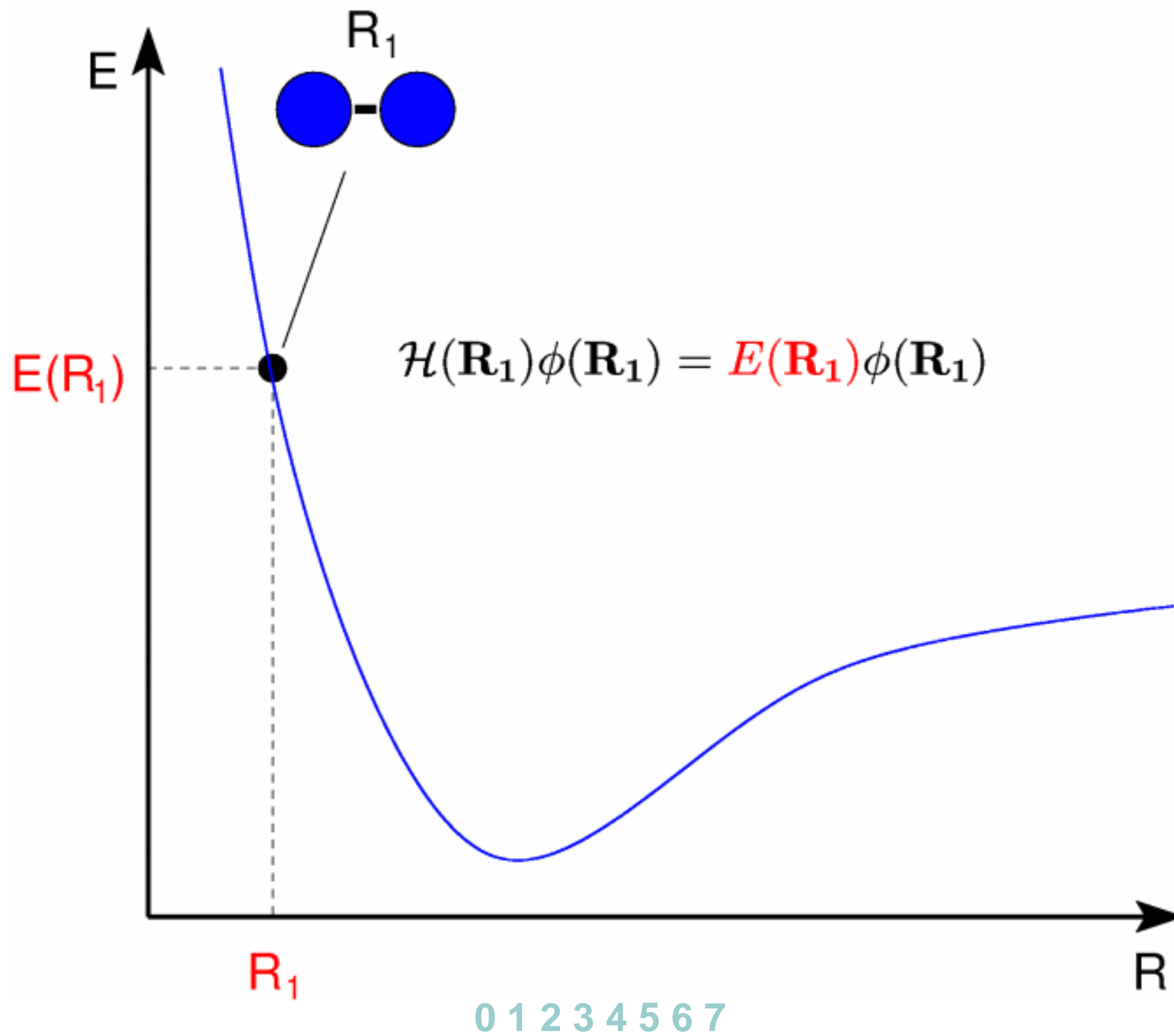
**Lehrstuhl für Theoretische Chemie  
Ruhr-Universität Bochum**



# Overview

- **Introduction and motivation**
  - Ab initio molecular dynamics (AIMD): the basics
  - Challenges: e.g. photochemistry, large biosystems
- **Photochemistry: AIMD beyond the Born-Oppenheimer approx.**
  - $S_0/S_1$  nonadiabatic ab initio surface hopping
    - OHBA:  $S_1$  proton transfer and internal conversion
    - Photoisomerisation (formaldimine, diazene, azobenzene)
    - Photochemistry of DNA / RNA - bases (guanine, uridine)
- **Large biosystems: hybrid quantum-classical simulations**
  - QM / MM simulation of proton transport in bacteriorhodopsin

# Ab initio molecular dynamics: basic principle



# Ab initio molecular dynamics: advantages

- nuclear forces "on the fly"

- no precalculated potential surface

← unfeasible for high-dimensional systems (~ 200 atoms)

- full dimensionality

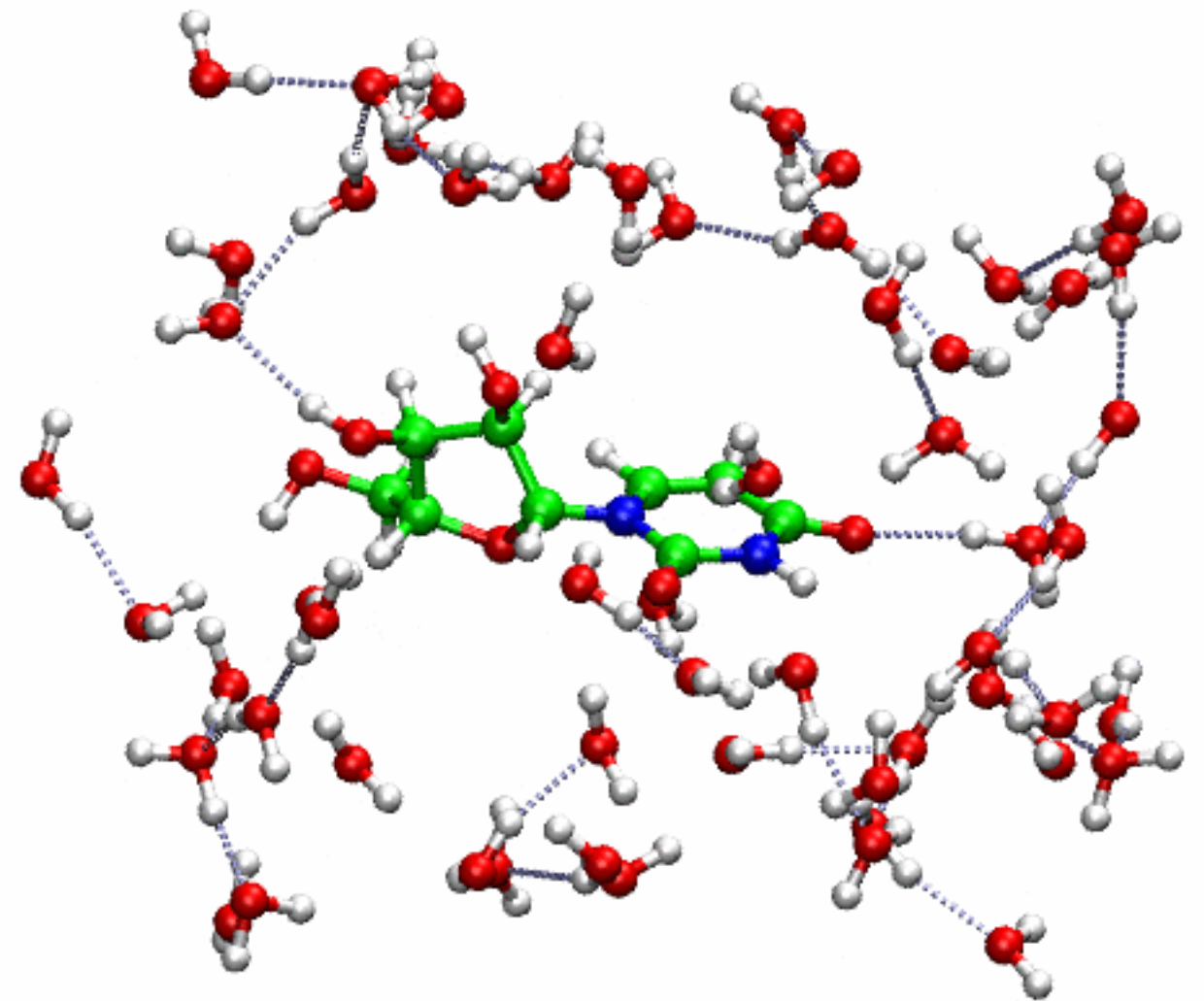
- no preselection of reactive modes to reduce dimensionality

⇒ no a priori

knowledge required !

