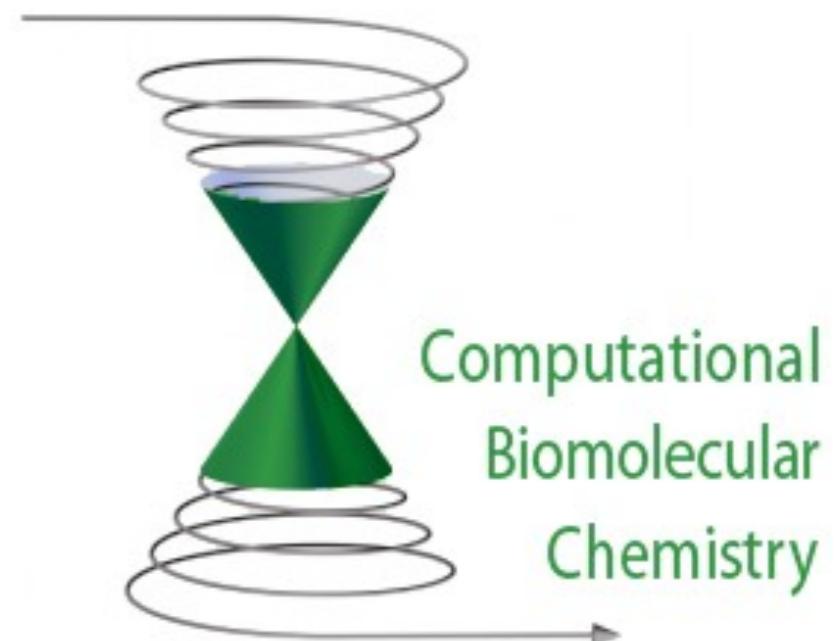


# Advanced Computational Chemistry

## KEMS4I3 (5 op)

Gerrit Groenhof

Department of chemistry & Nanoscience center  
University of Jyväskylä, Finland



<http://wwwuser.gwdg.de/~ggroenh>

# Content & goals of the course

## introduction

me: background, my research interests

you: background, expectations

overview of quantum mechanics: Schrödinger equations

## quick & dirty introduction to quantum chemistry

molecular orbital

self-consistent field

## matrix formulation of quantum mechanics

linear algebra (repeat?)

vector & function spaces

## Born-Oppenheimer approximation

non-crossing rule (diatomics!)

conical intersections (polyatomics)

## electronic wave function of molecules

# Content & goals of the course

electronic wave function of molecules

Hartree-Fock theory (HF)

configuration interaction (CI)

multi-configuration self-consistent field (MCSCF)

Møller-Plesset perturbation theory (MP<sub>x</sub>)

semi empirics (ZDO, MNDO, AMI, PM3)

Quantum Monte Carlo

density functional theory of molecules

Kohn-Sham theory

molecular mechanics

throw away electrons

hybrid quantum chemistry/molecular mechanics

molecular properties

# Content & goals of the course

molecular properties

potential energy surfaces

gradients

vibrational modes

spectra

free energy surfaces

# Goals of the course

Gain working knowledge of computational chemistry

understand papers

know limitations

choose level of theory for problem

getting the right answer for the right reason

set up and analysis of calculations

trouble-shooting calculations

develop critical mind (if not already)

Make you aware of power of computation

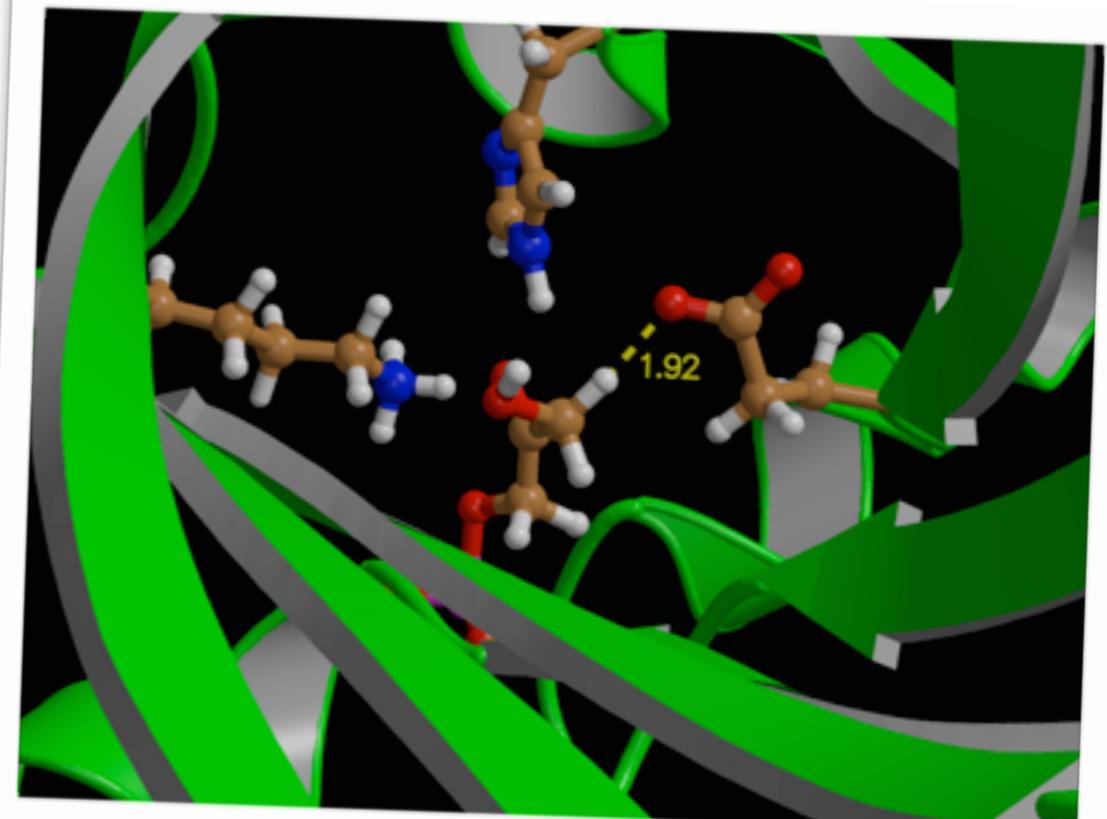
Bsc/Msc/PhD projects

# research interests

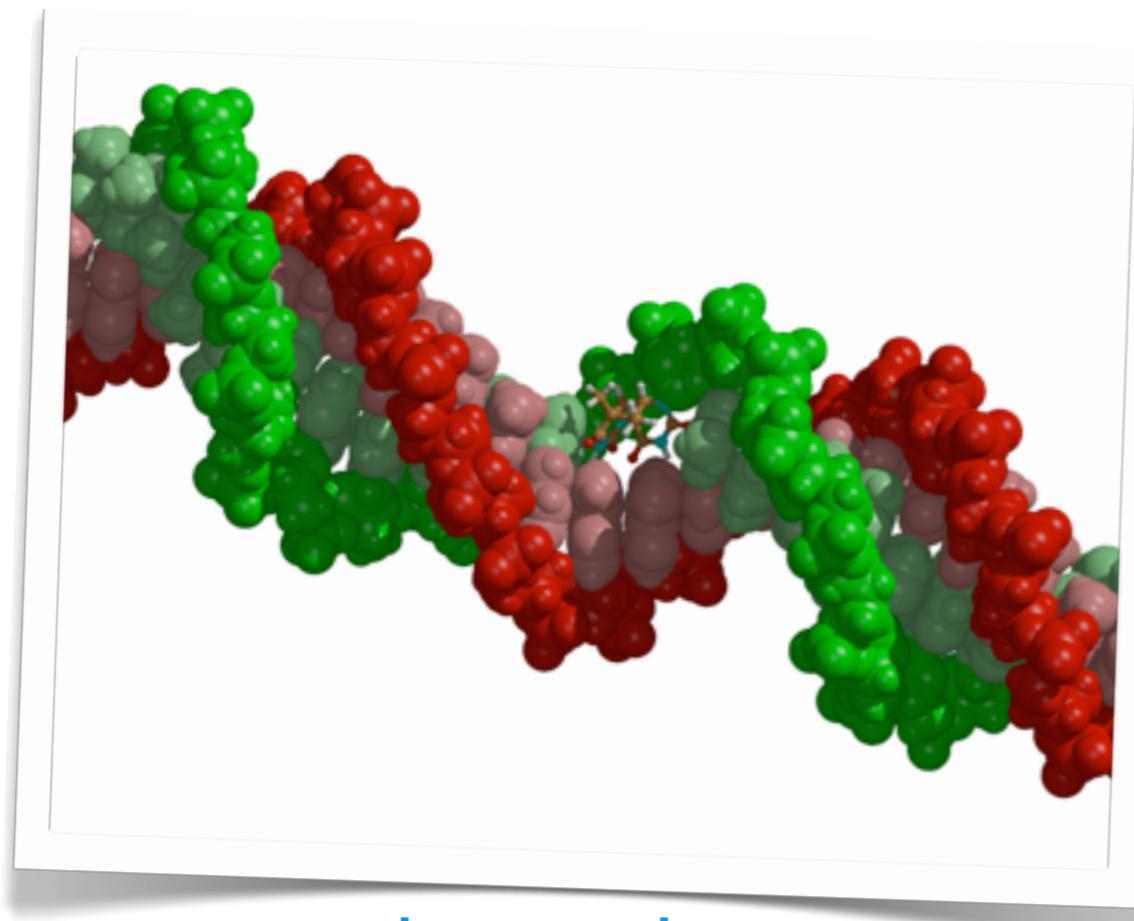
understand reactivity

control reactivity

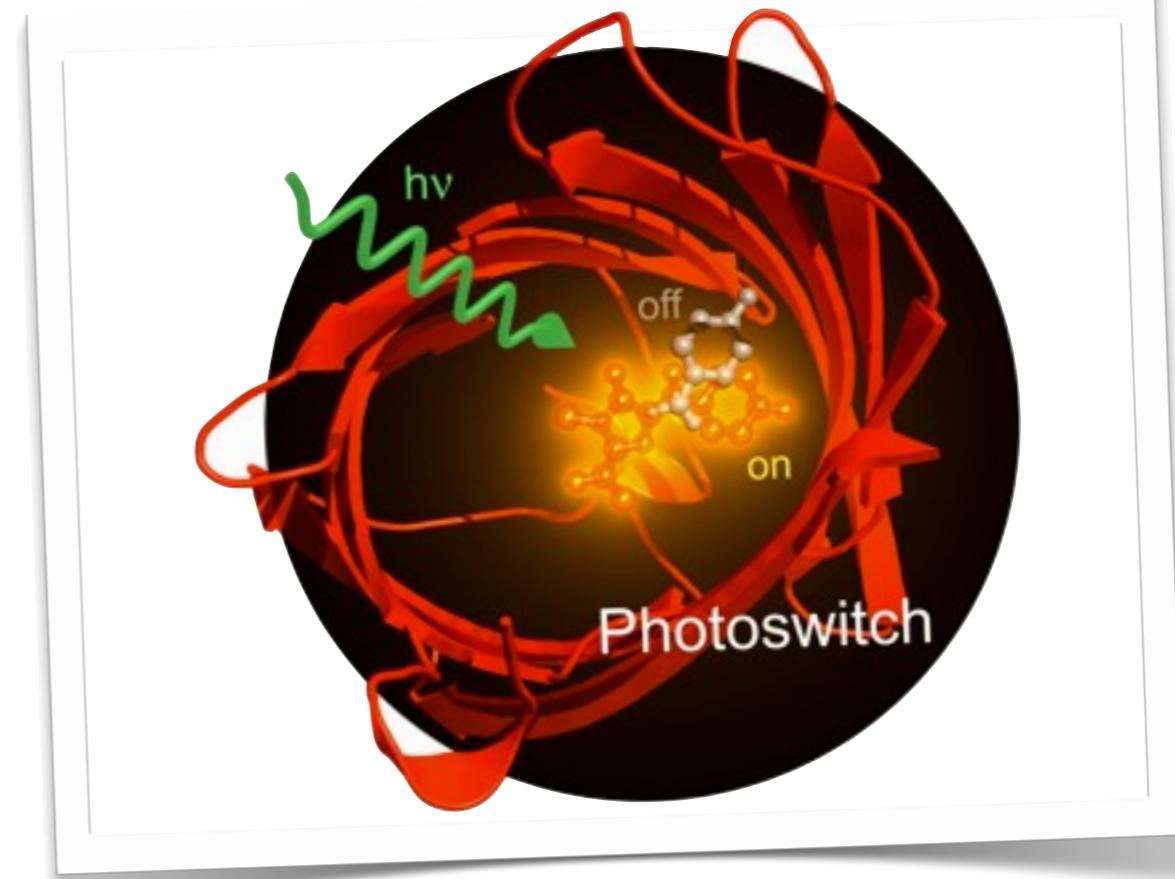
some examples



enzyme catalysis



radiation damage



photochemistry/photobiology

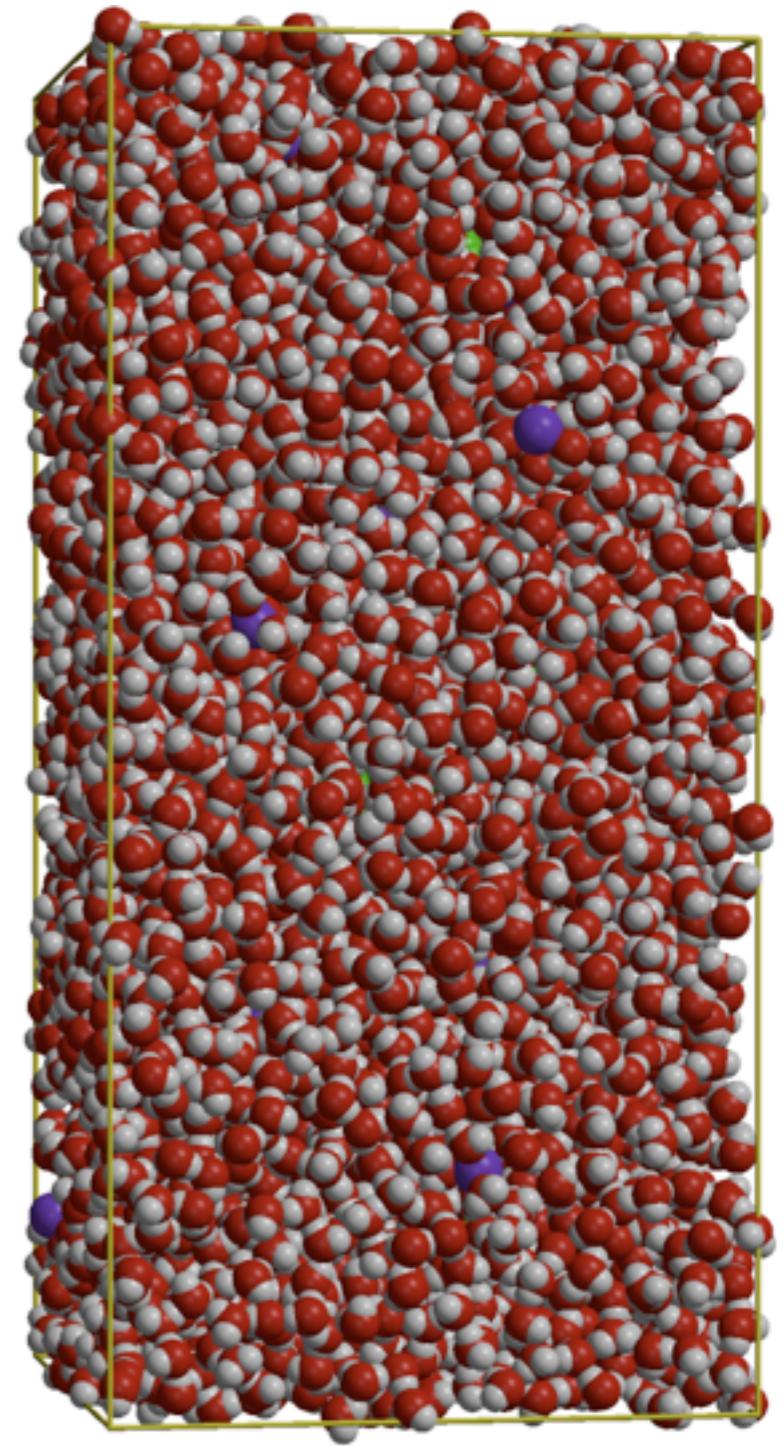
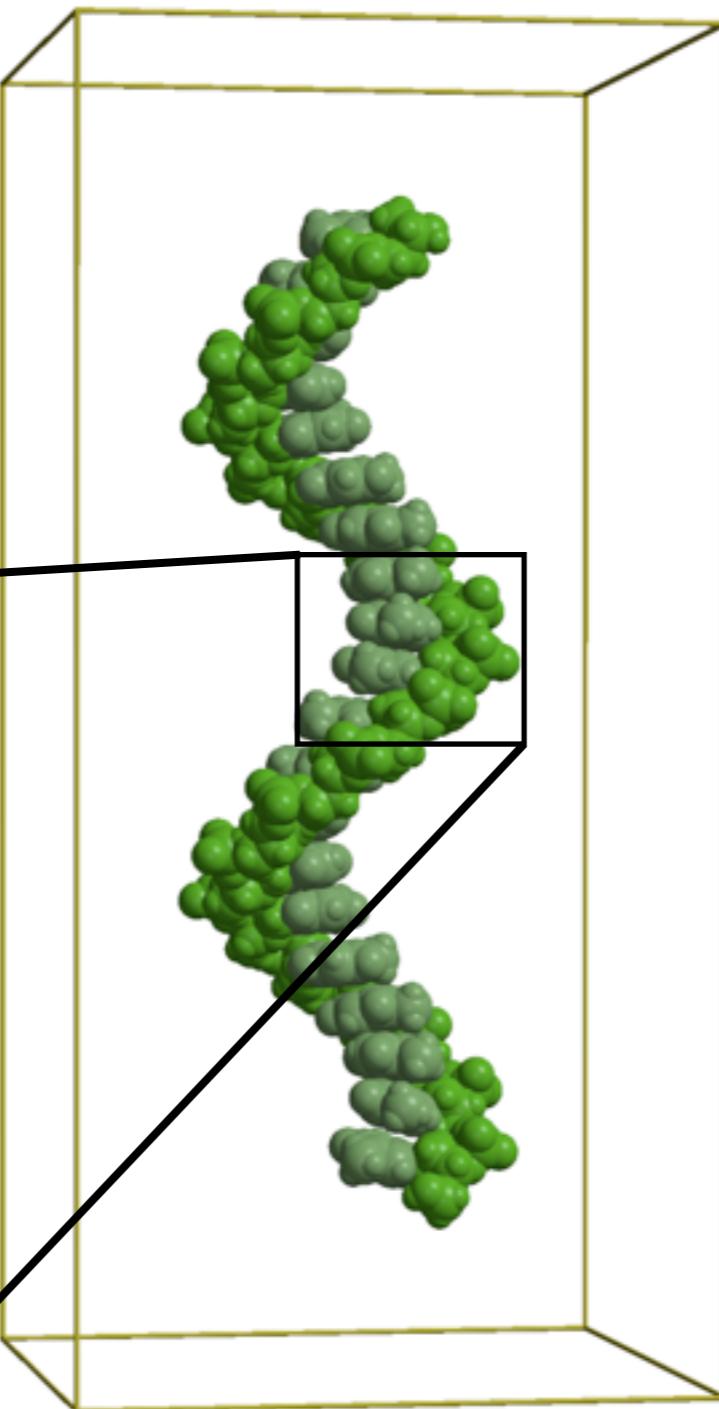
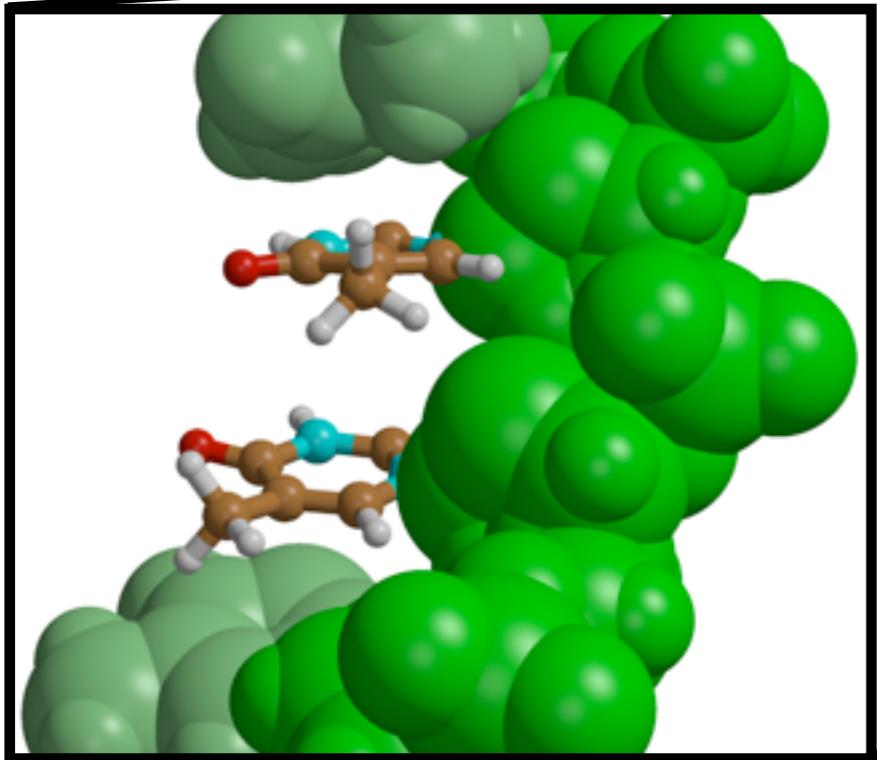
# Radiation damage: UV absorption in DNA

thymine dimerization

base stack (TT)

CASSCF(8,8)/6-31G

diabatic surface hop

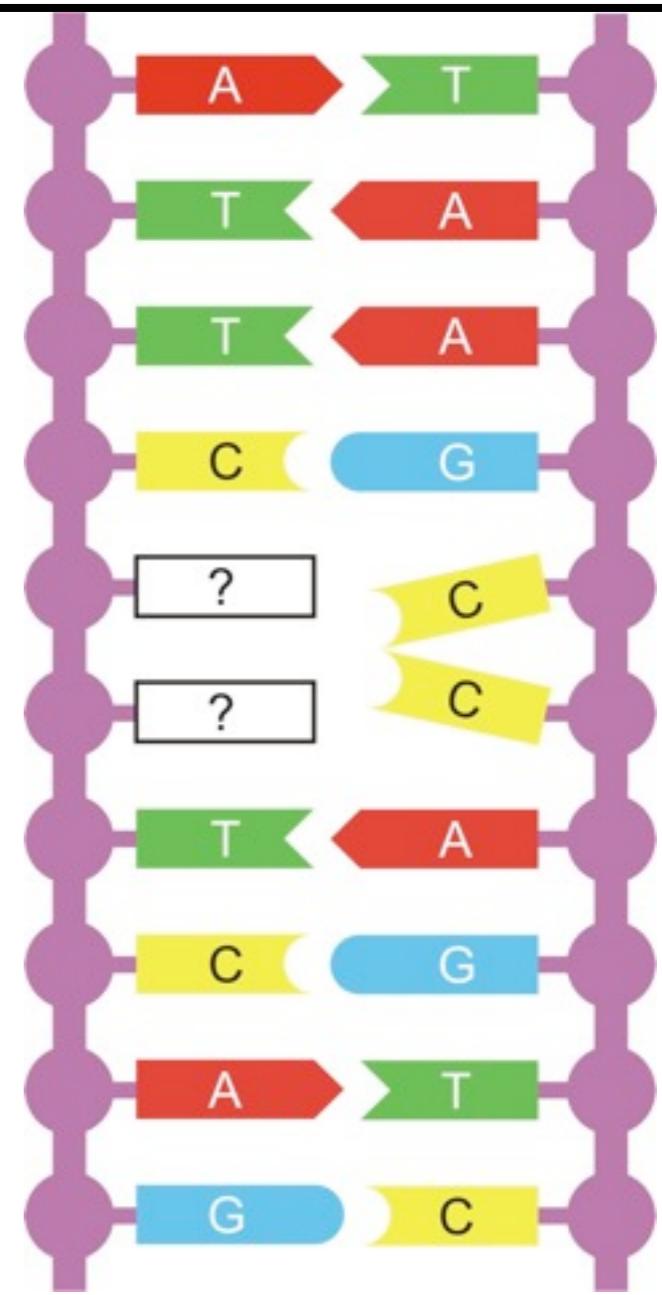


# Radiation damage: UV absorption in DNA

thymine dimerization

cell dead?

mutation?

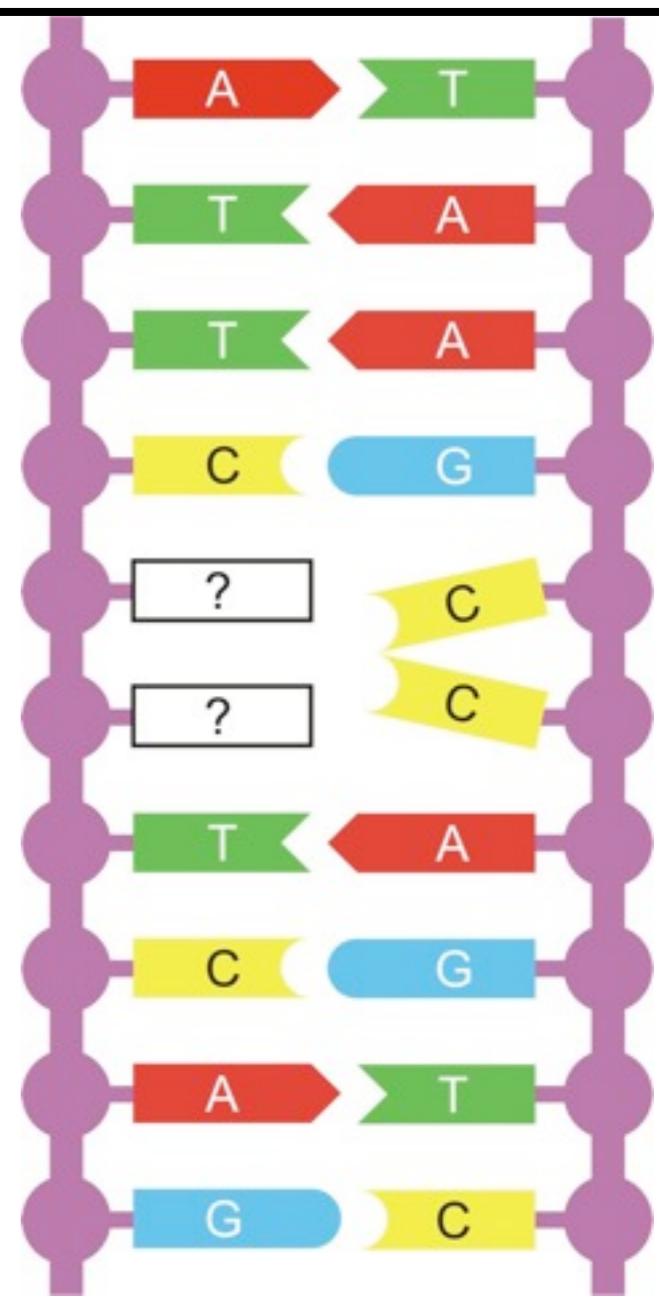
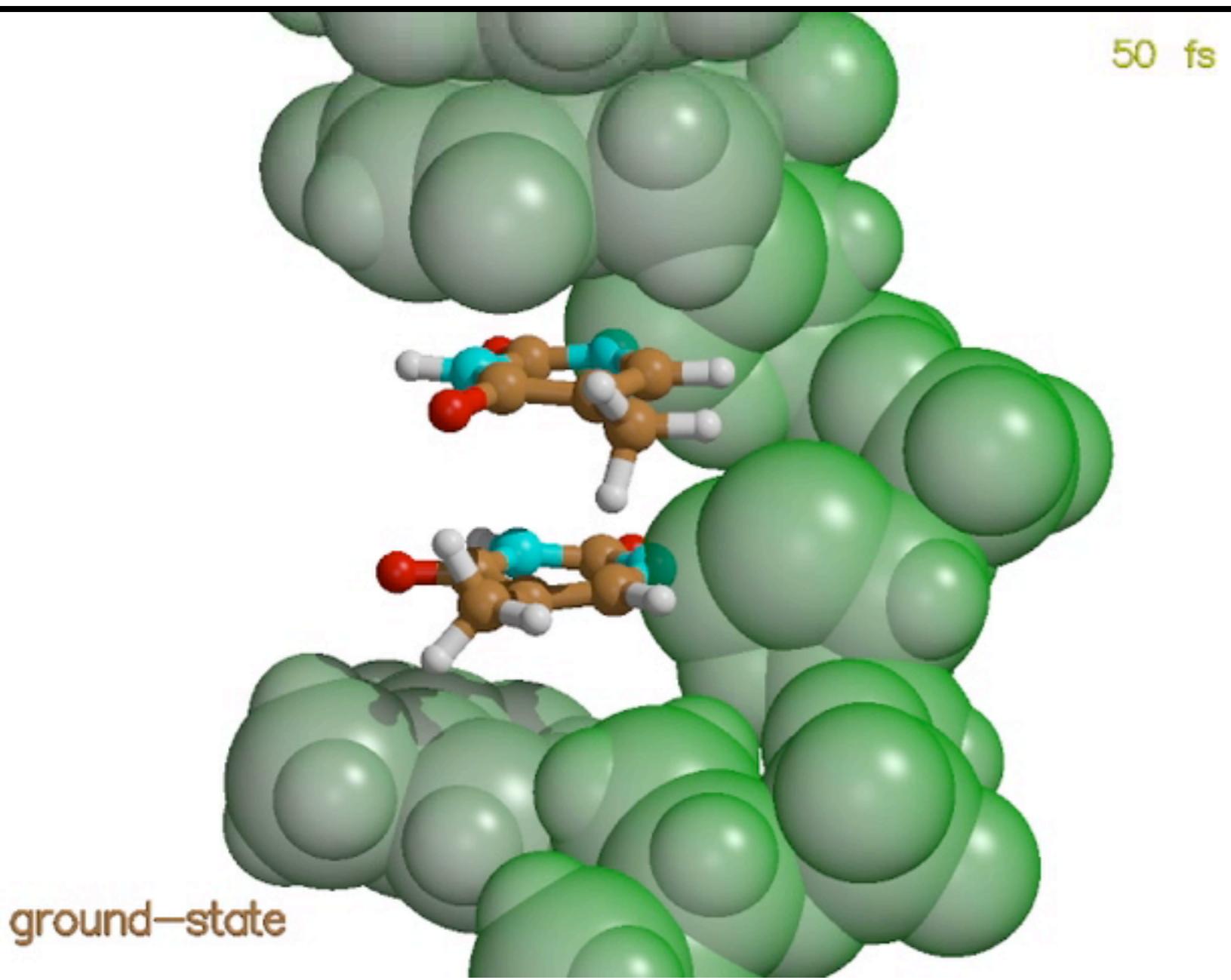


# Radiation damage: UV absorption in DNA

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cell dead?

mutation?



ground-state

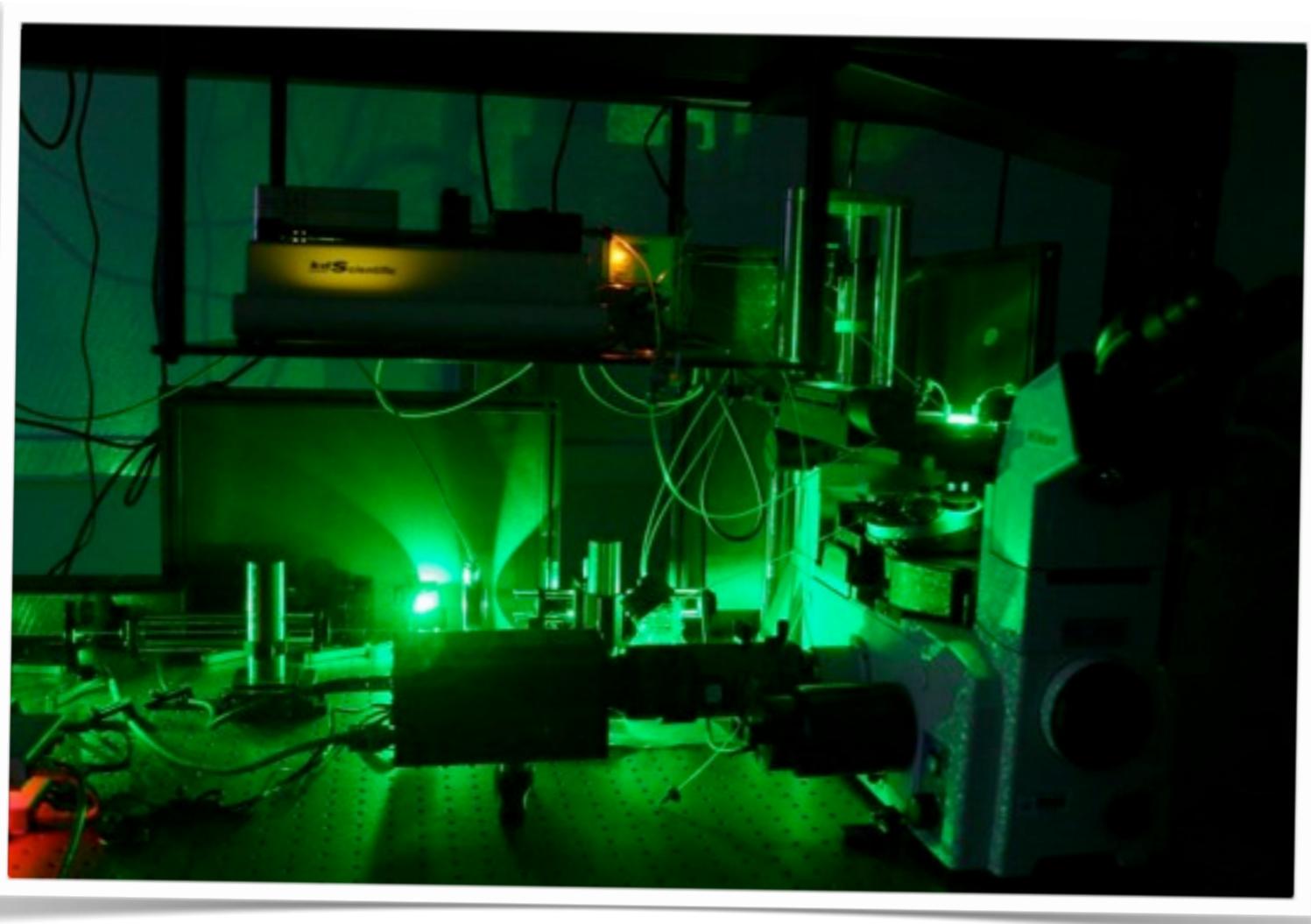
# Understanding & controlling chemistry

experiment

provides data

time-resolved spectroscopy (pump-probe)

UV/vis, IR/midIR, x-ray, ...