- reaction coordinate is

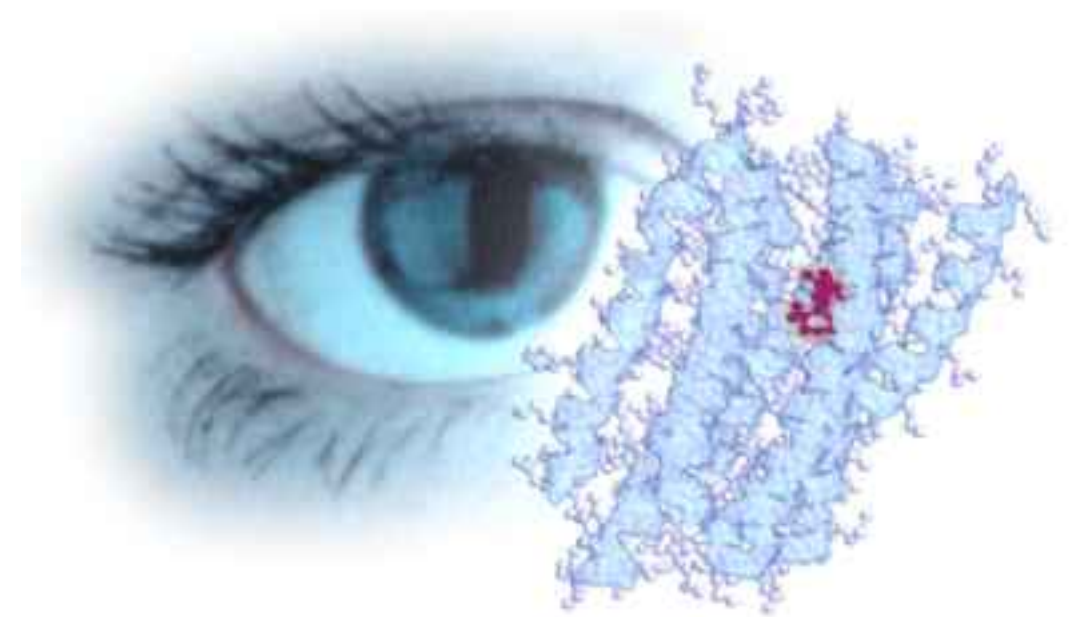
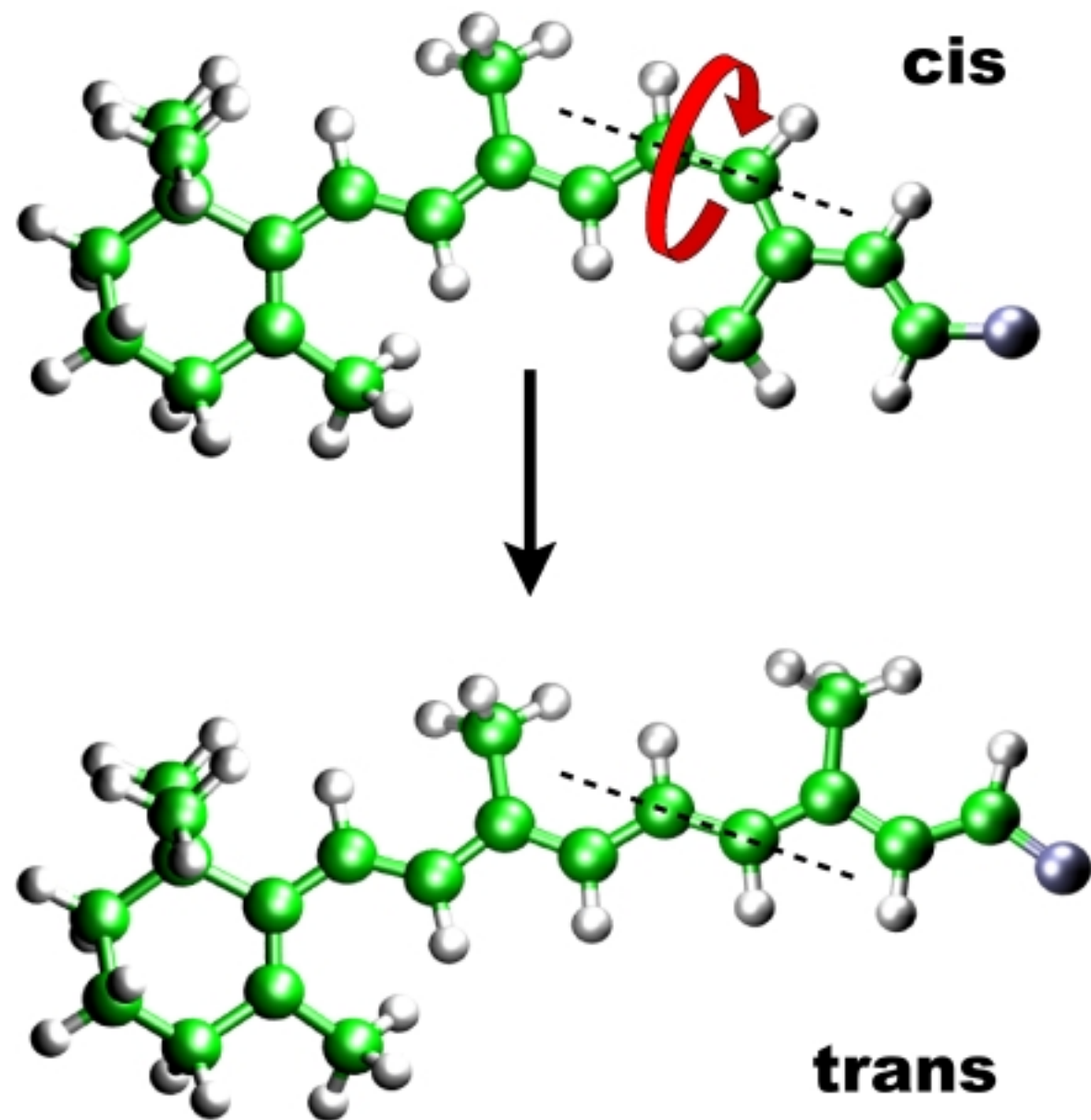
**output not input !**