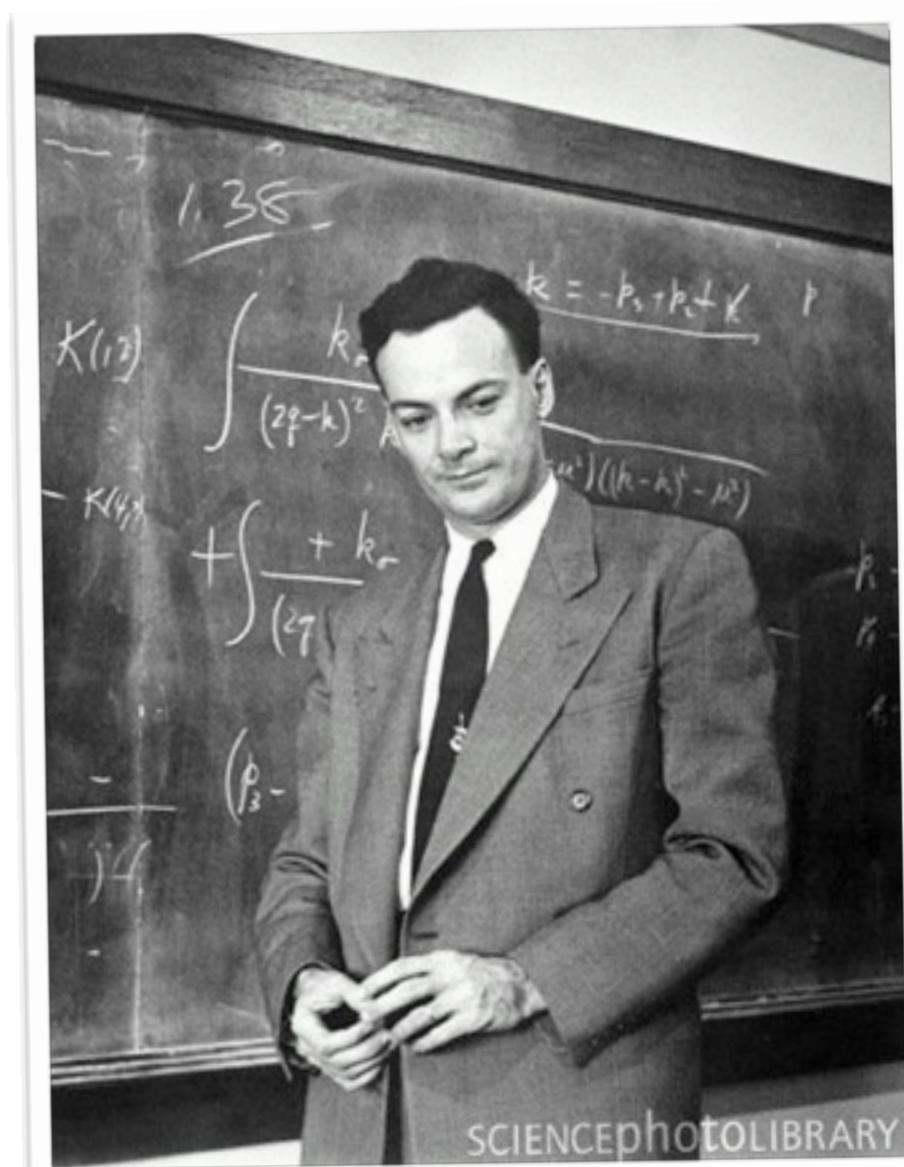
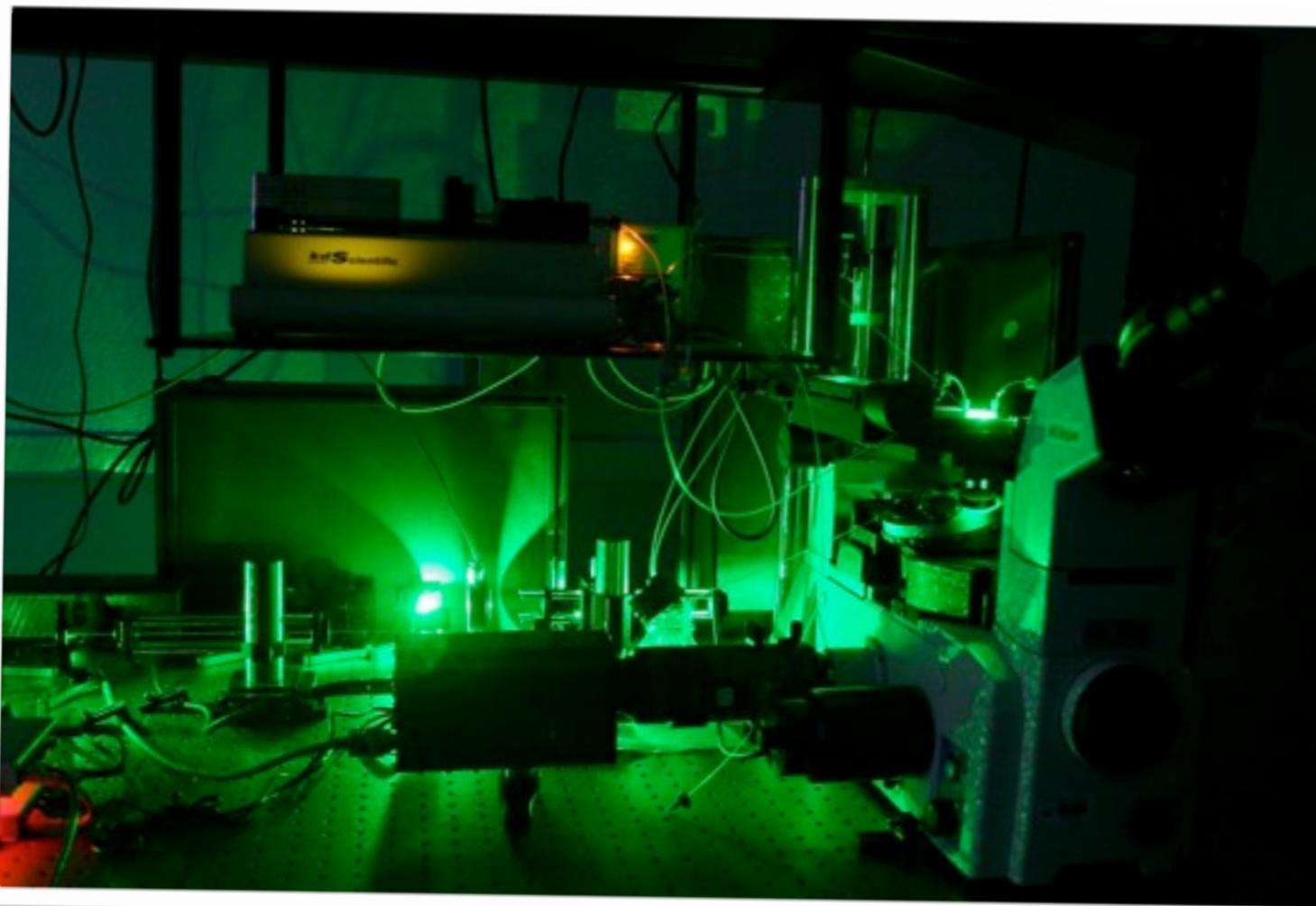
# Understanding & controlling chemistry

theory

provides concepts

explain

predict



SCIENCEphotOLIBRARY

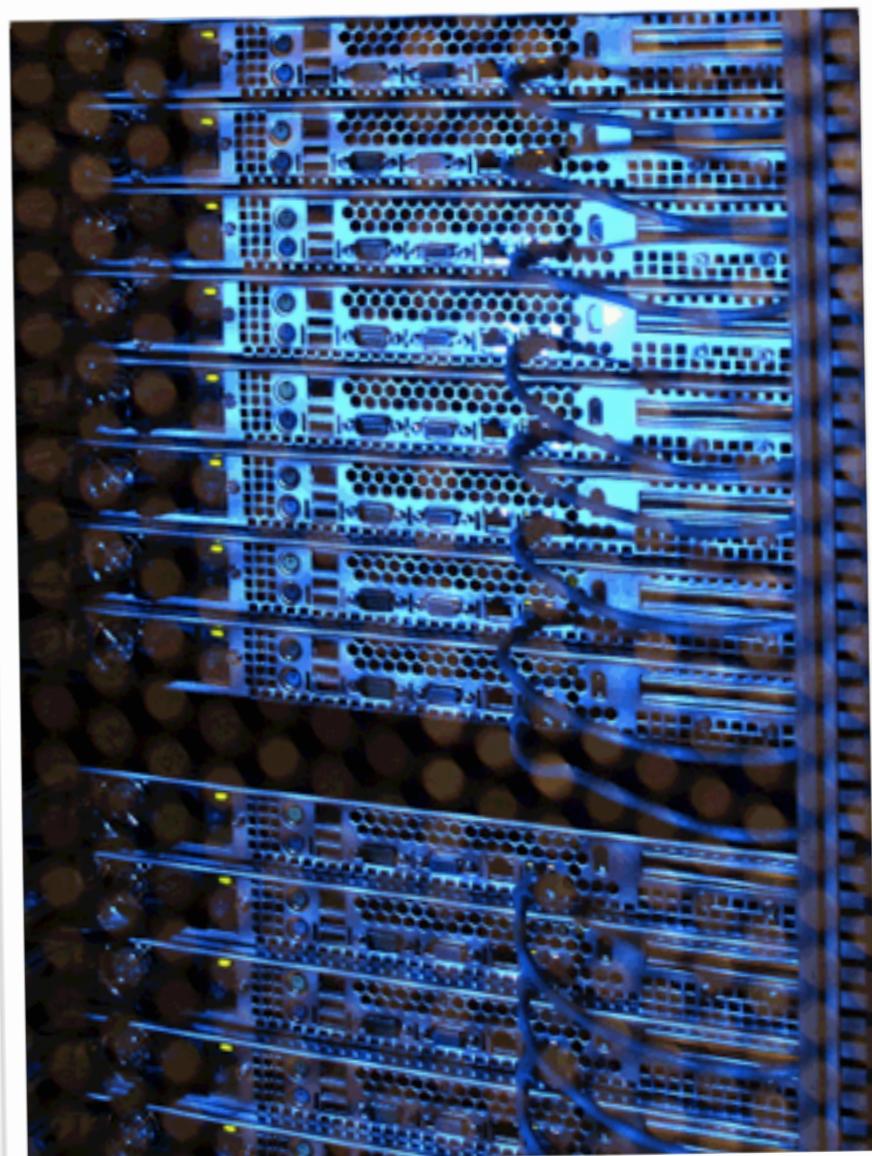
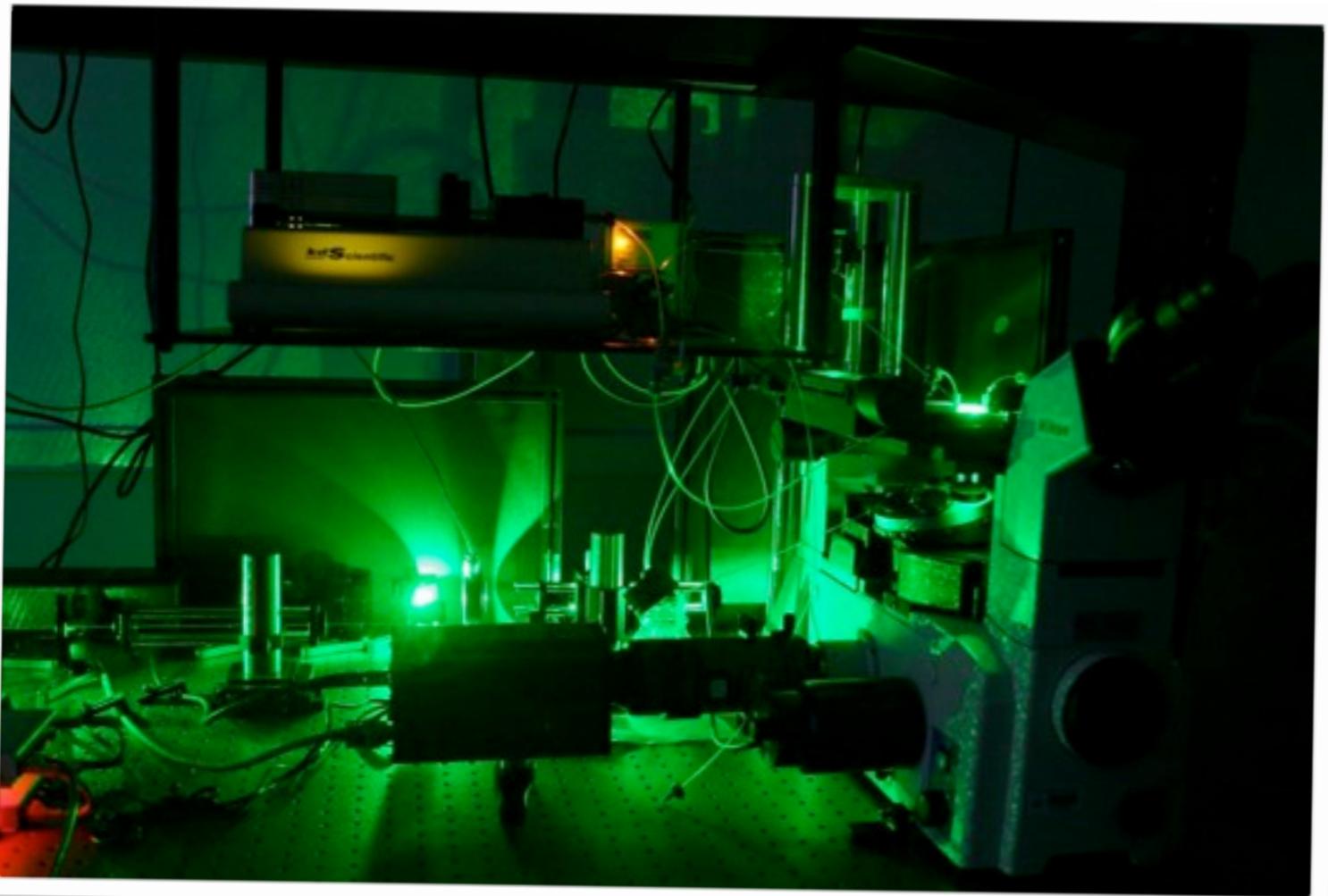
# Understanding & controlling chemistry

computation & simulation

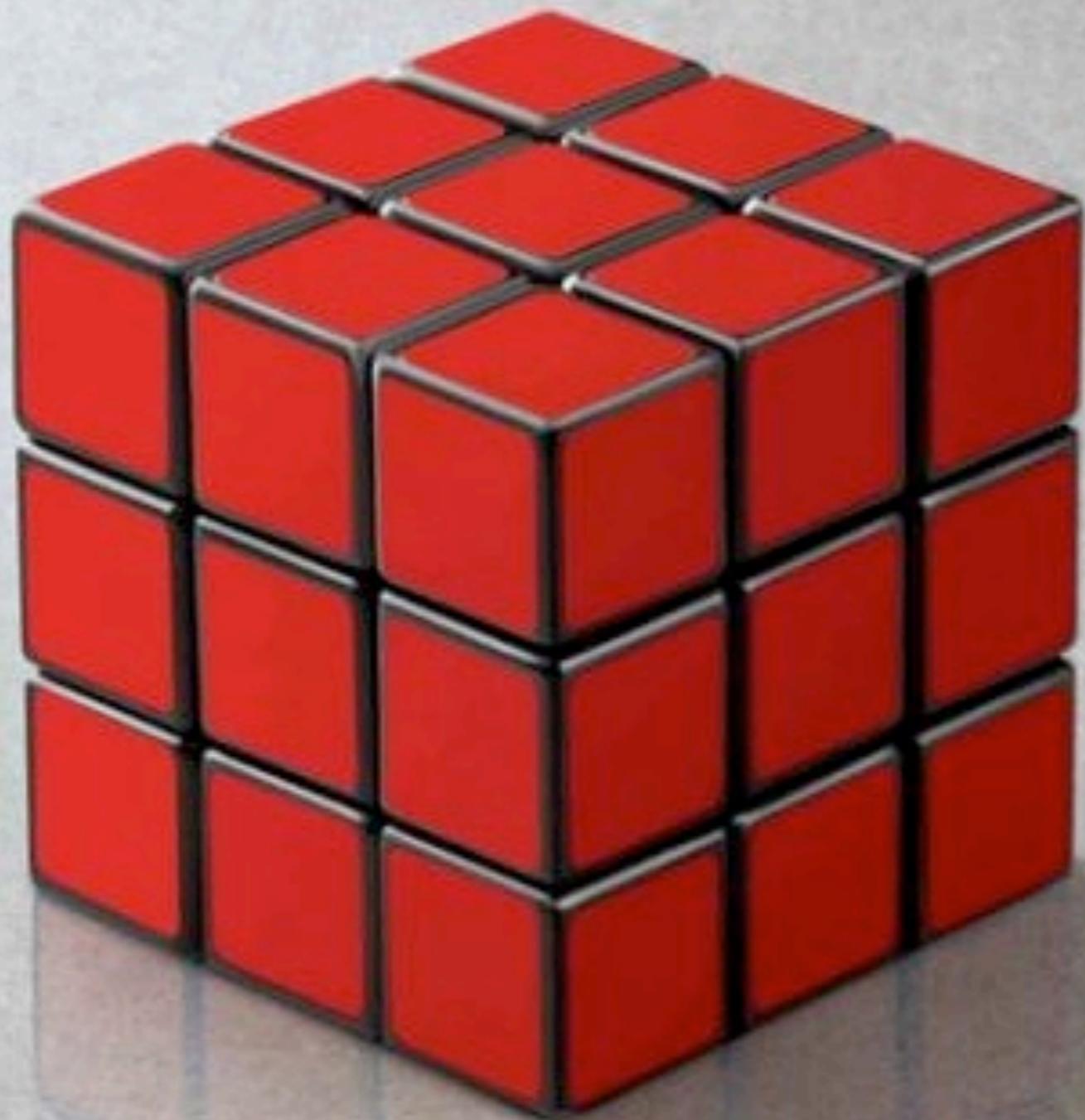
provides data (predictions)

like experiment (in my view)

fills gaps in time & length scale



Try to keep it simple.....



... and computable

# Physics of chemistry

## building blocks

electrons (-)

nuclei (+)

## theoretical foundations

electrostatic interactions: Coulomb's law

quantum mechanics: Schrödinger equation

## properties to calculate

static: reaction energy, structure, spectra

dynamic: trajectories, thermodynamics

# Quantum mechanics

small particles

wave/particle duality (de Broglie)

$$\lambda = \frac{h}{mv}$$

energy quantization (Planck)

# Foundations of quantum mechanics

classical mechanics

observables are presented by functions

quantum mechanics

observables are presented by operators

choice of operators determines the QM *representation*

position representation

$$\hat{x} = x \times$$

$$\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x}$$

momentum representation

$$\hat{p} = p \times$$

$$\hat{x} = -\frac{\hbar}{i} \frac{\partial}{\partial p}$$

# postulates of quantum mechanics

I. state of the system is given by wave function

$$\Psi(x, y, z, t)$$

# postulates of quantum mechanics

1. state of the system is given by wave function

$$\Psi(x, y, z, t)$$

2. all observables are represented by operators commuting as

$$[\hat{x}, \hat{p}_x] = i\hbar$$

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1. state of the system is given by wave function

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$$[\hat{x}, \hat{p}_x] = i\hbar$$

recipe for constructing operators in quantum mechanics

write classical expression in terms of position coordinates  $x$  and linear momentum  $p_x$

replace positions coordinates by multiplication

$$x \rightarrow \hat{x} = x \times$$

replace momentum by coordinates by differentiation

$$p_x \rightarrow \hat{p}_x = \frac{\hbar}{i} \frac{\partial}{\partial x}$$

# postulates of quantum mechanics

1. state of the system is given by wave function

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2. all observables are represented by operators commuting as

$$[\hat{x}, \hat{p}_x] = i\hbar$$

3. mean value of observable is expectation value

$$\langle \hat{\Omega} \rangle = \frac{\int_{-\infty}^{\infty} \Psi^* \hat{\Omega} \Psi d\mathbf{r}}{\int_{-\infty}^{\infty} \Psi^* \Psi d\mathbf{r}}$$

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4. probability distribution interpretation (Bohr)

$$p(\mathbf{r}, t) = \Psi(\mathbf{r}, t)^* \Psi(\mathbf{r}, t) d\mathbf{r}$$

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5. Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi = \hat{H} \Psi$$

# Quantum Chemistry in a nutshell

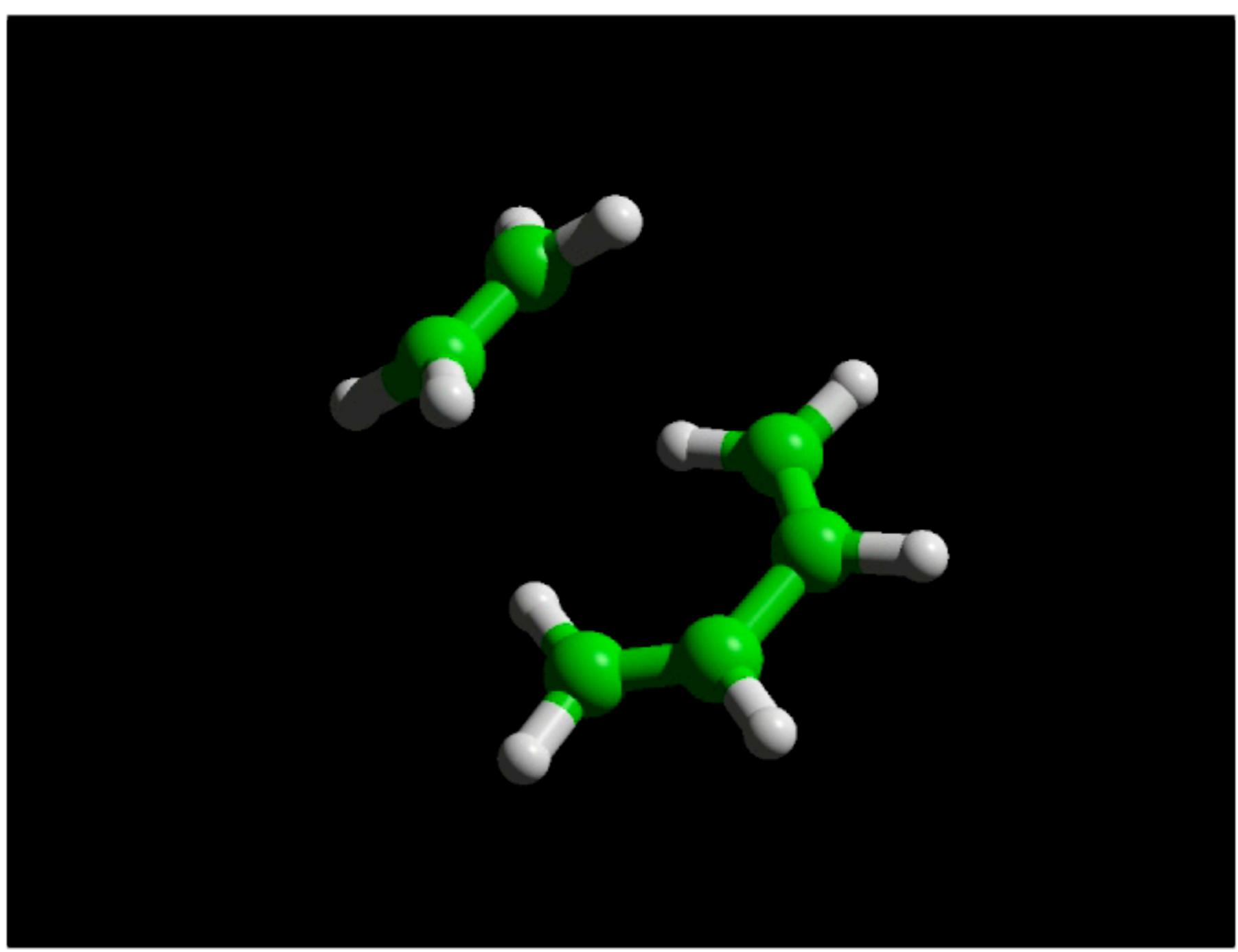
goal

get a feel for what computer is doing

# Quantum Chemistry in a nutshell

goal

get a feel for what computer is doing



# Chemistry on a computer

## chemical reactions

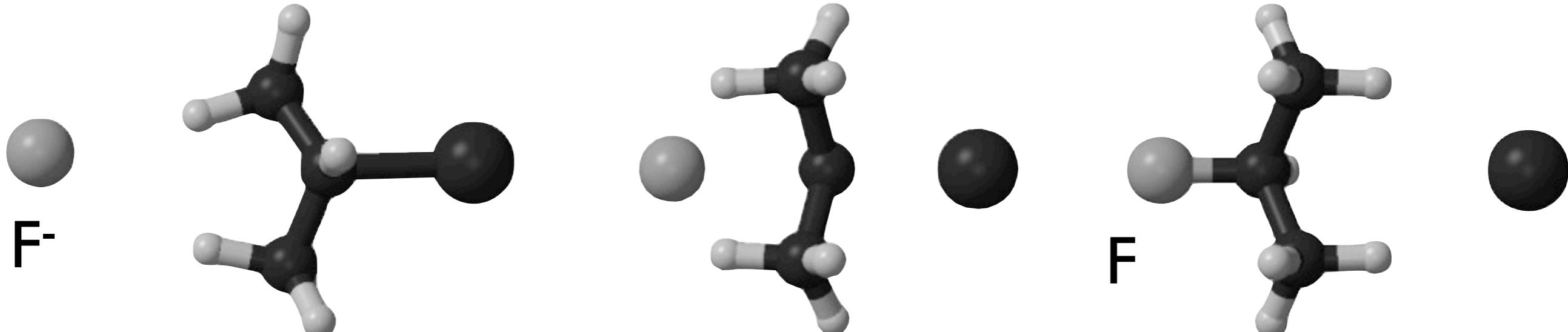
substitution

understand & predict

reactant

transition state

product



$\text{Cl}^-$       0 kJ/mol      17 kJ/mol      -204 kJ/mol

$\text{Br}^-$       0 kJ/mol      65 kJ/mol      -181 kJ/mol

# Chemistry on a computer

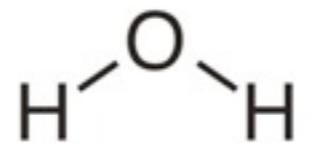
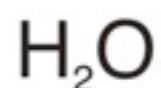
chemistry

electrons (-)

nuclei (+)

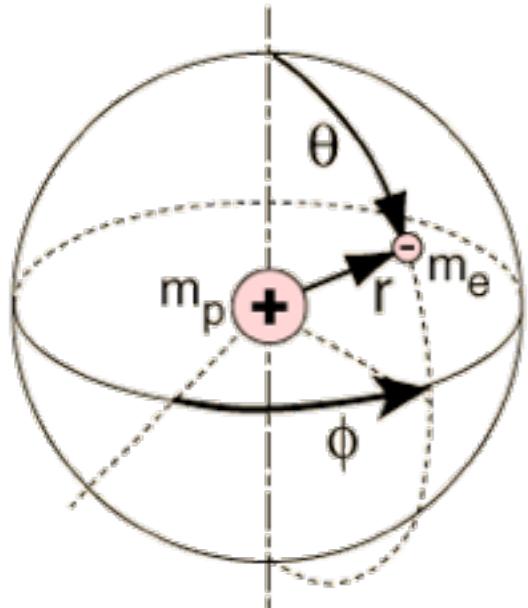
molecules

water (2 protons, 1 oxygen, 10 electrons)



90% of electrons

# Recall from quantum physics: Hydrogen atom



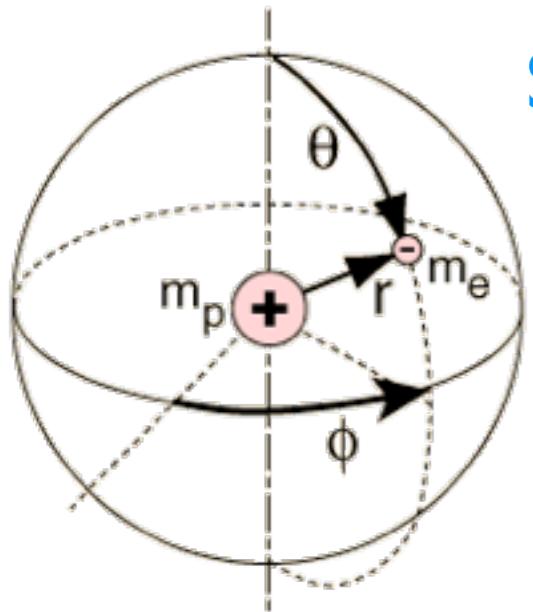
Spherical coordinates

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

# Recall from quantum physics: Hydrogen atom



Spherical coordinates

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

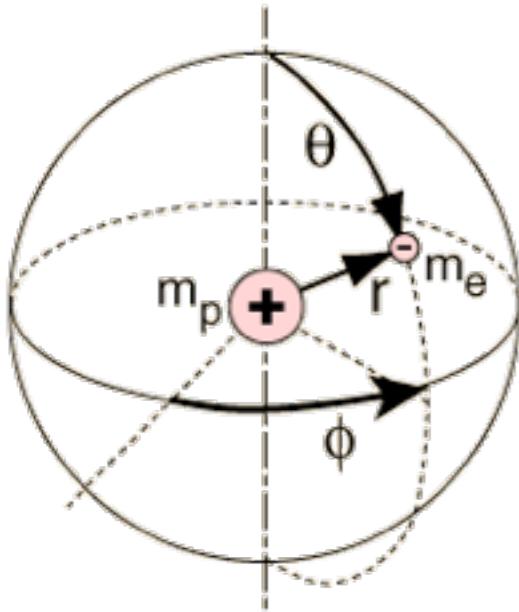
$$z = r \cos \theta$$

Schrödinger equation

$$H\psi(x, y, z) = E\psi(x, y, z)$$

$$H = -\frac{\hbar^2}{2m_e} \nabla^2 + \frac{Ze^2}{4\pi\epsilon_0 r}$$

# Recall from quantum physics: Hydrogen atom



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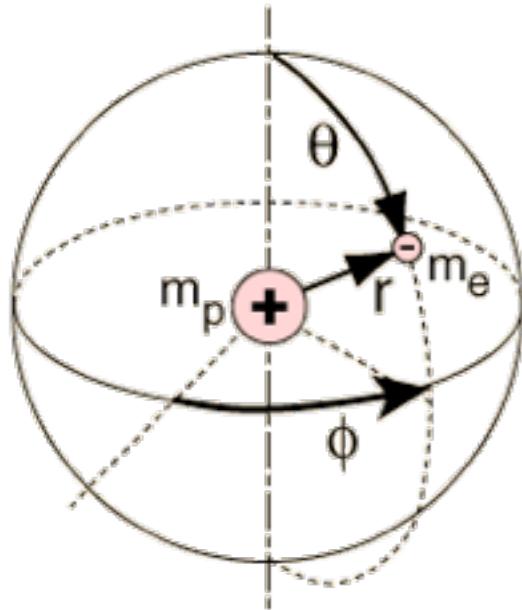
$$H = -\frac{\hbar^2}{2m_e} \nabla^2 + \frac{Ze^2}{4\pi\epsilon_0 r}$$

Wave function

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi)$$

$$\psi_{nlm}(r, \theta, \phi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n((n+l)!)^3}} \exp\left[-\frac{r}{na_0}\right] \left(\frac{2r}{na_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) Y_{lm}(\theta, \phi)$$

# Recall from quantum physics: Hydrogen atom

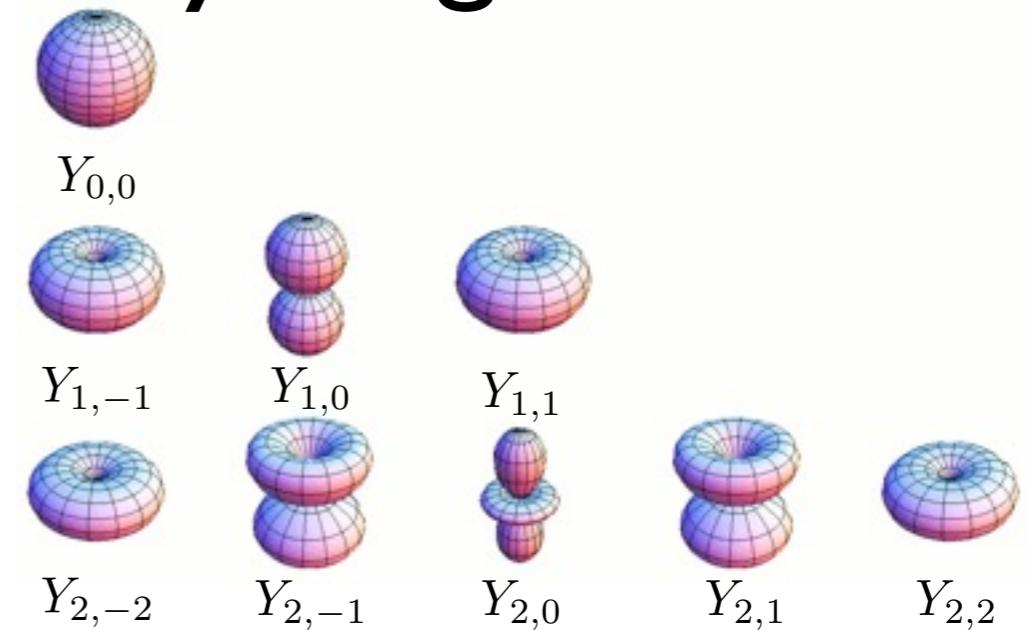


Spherical coordinates

$$x = r \sin \theta \cos \phi$$

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$$z = r \cos \theta$$



Schrödinger equation

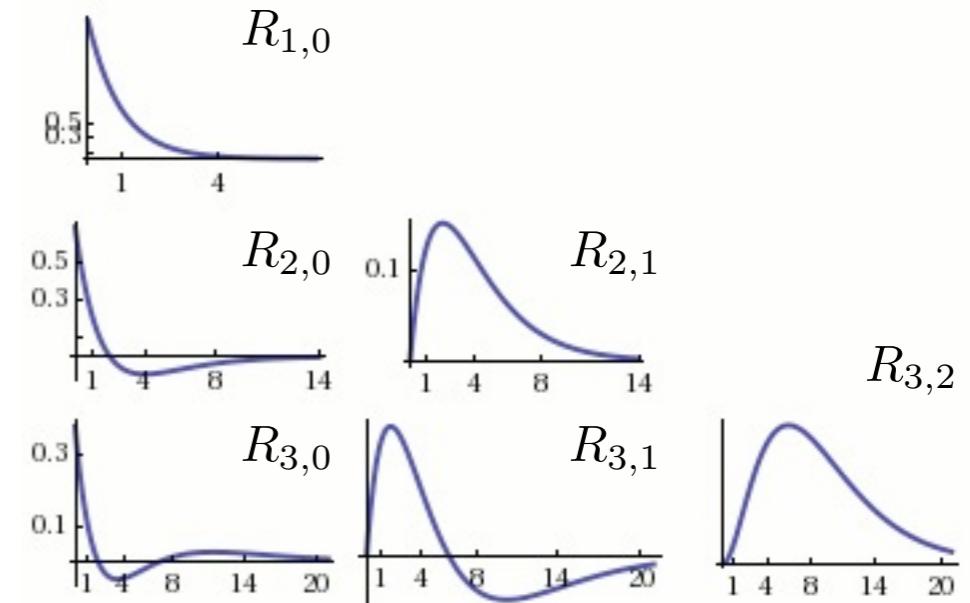
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Wave function

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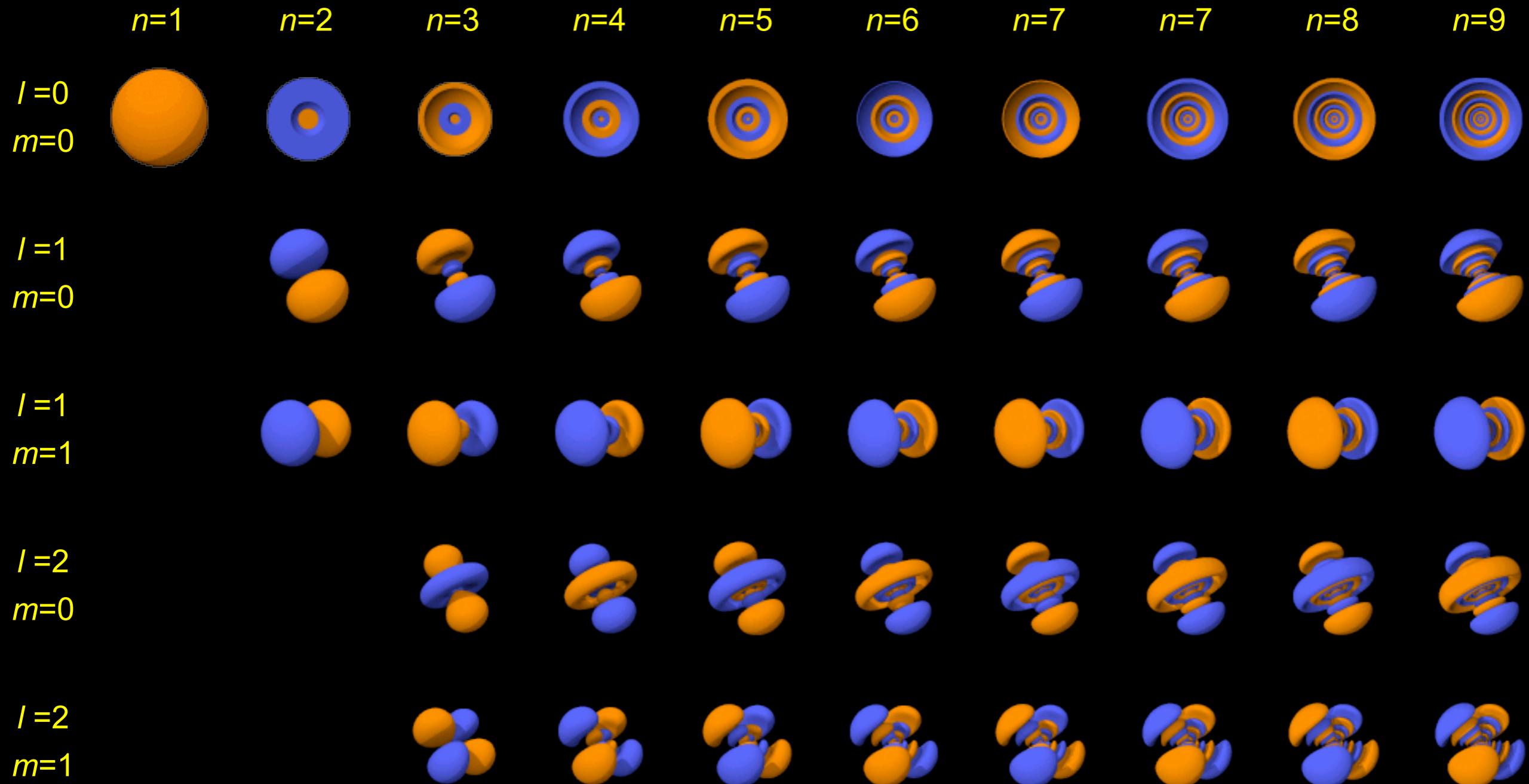
Spherical harmonics



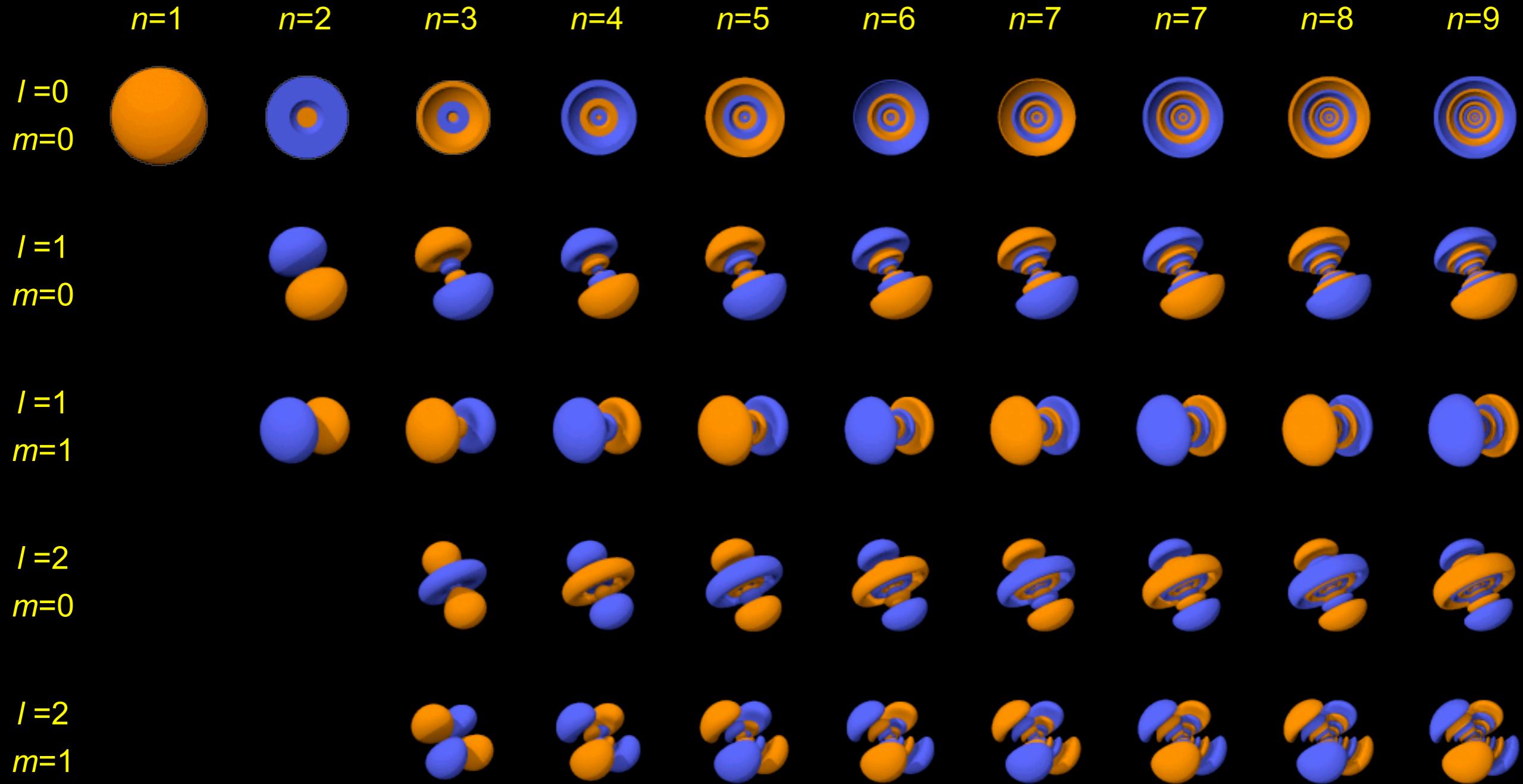
Associated Laguerre-Polynomials

$$\psi_{nlm}(r, \theta, \phi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n((n+l)!)^3}} \exp\left[-\frac{r}{na_0}\right] \left(\frac{2r}{na_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) Y_{lm}(\theta, \phi)$$

# Atomic orbitals



# Atomic orbitals



Complete set: any function can be expanded in  $\psi(r, \theta, \phi)$ :

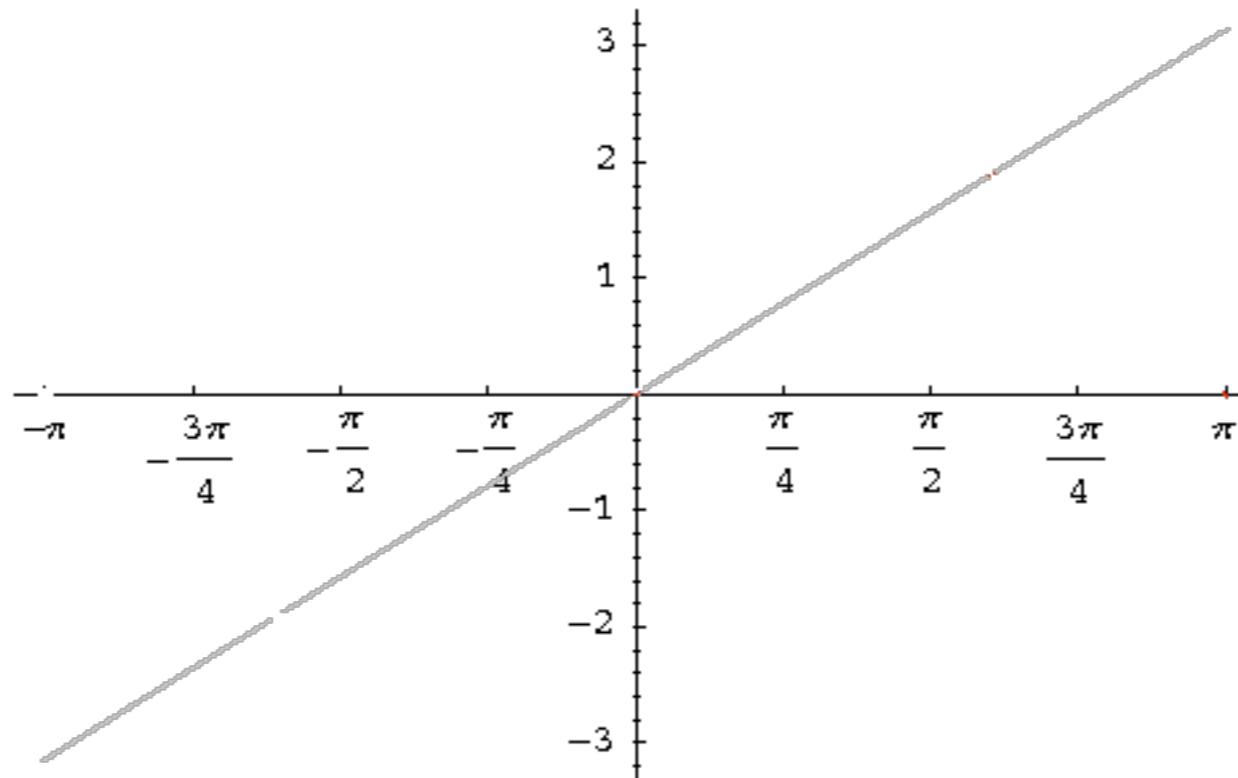
$$\Phi(r, \theta, \phi) = \sum_i \sum_{n=1}^{n-1} \sum_{l=0}^{m=+l} \sum_{m=-l} c_{inlm} \psi_{nlm}(r, \theta, \phi)$$

# Recall from Mathematics: Fourier Series

Linear combination of Cosine and Sine functions

example

$$f(x) = x \quad -\pi \leq x \leq \pi$$



# Recall from Mathematics: Fourier Series

Linear combination of Cosine and Sine functions

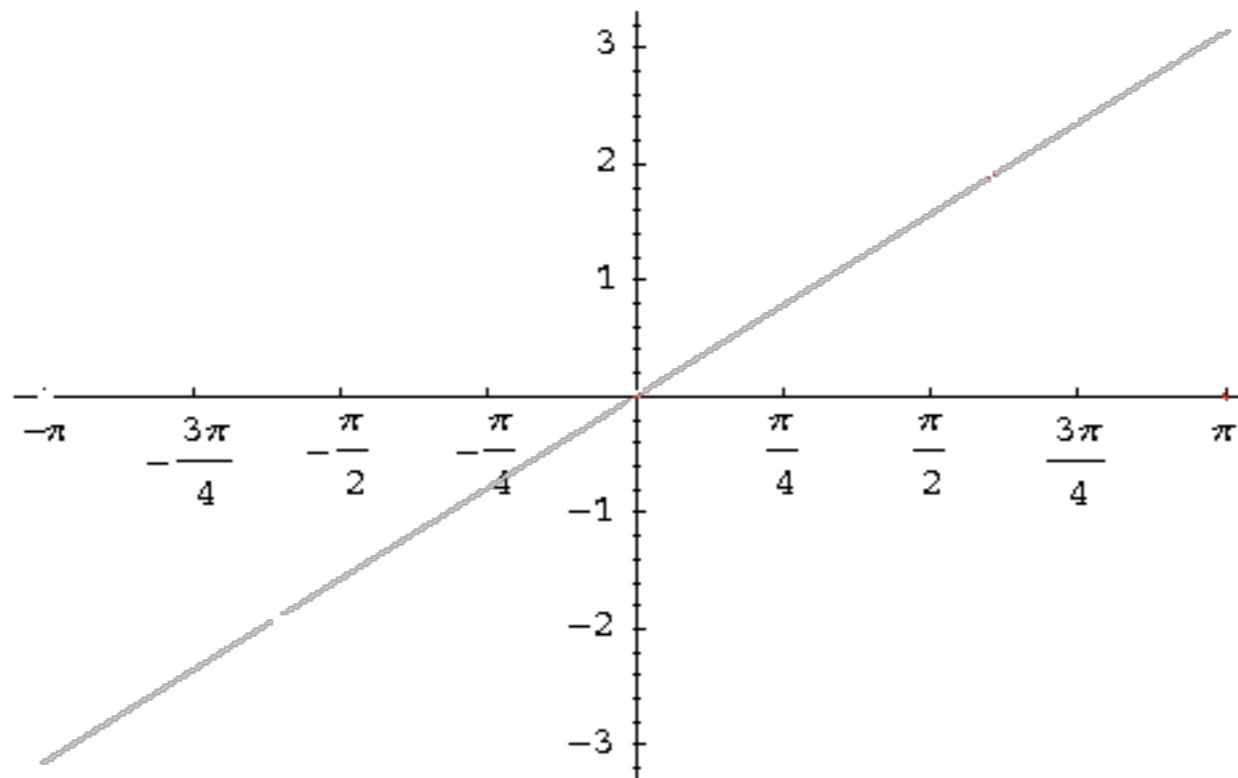
example

$$f(x) = x \quad -\pi \leq x \leq \pi$$

Fourier series

$$f(x) = \sum_{n=1}^{\infty} a_n \sin[nx] \quad a_n = \frac{2}{n}(-1)^{n+1}$$

$$f(x) \approx 2 \left( \sin[x] - \frac{1}{2} \sin[2x] + \frac{1}{3} \sin[3x] - \frac{1}{4} \sin[4x] + \dots \right)$$



# Recall from Mathematics: Fourier Series

Linear combination of Cosine and Sine functions

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# Recall from Mathematics: Fourier Series

Linear combination of Cosine and Sine functions

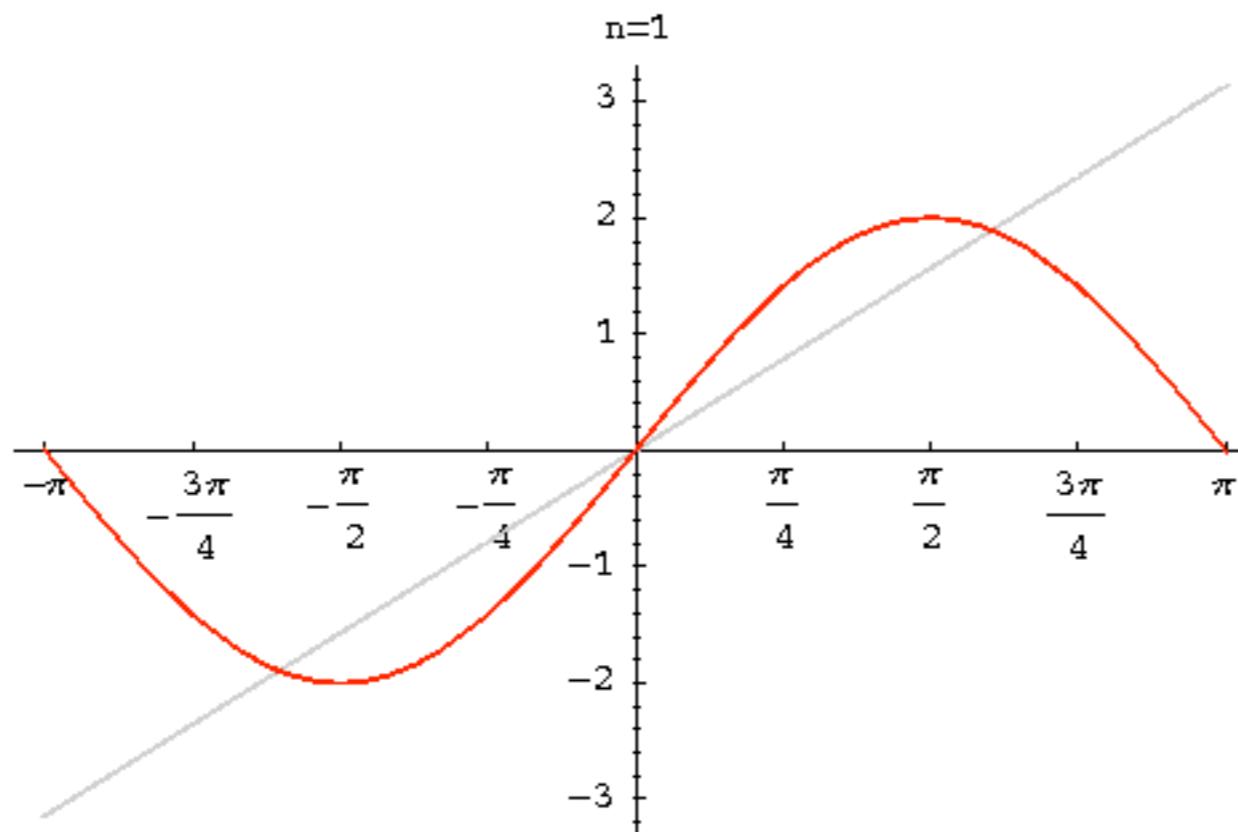
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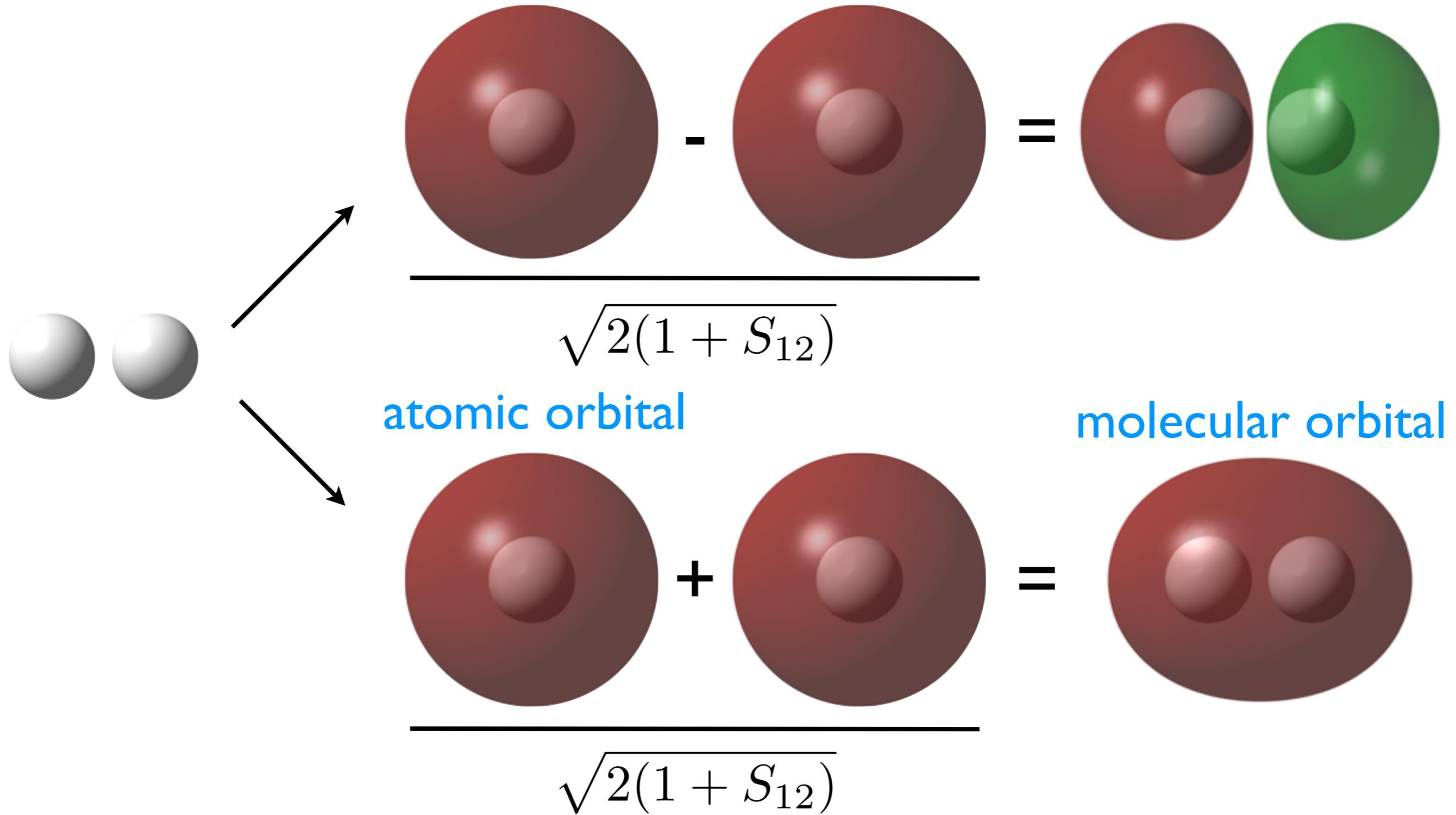
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# Hydrogen molecule

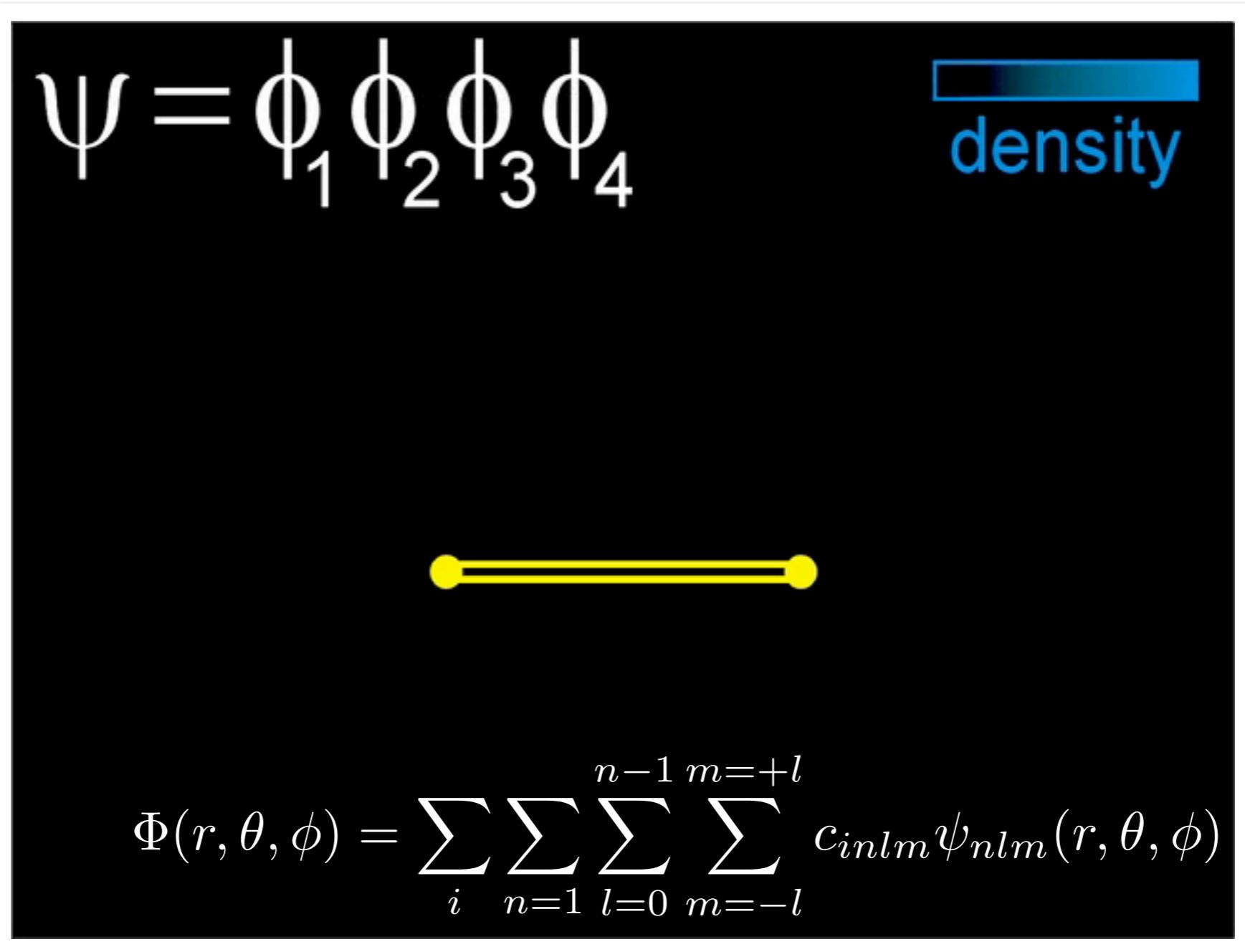
Linear Combination of single hydrogen orbitals



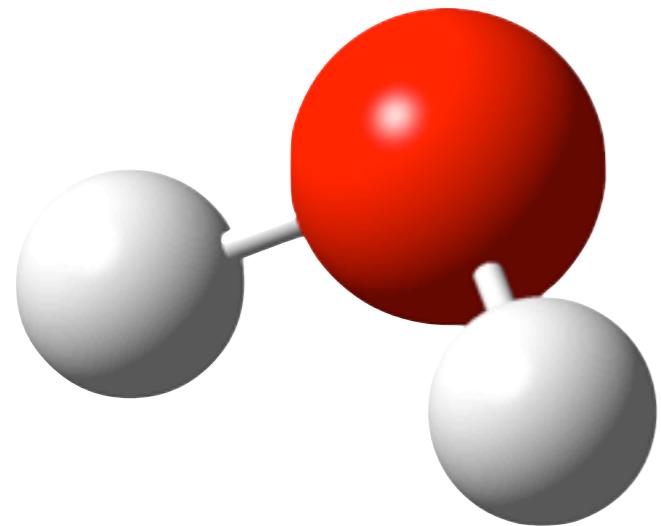
# simplified Hartree-Fock theory

mean field approach

vary orbitals until self-consistency (SCF)



# Water molecule



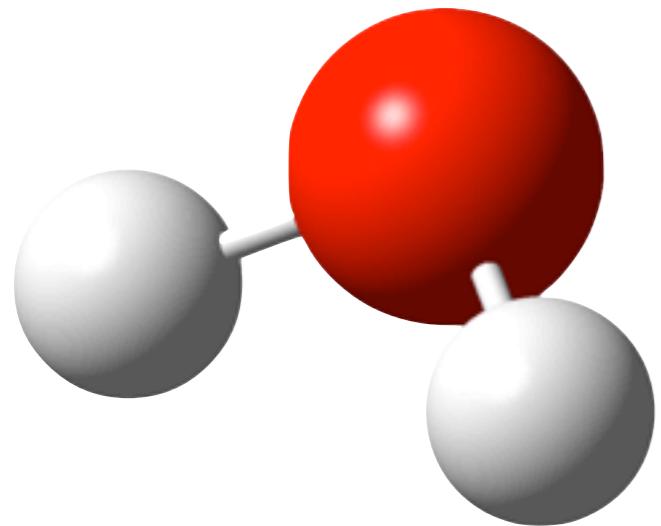
2 H<sup>+</sup>

1 O<sup>8+</sup>

10 electrons

10 molecular orbitals

# water molecule

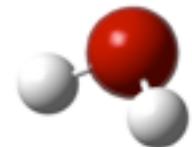
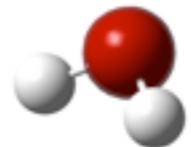
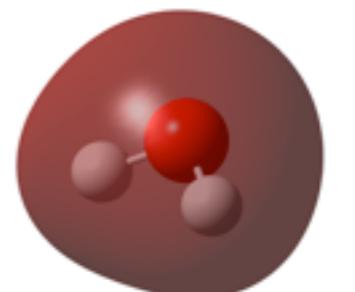
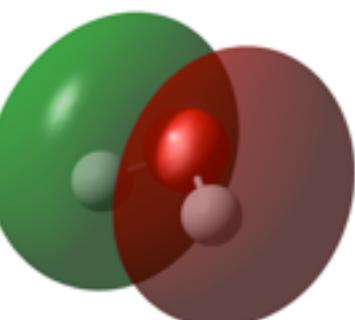
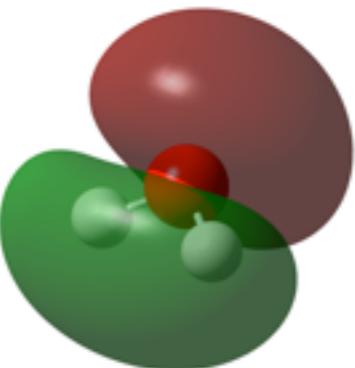
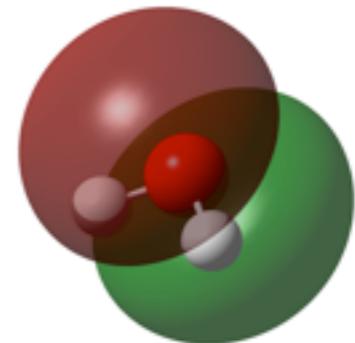
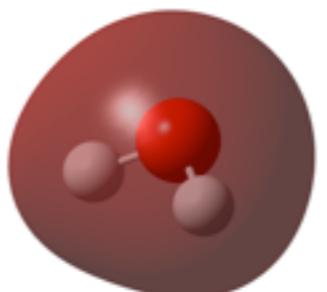
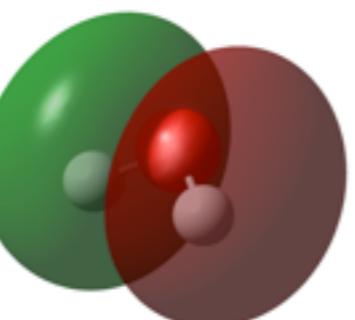
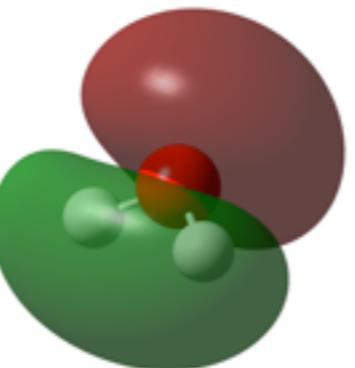
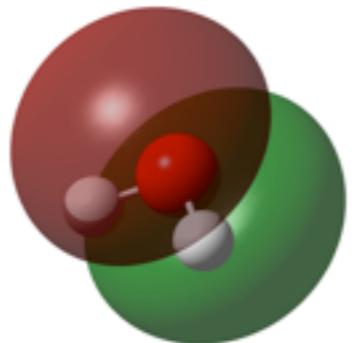


2 H<sup>+</sup>

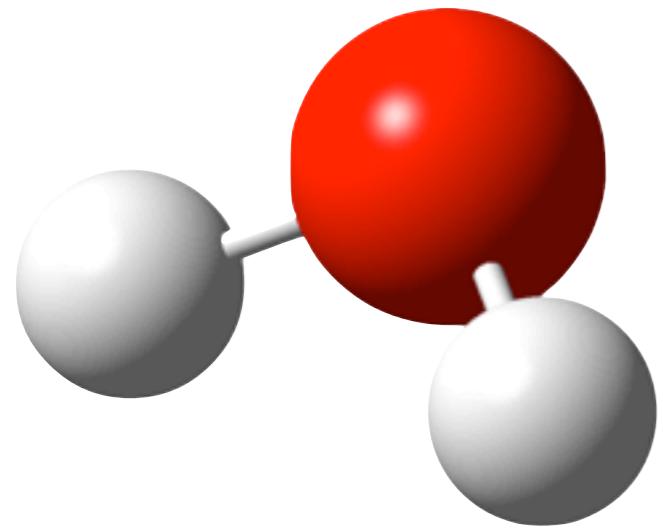
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10 electrons