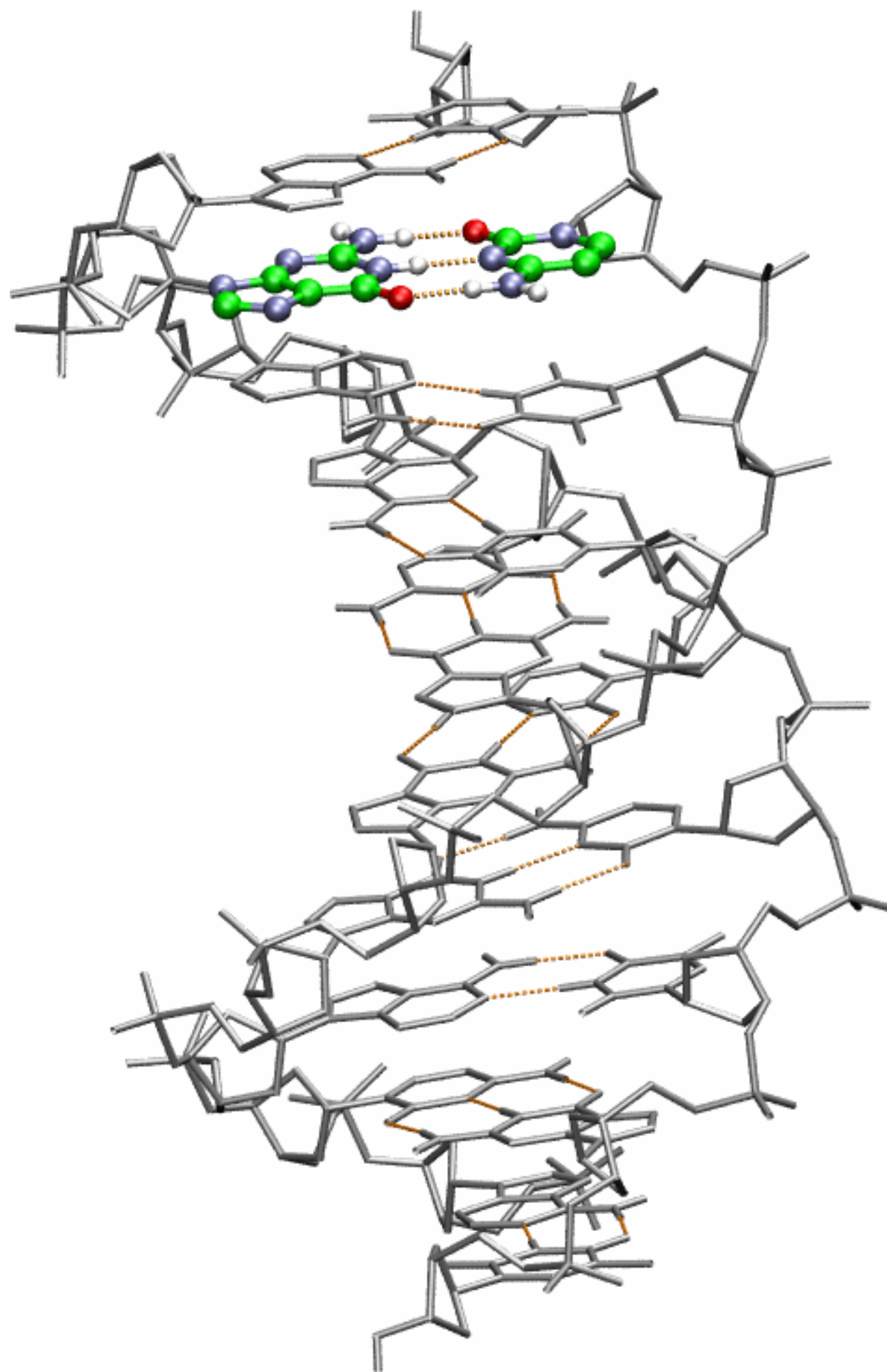
# Ab initio molecular dynamics: approximations in practice

- **approximative solution of Schrödinger equation:**  
Hartree-Fock, density functional theory
- **nuclei are classical particles**  $\Rightarrow$  extension: path integral AIMD
- **system in ground state**  $\Rightarrow$  extension: excited states (CIS, ROKS, TDDFT)  $\Rightarrow$  **photochemistry**
- **Born-Oppenheimer approximation: nuclear dynamics determined by **single** (adiab.) electronic state**  $\Rightarrow$  extension: nonadiabatic MD  $\Rightarrow$  **photochemistry**
- **finite simulation time (10 – 100 ps)**  $\Rightarrow$  solution: speeding up reactions using constraints
- **finite system size (~ 200 atoms)**  $\Rightarrow$  solution: QM / MM