10 molecular orbitals



# water molecule

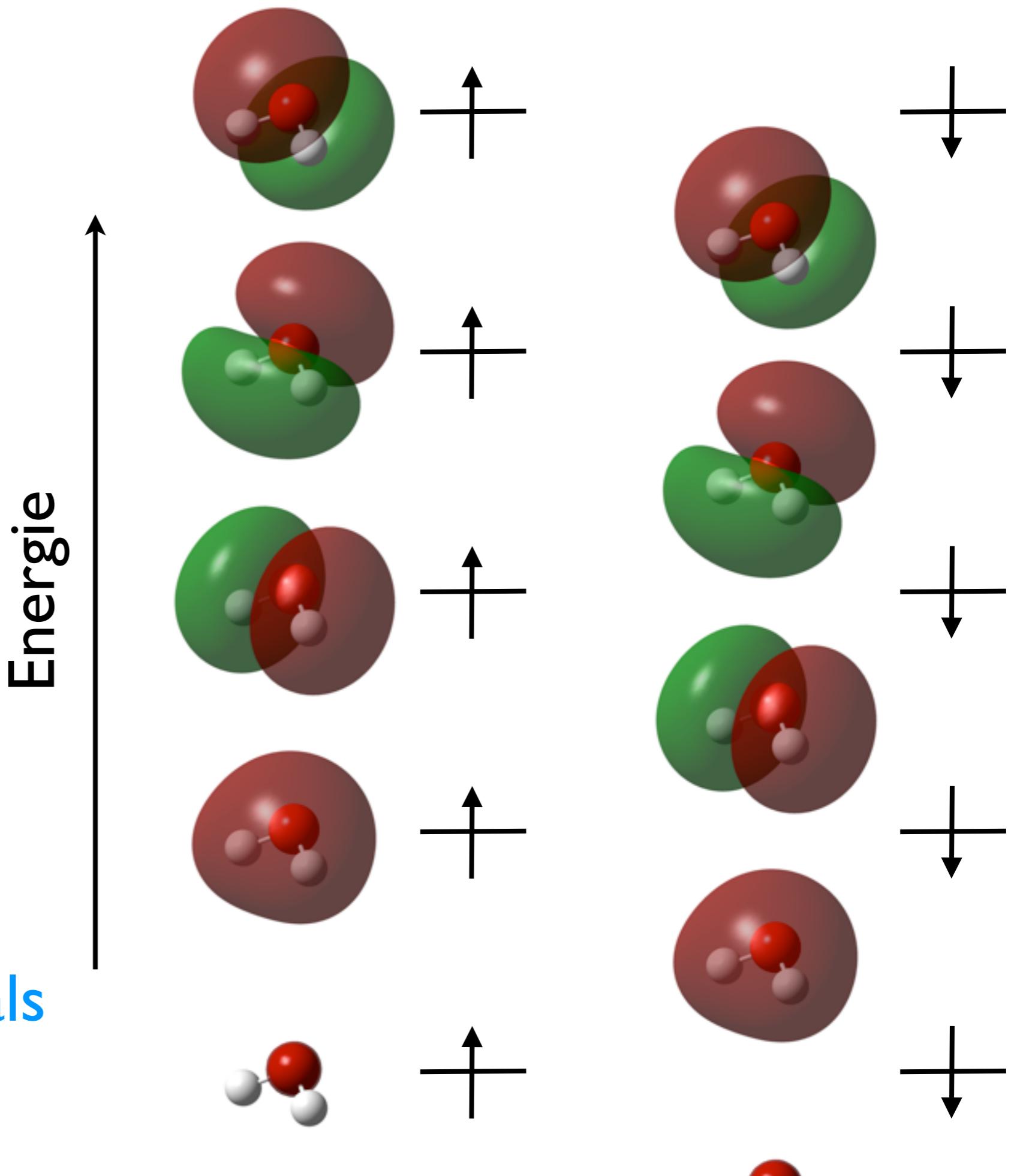


$2 \text{ H}^+$

$1 \text{ O}^{8+}$

10 electronen

10 molecular orbitals



# Molecular Quantum Mechanics

approaches for approximating  $\Psi_e$

Hartree-Fock and beyond (ab initio)

molecular orbitals

systematic improvement

precise, and only accurate with impossible computational effort

Density functional theory (semi-empirical)

many electron density

formally correct, if exact functional exists

precise, but not accurate

Quantum Monte Carlo (ab initio)

sample multi-dimensional wave function by Monte Carlo

quite accurate, but not precise

# Freshing up some mathematics

## linear algebra

vectors

basis

operators

matrices

transformations

eigenvalues & eigenvectors

## function spaces

Hilbert space

basis functions

eigenfunctions

## goals

re-acquire math skills to follow course

analogy between states in QM and vectors

familiarity with notations

# Matrices: properties and types

diagonal matrix

$$A_{ij} = A_{ii}\delta_{ij}$$

trace

$$\text{tr}\mathbf{A} = \sum_i A_{ii}$$

unit matrix

$$\mathbf{I}\mathbf{A} = \mathbf{A}\mathbf{I} = \mathbf{A} \quad (\mathbf{I})_{ij} = \delta_{ij}$$

inverse matrix

$$\mathbf{A}^{-1}\mathbf{A} = \mathbf{I} = \mathbf{A}\mathbf{A}^{-1}$$

unitary matrix

$$\mathbf{A}^{-1} = \mathbf{A}^\dagger$$

hermitian matrix

$$\mathbf{A}^\dagger = \mathbf{A} \quad A_{ji}^* = A_{ij}$$

# change of basis

states

not dependent on basis

$$|f\rangle = \sum_i^N |i\rangle f_i = \sum_{\alpha} |\alpha\rangle f_{\alpha}$$

$$\langle i|j\rangle = \delta_{ij} \quad \sum_i |i\rangle\langle i| = 1$$

$$\langle \alpha|\beta\rangle = \delta_{\alpha\beta} \quad \sum_{\alpha} |\alpha\rangle\langle \alpha| = 1$$

## matrix representation of operator

$$\hat{O}|f\rangle = |g\rangle$$

dependent on basis

$$\langle i|\hat{O}|j\rangle = O_{ij}$$

$$\langle \alpha|\hat{O}|\beta\rangle = \Omega_{\alpha\beta}$$

$$O_{ij} \neq \Omega_{\alpha\beta}$$

# Physics of chemistry

## building blocks

electrons (-)

nuclei (+)

## theoretical foundations

electrostatic interactions: Coulomb's law

quantum mechanics: Schrödinger equation

## properties to calculate

static: reaction energy, structure, spectra

dynamic: trajectories, thermodynamics

# Born-Oppenheimer Approximation

central to chemistry

separation slow (nuclear) and fast (electronic) motion

light electrons: QM (HF, DFT, ...), classical (MM)

heavy nuclei: QM (wavepacket/grid), classical (MD)

# Born-Oppenheimer Approximation

central to chemistry

separation slow (nuclear) and fast (electronic) motion

light electrons: QM (HF, DFT, ...), classical (MM)

heavy nuclei: QM (wavepacket/grid), classical (MD)

crux: nuclei move on single electronic PES

large energy gap between electronic states

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derivation of Born-Oppenheimer

terms couple nuclear motion on different electronic PES

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break down of Born-Oppenheimer approximation

small energy gap between electronic states

near surface crossings (degeneracies)

radiationless transition

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radiationless transition

adiabatic and diabatic electronic states

# Born-Oppenheimer Approximation

molecular Schrödinger equation

$$H\Psi = i\hbar \frac{\partial}{\partial t} \Psi \quad H\Psi = E\Psi$$

molecular Hamilton operator

$$H = T_N + T_e + U(\mathbf{r}, \mathbf{R})$$

with

$$T_N = -\frac{1}{2} \sum_i^{N_N} \frac{\hbar^2}{M_i} \nabla_{\mathbf{R}}^2$$

$$T_e = -\frac{\hbar^2}{2m_e} \sum_i^{n_e} \nabla_{\mathbf{r}}^2$$

$$U(\mathbf{r}, \mathbf{R}) = \frac{e^2}{4\pi\epsilon_0} \left( \sum_I^{N_N} \sum_{J>I}^{N_N} \frac{Z_I Z_J}{|\mathbf{R}_A - \mathbf{R}_B|} - \sum_I^{N_N} \sum_k^{n_e} \frac{Z_I}{|\mathbf{r}_k - \mathbf{R}_B|} + \sum_j^{n_e} \sum_{k>j}^{n_e} \frac{1}{|\mathbf{r}_k - \mathbf{r}_j|} \right)$$

# Born-Oppenheimer Approximation

molecular Hamilton operator

$$H = T_N + T_e + U(\mathbf{r}, \mathbf{R})$$

step I: clamped nuclei

separation of fast and slow degrees of freedom

$$T_N = 0$$

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always possible, not an approximation!

wrong choice: strong coupling between ‘fast’ and ‘slow’ motions

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consider only electronic degrees of freedom

$$H^e = T_e + U(\mathbf{r}, \mathbf{R})$$

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$$H^e = T_e + U(\mathbf{r}, \mathbf{R})$$

electronic Schrödinger equation in field of fixed nuclei

$$H^e \psi_i(\mathbf{r}; \mathbf{R}) = V_i(\mathbf{R}) \psi_i(\mathbf{r}; \mathbf{R})$$

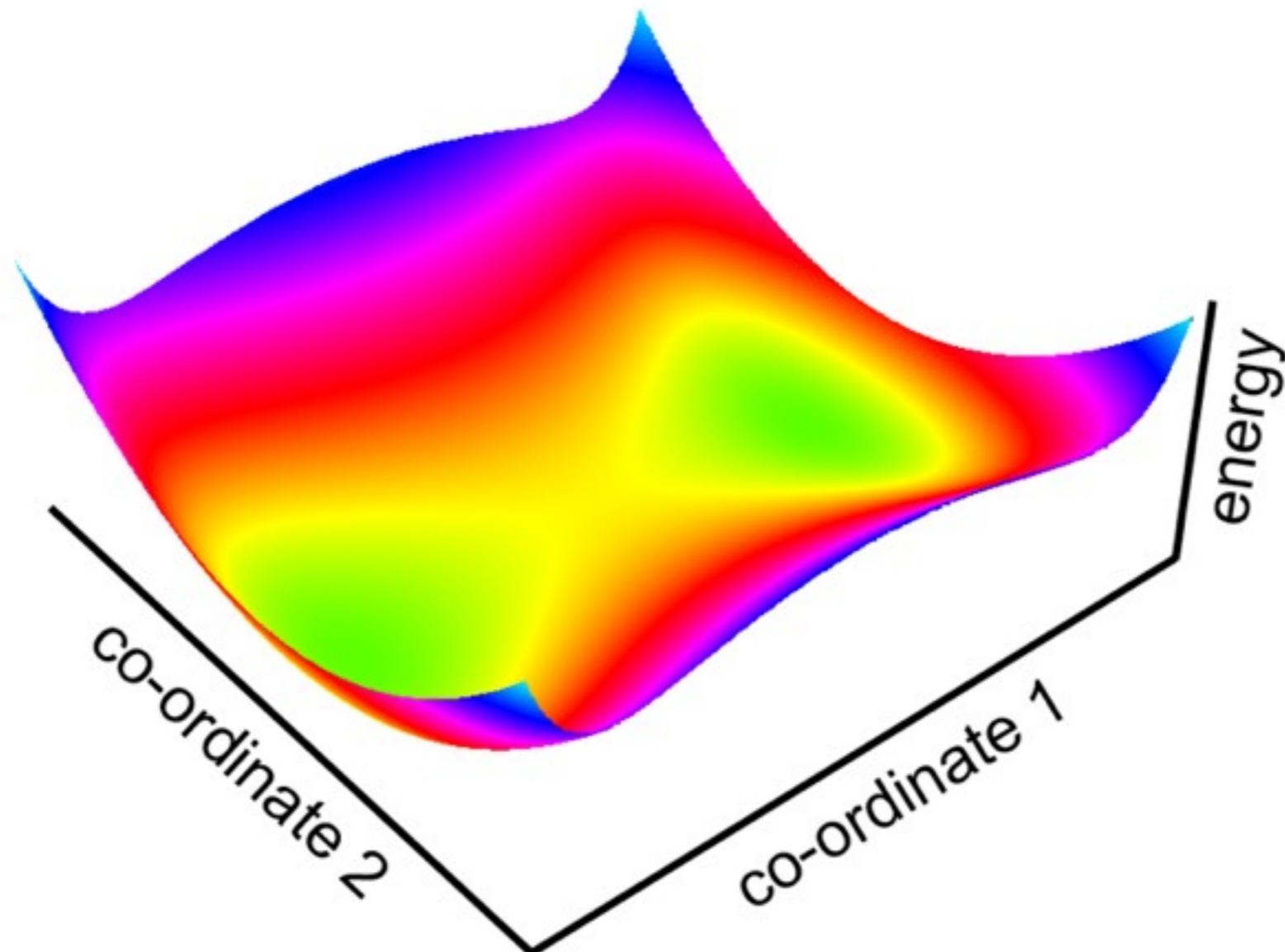
$i \geq 1$ : CI, SA-CASSCF, MRCI

# Born-Oppenheimer Approximation

electronic Schrödinger equation in field of fixed nuclei

$$H^e \psi_i(\mathbf{r}; \mathbf{R}) = V_i(\mathbf{R}) \psi_i(\mathbf{r}; \mathbf{R})$$

electronic potential energy surface (PES)



# Born-Oppenheimer Approximation

electronic Schrödinger equation in field of fixed nuclei

diagonalize electronic Hamiltonian

$$H^e \psi_i(\mathbf{r}; \mathbf{R}) = V_i(\mathbf{R}) \psi_i(\mathbf{r}; \mathbf{R})$$

solution form orthogonal basis (or can be made so)

adiabatic electronic states

$$\langle \psi_i | \psi_j \rangle = \int_{-\infty}^{\infty} \psi_i(\mathbf{r}; \mathbf{R})^* \psi_j(\mathbf{r}; \mathbf{R}) d\mathbf{r} = \delta_{ij}$$

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Born representation: expansion in electronic basis

expansion coefficients are nuclear wavefunctions

$$\Psi(\mathbf{r}, \mathbf{R}) = \sum_j \chi_j(\mathbf{R}) \psi_j(\mathbf{r}; \mathbf{R}),$$

no approximations so far!

# Born-Oppenheimer Approximation

molecular wavefunction in Born representation

$$\Psi(\mathbf{r}, \mathbf{R}) = \sum_j \chi_j(\mathbf{R}) \psi_j(\mathbf{r}; \mathbf{R}),$$

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molecular hamiltonian

$$H = T_N + T_e + U(\mathbf{r}, \mathbf{R}) = T_N + H^e(\mathbf{R})$$

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$$H = T_N + T_e + U(\mathbf{r}, \mathbf{R}) = T_N + H^e(\mathbf{R})$$

substitute and multiply from left by  $\langle \psi_i |$  and integrate

$$\sum_j \langle \psi_i | H | \psi_j \rangle \chi_j(\mathbf{R}) = i\hbar \frac{\partial}{\partial t} \sum_j \langle \psi_i | \psi_j \rangle \chi_j(\mathbf{R})$$

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using short-hand notation

$$\begin{aligned} H_{ij}(\mathbf{R}) &= \langle \psi_i(\mathbf{r}; \mathbf{R}) | H | \psi_j(\mathbf{r}; \mathbf{R}) \rangle \\ &= \langle \psi_i(\mathbf{r}; \mathbf{R}) | T_N | \psi_j(\mathbf{r}; \mathbf{R}) \rangle + V_i(\mathbf{R}) \delta_{ij} \end{aligned}$$

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coupled differential equations

$$\sum_j H_{ij}(\mathbf{R}) \chi_j(\mathbf{R}) = i\hbar \frac{\partial}{\partial t} \chi_i(\mathbf{R})$$

# Born-Oppenheimer Approximation

elements of nuclear kinetic energy matrix

$$\begin{aligned}\langle \psi_i | T_N | \psi_j \rangle &= \frac{-\hbar^2}{2M_k} \langle \psi_i | \nabla_{\mathbf{R}}^2 | \psi_j \rangle \\ &= \frac{-\hbar^2}{2M_k} (\langle \psi_i | \nabla_{\mathbf{R}} \cdot \underline{\nabla_{\mathbf{R}}} | \psi_j \rangle) \\ &= \frac{-\hbar^2}{2M_k} (\langle \psi_i | \underline{\nabla_{\mathbf{R}}} | \underline{[\nabla_{\mathbf{R}} \psi_j]} \rangle + \langle \psi_i | \nabla_{\mathbf{R}} | \psi_j \rangle \underline{\nabla_{\mathbf{R}}}) \\ &= \frac{-\hbar^2}{2M_k} (\langle \psi_i | \underline{[\nabla_{\mathbf{R}}^2 \psi_j]} \rangle + \langle \psi_i | \underline{[\nabla_{\mathbf{R}} \psi_j]} \rangle \nabla_{\mathbf{R}} + \\ &\quad \langle \psi_i | \underline{[\nabla_{\mathbf{R}} \psi_j]} \rangle \nabla_{\mathbf{R}} + \langle \psi_i | \psi_j \rangle \underline{\nabla_{\mathbf{R}}^2}) \\ &= \frac{-\hbar^2}{2M_k} (\langle \psi_i | [\nabla_{\mathbf{R}}^2 \psi_j] \rangle + 2\langle \psi_i | [\nabla_{\mathbf{R}} \psi_j] \rangle \nabla_{\mathbf{R}} + \langle \psi_i | \psi_j \rangle \nabla_{\mathbf{R}}^2) \\ &= \frac{-\hbar^2}{2M_k} (G_{ij} + 2\mathbf{F} \nabla_{\mathbf{R}}) + T_N \\ &= T_N \delta_{ij} - \Lambda_{ij}\end{aligned}$$

# Born-Oppenheimer Approximation

substitute and multiply from left by  $\langle \psi_i |$  and integrate

$$\sum_j H_{ij}(\mathbf{R}) \chi_j(\mathbf{R}) = i\hbar \frac{\partial}{\partial t} \chi_i(\mathbf{R})$$

collect all couplings in special operator

$$H_{ij}(\mathbf{R}) = [T_N + V_i(\mathbf{R})] \delta_{ij} - \Lambda_{ij}$$

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coupled equations

coupling between nuclear wave packets on different electronic PES

coupling due to nuclear kinetic energy operator operating on electrons

kind of resonance with energy exchange

$$[T_N + V_i(\mathbf{R})]\chi_i(\mathbf{R}) - \sum_j \Lambda_{ij}\chi_j(\mathbf{R}) = i\hbar \frac{\partial}{\partial t} \chi_i(\mathbf{R})$$

# Born-Oppenheimer Approximation

coupled equations

$$[T_N + V_i(\mathbf{R})]\chi_i(\mathbf{R}) - \sum_j \Lambda_{ij}\chi_j(\mathbf{R}) = i\hbar \frac{\partial}{\partial t} \chi_i(\mathbf{R})$$

non-adiabatic coupling operator matrix elements

$$\Lambda_{ij}(\mathbf{R}) = \sum_k \frac{\hbar^2}{2M_k} [2\mathbf{F}_{ij}^k(\mathbf{R})\nabla_{\mathbf{R}_k} + G_{ij}^k(\mathbf{R})]$$

with elements

$$\mathbf{F}_{ij}^k(\mathbf{R}) = \langle \psi_i(\mathbf{r}; \mathbf{R}) | \nabla_{\mathbf{R}_k} \psi_j(\mathbf{r}; \mathbf{R}) \rangle$$

$$G_{ij}^k(\mathbf{R}) = \langle \psi_i(\mathbf{r}; \mathbf{R}) | \nabla_{\mathbf{R}_k}^2 \psi_j(\mathbf{r}; \mathbf{R}) \rangle$$

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 non-adiabatic coupling vector

$$G_{ij}^k(\mathbf{R}) = \langle \psi_i(\mathbf{r}; \mathbf{R}) | \nabla_{\mathbf{R}_k}^2 \psi_j(\mathbf{r}; \mathbf{R}) \rangle$$
 scalar coupling

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 scalar coupling

inversely proportional to nuclear mass!

small terms due to mass difference, but...

# Born-Oppenheimer Approximation

non-adiabatic coupling vector

$$\mathbf{F}_{ij}^k(\mathbf{R}) = \langle \psi_i(\mathbf{r}; \mathbf{R}) | \nabla_{\mathbf{R}_k} \psi_j(\mathbf{r}; \mathbf{R}) \rangle$$

using the following relation

$$\nabla_{\mathbf{R}} H^e(\mathbf{r}; \mathbf{R}) \psi_j(\mathbf{r}; \mathbf{R}) = \nabla_{\mathbf{R}} V_j(\mathbf{R}) \psi_j(\mathbf{r}; \mathbf{R})$$

and some lines of algebra to show that

$$\mathbf{F}_{ij}^k(\mathbf{R}) = \frac{\langle \psi_i(\mathbf{r}; \mathbf{R}) | \nabla_{\mathbf{R}_k} H^e | \psi_j(\mathbf{r}; \mathbf{R}) \rangle}{V_j - V_i}$$

... coupling inversely proportional to energy gap!

# Born-Oppenheimer Approximation

non-adiabatic coupling vector

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Hellman-Feynmann term

$$\mathbf{F}_{ij}^k(\mathbf{R}) = \frac{\langle \psi_i(\mathbf{r}; \mathbf{R}) | \nabla_{\mathbf{R}_k} H^e | \psi_j(\mathbf{r}; \mathbf{R}) \rangle}{V_j - V_i}$$

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# Born-Oppenheimer Approximation

non-adiabatic coupling matrix element

$$F_{ij}^k(R) = \langle \psi_i(\mathbf{r}; R) | \nabla_{R_k} \psi_j(\mathbf{r}; R) \rangle$$

no diagonal elements

$$F_{ii}^k(R) = 0$$

because

$$\nabla_R \langle \psi_i | \psi_i \rangle = 0$$

$$\langle \nabla_R \psi_i | \psi \rangle + \langle \psi_i | \nabla_R \psi_i \rangle = 0$$

$$\langle \psi_i | \nabla_R \psi \rangle + \text{c.c} = 0$$

# Born-Oppenheimer Approximation

nuclear Schrödinger in Born representation

$$[T_N + V_i(\mathbf{R})]\chi_i(\mathbf{R}) - \sum_j \Lambda_{ij}\chi_j(\mathbf{R}) = i\hbar \frac{\partial}{\partial t} \chi_i(\mathbf{R})$$

coupling between nuclear wavepackets on different PES

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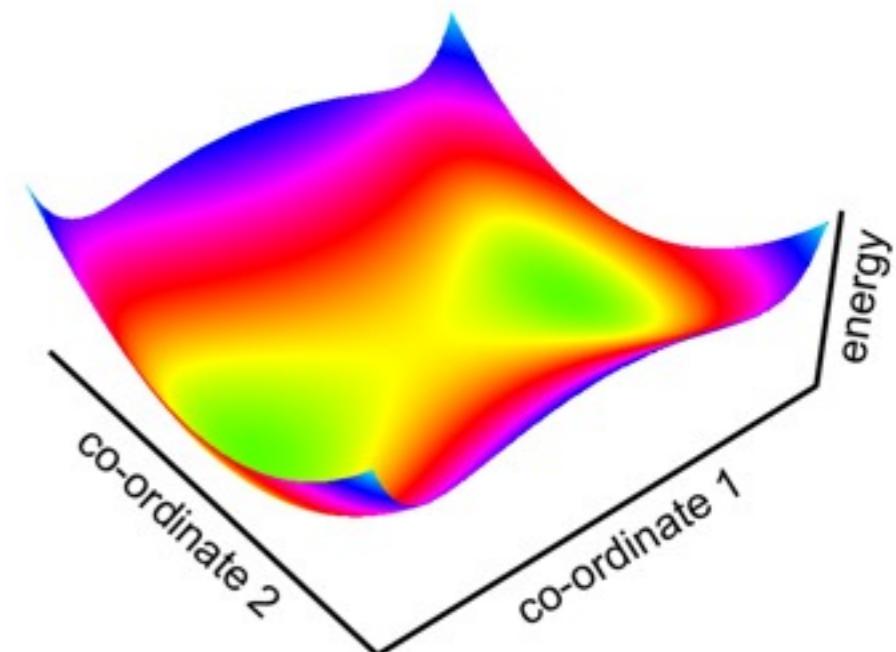
coupling between nuclear wavepackets on different PES

Born-Oppenheimer approximation:  $\Lambda = \Lambda_{ii}$

$$[T_N + V_i(\mathbf{R}) + \Lambda_{ii}] \chi_i(\mathbf{R}) = i\hbar \frac{\partial}{\partial t} \chi_i(\mathbf{R})$$

nuclear wavepackets restricted to single electronic PES

$$\Psi_i^{\text{tot}}(\mathbf{R}, \mathbf{r}) = \chi_i(\mathbf{R})\psi_i(\mathbf{r}; \mathbf{R})$$



# Born-Oppenheimer Approximation

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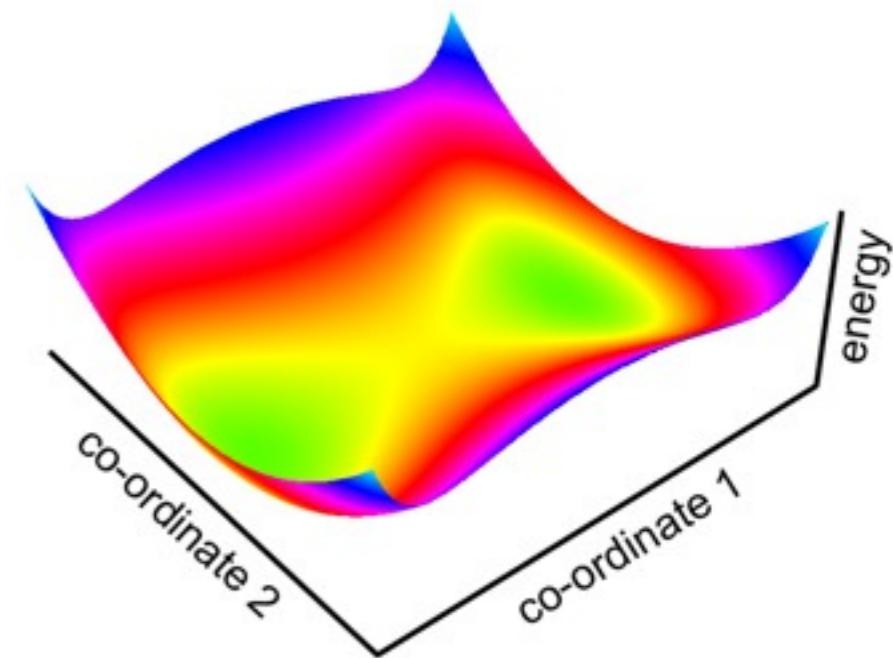
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$$\Psi_i^{\text{tot}}(\mathbf{R}, \mathbf{r}) = \chi_i(\mathbf{R})\psi_i(\mathbf{r}; \mathbf{R})$$

adiabatic approximation:  $\Lambda = 0$

$$[T_N + V_i(\mathbf{R})] \chi_i(\mathbf{R}) = i\hbar \frac{\partial}{\partial t} \chi_i(\mathbf{R})$$

mostly used in quantum chemistry



# Born-Oppenheimer Approximation

nuclear Schrödinger in Born representation

$$[T_N + V_i(\mathbf{R})]\chi_i(\mathbf{R}) - \sum_j \Lambda_{ij}\chi_j(\mathbf{R}) = i\hbar \frac{\partial}{\partial t} \chi_i(\mathbf{R})$$

using atomic units and scaled coordinates

$$T_N = -\frac{1}{M} \nabla_{\mathbf{R}}^2$$

$$\Lambda_{ij} = \frac{1}{2M} (2\mathbf{F}_{ij} \cdot \nabla_{\mathbf{R}} + G_{ij}))$$

$$\mathbf{F}_{ij} = \langle \psi_i | \nabla_{\mathbf{R}} \psi_j \rangle \quad G_{ij} = \langle \psi_i | \nabla_{\mathbf{R}}^2 \psi_j \rangle$$

# Born-Oppenheimer Approximation

using atomic units and scaled coordinates

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using the relation

$$\mathbf{G} = \nabla_{\mathbf{R}} \cdot \mathbf{F} + \mathbf{F} \cdot \mathbf{F}$$

one arrives at

$$\left[ -\frac{1}{2M} (\nabla_{\mathbf{R}} + \mathbf{F})^2 + \mathbf{V} \right] \chi = i \frac{\partial}{\partial t} \chi$$

# Born-Oppenheimer Approximation

nuclear Schrödinger in vector notation

$$\left[ -\frac{1}{2M} (\nabla_{\mathbf{R}} + \mathbf{F})^2 + \mathbf{V} \right] \chi = i \frac{\partial}{\partial t} \chi$$

dressed kinetic energy operator

$$\tilde{T}_N = -\frac{1}{2M} (\nabla_{\mathbf{R}} + \mathbf{F})^2 \quad \mathbf{F}_{ij} = \langle \psi_i | \nabla_{\mathbf{R}} \psi_j \rangle$$

non local & non diagonal

couples nuclear dynamics on multiple electronic PES

induces radiationless transitions!

potential energy operator

local & diagonal

no coupling

# Born-Oppenheimer Approximation

non-adiabatic coupling vector

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inversely proportional with gap!

break down of adiabatic approximation!

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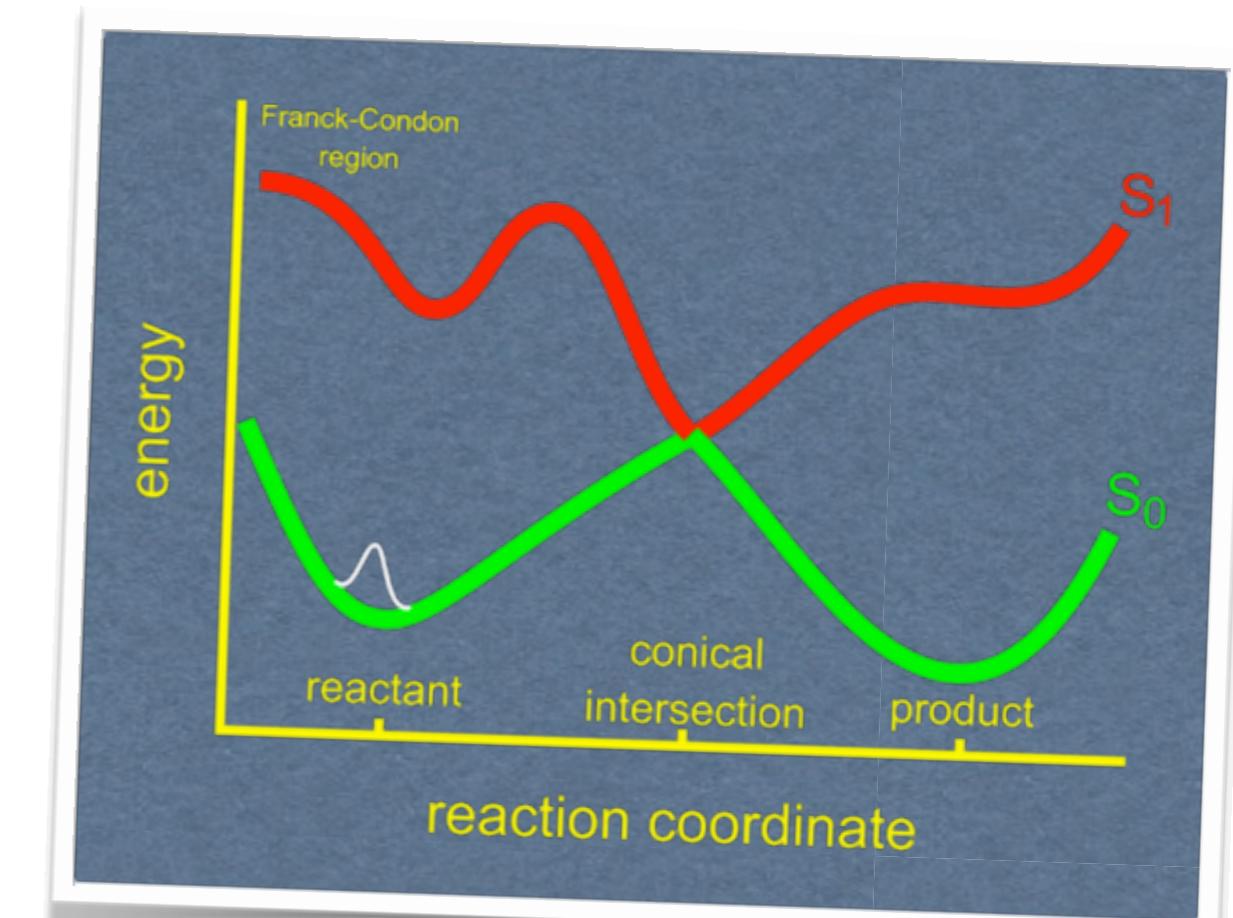
non-adiabatic dynamics

multiple surfaces

branching

interference/coherence

photochemistry



intersection between adiabatic surfaces

# Born-Oppenheimer Approximation

adiabatic electronic basis

diagonal & local potential matrix

$$\langle \psi_i | H^e | \psi_j \rangle = \delta_{ij} V_j$$

non-diagonal & non-local nuclear kinetic energy matrix

$$\langle \psi_i | T_N | \psi_j \rangle = -\frac{1}{2M} (\nabla_{\mathbf{R}} + \boxed{\langle \psi_i | \nabla_{\mathbf{R}} | \psi_j \rangle})^2$$

coupling in F

# Born-Oppenheimer Approximation

adiabatic electronic basis

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coupling in  $\mathbf{F}$

diabatic representation

non-diagonal & local potential matrix

$$\langle \varphi_i | H^e | \varphi_j \rangle = W_{ij}$$

coupling in  $\mathbf{W}$

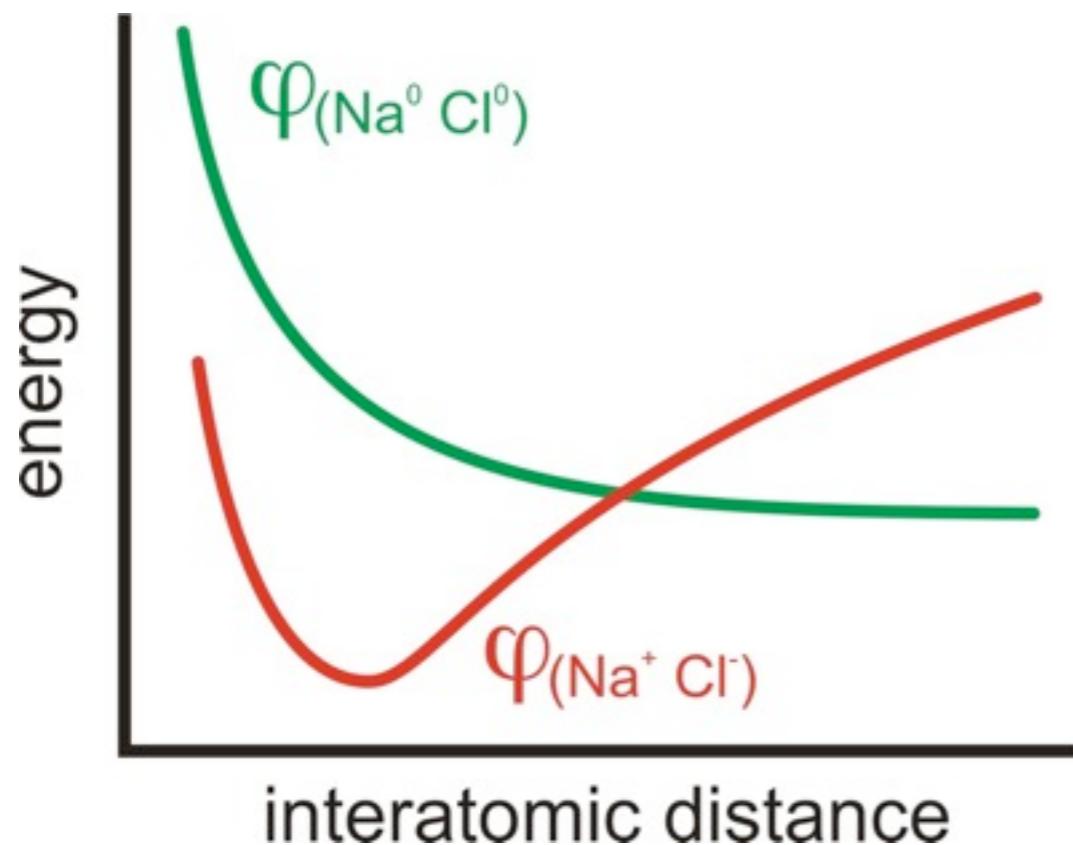
diagonal nuclear kinetic energy matrix

$$\langle \varphi_i | T_N | \varphi_j \rangle = -\frac{\delta_{ij}}{2M} \nabla_{\mathbf{R}}^2$$

# Born-Oppenheimer Approximation

diabatic electronic basis

electronic character preserved



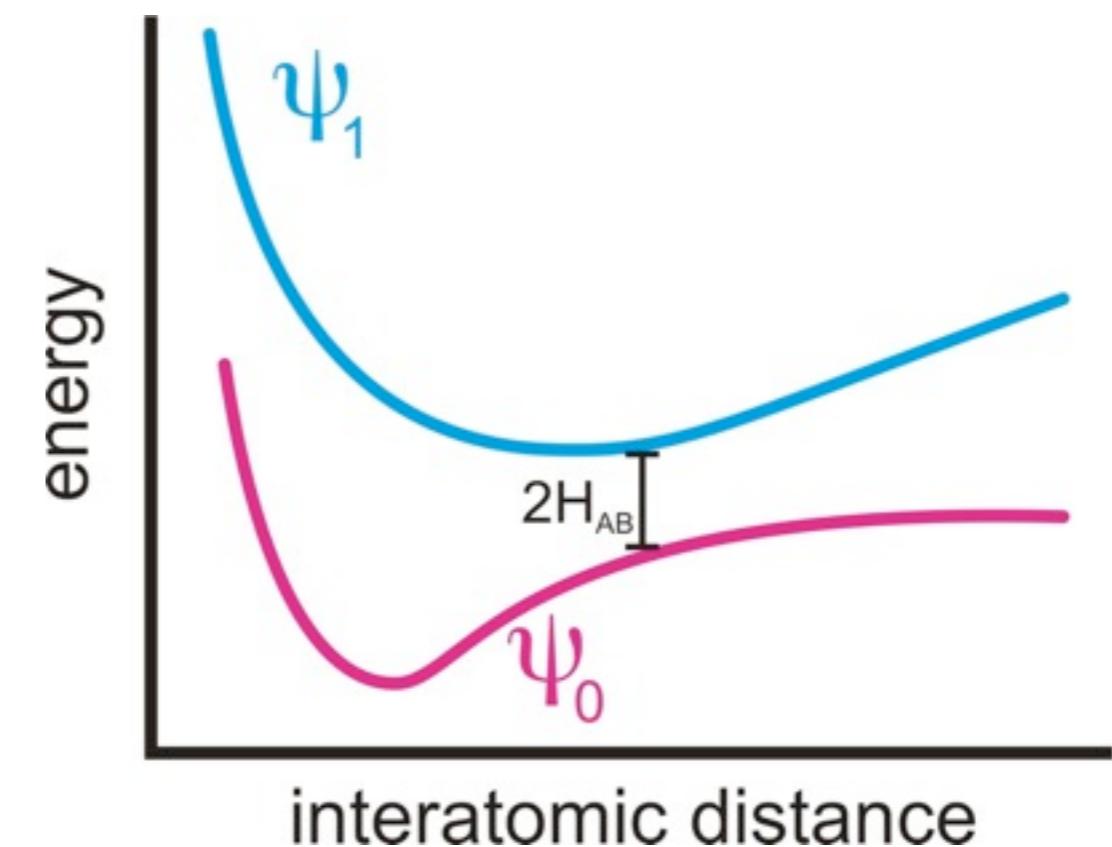
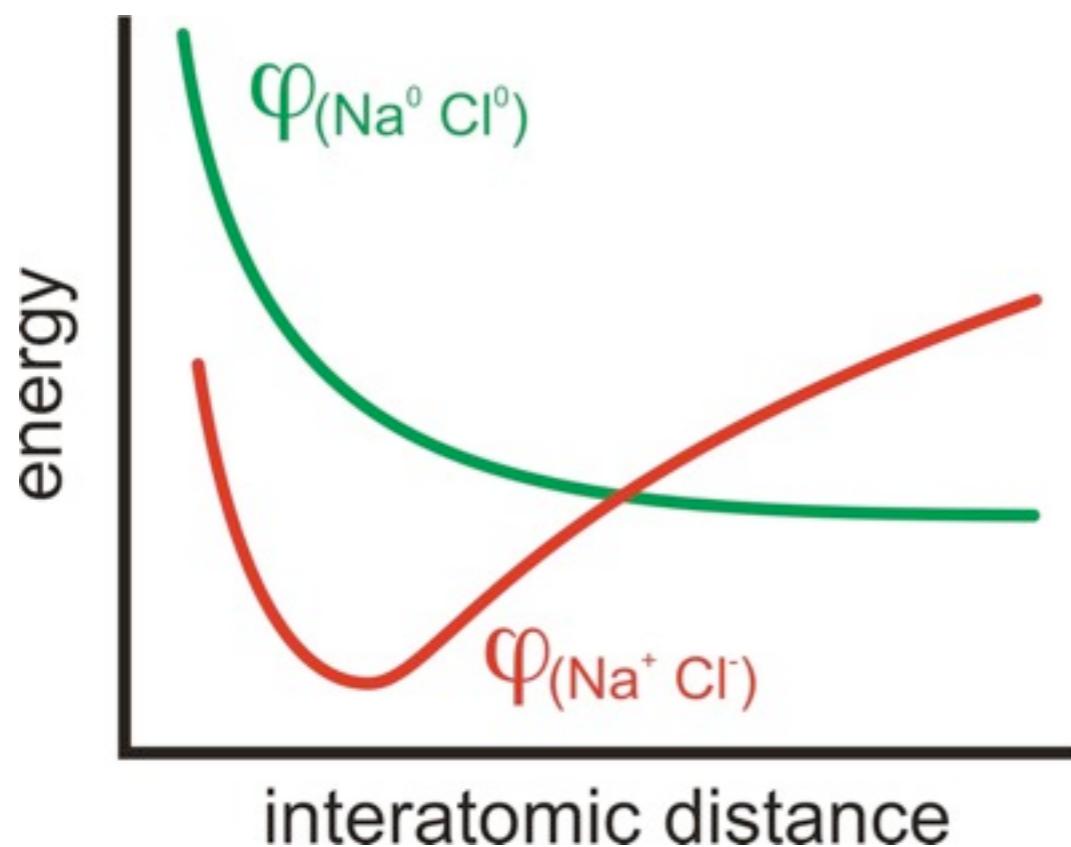
# Born-Oppenheimer Approximation

diabatic electronic basis

electronic character preserved

adiabatic electronic basis

electronic character mixed



# Born-Oppenheimer Approximation

diabatic representation

non-diagonal & local potential matrix

$$\langle \varphi_i | H^e | \varphi_j \rangle = W_{ij}$$

diagonal nuclear kinetic energy matrix

$$\langle \varphi_i | T_N | \varphi_j \rangle = -\frac{\delta_{ij}}{2M} \nabla_{\mathbf{R}}^2$$

molecular Hamiltonian

$$H_{ij} = T_N \delta_{ij} + W_{ij}$$

molecular Schrödinger equation

$$\sum_j H_{ij} \chi_j = T_N \chi_i + \sum_j W_{ij} \chi_j = i \frac{\partial}{\partial t} \chi_i$$

$$\mathbf{H} \boldsymbol{\chi} = [T_N \mathbf{I} + \mathbf{W}(\mathbf{R})] \boldsymbol{\chi} = i \frac{\partial}{\partial t} \boldsymbol{\chi}$$

# Born-Oppenheimer Approximation

construction of diabatic basis

unitary transformation for each nuclear configuration

$$\varphi_i(\mathbf{r}; \mathbf{R}) = \sum_j \psi_j(\mathbf{r}; \mathbf{R}) U_{ji}(\mathbf{R})$$

# Born-Oppenheimer Approximation

construction of diabatic basis

unitary transformation for each nuclear configuration

$$\varphi_i(\mathbf{r}; \mathbf{R}) = \sum_j \psi_j(\mathbf{r}; \mathbf{R}) U_{ji}(\mathbf{R})$$

construction of diabatic Hamiltonian

potential matrix

$$\mathbf{W} = \mathbf{U}^T \mathbf{V} \mathbf{U}$$

kinetic energy (diagonal)

$$T_N \mathbf{I} = \mathbf{U}^T \tilde{\mathbf{T}}_N \mathbf{U}$$

# Born-Oppenheimer Approximation

construction of diabatic basis

unitary transformation for each nuclear configuration

$$\varphi_i(\mathbf{r}; \mathbf{R}) = \sum_j \psi_j(\mathbf{r}; \mathbf{R}) U_{ji}(\mathbf{R})$$

construction of diabatic Hamiltonian

kinetic energy (diagonal)

$$T_N^d \mathbf{1} = \mathbf{U}^\dagger \tilde{\mathbf{T}}_N \mathbf{U}$$

dressed kinetic energy operator

$$\tilde{\mathbf{T}}_N = -\frac{1}{2M} (\nabla_{\mathbf{R}} + \mathbf{F})^2 \quad \mathbf{F}_{ij} = \langle \psi_i | \nabla_{\mathbf{R}} \psi_j \rangle$$

transformation should nullify non-adiabatic coupling

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transformation should nullify non-adiabatic coupling

$$\begin{aligned} \langle \varphi_i | \nabla_{\mathbf{R}} \varphi_j \rangle &= \sum_k \sum_l U_{ki}^*(\mathbf{R}) \langle \psi_k | \nabla_{\mathbf{R}} U_{lj}(\mathbf{R}) \psi_l \rangle \\ &= \sum_k \sum_l [U_{ki}^*(\mathbf{R}) \langle \psi_k | \psi_l \rangle \nabla_{\mathbf{R}} U_{lj}(\mathbf{R}) + U_{ki}^*(\mathbf{R}) \langle \psi_k | \nabla_{\mathbf{R}} | \psi_l \rangle U_{lj}(\mathbf{R})] \\ &= \underline{\sum_k U_{ki}^* \nabla_{\mathbf{R}} U_{kj}} + \underline{\sum_k \sum_l U_{ki}^*(\mathbf{R}) \langle \psi_k | \nabla_{\mathbf{R}} | \psi_l \rangle U_{lj}(\mathbf{R})} \end{aligned}$$

# Born-Oppenheimer Approximation

construction of diabatic Hamiltonian

dressed kinetic energy operator

$$\tilde{\mathbf{T}}_N = -\frac{1}{2M} (\nabla_{\mathbf{R}} + \mathbf{F})^2 \quad \mathbf{F}_{ij} = \langle \psi_i | \nabla_{\mathbf{R}} \psi_j \rangle$$

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find  $\mathbf{U}$  such that

$$\underline{\mathbf{U}^T \mathbf{F} \mathbf{U}} + \underline{\mathbf{U}^T \nabla_{\mathbf{R}} \mathbf{U}} = \mathbf{0}$$

# Born-Oppenheimer Approximation

derivation

separation between fast and slow degrees of freedom

nuclei move on single adiabatic PES

ignore non-adiabatic coupling

breakdown

small energy gap between electronic PES

at intersections infinite non-adiabatic coupling

nuclear displacement couple different adiabatic states

highly complicated nuclear wave function

switch to diabatic basis

only electronic coupling

unitary transformation

# Conical Intersection

surface crossings

funnels for photochemical reactions

conditions for crossing

adiabatic representation

two coordinates needed to locate intersection

two coordinates needed to lift degeneracy

topology of intersection

double cone

$2N-8$  dimensional hyperline

properties of intersection

Berry phase

singularity due to separation between electronic and nuclear motion

compensated by nuclear wavefunction (complicated!)

# Conical Intersection

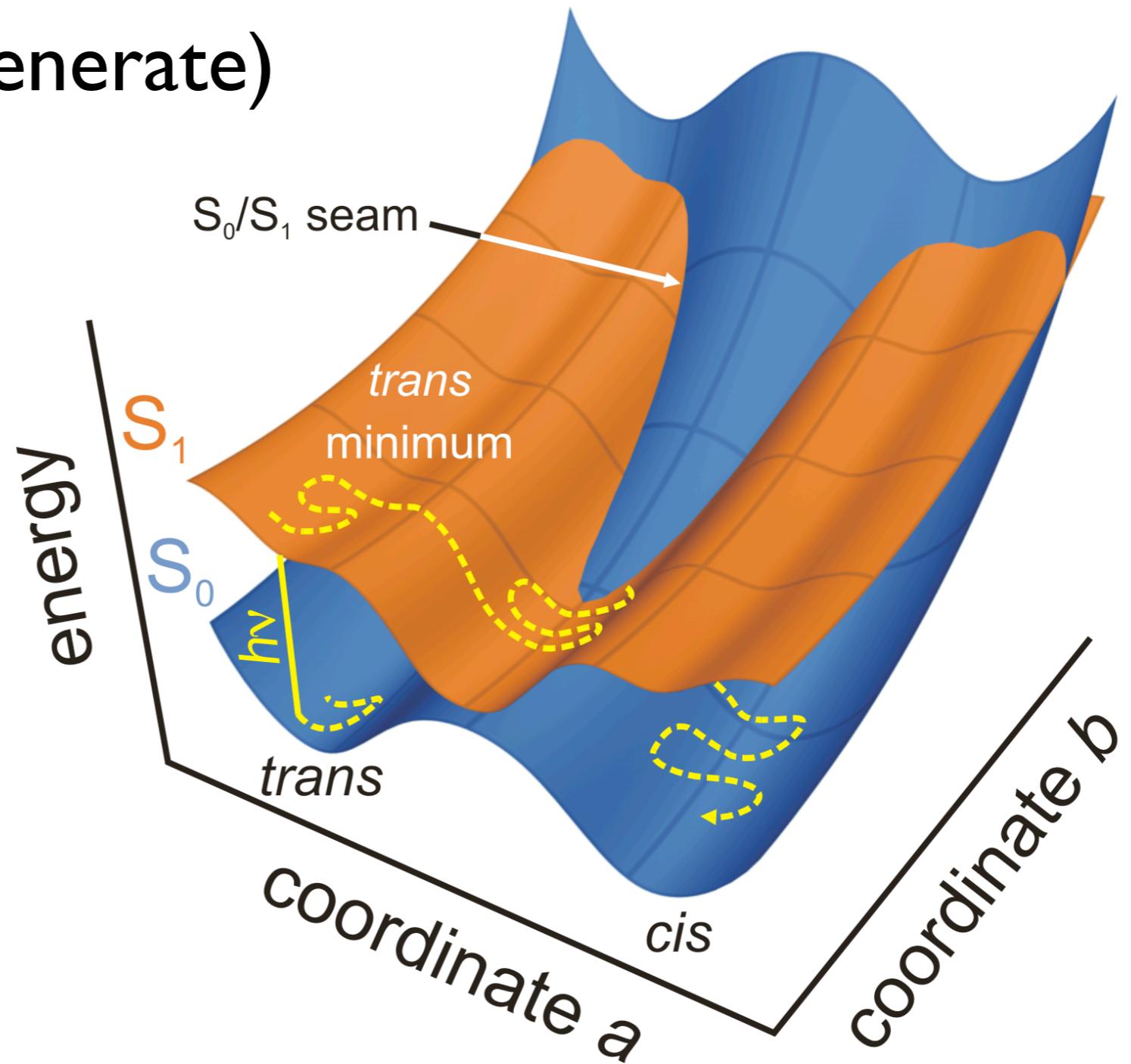
adiabatic surfaces

$$H^e \psi_i(\mathbf{r}; \mathbf{R}) = V_i(\mathbf{R}) \psi_i(\mathbf{r}; \mathbf{R})$$

can cross (are degenerate)

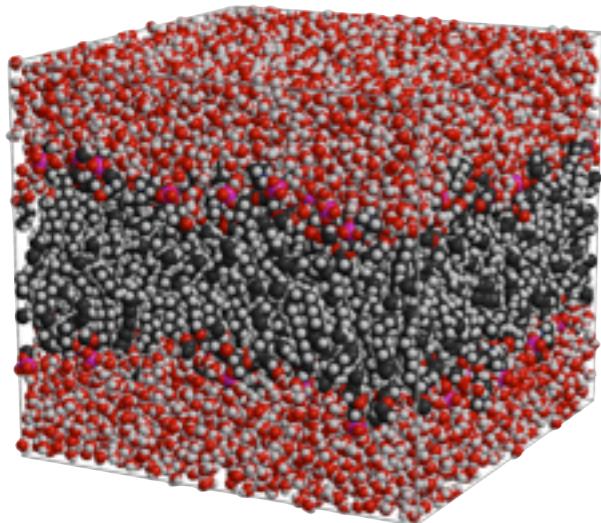
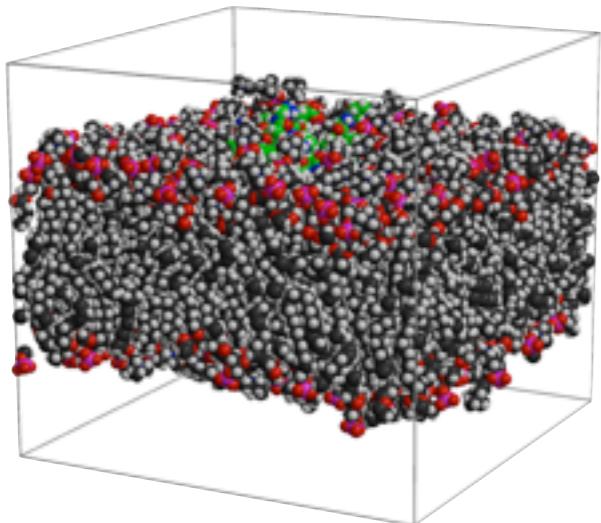
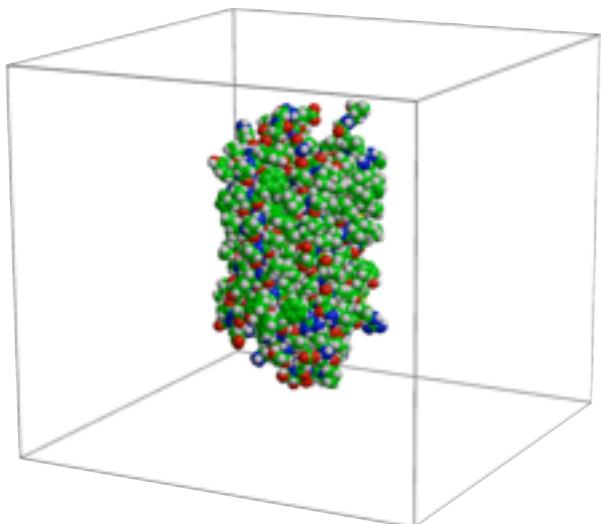
$$V_i(\mathbf{R}) = V_j(\mathbf{R})$$

radiationless decay



# photoisomerization in bacteriorhodopsin

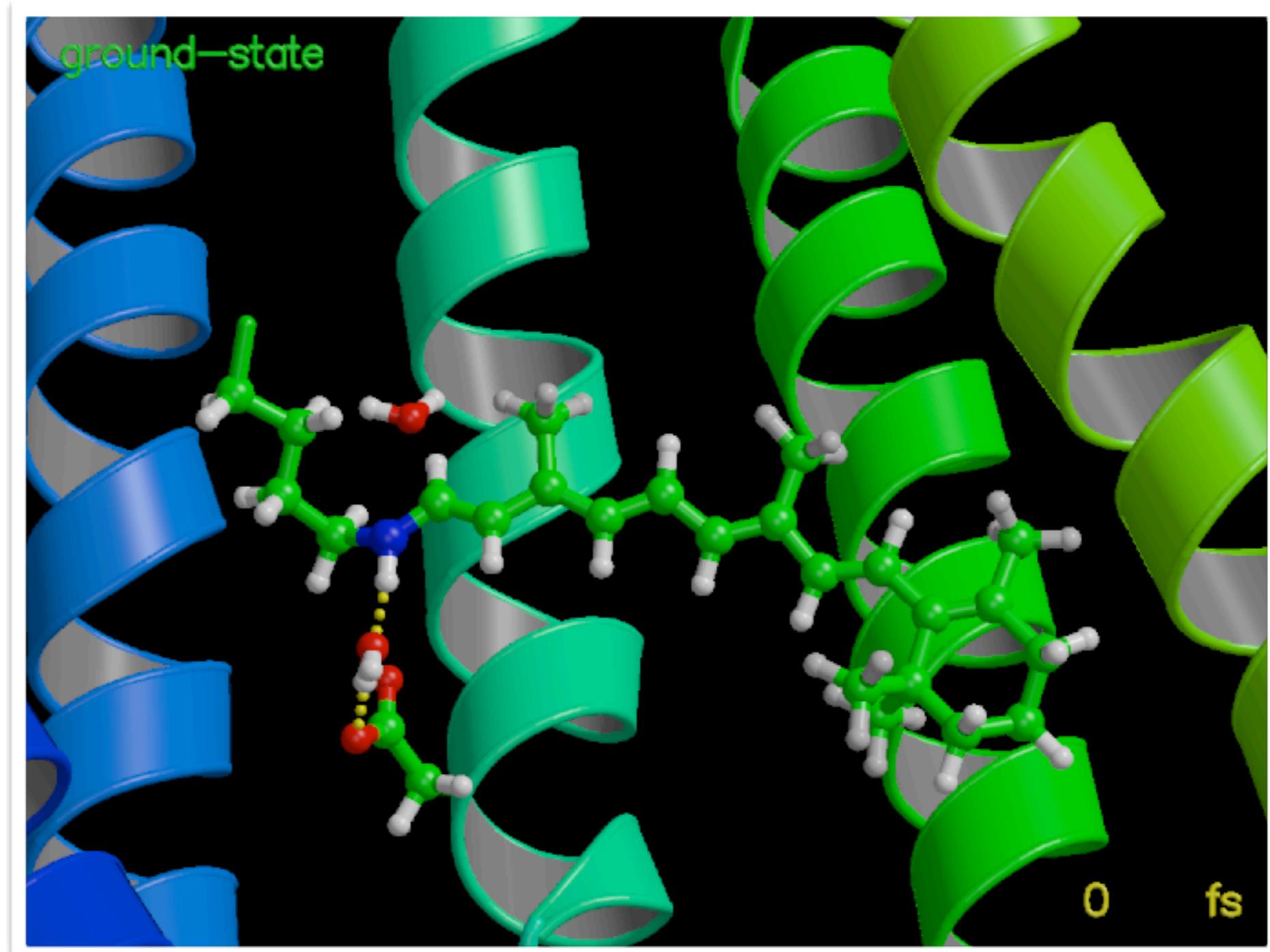
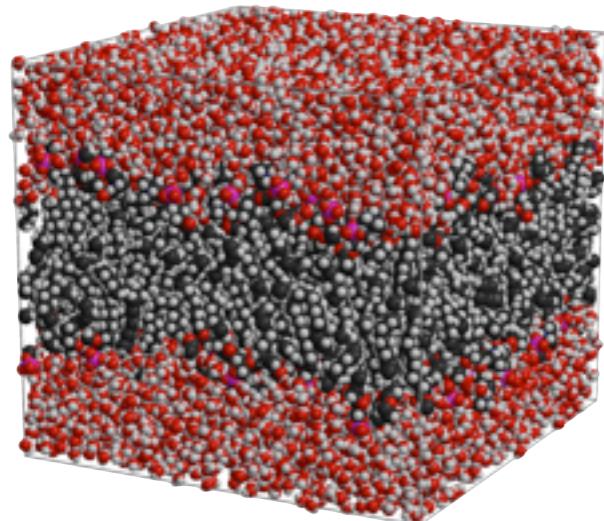
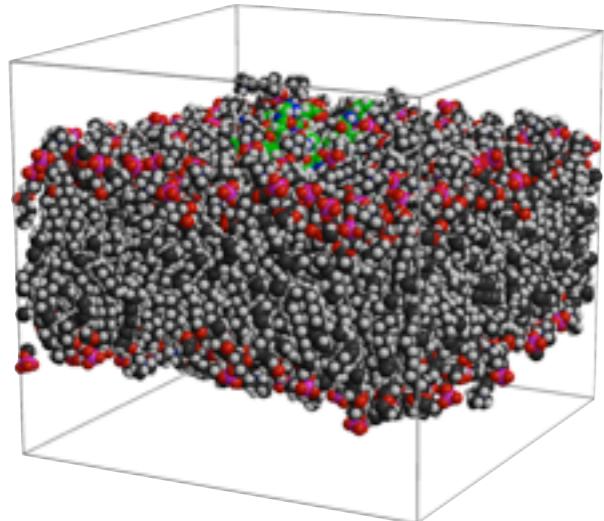
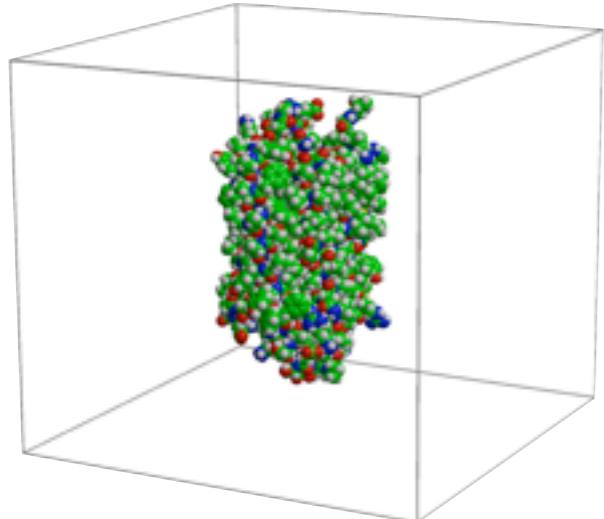
## excited state decay via $S_1/S_0$ conical intersection



CASSCF/OPLS & diabatic hopping

# photoisomerization in bacteriorhodopsin

excited state decay via  $S_1/S_0$  conical intersection



CASSCF/OPLS & diabatic hopping

# Conical Intersection

adiabatic surfaces

$$H^e \psi_i(\mathbf{r}; \mathbf{R}) = V_i(\mathbf{R}) \psi_i(\mathbf{r}; \mathbf{R})$$

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can cross (are degenerate)

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break-down of Born-Oppenheimer

non-adiabatic coupling becomes infinite!

$$\mathbf{F}_{ij}^k(\mathbf{R}) = \frac{\langle \psi_i(\mathbf{r}; \mathbf{R}) | \nabla_{\mathbf{R}_k} H^e | \psi_j(\mathbf{r}; \mathbf{R}) \rangle}{V_j - V_i}$$

# Conical Intersection

adiabatic surfaces

$$H^e \psi_i(\mathbf{r}; \mathbf{R}) = V_i(\mathbf{R}) \psi_i(\mathbf{r}; \mathbf{R})$$

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switch to diabatic basis

no non-adiabatic coupling

back to adiabatic basis by diagonalizing  $\mathbf{W}$

# Conical Intersection

degeneracy between two electronic states at  $\mathbf{R}_0$

$$V_1(\mathbf{R}_0) = V_2(\mathbf{R}_0)$$

construct mixed diabatic/adiabatic basis at  $\mathbf{R}_0$

via unitary transformation

$$\{\varphi_2, \varphi_1, \psi_3, \dots, \psi_n\}$$

orthonormal

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} \quad \langle \varphi_I | \varphi_J \rangle = \delta_{IJ} \quad \langle \varphi_I | \psi_j \rangle = 0$$

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diabatic and adiabatic energies for two lowest states

$$E_1(\mathbf{R}_0) = E_2(\mathbf{R}_0) = V_1(\mathbf{R}_0) = V_2(\mathbf{R}_0)$$

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diabatic and adiabatic energies for two lowest states

$$E_1(\mathbf{R}_0) = E_2(\mathbf{R}_0) = V_1(\mathbf{R}_0) = V_2(\mathbf{R}_0)$$

adiabatic wavefunctions

$$\psi_1 = c_{11}\varphi_1 + c_{12}\varphi_2 \quad \psi_2 = c_{21}\varphi_1 + c_{22}\varphi_2$$

# Conical Intersection

degeneracy between two electronic states at  $\mathbf{R}_0$

$$V_1(\mathbf{R}_0) = V_2(\mathbf{R}_0)$$

transformation to mixed diabatic/adiabatic basis at  $\mathbf{R}_0$

**diabatic electronic energies**

$$E_1(\mathbf{R}_0) = E_2(\mathbf{R}_0) = V_1(\mathbf{R}_0) = V_2(\mathbf{R}_0)$$

$$\mathbf{W}(\mathbf{R}_0) = \mathbf{V}(\mathbf{R}_0)$$

# Conical Intersection

degeneracy between two electronic states at  $\mathbf{R}_0$

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$$W_{ij} = H_{ij} = \langle \varphi_i | H^e | \varphi_j \rangle$$

# Conical Intersection

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$$\mathbf{W}(\mathbf{R}_0) = \begin{pmatrix} H_{11}(\mathbf{R}_0) & H_{12}(\mathbf{R}_0) \\ H_{12}(\mathbf{R}_0) & H_{22}(\mathbf{R}_0) \end{pmatrix}$$

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adiabatic electronic energies

diagonalize  $\mathbf{W}$

$$V_1(\mathbf{R}_0) = \left( \frac{H_{11} + H_{22}}{2} \right) - \sqrt{\left( \frac{H_{11} - H_{22}}{2} \right)^2 + H_{12}^2}$$

$$V_2(\mathbf{R}_0) = \left( \frac{H_{11} + H_{22}}{2} \right) + \sqrt{\left( \frac{H_{11} - H_{22}}{2} \right)^2 + H_{12}^2}$$

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degeneracy between two electronic states at  $\mathbf{R}_0$

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degeneracy (crossing) if

$$H_{11} = H_{22} \wedge H_{12} = 0$$

independent: 2 coordinates required to locate degeneracy

degeneracy preserved in  $N-8$  remaining internal coordinates

# Conical Intersection

degeneracy between two electronic states at  $R_0$

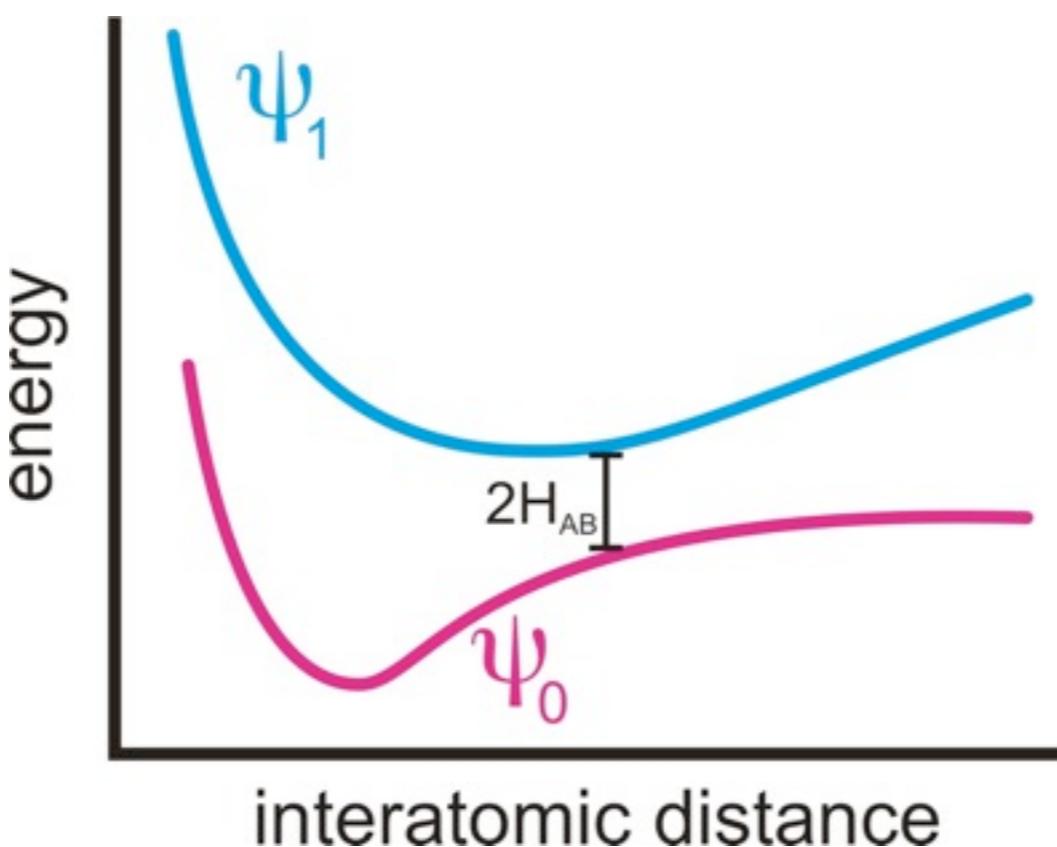
two coordinates required to locate degeneracy

degeneracy (crossing) if

$$H_{11} = H_{22} \wedge H_{12} = 0$$

non-crossing rule

diatomics



# Conical Intersection

topology of intersection

expand  $\mathbf{W}$  around  $\mathbf{R}_0$

$$\mathbf{W}(\mathbf{R} - \mathbf{R}_0) = \mathbf{W}^{(0)} + \mathbf{W}^{(1)} + \mathbf{W}^{(2)} + \dots$$

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zeroth order term

$$\mathbf{W}^{(0)} = \frac{E_A + E_B}{2} \mathbf{1} + \begin{pmatrix} -\frac{E_B - E_A}{2} & 0 \\ 0 & \frac{E_B - E_A}{2} \end{pmatrix}$$

# Conical Intersection

topology of intersection

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offset, set to zero for convenience

$$\mathbf{W}^{(0)} = 0$$

# Conical Intersection

topology of intersection

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offset, set to zero for convenience

$$\mathbf{W}^{(0)} = 0$$

first order term

$$\mathbf{W}^{(1)} = \begin{pmatrix} \nabla_{\mathbf{R}} \left( \frac{H_{11} + H_{22}}{2} \right) \cdot \Delta \mathbf{R} + \nabla_{\mathbf{R}} \left( \frac{H_{11} - H_{22}}{2} \right) \Delta \mathbf{R} & \nabla_{\mathbf{R}} H_{12} \cdot \Delta \mathbf{R} \\ \nabla_{\mathbf{R}} H_{12} \cdot \Delta \mathbf{R} & \nabla_{\mathbf{R}} \left( \frac{H_{11} + H_{22}}{2} \right) \cdot \Delta \mathbf{R} - \nabla_{\mathbf{R}} \left( \frac{H_{11} - H_{22}}{2} \right) \Delta \mathbf{R} \end{pmatrix}$$

$$\Delta \mathbf{R} = \mathbf{R}_0 - \mathbf{R}$$

# Conical Intersection

## topology of intersection

first order term

$$\mathbf{W}^{(1)} = \begin{pmatrix} \nabla_{\mathbf{R}} \left( \frac{H_{11}+H_{22}}{2} \right) \cdot \Delta\mathbf{R} + \nabla_{\mathbf{R}} \left( \frac{H_{11}-H_{22}}{2} \right) \Delta\mathbf{R} & \nabla_{\mathbf{R}} H_{12} \cdot \Delta\mathbf{R} \\ \nabla_{\mathbf{R}} H_{12} \cdot \Delta\mathbf{R} & \nabla_{\mathbf{R}} \left( \frac{H_{11}+H_{22}}{2} \right) \cdot \Delta\mathbf{R} - \nabla_{\mathbf{R}} \left( \frac{H_{11}-H_{22}}{2} \right) \Delta\mathbf{R} \end{pmatrix}$$
$$\mathbf{W}^{(1)} = \begin{pmatrix} \mathbf{s} \cdot \Delta\mathbf{R} + \mathbf{g} \cdot \Delta\mathbf{R} & \mathbf{h} \cdot \Delta\mathbf{R} \\ \mathbf{h} \cdot \Delta\mathbf{R} & \mathbf{s} \cdot \Delta\mathbf{R} - \mathbf{g} \cdot \Delta\mathbf{R} \end{pmatrix}$$