# cis-trans isomerisation of retinal in rhodopsin

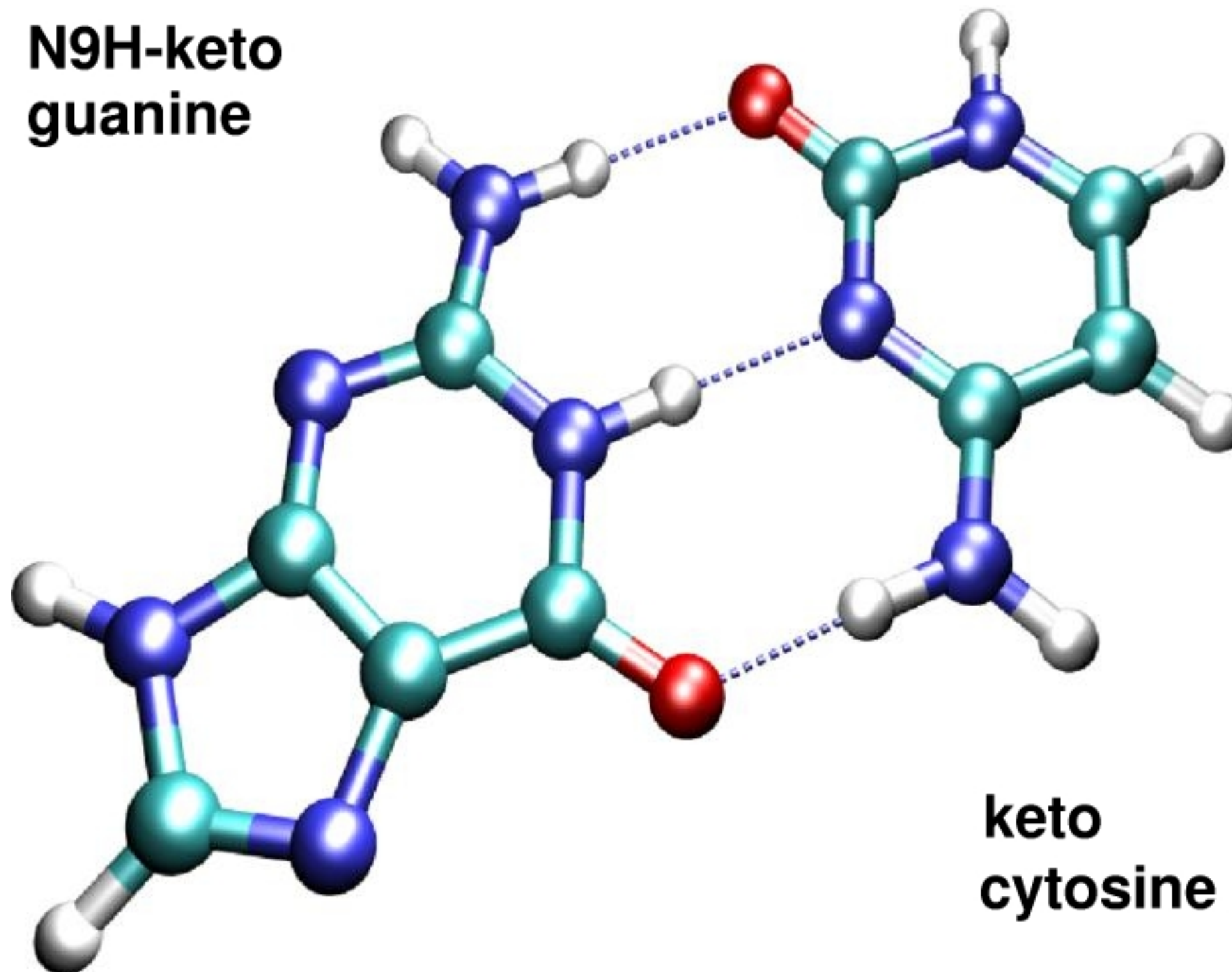


DNA  
radiation-  
induced  
damage

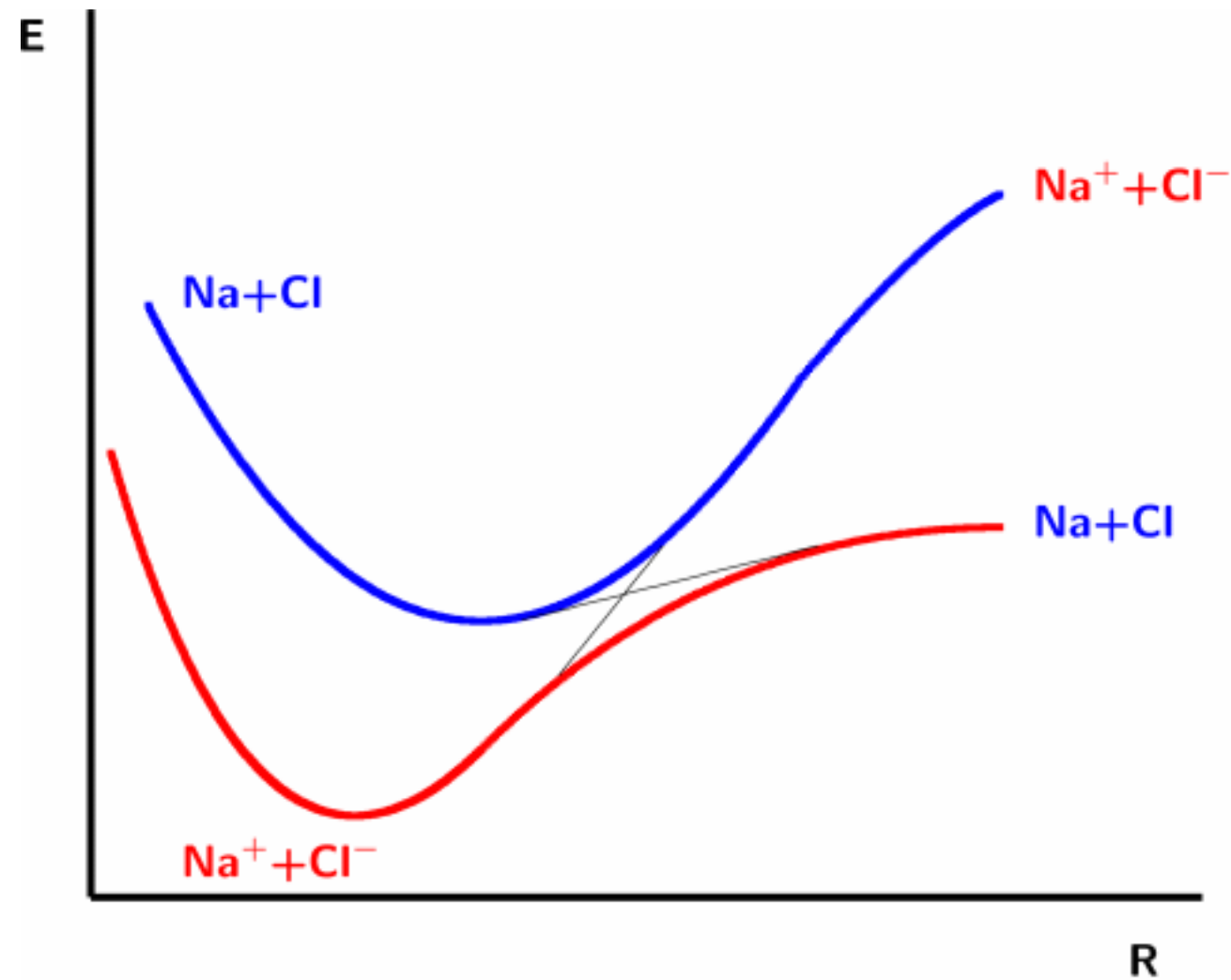


# Motivation: radiation-induced DNA damage

[E. Nir, K. Kleinermanns, and M.S. de Vries; Nature 408 (2000) 949]



# Nonadiabatic effects: breakdown of Born-Oppenheimer



➔ **nonadiabatic effects**

in case of:

- avoided crossing
- conical intersection

Massey parameter


$$\xi = \frac{\Delta E l}{\hbar \dot{R}} = \frac{\text{passage time}}{\text{inverse transition frequency}}$$

→ adiabaticity if  $\xi \gg 1$


# nonadiabatic MD: mixed quantum-classical approach

classical nuclei:  $\mathbf{R} = \mathbf{R}(t)$

quantum-mechanical electrons:  $\Phi(\mathbf{r}, t)$

 solve:  $\mathcal{H}_{\text{el}}(\mathbf{r}, \mathbf{R}(t))\Phi(\mathbf{r}; t) = i\hbar \frac{\partial}{\partial t} \Phi(\mathbf{r}; t)$

ansatz:  $\Phi(\mathbf{r}; t) = \sum_j a_j(t) \phi_j(\mathbf{r}, \mathbf{R})$

  $\dot{a}_i(t) = -\frac{i}{\hbar} a_i(t) E_i - \sum_j a_j(t) C_{ij}$

nonadiabatic coupling matrix elements:  $C_{ij} \equiv \langle \phi_i | \frac{\partial}{\partial t} | \phi_j \rangle = \dot{\mathbf{R}} \mathbf{d}_{ij}$

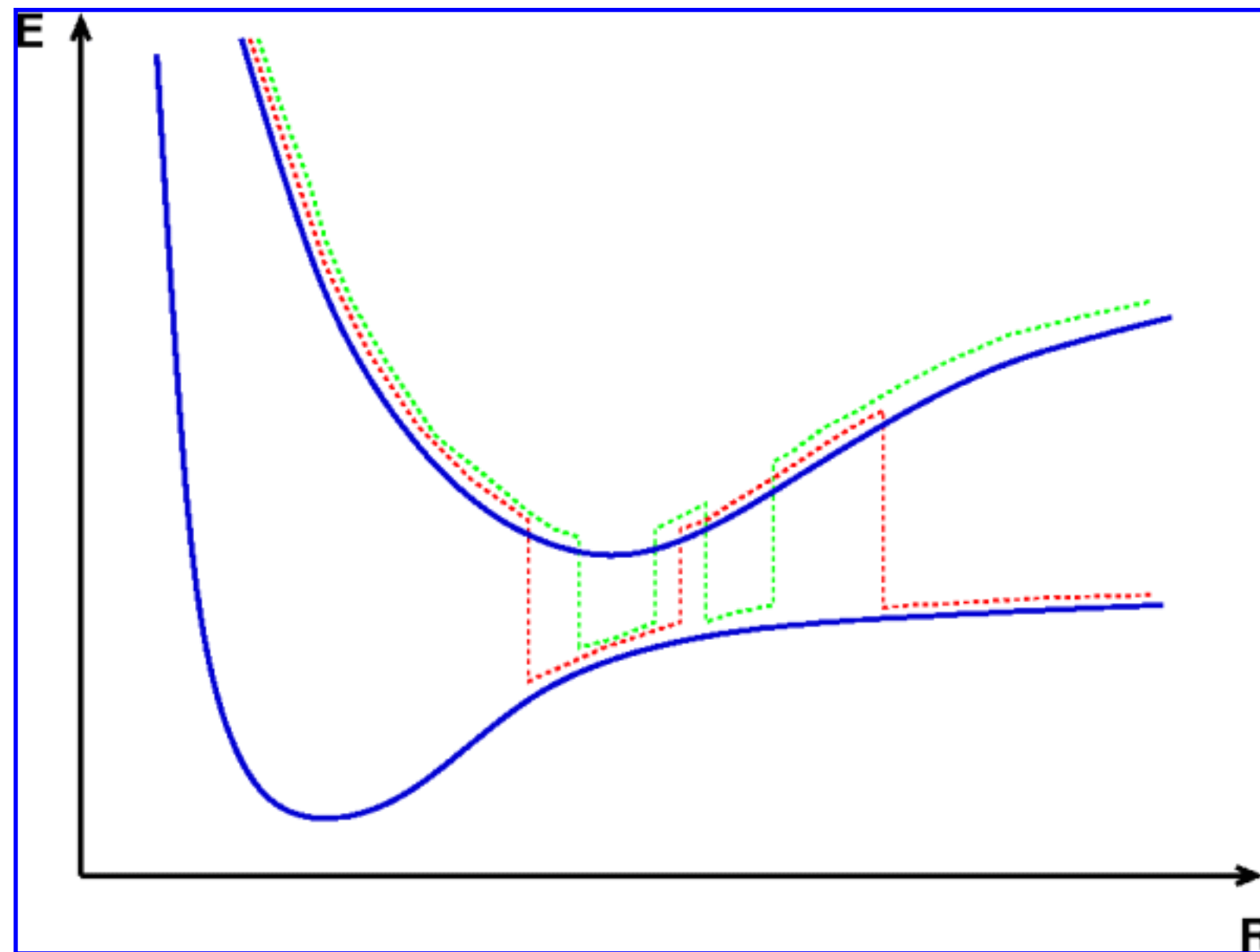
nonadiabatic coupling vector:  $\mathbf{d}_{ij} = \langle \phi_i | \nabla | \phi_j \rangle$

  $|a_i(t)|^2$  = probability to find system in adiabatic state  $i$  at time  $t$

# Surface Hopping approach

[J. C. Tully and R. K. Preston, J. Chem. Phys. 55 (1971) 562]

[J. C. Tully, J. Chem. Phys. 93 (1990) 1061]



→ 1000 - 10000 trajectories necessary !! → NIC project: 6 in 3 years

# New method: Ab Initio MD + Surface Hopping

[ N. L. Doltsinis and D. Marx, Phys. Rev. Lett. 88 (2002) 166402 ]

## previously:

- mostly semiempirical or model potentials
  - few atoms
- no generally applicable code

## new method:

- electronic states: ab initio (DFT)
- large systems (complexity  $\approx$  ground state AIMD)
- nonadiabatic coupling

$$C_{ij} \equiv \langle \phi_i | \frac{\partial}{\partial t} | \phi_j \rangle = \dot{\mathbf{R}} \mathbf{d}_{ij}$$

"for free" from AIMD

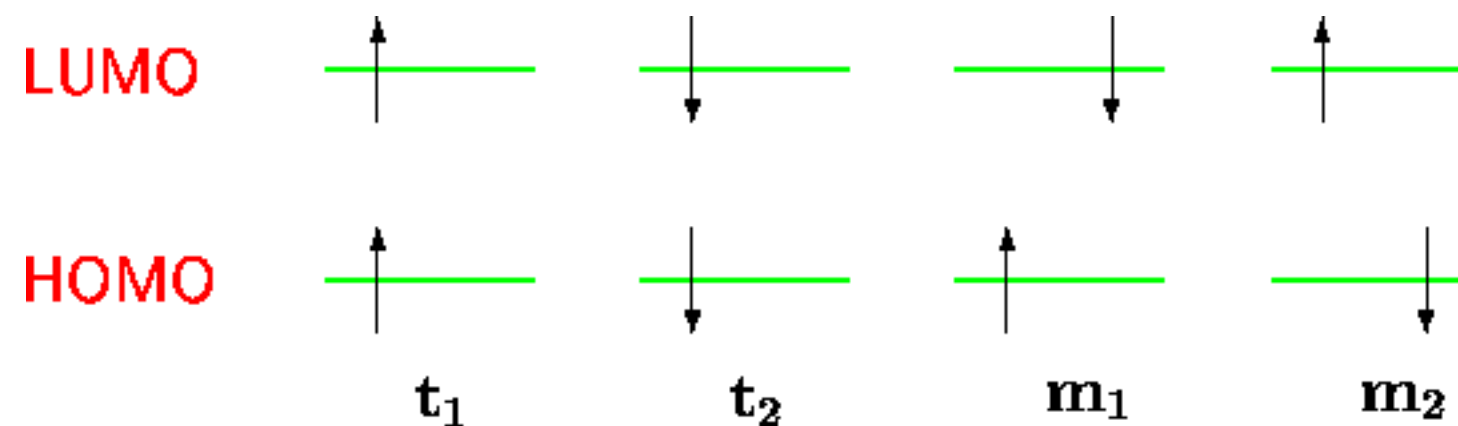
# Ab Initio (Car-Parrinello) Surface Hopping

[ N. L. Doltsinis and D. Marx, Phys. Rev. Lett. 88 (2002) 166402 ]

- Ground state  $S_0$ : **Kohn-Sham DFT**

➔  $\phi_0 = |\varphi_1^{(0)} \bar{\varphi}_1^{(0)} \varphi_2^{(0)} \bar{\varphi}_2^{(0)} \cdots \varphi_l^{(0)} \bar{\varphi}_l^{(0)}\rangle$

- excited state  $S_1$ : restricted open-shell Kohn-Sham



$$\phi_1 = \frac{1}{\sqrt{2}} \{ |m_1\rangle + |m_2\rangle \}, \quad E(S_1) = 2 E(m) - E(t)$$

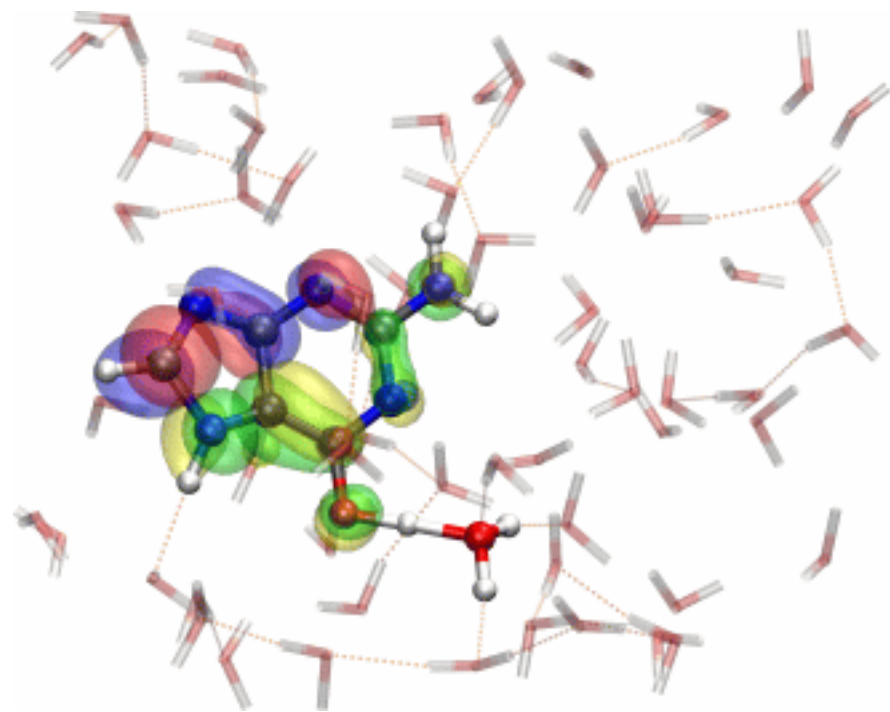
[I. Frank et al., J. Chem. Phys. 108 (1998) 4060]

# Coordination constraint dynamics

H. Langer, N. L. Doltsinis, and D. Marx; ChemPhysChem, 6 (2005) 1734

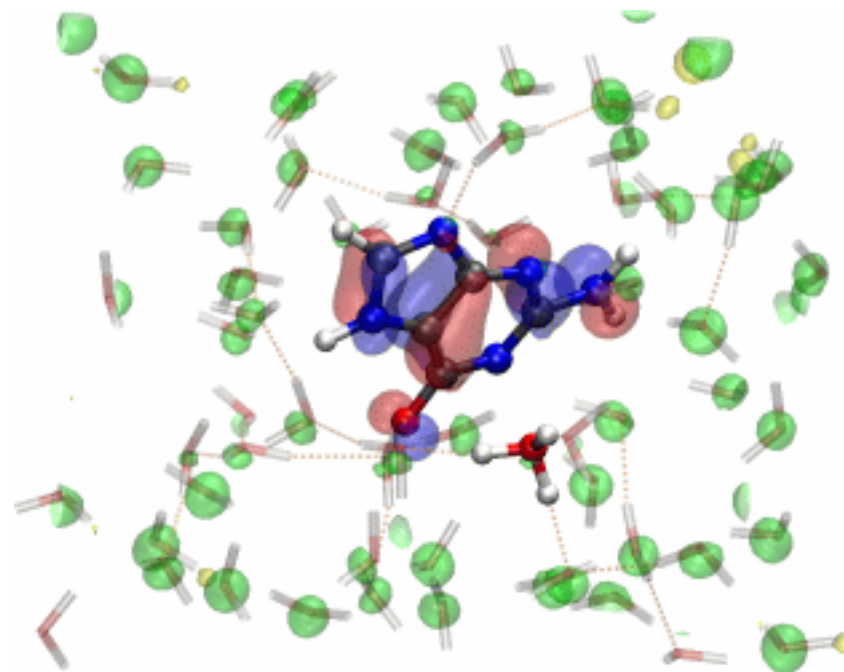
$$\text{coordination number } n_{\text{H}} = \sum_i \{ \exp[ \kappa(r_i - r_c) ] + 1 \}^{-1}$$