# Conical Intersection

## topology of intersection

first order term

$$\mathbf{W}^{(1)} = \begin{pmatrix} \nabla_{\mathbf{R}} \left( \frac{H_{11}+H_{22}}{2} \right) \cdot \Delta \mathbf{R} + \nabla_{\mathbf{R}} \left( \frac{H_{11}-H_{22}}{2} \right) \Delta \mathbf{R} & \nabla_{\mathbf{R}} H_{12} \cdot \Delta \mathbf{R} \\ \nabla_{\mathbf{R}} H_{12} \cdot \Delta \mathbf{R} & \nabla_{\mathbf{R}} \left( \frac{H_{11}+H_{22}}{2} \right) \cdot \Delta \mathbf{R} - \nabla_{\mathbf{R}} \left( \frac{H_{11}-H_{22}}{2} \right) \Delta \mathbf{R} \end{pmatrix}$$
$$\mathbf{W}^{(1)} = \begin{pmatrix} \mathbf{s} \cdot \Delta \mathbf{R} + \mathbf{g} \cdot \Delta \mathbf{R} & \mathbf{h} \cdot \Delta \mathbf{R} \\ \mathbf{h} \cdot \Delta \mathbf{R} & \mathbf{s} \cdot \Delta \mathbf{R} - \mathbf{g} \cdot \Delta \mathbf{R} \end{pmatrix}$$

average gradient vector

$$\mathbf{s} = \nabla_{\mathbf{R}} \frac{H_{11} + H_{22}}{2} | \mathbf{R}_0$$

gradient difference vector

$$\mathbf{g} = \nabla_{\mathbf{R}} \frac{H_{11} - H_{22}}{2} | \mathbf{R}_0$$

derivative coupling vector

$$\mathbf{h} = \nabla_{\mathbf{R}} H_{12} | \mathbf{R}_0$$

# Conical Intersection

topology of intersection

keeping only terms to first order

$$\mathbf{W}(\Delta \mathbf{R}) \approx \mathbf{W}^{(0)} + \mathbf{W}^{(1)}$$

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$$\mathbf{W}(\Delta \mathbf{R}) \approx \mathbf{W}^{(0)} + \mathbf{W}^{(1)}$$

set zero<sup>th</sup> order term to zero (just an offset)

$$\mathbf{W}(\Delta \mathbf{R}) \approx \begin{pmatrix} s \cdot \Delta \mathbf{R} + g \cdot \Delta \mathbf{R} & h \cdot \Delta \mathbf{R} \\ h \cdot \Delta \mathbf{R} & s \cdot \Delta \mathbf{R} - g \cdot \Delta \mathbf{R} \end{pmatrix}$$

# Conical Intersection

topology of intersection

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diagonalize to get adiabatic PES

$$V_1(\Delta\mathbf{R}) = s \cdot \Delta\mathbf{R} - \sqrt{(g \cdot \Delta\mathbf{R})^2 + (h \cdot \Delta\mathbf{R})^2}$$

$$V_2(\Delta\mathbf{R}) = s \cdot \Delta\mathbf{R} + \sqrt{(g \cdot \Delta\mathbf{R})^2 + (h \cdot \Delta\mathbf{R})^2}$$

# Conical Intersection

topology of intersection

eigenvalues of  $\mathbf{W}$

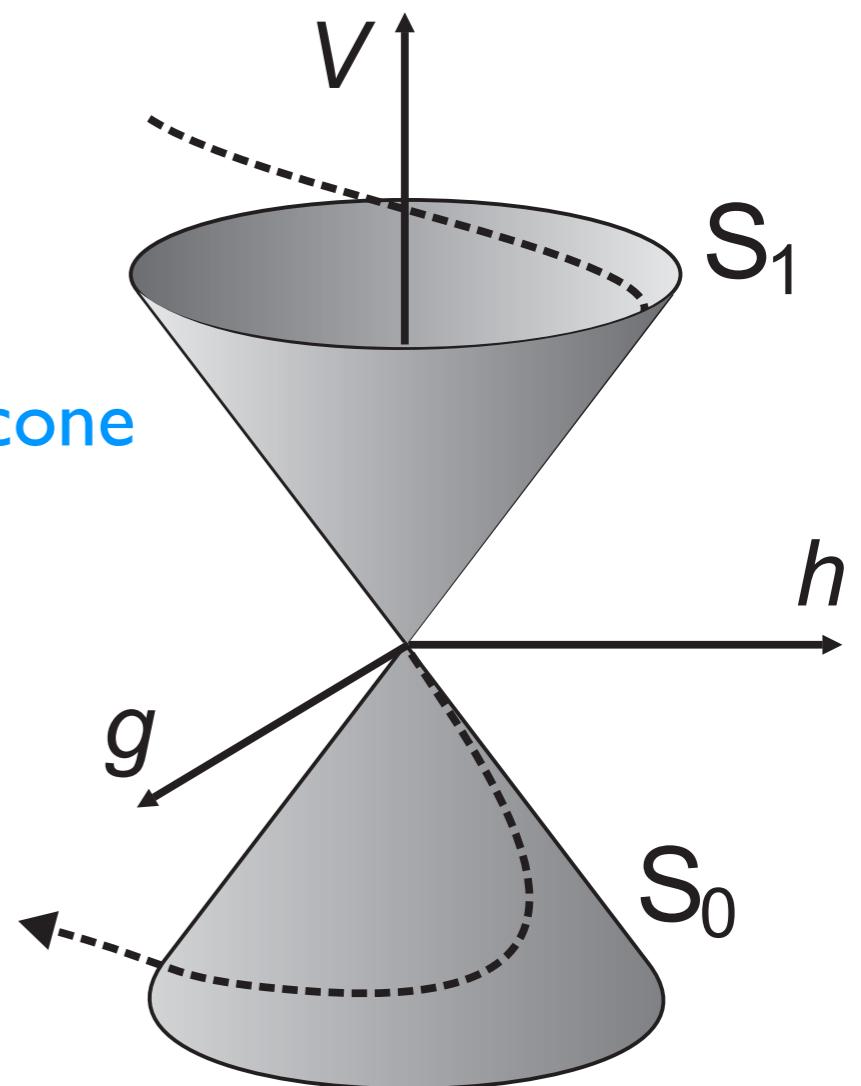
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double cone in branching space (g-h space)

adiabatic surfaces touch at tip

average gradient projected on g-h gives tilt of cone



# Conical Intersection

topology of intersection

eigenvalues of  $\mathbf{W}$

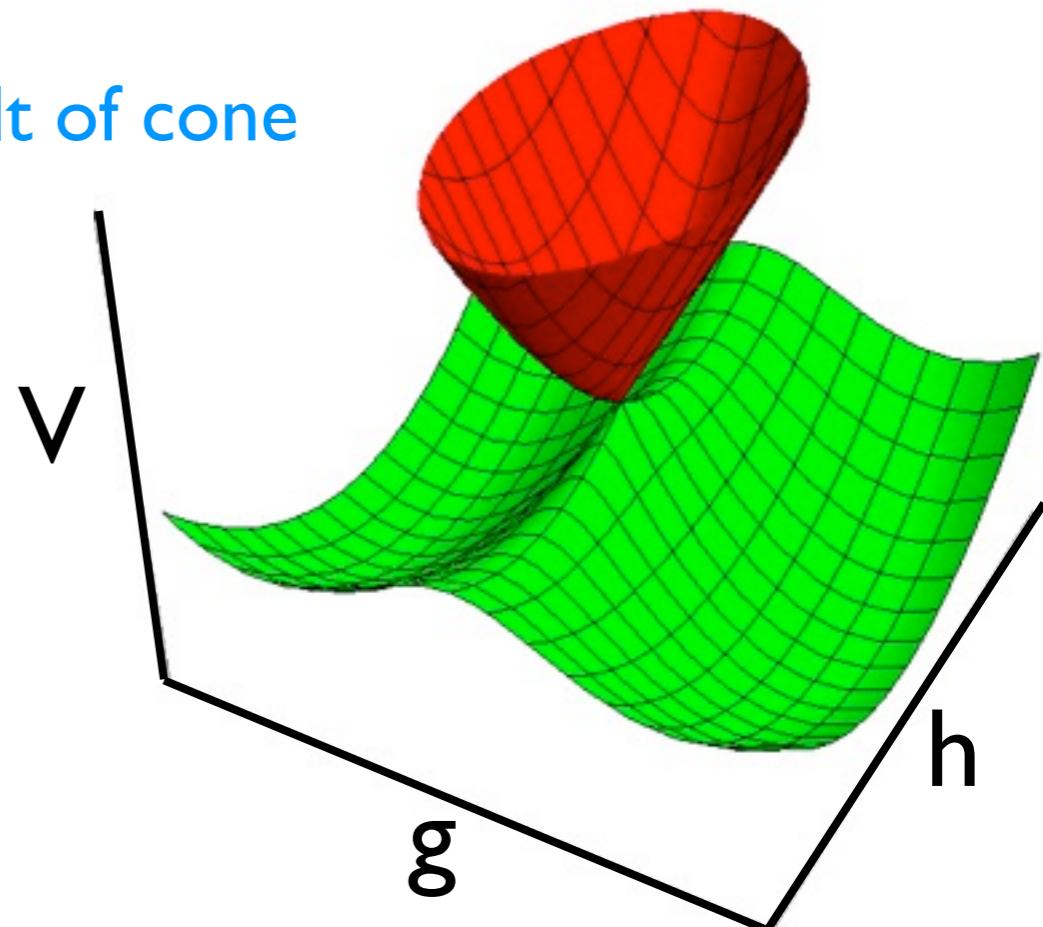
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double cone in branching space (g-h space) to first order!

adiabatic surfaces touch at tip

average gradient projected on g-h gives tilt of cone



# Conical Intersection

back to adiabatic basis

degeneracy requires (to first order) that

$$\mathbf{g} \cdot \Delta \mathbf{R} = 0 \wedge \mathbf{h} \cdot \Delta \mathbf{R}$$

independent: accidental same-symmetry intersection

two coordinate need to change to locate intersection

single degree of freedom: non-crossing rule in diatomics

degeneracy lifted in branching space

degeneracy maintained in  $3N-8$  remaining degree of freedom

# Conical Intersection

back to adiabatic basis

degeneracy lifted in branching space

$$\mathbf{x}_1 = \|\mathbf{g}\| \quad \mathbf{x}_2 = \|\mathbf{h}\|$$

# Conical Intersection

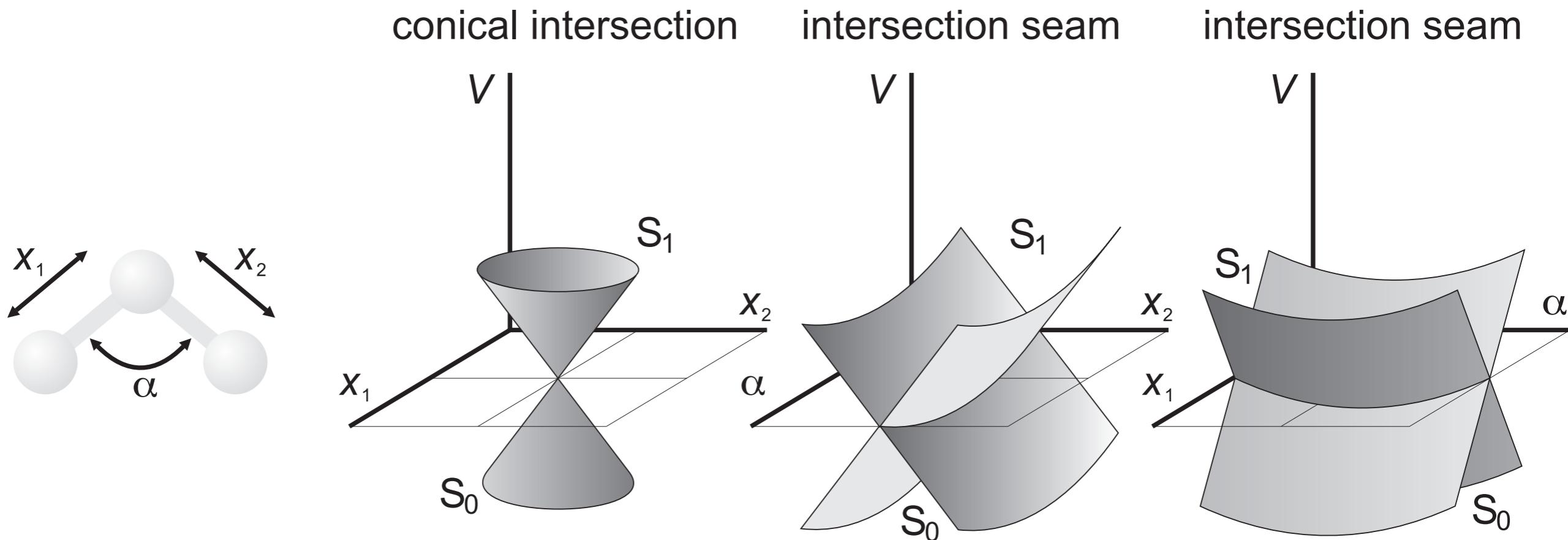
back to adiabatic basis

degeneracy lifted in branching space

$$\mathbf{x}_1 = \|\mathbf{g}\| \quad \mathbf{x}_2 = \|\mathbf{h}\|$$

degeneracy maintained in  $3N-8$  remaining degree of freedom

tri-atomics: hypothetical example



# Conical Intersection

back to adiabatic basis

derivative coupling parallel to non-adiabatic coupling

$$\mathbf{h} = \nabla_{\mathbf{R}} \langle \psi_1 | H | \psi_2 \rangle$$

$$= V_2 \langle \nabla_{\mathbf{R}} \psi_1 | \psi_2 \rangle + V_1 \langle \psi_1 | \nabla_{\mathbf{R}} \psi_2 \rangle + \langle \psi_1 | \nabla_{\mathbf{R}} H | \psi_2 \rangle$$

adiabatic basis

$$\nabla_{\mathbf{R}} \langle \psi_l | \psi_j \rangle = 0$$

$$\langle \nabla_{\mathbf{R}} \psi_l | \psi_j \rangle + \langle \psi_l | \nabla_{\mathbf{R}} \psi_j \rangle = 0$$

$$\langle \nabla_{\mathbf{R}} \psi_l | \psi_j \rangle = -\langle \psi_l | \nabla_{\mathbf{R}} \psi_j \rangle$$

at conical intersection  $V_1 = V_2$

$$\mathbf{h} = -V_2 \langle \psi_1 | \nabla_{\mathbf{R}} \psi_2 \rangle + V_1 \langle \psi_1 | \nabla_{\mathbf{R}} \psi_2 \rangle + \langle \psi_1 | \nabla_{\mathbf{R}} H | \psi_2 \rangle$$

$$= \langle \psi_1 | \nabla_{\mathbf{R}} H | \psi_2 \rangle$$

remember: non-adiabatic coupling vector

$$\mathbf{F}_{12} = \langle \psi_1 | \nabla_{\mathbf{R}} | \psi_2 \rangle = \frac{\langle \psi_1 | \nabla_{\mathbf{R}} H | \psi_2 \rangle}{V_2 - V_1}$$

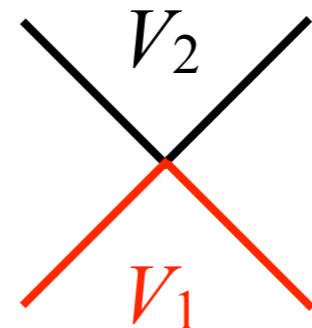
# Conical Intersection

average gradient ( $s$ ) determines tilt of double cone

peaked

photoreactivity

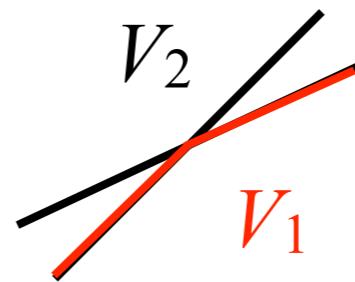
$$s \cdot g \approx 0 \quad s \cdot h \approx 0$$



sloped

photostability

$$s \cdot g > 0$$



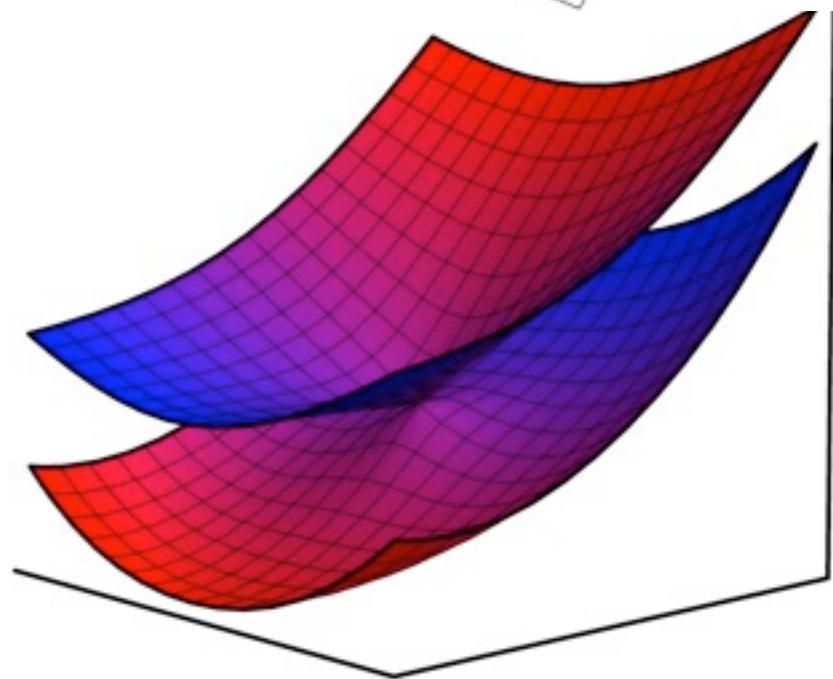
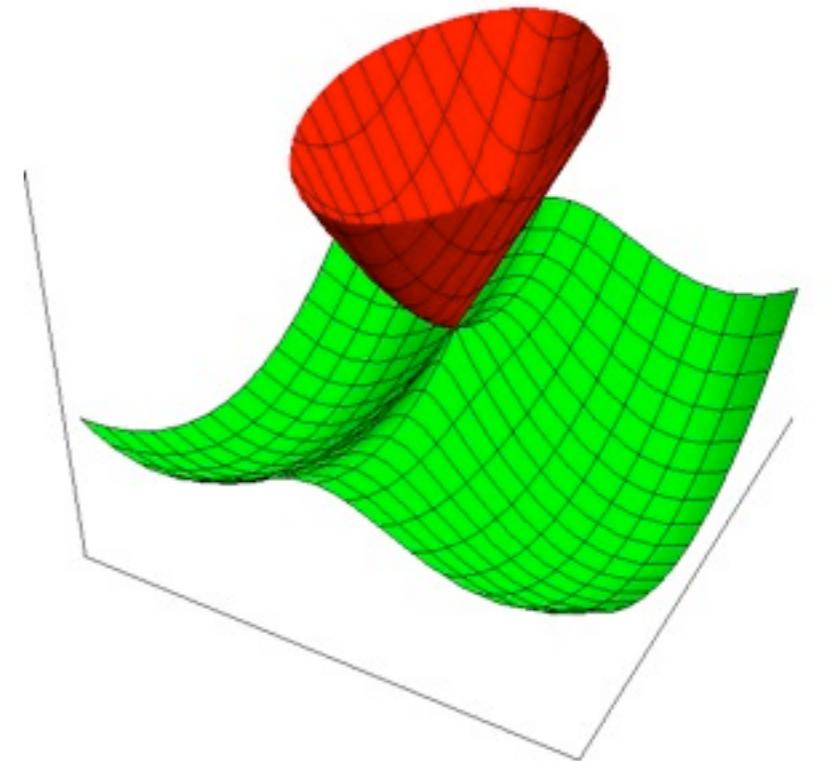
all are  $3N-8$  dimensional hyperlines

impossible to hit

compare point in plane

possible to get near

coupling strong enough for transition



# Conical Intersection

they are everywhere!



# Conical Intersection

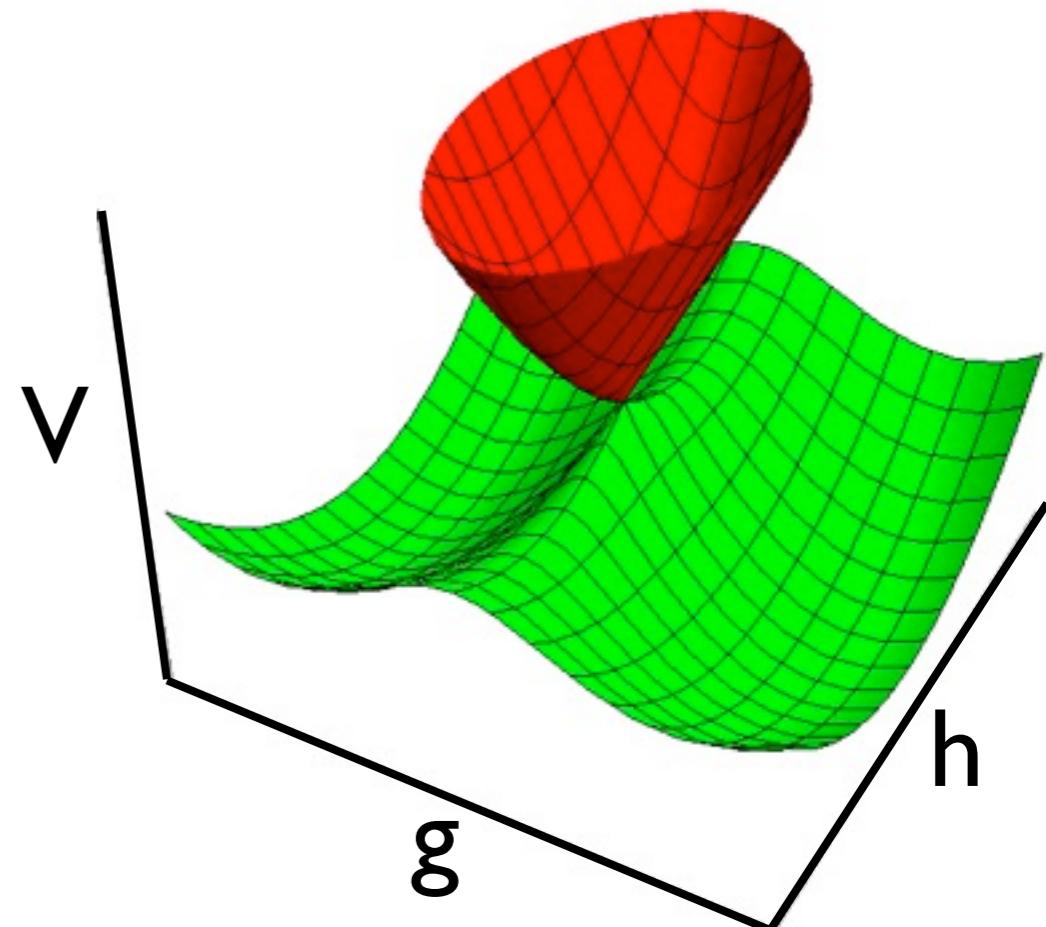
finding them

electronic structure of excited & ground state: SA-CASSCF

optimization on  $S_1$  in N-2 internal degrees of freedom

minimize gap in g-h plane

example for practical



# Conical Intersection

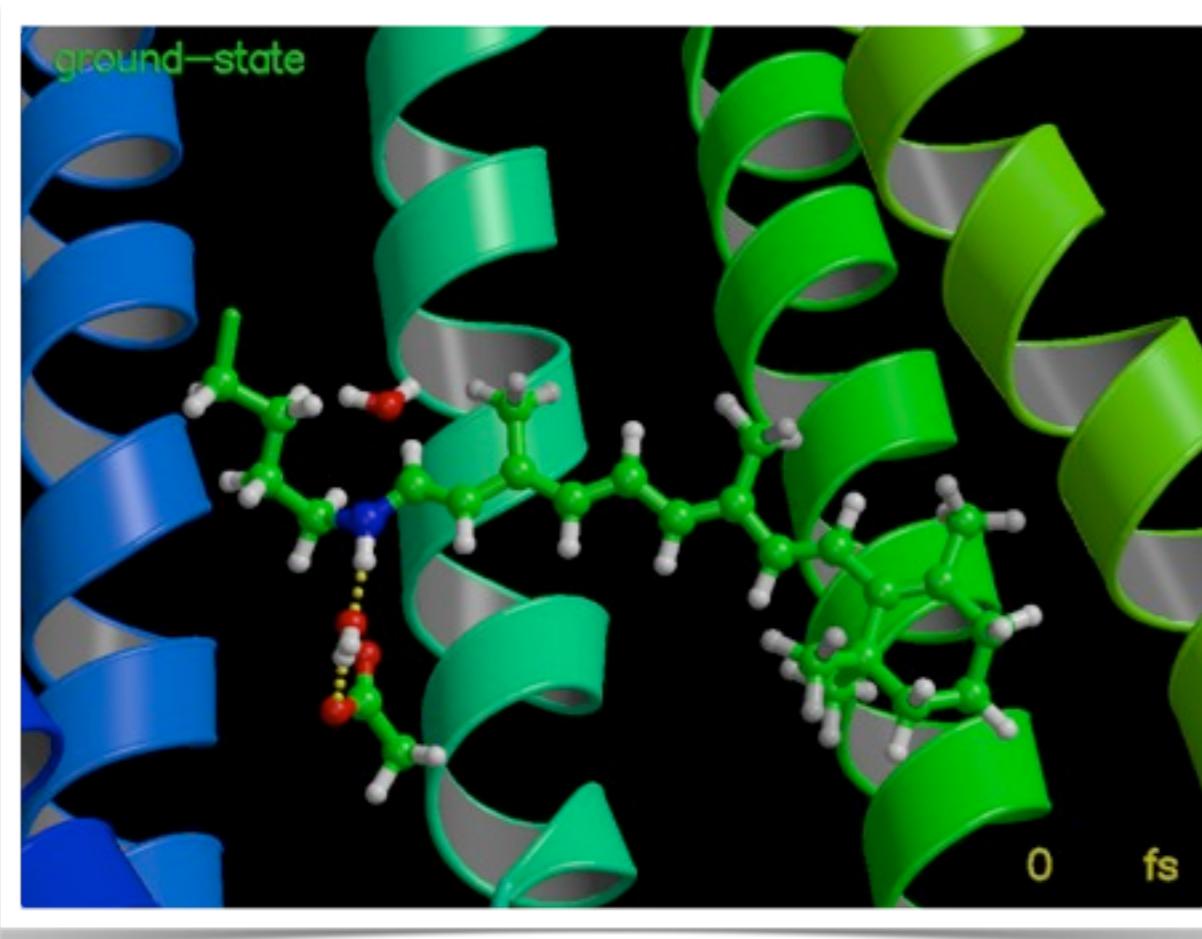
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example for practical: photoisomerization



# Conical Intersection

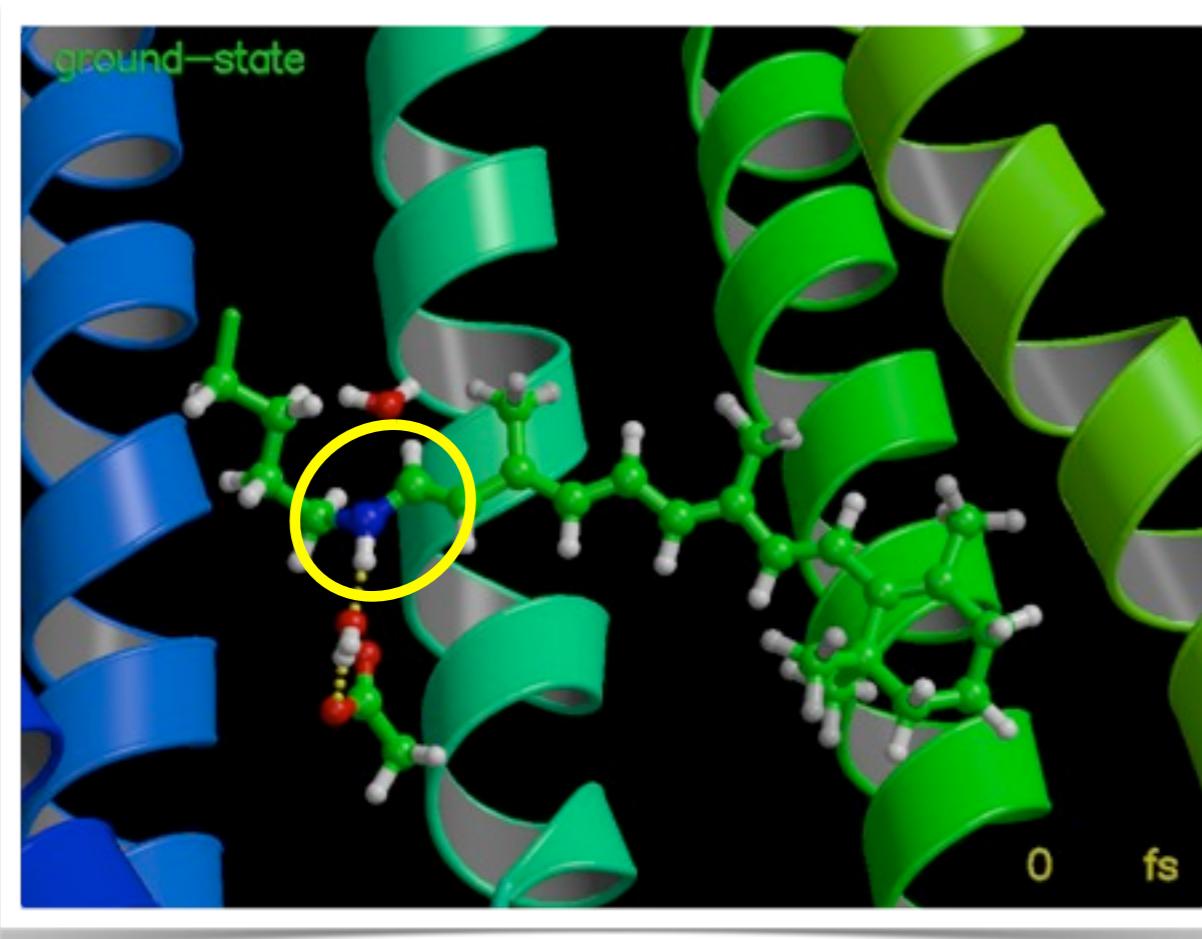
finding them

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example for practical: photoisomerization