→ thermodynamic integration →  $\Delta A = 27$  kJ/mol (gas phase: 52 kJ/mol)



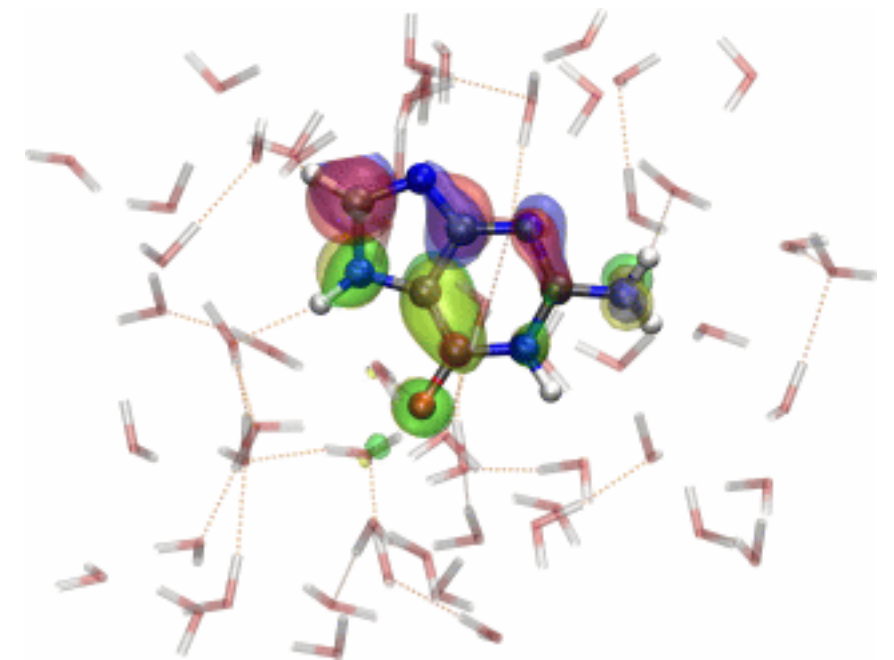
$\pi\pi^*$

localised on G



$\pi\sigma^*$

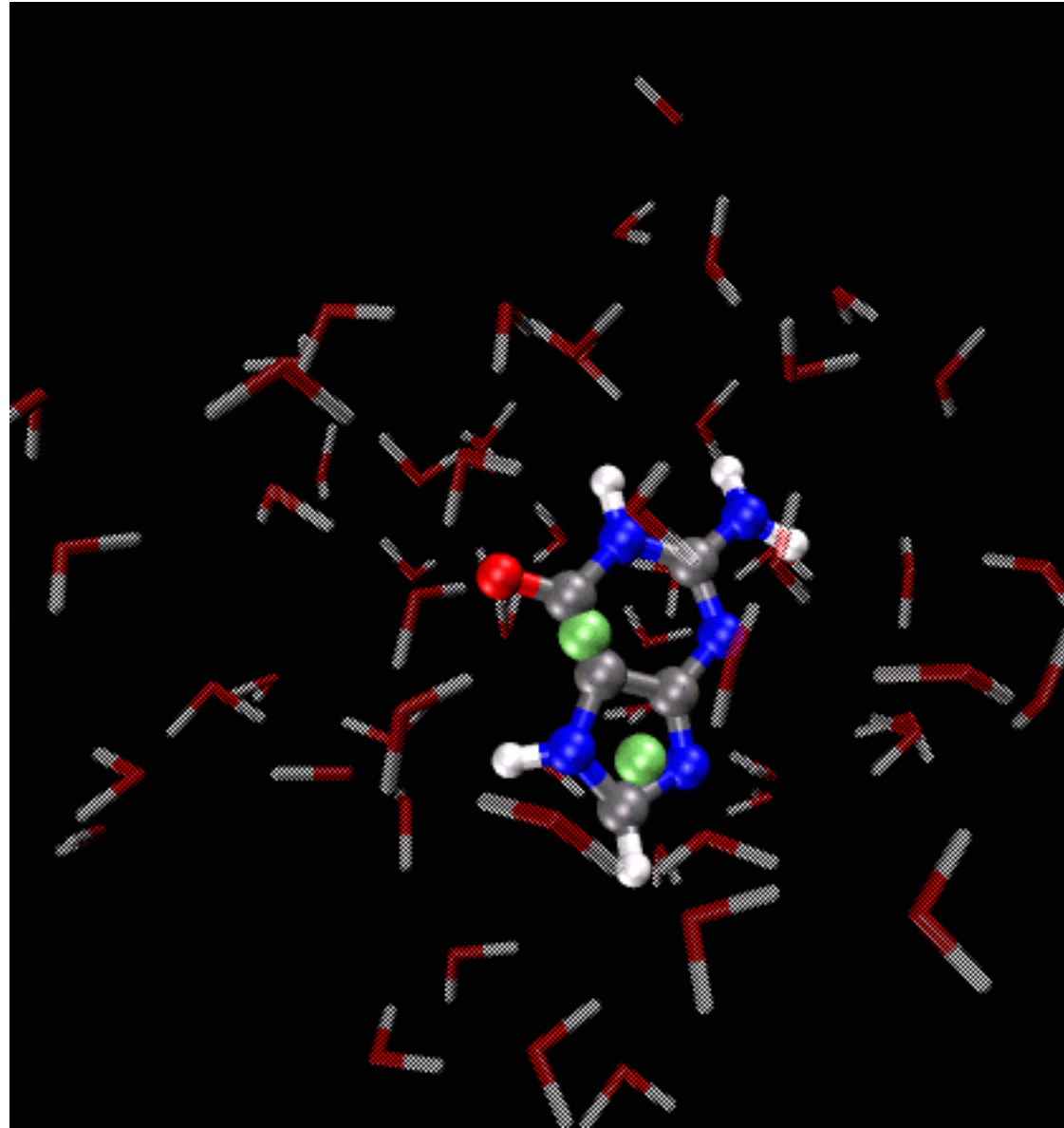
delocalised in water



$\pi\pi^*$

localised on G

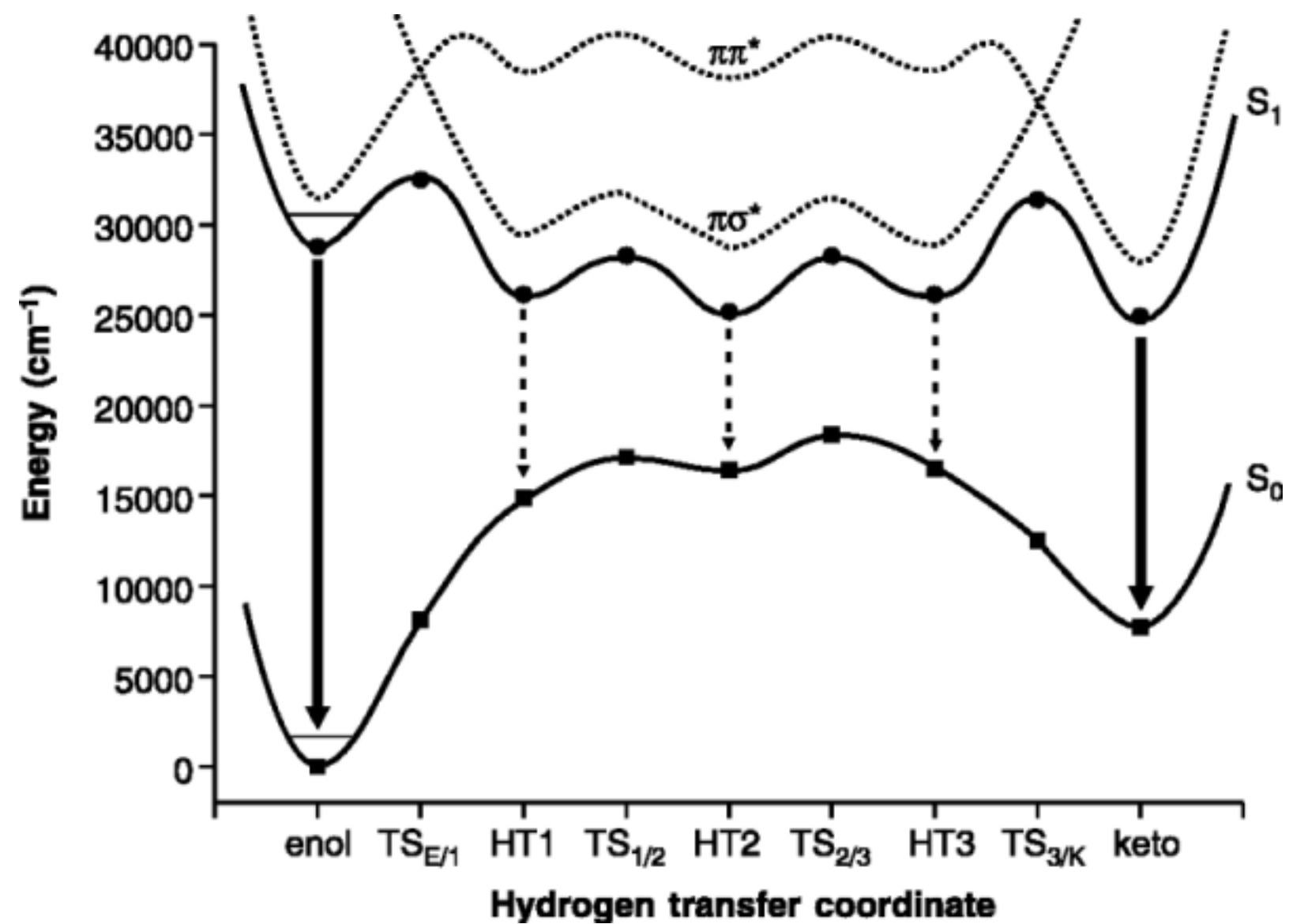
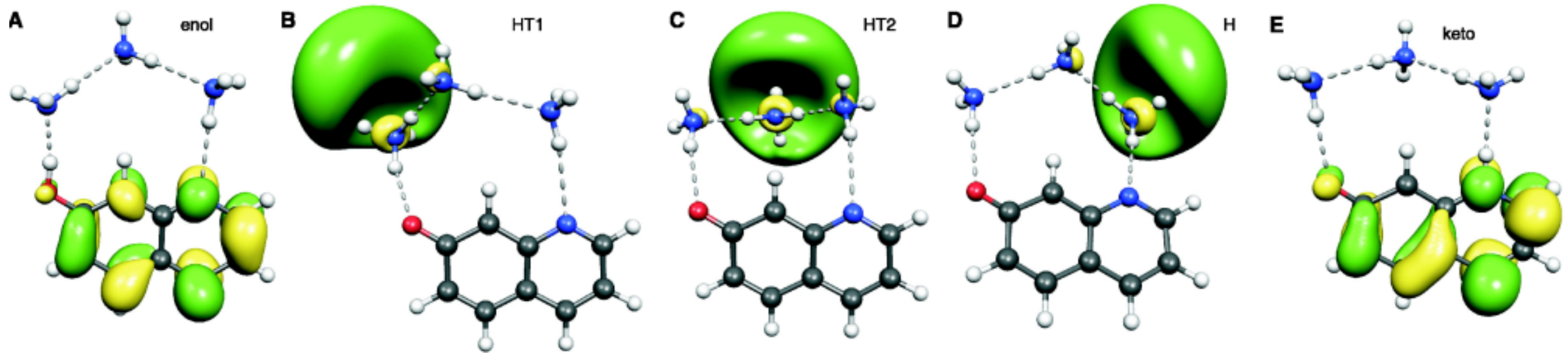
# Dynamics of singly occupied orbitals



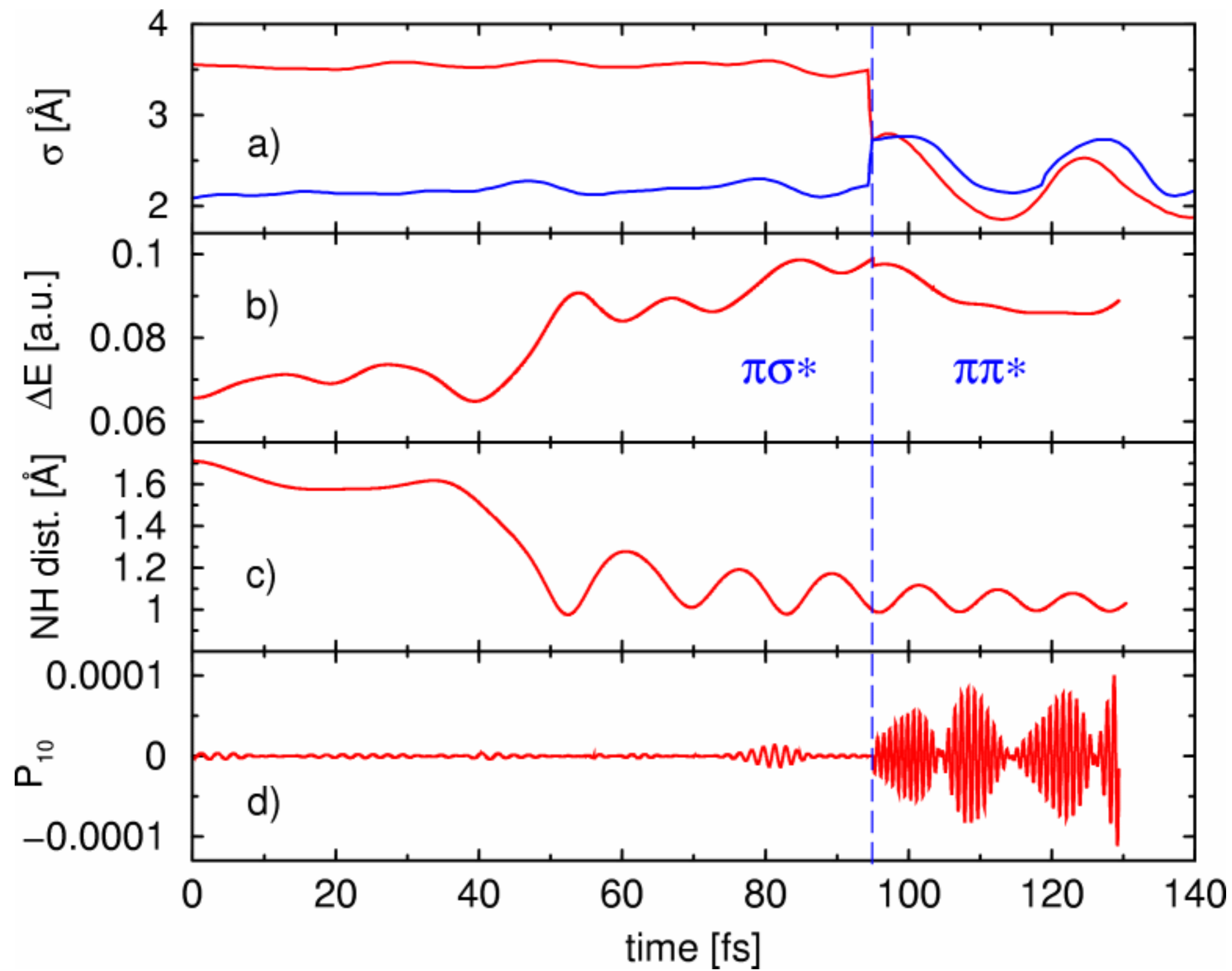
green balls (●): centres of localised orbitals

# H-transfer along ammonia wire

[Tanner, Manca, and Leutwyler, Science 302 (2003) 1736]