# Conical Intersection

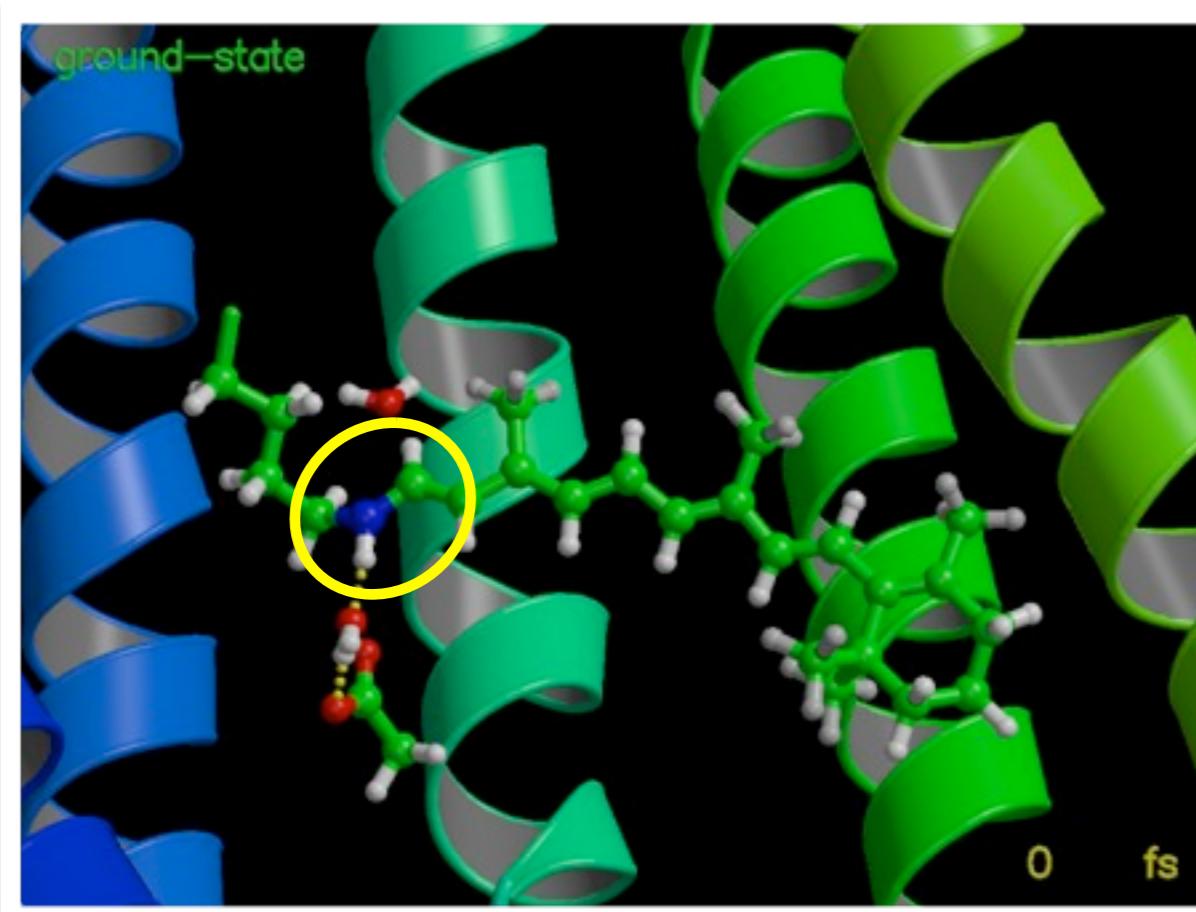
finding them

electronic structure of excited & ground state: SA-CASSCF

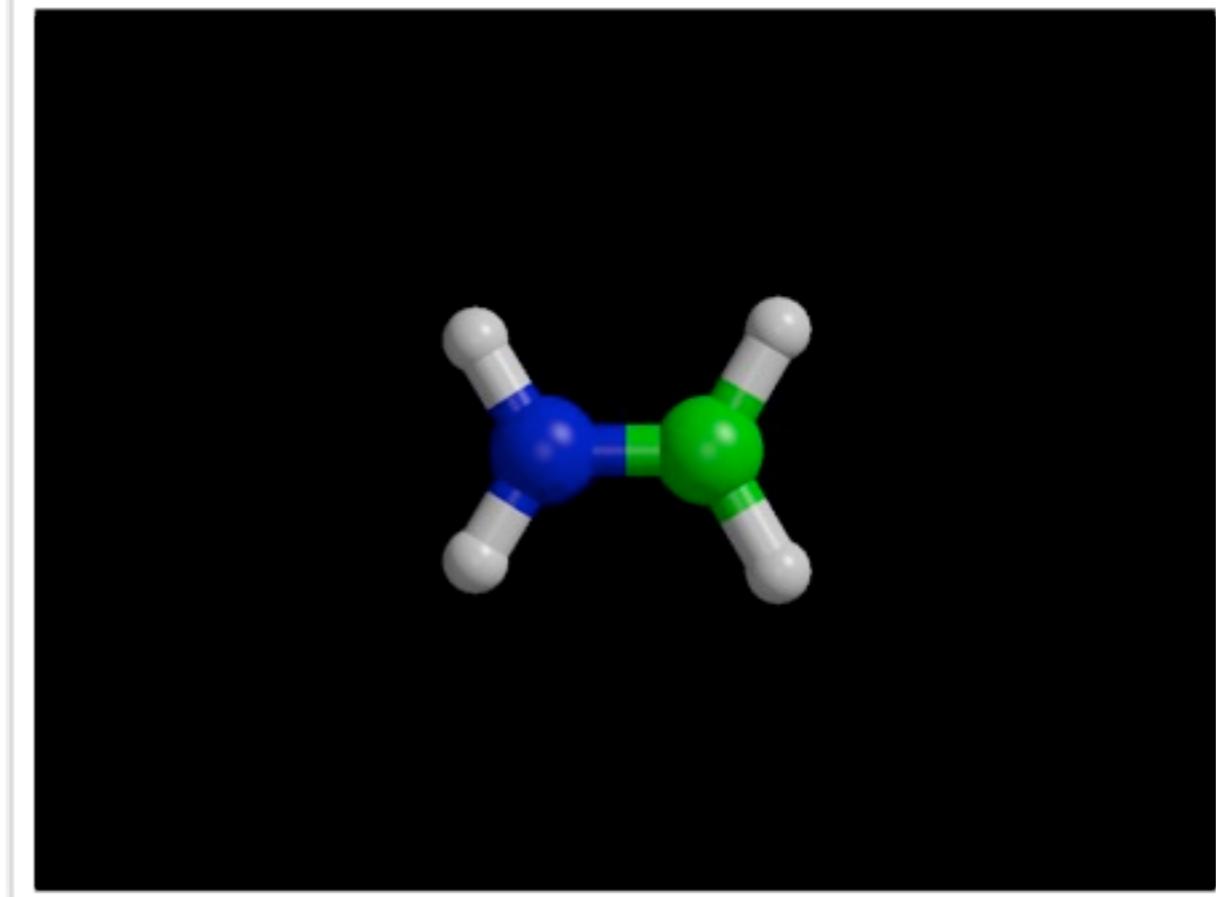
optimization on  $S_1$  in N-2 internal degrees of freedom

minimize gap in g-h plane

example for practical: photoisomerization



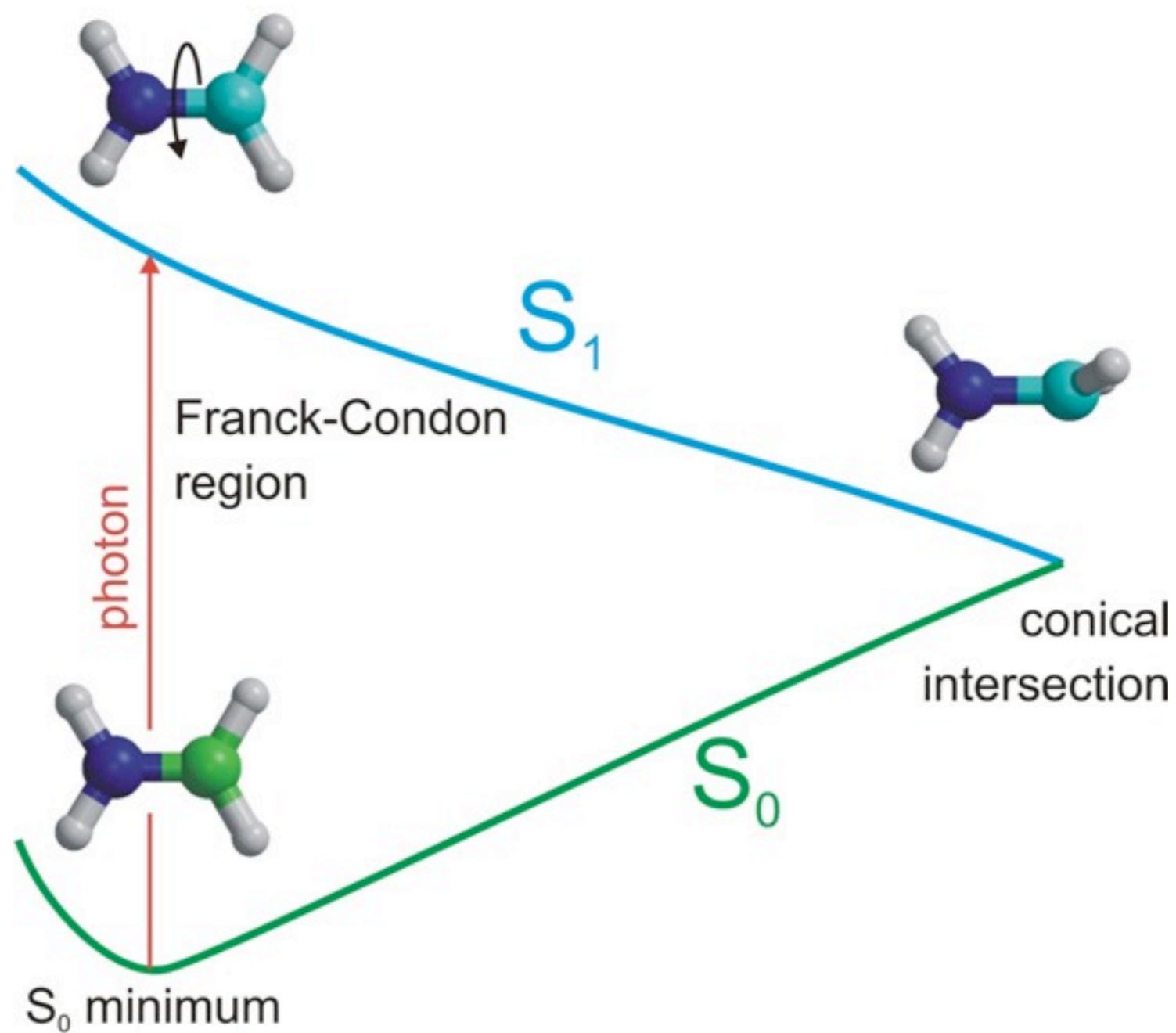
$\approx$



# Conical Intersection

example for practical: photoisomerization

optimizing conical intersection in protonated formaldimine



# Quantum chemistry

isolated molecules

molecular Schrödinger equation

$$H^{\text{tot}}(\mathbf{r}_e, \mathbf{R}_N) \Phi^{\text{tot}}(\mathbf{r}_e, \mathbf{R}_N) = E^{\text{tot}} \Phi^{\text{tot}}(\mathbf{r}_e, \mathbf{R}_N)$$

molecular Hamiltonian

$$H^{\text{tot}}(\mathbf{r}_e, \mathbf{R}_N) = T^{\text{nuc}}(\mathbf{R}_N) + T^{\text{eln}}(\mathbf{r}_e, \mathbf{R}_N) + U(\mathbf{r}_e, \mathbf{R}_N)$$

# Quantum chemistry

## Born-Oppenheimer approximation

$$m_e/m_p \approx 1/2000$$

electrons much faster than nuclei

electrons adapt instantly (assumption)

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## Born-Oppenheimer approximation

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$$\Phi^{\text{tot}}(\mathbf{r}_e, \mathbf{R}_N) = \Xi^{\text{nuc}}(\mathbf{R}_N) \Psi^{\text{eln}}(\mathbf{r}_e; \mathbf{R}_N)$$

## electronic Schrödinger equation

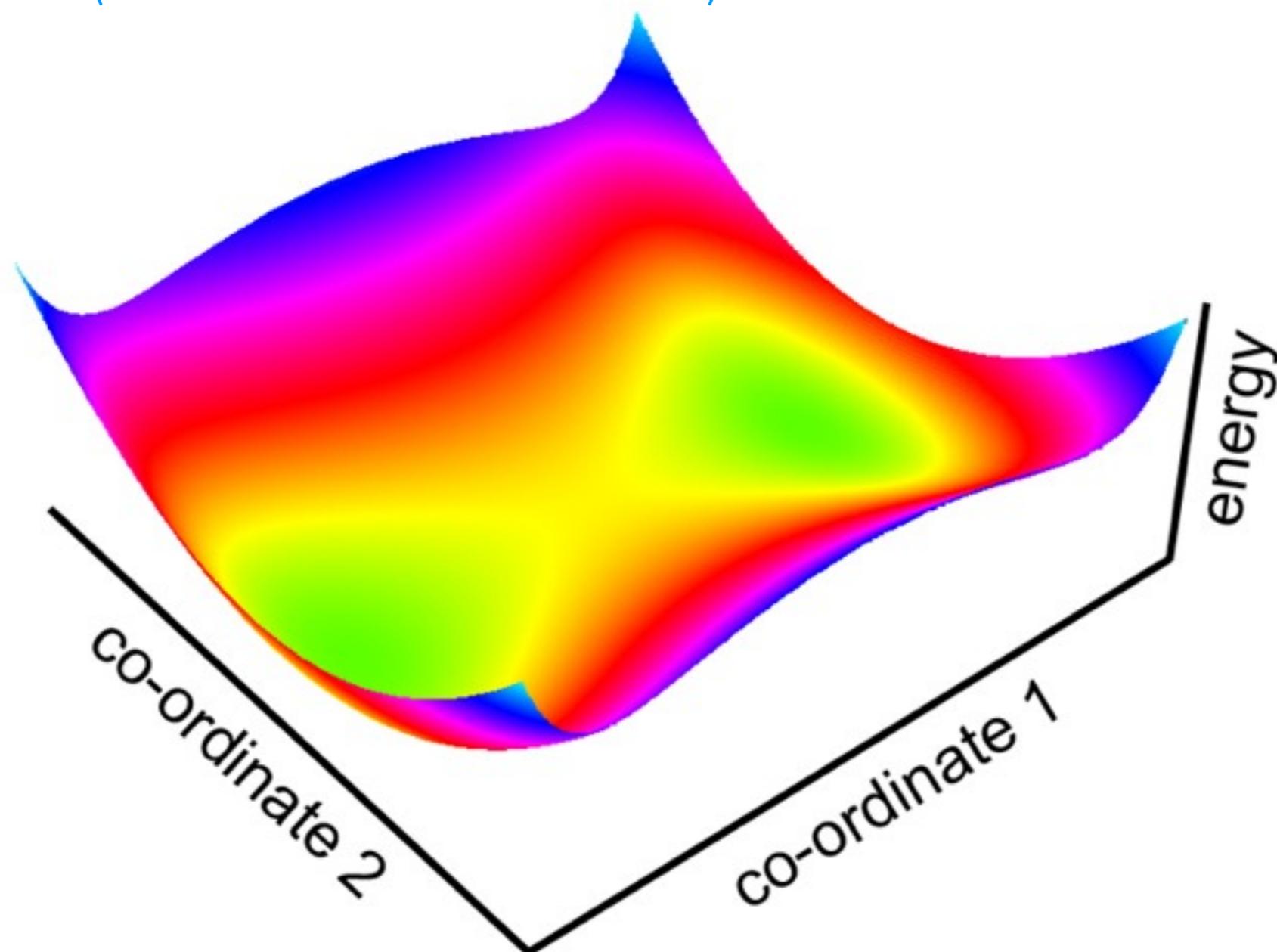
$$H^{\text{eln}}(\mathbf{R}_N, \mathbf{r}_e) \Psi^{\text{eln}}(\mathbf{r}_e; \mathbf{R}_N) = V(\mathbf{R}_N) \Psi^{\text{eln}}(\mathbf{r}_e; \mathbf{R}_N)$$

$$H^{\text{eln}}(\mathbf{R}_N, \mathbf{r}_e) = T^{\text{eln}}(\mathbf{r}_e) + U(\mathbf{r}_e, \mathbf{R}_N)$$

# Quantum chemistry

adiabatic potential energy surface for nuclei

$$V(\mathbf{R}) = \langle \Psi^{\text{eln}} | H^{\text{eln}}(\mathbf{R}) | \Psi^{\text{eln}} \rangle$$



# Molecular Dynamics

nuclei are classical particles (assumption)

$$F_n = m_n \ddot{x}_n = -\nabla_{x_n} V(x_1, x_2, \dots, x_N)$$

$$x_n(t) = x_n(t_0) + \dot{x}_n(t_0)(t - t_0) + \frac{1}{2} \ddot{x}_n^2 (t - t_0)^2$$

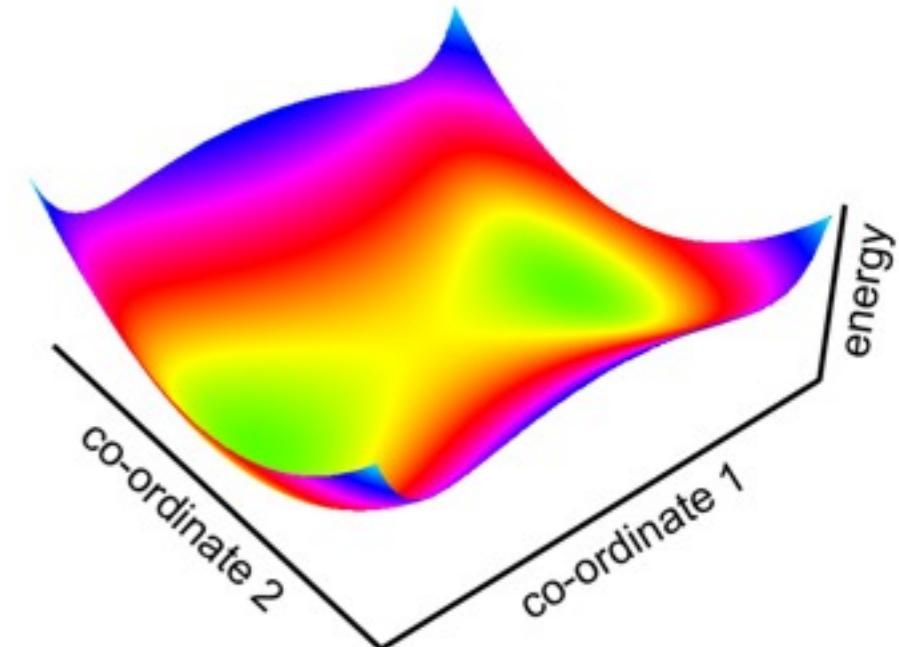
potential energy and forces

$$V(x_1, x_2, \dots, x_N) = \langle \Psi_e | \hat{H}(x_1, x_2, \dots, x_N) | \Psi_e \rangle$$

limitations

protons (low mass): tunneling through barrier

H/D isotope effect



# Molecular Dynamics

Hellmann-Feynmann forces

$$F_n = -\langle \Psi_e | \nabla H(R_1, R_2, \dots, R_N) | \Psi_e \rangle$$

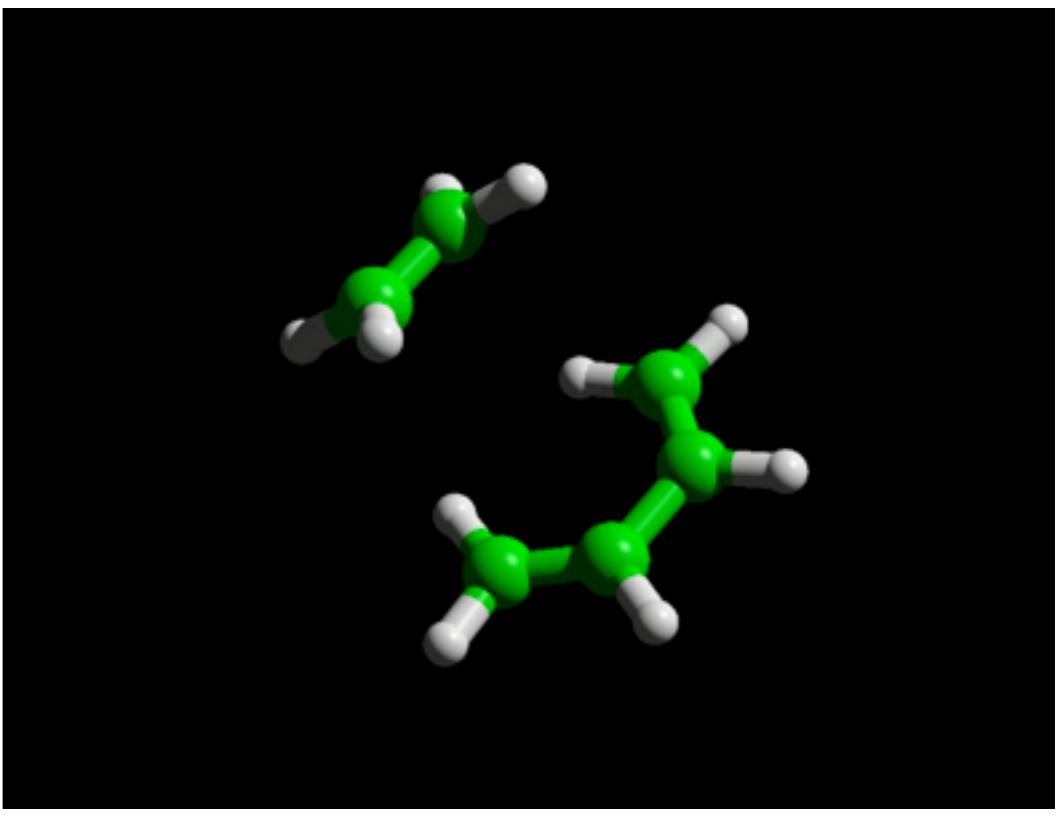
electrons adapt instantly!!

on-the-fly molecular dynamics

reactions

photochemistry

electron transfer



**So far so good ...**

So far so good ...

... but how can we calculate  $\Psi_e$ ?

So far so good ...

... but how can we calculate  $\Psi_e$ ?

except for the hydrogen atom we can't ...

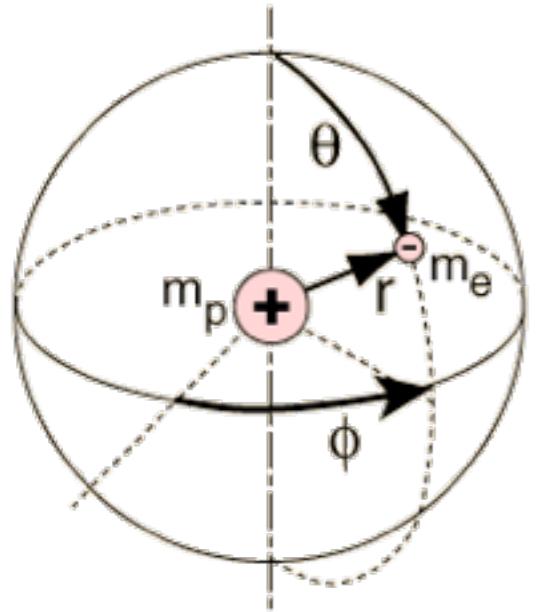
So far so good ...

... but how can we calculate  $\Psi_e$ ?

except for the hydrogen atom we can't ...

... but we can approximate  $\Psi_e$ !

# Wasserstoffatom



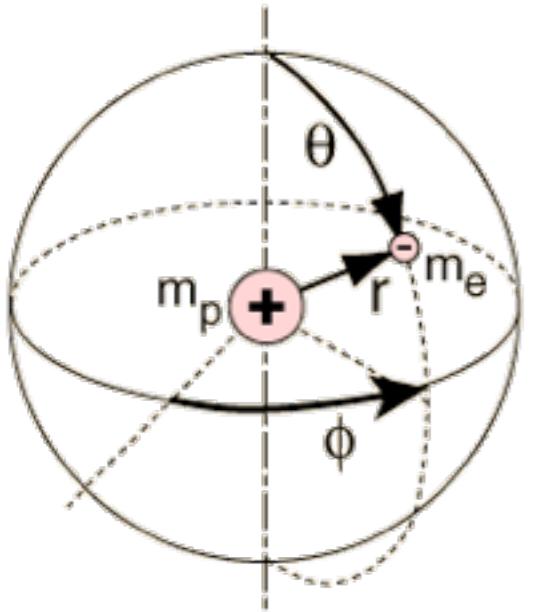
## Kugelkoordinaten

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

# Wasserstoffatom



## Kugelkoordinaten

$$x = r \sin \theta \cos \phi$$

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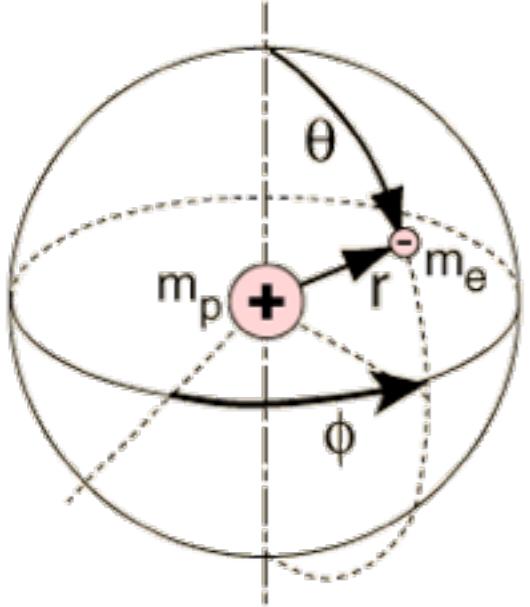
$$z = r \cos \theta$$

## Schrödinger-Gleichung

$$H\psi(x, y, z) = E\psi(x, y, z)$$

$$H = -\frac{\hbar^2}{2m_e} \nabla^2 + \frac{Ze^2}{4\pi\epsilon_0 r}$$

# Wasserstoffatom



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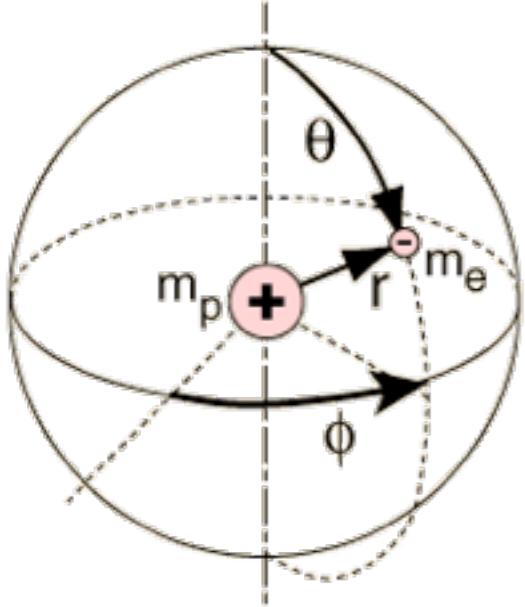
$$H = -\frac{\hbar^2}{2m_e} \nabla^2 + \frac{Ze^2}{4\pi\epsilon_0 r}$$

## Wellenfunktion

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi)$$

$$\psi_{nlm}(r, \theta, \phi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n((n+l)!)^3}} \exp\left[-\frac{r}{na_0}\right] \left(\frac{2r}{na_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) Y_{lm}(\theta, \phi)$$

# Wasserstoffatom

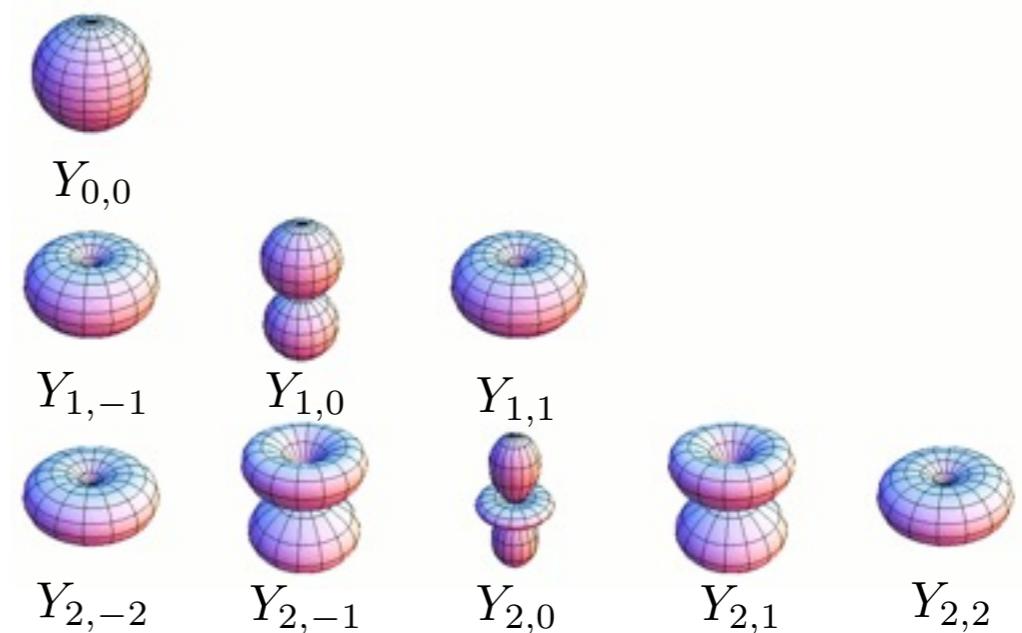


## Kugelkoordinaten

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$



## Kugelflächenfunktionen

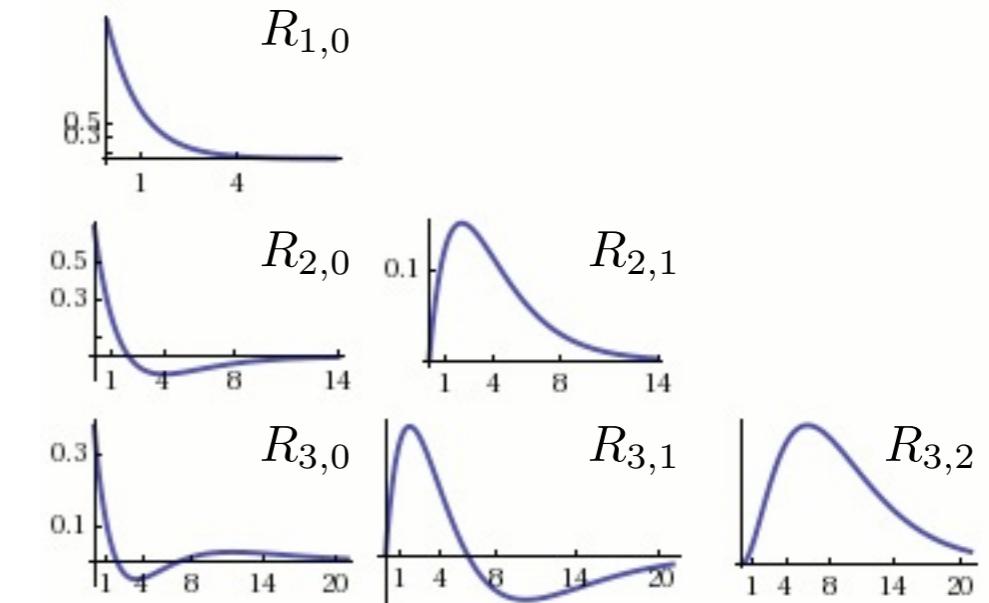
## Schrödinger-Gleichung

$$H\psi(x, y, z) = E\psi(x, y, z)$$

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## Wellenfunktion

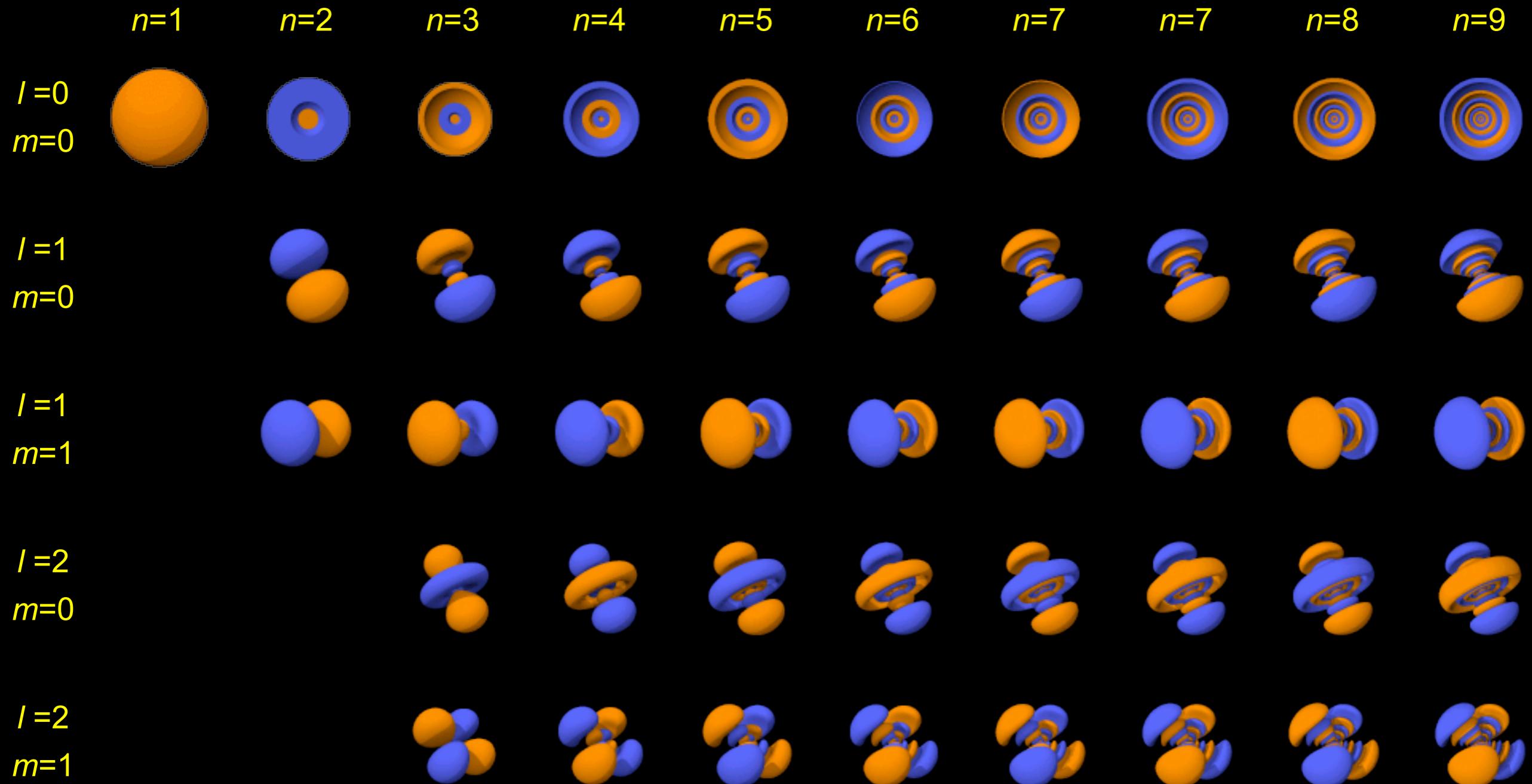
$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi)$$



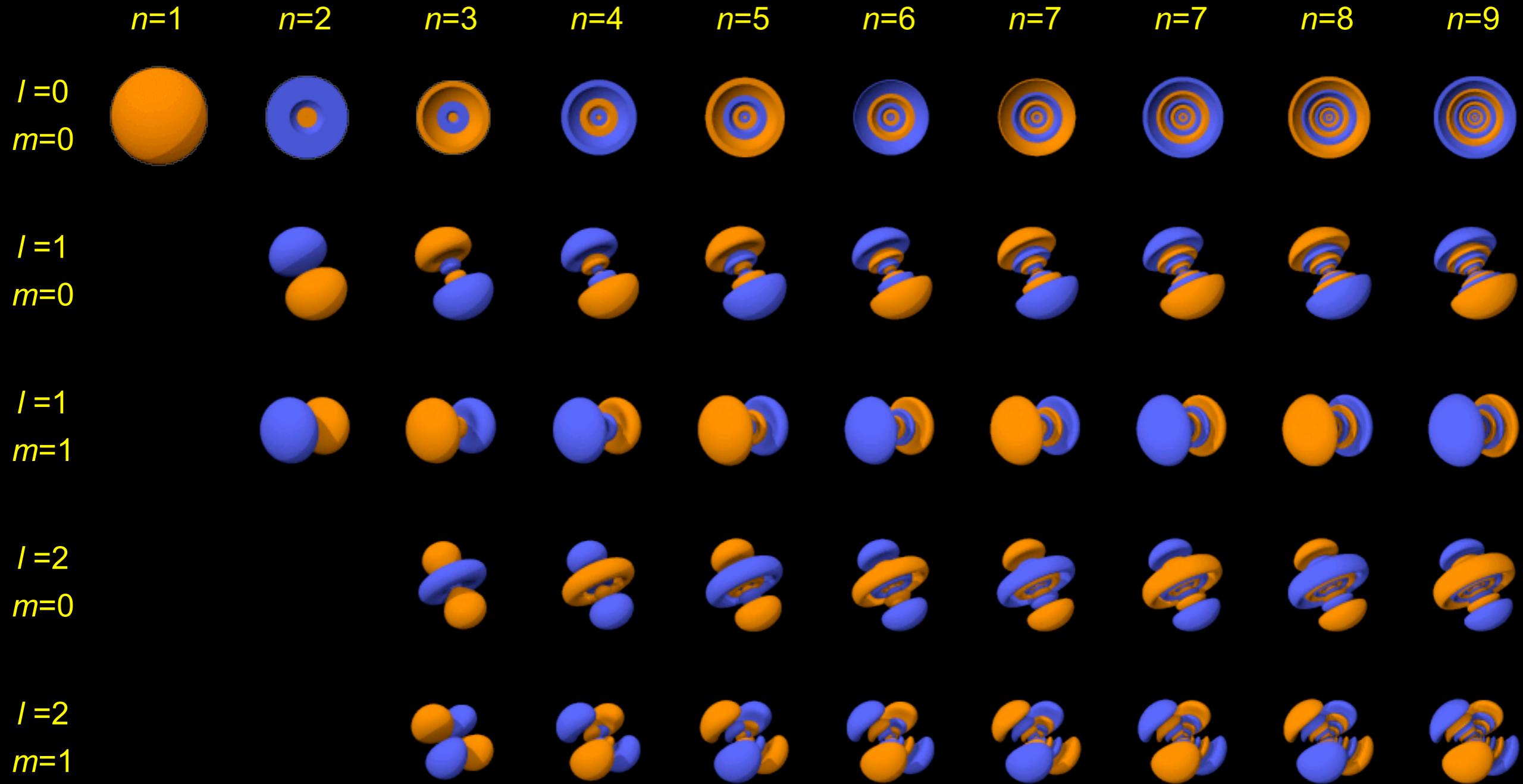
## Zugeordnete Laguerre-Polynome

$$\psi_{nlm}(r, \theta, \phi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n((n+l)!)^3}} \exp\left[-\frac{r}{na_0}\right] \left(\frac{2r}{na_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) Y_{lm}(\theta, \phi)$$