# nonadiabatic transition parameter at H-recombination



**decay in  $\pi\pi^*$  more likely by 1 order of magnitude!**

# Summary

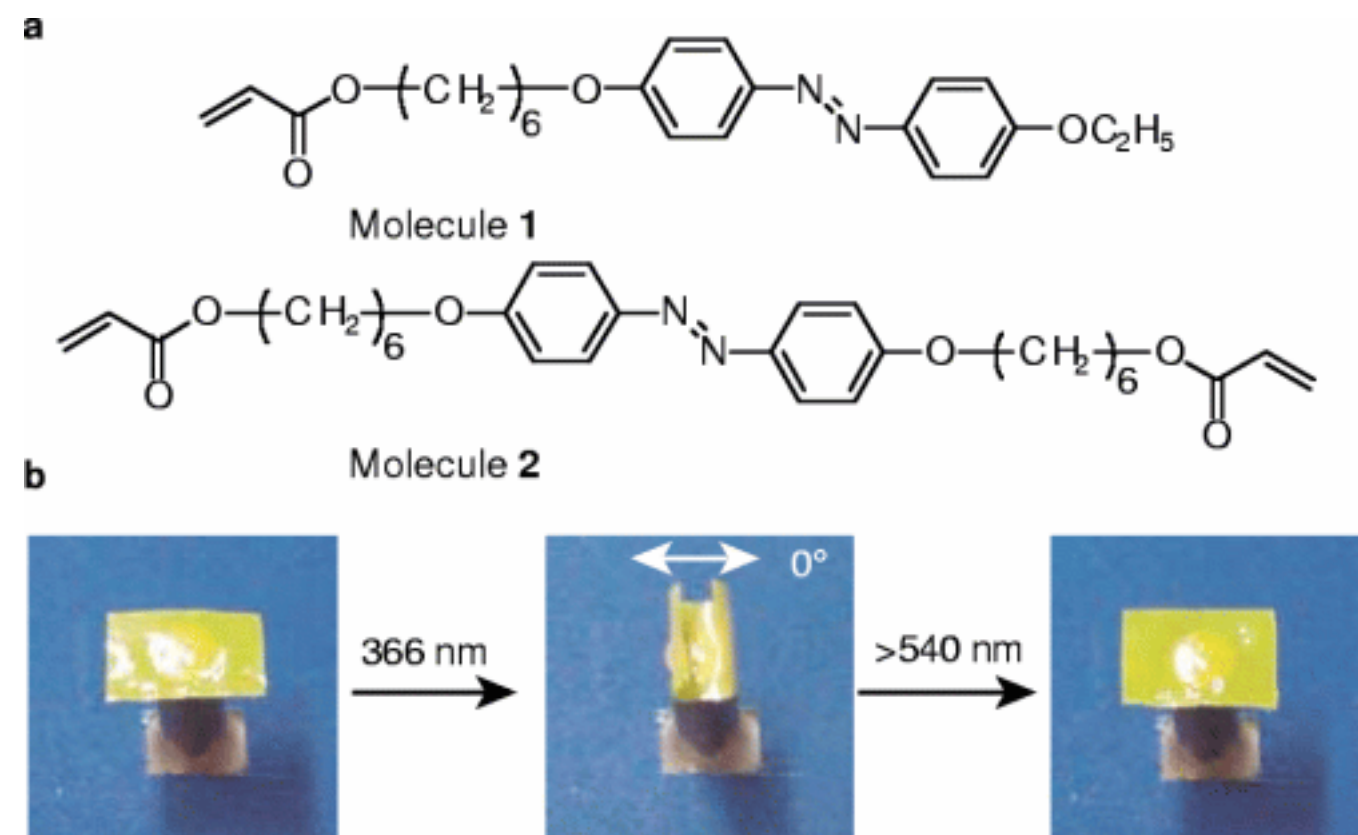
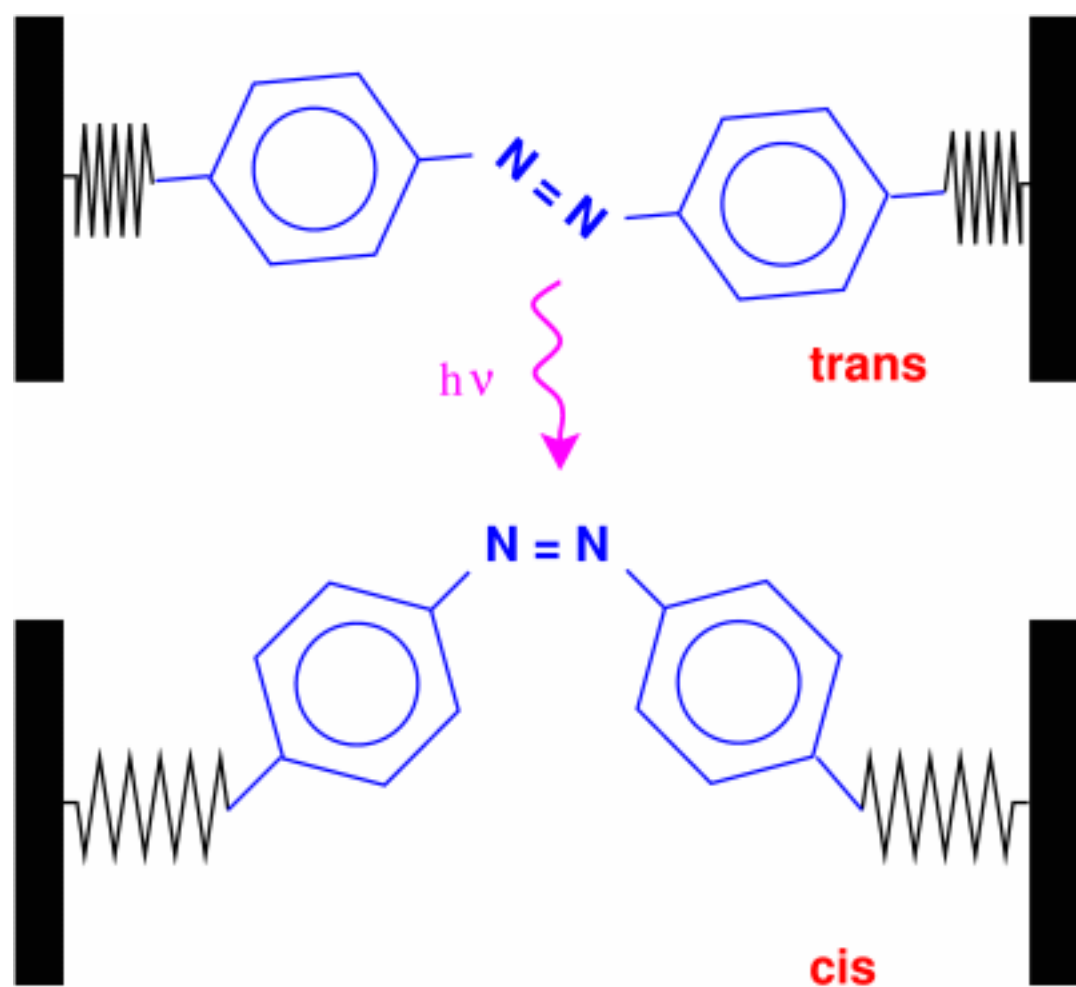
- **Ab initio MD beyond the Born-Oppenheimer approximation**
  - simulation of complex systems (condensed phase / large molecules)
  - all degrees of freedom
  - reaction coordinate is output!
- **Photochemistry / photophysics of guanine**
  - special role of biologically relevant 9-keto G
    - shortest lifetime ~ 1 ps
    - large excited state structural distortion
  - enol - keto phototautomerisation via  $\pi\sigma^*$  state
    - coupled proton-electron transfer
    - delocalised  $\sigma^*$  orbital in aqueous solution

# Volkswagen initiative "New Conceptual Approaches to Modeling and Simulation of Complex Systems"

## "Adaptive Multiscale Simulation: Connecting the Quantum to the Mesoscopic Level"

[ collaboration with Marx (Bochum), Kremer / Delle Site (Mainz) ]

- nonadiabatic QM / MM simulations of optical switches
- "coarse graining" for mesoscopic simulations of optically active materials



[ Y. Yu, M. Nakano, and T. Ikeda, Nature 425 (2003) 145 ]

# Acknowledgements

- **Co-workers**

- Dipl. Chem. Holger Langer
- Dr. Marcus Böckmann
- Prof. Dominik Marx

- **Software**

- CPMD, J. Hutter et al., MPI Stuttgart / IBM Zürich

- **Funding**

- German Science Foundation (DO-768), Volkswagen Foundation

- **Computer resources**

- John von Neumann Institute for Computing, Jülich
- Theoretical Chemistry & Computer Centre Bochum
- Computing Network Northrhine-Westphalia