# Atomic orbitals



# Atomic orbitals



Complete set: any function can be expanded in  $\psi(r, \theta, \phi)$ :

$$\Phi(r, \theta, \phi) = \sum_i \sum_{n=1}^{n-1} \sum_{l=0}^{m=+l} \sum_{m=-l} c_{inlm} \psi_{nlm}(r, \theta, \phi)$$

# Orthogonal function spaces

eigenfunctions of an hermitian operator form a complete set

$$\hat{O}g_i(x) = \omega_i g_i(x)$$

any function can be expanded in terms of eigenfunctions

$$f(x) = \sum_i a_i g_i(x)$$

advantage

deduce effect of an operator on any function that is not by itself an eigenfunction of the operator:

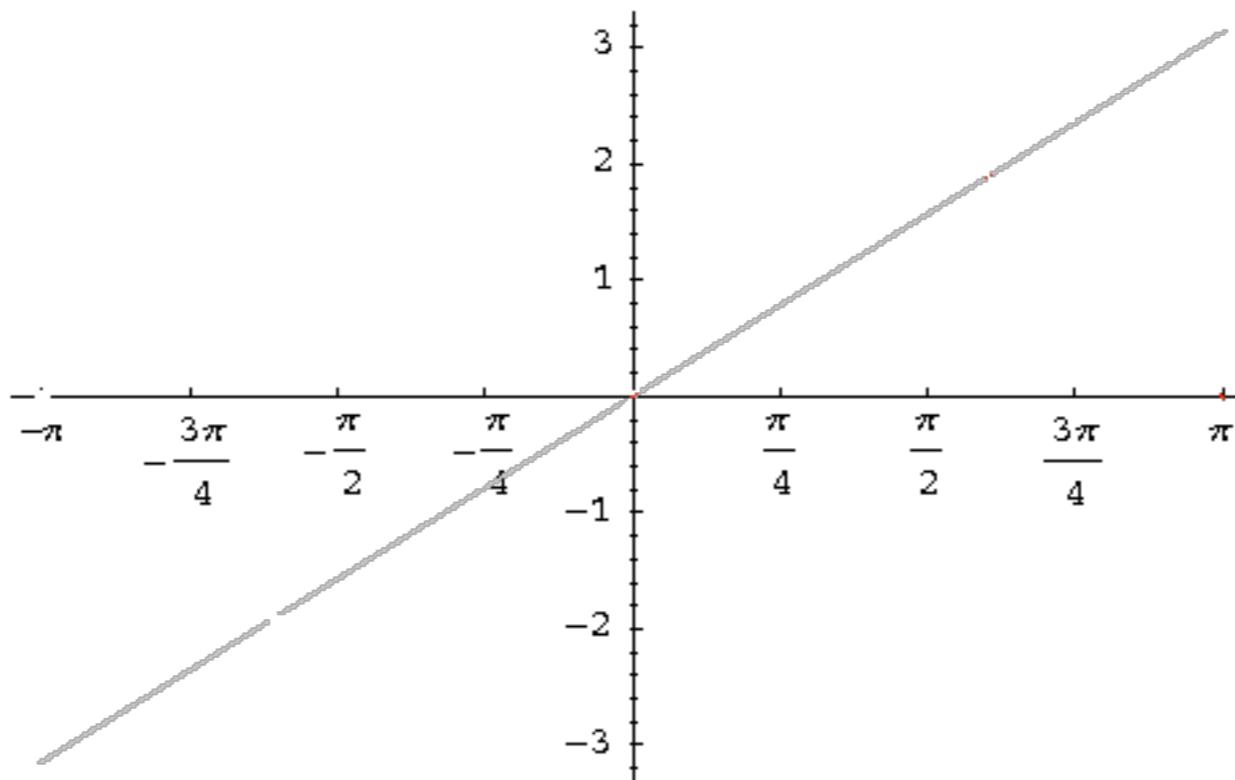
$$\hat{O}f(x) = \hat{O} \sum_i a_i g_i(x) = \sum_i a_i \hat{O}g_i(x) = \sum_i c_i \omega_i g_i(x)$$

# Recall from Mathematics: Fourier Series

Linear combination of Cosine and Sine functions

example

$$f(x) = x \quad -\pi \leq x \leq \pi$$



# Recall from Mathematics: Fourier Series

Linear combination of Cosine and Sine functions

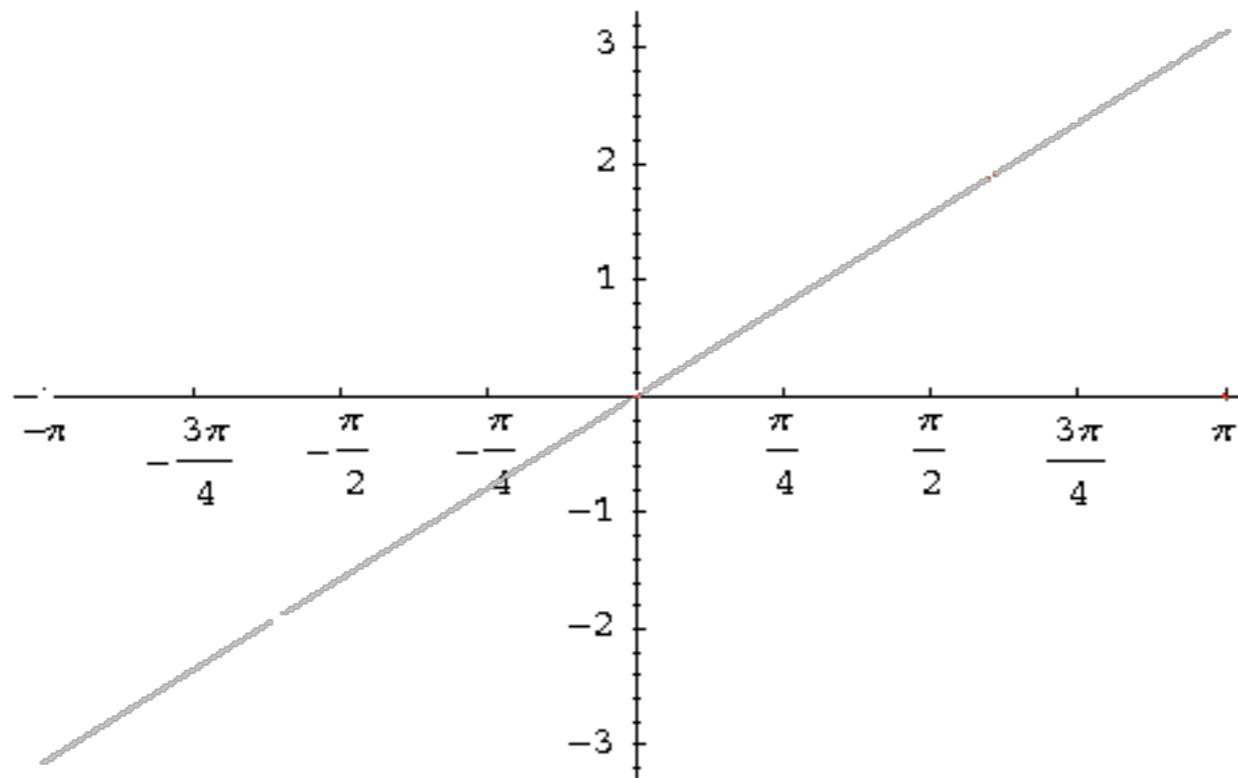
example

$$f(x) = x \quad -\pi \leq x \leq \pi$$

Fourier series

$$f(x) = \sum_{n=1}^{\infty} a_n \sin[nx] \quad a_n = \frac{2}{n}(-1)^{n+1}$$

$$f(x) \approx 2 \left( \sin[x] - \frac{1}{2} \sin[2x] + \frac{1}{3} \sin[3x] - \frac{1}{4} \sin[4x] + \dots \right)$$



# Recall from Mathematics: Fourier Series

Linear combination of Cosine and Sine functions

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# Recall from Mathematics: Fourier Series

Linear combination of Cosine and Sine functions

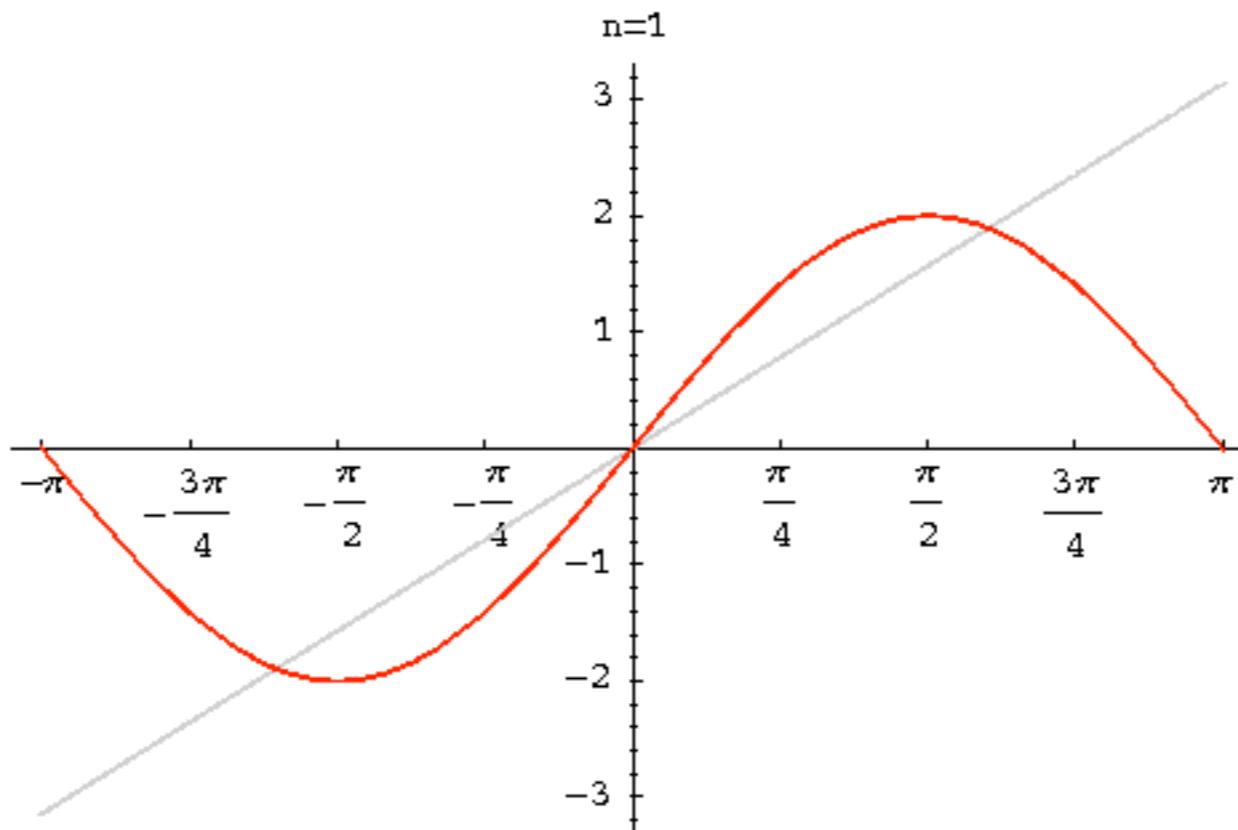
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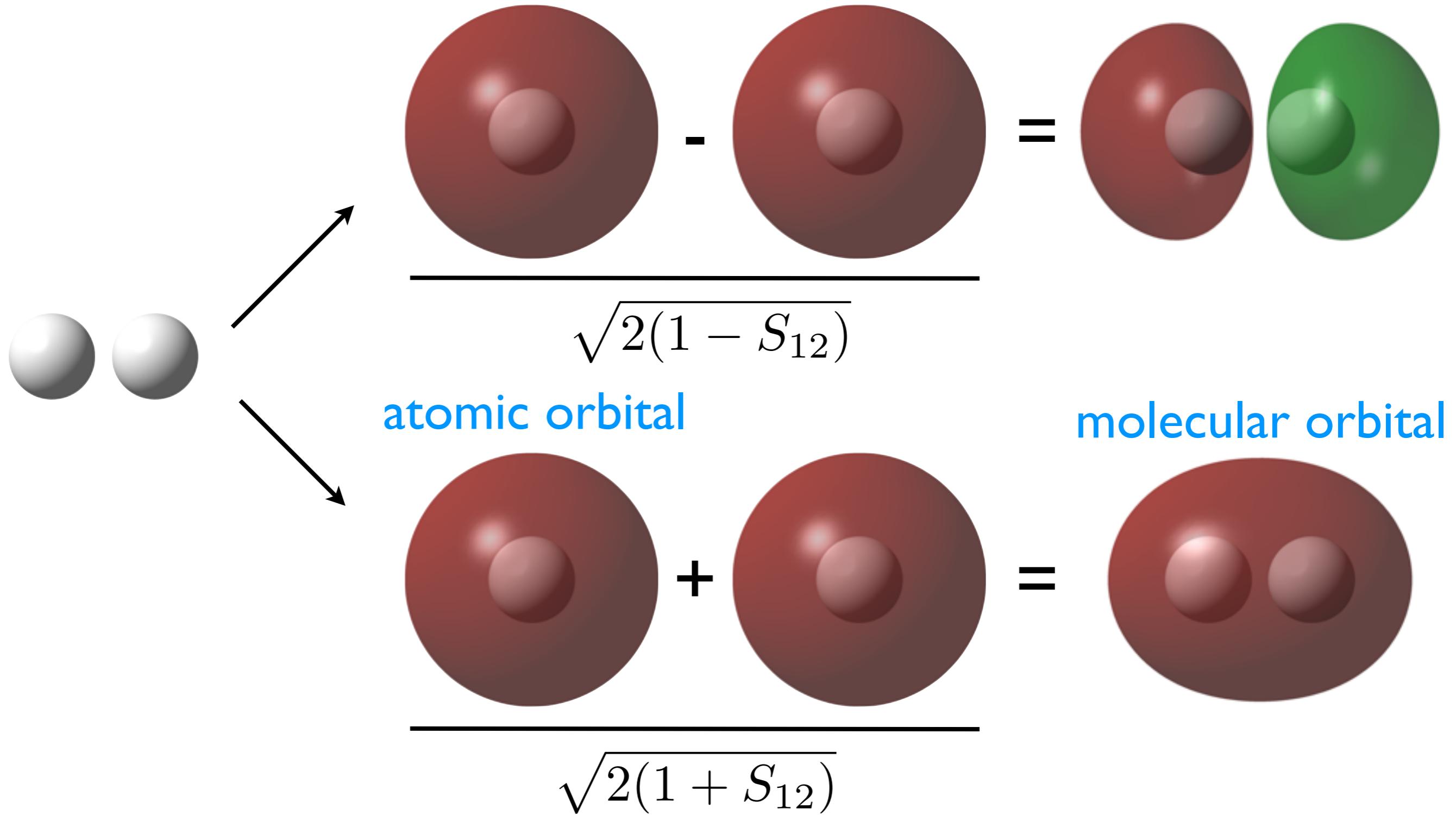
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# Hydrogen molecule

Linear Combination of single hydrogen orbitals



# Molecular Quantum Mechanics

many-electron Schrödinger equation

$$H^{\text{eln}} \Psi^{\text{eln}}(\mathbf{r}) = E \Psi^{\text{eln}}(\mathbf{r})$$

$$H = -\frac{\hbar^2}{2m_e} \sum_i^{n_e} \nabla_i^2 + \sum_i^{n_e} \sum_{j>i}^{n_e} \frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_i^{n_e} \sum_A^{N_{\text{QM}}} \frac{e^2 Z_A}{4\pi\epsilon_0 r_{iA}}$$

kinetic energy

electron-electron

electron-nuclei

$$+ \sum_A^{N_{\text{QM}}} \sum_{B>A}^{N_{\text{QM}}} \frac{e^2 Z_A Z_B}{4\pi\epsilon_0 R_{AB}}$$

nuclei-nuclei

# Molecular Quantum Mechanics

approaches for approximating  $\Psi_e$

Hartree-Fock and beyond (ab initio)

molecular orbitals

systematic improvement

precise, and only accurate with impossible computational effort

Density functional theory (semi-empirical)

many electron density

formally correct, if exact functional exists

precise, but not accurate

Quantum Monte Carlo (ab initio)

sample multi-dimensional wavefunction by Monte Carlo

quite accurate, but not precise

# Hartree-Fock Theory

Solving electronic structure problem on computers

Hartree product of non-interacting electrons

mean field

molecular orbitals

expectations values one and two electron operators

Pauli Principle

slater determinant of molecular orbitals

expectations values of one and two electron operators

energy of slater determinant

variation principle

optimizing the orbitals in slater determinant

one-particle mean-field fock operator

self-consistent-field

linear combinations atomic orbitals & basissets

Roothaan Hall equations

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Slater determinant of molecular orbitals

one-electron basisfunctions

many-electron basisfunctions

configuration interaction

Lagrange undetermined multipliers

linear variation principle

# Hartree-Fock Theory for $n$ electrons

mean-field approach

$$H = \sum_i \left\{ -\frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_A \frac{e^2 Z_A}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{R}_A|} + v_i^{\text{mf}}(\mathbf{r}_i) \right\}$$

atomic units

$$h_i(\mathbf{r}_i) = -\nabla_i^2 + \sum_A \frac{Z_A}{r_{iA}} + v_i^{\text{mf}}(\mathbf{r}_i)$$

independent electrons

$$H = \sum_i h_i(\mathbf{r}_i)$$

one-electron wavefunctions (molecular orbitals)

$$h_i(\mathbf{r})\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

orthonormal

$$\int \phi_i^*(\mathbf{r})\phi_j(\mathbf{r})d\mathbf{r} = \delta_{ij}$$

Hartree product of  $n$  distinguishable electrons

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\dots\phi_n(\mathbf{r}_n)$$

# Hartree-Fock Theory for $n$ electrons

indistinguishable electrons

fermions with 3 spatial and 1 spin coordinate (4D)

$$\{\mathbf{x}\} = \{\mathbf{r}, s\}$$

Pauli principle

$$\Psi(\mathbf{r}_1, \mathbf{x}_2, \dots, \mathbf{x}_i, \mathbf{x}_j, \dots, \mathbf{x}_n) = -\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_j, \mathbf{x}_i, \dots, \mathbf{x}_n)$$

spin orbitals

$$\varphi_i(\mathbf{x}) = \begin{cases} \phi_i(\mathbf{r})\alpha(s) \\ \phi_i(\mathbf{r})\beta(s) \end{cases}$$

spin functions

$$\int \alpha(s)\beta(s)ds = \delta_{\alpha\beta}$$

# Hartree-Fock Theory for $n$ electrons

antisymmetric linear combination of Hartree products:

i.e. 2 electrons

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} [\varphi_1(\mathbf{x}_1)\varphi_2(\mathbf{x}_2) - \varphi_2(\mathbf{x}_1)\varphi_1(\mathbf{x}_2)]$$

$n$  electrons: Slater determinant

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \varphi_1(\mathbf{x}_1) & \varphi_1(\mathbf{x}_2) & \dots & \varphi_1(\mathbf{x}_n) \\ \varphi_2(\mathbf{x}_1) & \varphi_2(\mathbf{x}_2) & \dots & \varphi_2(\mathbf{x}_n) \\ \dots & \dots & \dots & \dots \\ \varphi_n(\mathbf{x}_1) & \varphi_n(\mathbf{x}_2) & \dots & \varphi_n(\mathbf{x}_n) \end{vmatrix}$$

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# Hartree-Fock Theory for $n$ electrons

anitsymmetric linear combination of Hartree products:

i.e. 2 electrons ( $\text{H}_2$ ,  $\text{HeH}^+$ )

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} [\varphi_1(\mathbf{x}_1)\varphi_2(\mathbf{x}_2) - \varphi_2(\mathbf{x}_1)\varphi_1(\mathbf{x}_2)]$$

molecular orbitals: spatial & spin part

$$\varphi_i(\mathbf{x}) = \begin{cases} \phi_i(\mathbf{r})\alpha(s) \\ \phi_i(\mathbf{r})\beta(s) \end{cases}$$

joint/pair probability density

$$P(\mathbf{r}_1, \mathbf{r}_2) = \int \int P(\mathbf{x}_1, \mathbf{x}_2) ds_1 ds_2$$

$$= \int \int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, s_1, s_2) \Psi^*(\mathbf{r}_1, \mathbf{r}_2, s_1, s_2) ds_1 ds_2$$

# Hartree-Fock Theory for $n$ electrons

joint/pair probability

opposite spin

$$\begin{aligned} P(\mathbf{r}_1, \mathbf{r}_2) = & \frac{1}{2} \int \int \phi_1^*(\mathbf{r}_1) \alpha^*(s_1) \phi_2^*(\mathbf{r}_2) \beta^*(s_2) \phi_1(\mathbf{r}_1) \alpha(s_1) \phi_2(\mathbf{r}_2) \beta(s_2) ds_1 ds_2 - \\ & \frac{1}{2} \int \int \phi_1^*(\mathbf{r}_1) \alpha^*(s_1) \phi_2^*(\mathbf{r}_2) \beta^*(s_2) \phi_2(\mathbf{r}_1) \beta(s_1) \phi_1(\mathbf{r}_2) \alpha(s_2) ds_1 ds_2 - \\ & \frac{1}{2} \int \int \phi_2^*(\mathbf{r}_1) \beta^*(s_1) \phi_1^*(\mathbf{r}_2) \alpha^*(s_2) \phi_1(\mathbf{r}_1) \alpha(s_1) \phi_2(\mathbf{r}_2) \beta(s_2) ds_1 ds_2 + \\ & \frac{1}{2} \int \int \phi_2^*(\mathbf{r}_1) \beta^*(s_1) \phi_1^*(\mathbf{r}_2) \alpha^*(s_2) \phi_2(\mathbf{r}_1) \beta(s_1) \phi_1(\mathbf{r}_2) \alpha(s_2) ds_1 ds_2 \end{aligned}$$

uncorrelated

$$\begin{aligned} P(\mathbf{r}_1, \mathbf{r}_2) &= \frac{1}{2} \left[ |\phi_1(\mathbf{r}_1)|^2 |\phi_2(\mathbf{r}_2)|^2 + |\phi_2(\mathbf{r}_1)|^2 |\phi_1(\mathbf{r}_2)|^2 \right] \\ &= |\phi_1(\mathbf{r}_1)|^2 |\phi_2(\mathbf{r}_2)|^2 \end{aligned}$$

same spatial orbital:

$$P(\mathbf{r}_1, \mathbf{r}_2) = |\phi_1(\mathbf{r}_1)|^2 |\phi_1(\mathbf{r}_2)|^2 \geq 0$$

# Hartree-Fock Theory for $n$ electrons

joint/pair probability

same spin

$$\begin{aligned} P(\mathbf{r}_1, \mathbf{r}_2) = & \frac{1}{2} \int \int \phi_1^*(\mathbf{r}_1) \alpha^*(s_1) \phi_2^*(\mathbf{r}_2) \alpha^*(s_2) \phi_1(\mathbf{r}_1) \alpha(s_1) \phi_2(\mathbf{r}_2) \alpha(s_2) ds_1 ds_2 - \\ & \frac{1}{2} \int \int \phi_1^*(\mathbf{r}_1) \alpha^*(s_1) \phi_2^*(\mathbf{r}_2) \alpha^*(s_2) \phi_2(\mathbf{r}_1) \alpha(s_1) \phi_1(\mathbf{r}_2) \alpha(s_2) ds_1 ds_2 - \\ & \frac{1}{2} \int \int \phi_2^*(\mathbf{r}_1) \alpha^*(s_1) \phi_1^*(\mathbf{r}_2) \alpha^*(s_2) \phi_1(\mathbf{r}_1) \alpha(s_1) \phi_2(\mathbf{r}_2) \alpha(s_2) ds_1 ds_2 + \\ & \frac{1}{2} \int \int \phi_2^*(\mathbf{r}_1) \alpha^*(s_1) \phi_1^*(\mathbf{r}_2) \alpha^*(s_2) \phi_2(\mathbf{r}_1) \alpha(s_1) \phi_1(\mathbf{r}_2) \alpha(s_2) ds_1 ds_2 \end{aligned}$$

correlated

$$\begin{aligned} P(\mathbf{r}_1, \mathbf{r}_2) = & \frac{1}{2} [ |\phi_1(\mathbf{r}_1)|^2 |\phi_2(\mathbf{r}_2)|^2 + |\phi_2(\mathbf{r}_1)|^2 |\phi_1(\mathbf{r}_2)|^2 \\ & - \phi_1^*(\mathbf{r}_1) \phi_2(\mathbf{r}_1) \phi_2^*(\mathbf{r}_2) \phi_1(\mathbf{r}_2) - \phi_2^*(\mathbf{r}_1) \phi_1(\mathbf{r}_1) \phi_1^*(\mathbf{r}_2) \phi_2(\mathbf{r}_2) ] \end{aligned}$$

Pauli repulsion

$$P^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) < P^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2)$$

# Hartree-Fock Theory for $n$ electrons

joint/pair probability

same spin

$$\begin{aligned} P(\mathbf{r}_1, \mathbf{r}_2) = & \frac{1}{2} \int \int \phi_1^*(\mathbf{r}_1) \alpha^*(s_1) \phi_2^*(\mathbf{r}_2) \alpha^*(s_2) \phi_1(\mathbf{r}_1) \alpha(s_1) \phi_2(\mathbf{r}_2) \alpha(s_2) ds_1 ds_2 - \\ & \frac{1}{2} \int \int \phi_1^*(\mathbf{r}_1) \alpha^*(s_1) \phi_2^*(\mathbf{r}_2) \alpha^*(s_2) \phi_2(\mathbf{r}_1) \alpha(s_1) \phi_1(\mathbf{r}_2) \alpha(s_2) ds_1 ds_2 - \\ & \frac{1}{2} \int \int \phi_2^*(\mathbf{r}_1) \alpha^*(s_1) \phi_1^*(\mathbf{r}_2) \alpha^*(s_2) \phi_1(\mathbf{r}_1) \alpha(s_1) \phi_2(\mathbf{r}_2) \alpha(s_2) ds_1 ds_2 + \\ & \frac{1}{2} \int \int \phi_2^*(\mathbf{r}_1) \alpha^*(s_1) \phi_1^*(\mathbf{r}_2) \alpha^*(s_2) \phi_2(\mathbf{r}_1) \alpha(s_1) \phi_1(\mathbf{r}_2) \alpha(s_2) ds_1 ds_2 \end{aligned}$$

correlated

$$\begin{aligned} P(\mathbf{r}_1, \mathbf{r}_2) = & \frac{1}{2} [ |\phi_1(\mathbf{r}_1)|^2 |\phi_2(\mathbf{r}_2)|^2 + |\phi_2(\mathbf{r}_1)|^2 |\phi_1(\mathbf{r}_2)|^2 \\ & - \phi_1^*(\mathbf{r}_1) \phi_2(\mathbf{r}_1) \phi_2^*(\mathbf{r}_2) \phi_1(\mathbf{r}_2) - \phi_2^*(\mathbf{r}_1) \phi_1(\mathbf{r}_1) \phi_1^*(\mathbf{r}_2) \phi_2(\mathbf{r}_2) ] \end{aligned}$$

same orbital?

$$\begin{aligned} P(\mathbf{r}_1, \mathbf{r}_2) = & \frac{1}{2} [ |\phi_1(\mathbf{r}_1)|^2 |\phi_2(\mathbf{r}_2)|^2 + |\phi_2(\mathbf{r}_1)|^2 |\phi_1(\mathbf{r}_2)|^2 \\ & - |\phi_1(\mathbf{r}_1)|^2 |\phi_2(\mathbf{r}_2)|^2 - |\phi_2(\mathbf{r}_1)|^2 |\phi_1(\mathbf{r}_2)|^2 ] = 0 \end{aligned}$$

Pauli exclusion: Fermi hole

# Spin of Slater determinant

## Spin operators

total spin

$$\hat{s} = \hat{s}_x \mathbf{x} + \hat{s}_y \mathbf{y} + \hat{s}_z \mathbf{z} \quad \hat{s}^2 = \hat{s}_x^2 + \hat{s}_y^2 + \hat{s}_z^2$$

commutation relations

$$[\hat{s}_x, \hat{s}_y] = \hat{s}_x \hat{s}_y - \hat{s}_y \hat{s}_x = i \hat{s}_z$$
$$[\hat{s}_y, \hat{s}_z] = i \hat{s}_x \quad [\hat{s}_z, \hat{s}_x] = i \hat{s}_y$$

step operators

$$\hat{s}_+ = \hat{s}_x + i \hat{s}_y \quad \hat{s}_+ |\alpha\rangle = 0 \quad \hat{s}_+ |\beta\rangle = |\alpha\rangle$$
$$\hat{s}_- = \hat{s}_x - i \hat{s}_y \quad \hat{s}_- |\alpha\rangle = |\beta\rangle \quad \hat{s}_- |\beta\rangle = |\alpha\rangle$$
$$\hat{s}^2 = \hat{s}_+ \hat{s}_- - \hat{s}_z + \hat{s}_z^2 \quad \hat{s}^2 = \hat{s}_- \hat{s}_+ + \hat{s}_z + \hat{s}_z^2$$

## Spin eigenfunctions

$$\hat{s}^2 |s, m_s\rangle = s(s+1) |s, m_s\rangle \quad s = 0, \frac{1}{2}, 1, 1\frac{1}{2}, \dots$$
$$\hat{s}_z |s, m_s\rangle = m_s |s, m_s\rangle \quad m_s = -s, -s+1, \dots, s-1, s$$

# Spin of Slater determinant

many electron spin operators

$$\hat{S}^2 = \sum_k^N \hat{s}^2(k) \quad \hat{S}_z = \sum_k^N \hat{s}_z(k)$$

$$\hat{S}_+ = \sum_k^N \hat{s}_+(k) \quad \hat{S}_- = \sum_k^N \hat{s}_-(k)$$

Spin eigenfunctions

$$\hat{S}_z |\phi_1 \phi_2 \dots \phi_3\rangle = \frac{1}{2}(N^\alpha - N^\beta) |\phi_1 \phi_2 \dots \phi_3\rangle$$

closed shell

$$\hat{S}^2 |\phi_1 \phi_2 \dots \phi_3\rangle = |\phi_1 \phi_2 \dots \phi_3\rangle$$

open shell: all parallel

$$\hat{S}^2 |\phi_1 \phi_2 \dots \phi_3\rangle = N^\alpha |\phi_1 \phi_2 \dots \phi_3\rangle$$

open shell: configuration state functions

# Hartree-Fock Theory for $n$ electrons

Expectations values for one and two electron operators

Hartree product (no spin)

$$\langle \hat{O}_1 \rangle = \sum_a \int \phi_a^*(\mathbf{x}_1) \hat{o}(\mathbf{r}_1) \phi_a(\mathbf{r}_1) d\mathbf{r}_1$$

$$\langle \hat{O}_2 \rangle = \frac{1}{2} \sum_a \sum_b \int \int \phi_a^*(\mathbf{r}_1) \phi_b^*(\mathbf{r}_2) \hat{o}(\mathbf{r}_1, \mathbf{r}_2) \phi_a(\mathbf{r}_1) \phi_b(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

Slater determinant (spin, Pauli principle)

$$\langle \hat{O}_1 \rangle = \sum_a \int \phi_a^*(\mathbf{x}_1) \hat{o}(\mathbf{r}_1) \phi_a(\mathbf{x}_1) d\mathbf{x}_1$$

$$\langle \hat{O}_2 \rangle = \frac{1}{2} \sum_a \sum_b \int \int \phi_a^*(\mathbf{x}_1) \phi_b^*(\mathbf{x}_2) \hat{o}(\mathbf{r}_1, \mathbf{r}_2) \phi_a(\mathbf{x}_1) \phi_b(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2$$

$$- \frac{1}{2} \sum_a \sum_b \int \int \phi_a^*(\mathbf{x}_1) \phi_b^*(\mathbf{x}_2) \hat{o}(\mathbf{r}_1, \mathbf{r}_2) \phi_b(\mathbf{x}_1) \phi_a(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2$$

$$\langle \hat{O}_2 \rangle = \frac{1}{2} \sum_a \sum_b \int \int \phi_a^*(\mathbf{x}_1) \phi_b^*(\mathbf{x}_2) \hat{o}(\mathbf{r}_1, \mathbf{r}_2) (1 - \hat{p}_{12}) \phi_a(\mathbf{x}_1) \phi_b(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2$$

# Hartree-Fock Theory for $n$ electrons

Expectations values for one and two electron operators

Hartree product (no spin)

$$\langle \hat{O}_1 \rangle = \sum_a \int \phi_a^*(\mathbf{x}_1) \hat{o}(\mathbf{r}_1) \phi_a(\mathbf{r}_1) d\mathbf{r}_1$$

$$\langle \hat{O}_2 \rangle = \frac{1}{2} \sum_a \sum_b \int \int \phi_a^*(\mathbf{r}_1) \phi_b^*(\mathbf{r}_2) \hat{o}(\mathbf{r}_1, \mathbf{r}_2) \phi_a(\mathbf{r}_1) \phi_b(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

Slater determinant (spin, Pauli principle)

$$\langle \hat{O}_1 \rangle = \sum_a \int \phi_a^*(\mathbf{x}_1) \hat{o}(\mathbf{r}_1) \phi_a(\mathbf{x}_1) d\mathbf{x}_1$$

$$\langle \hat{O}_2 \rangle = \frac{1}{2} \sum_a \sum_b \int \int \phi_a^*(\mathbf{x}_1) \phi_b^*(\mathbf{x}_2) \hat{o}(\mathbf{r}_1, \mathbf{r}_2) \phi_a(\mathbf{x}_1) \phi_b(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2$$

$$-\frac{1}{2} \sum_a \sum_b \int \int \phi_a^*(\mathbf{x}_1) \phi_b^*(\mathbf{x}_2) \hat{o}(\mathbf{r}_1, \mathbf{r}_2) \phi_b(\mathbf{x}_1) \phi_a(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2$$

$$\langle \hat{O}_2 \rangle = \frac{1}{2} \sum_a \sum_b \int \int \phi_a^*(\mathbf{x}_1) \phi_b^*(\mathbf{x}_2) \hat{o}(\mathbf{r}_1, \mathbf{r}_2) (1 - \hat{p}_{12}) \phi_a(\mathbf{x}_1) \phi_b(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2$$

# Hartree-Fock Theory for $n$ electrons

task: finding the best orbitals that minimize total energy

Variational principle

$$E \geq E^0$$

minimum

$$\partial E = 0$$

when for all orbitals

$$\varphi_i(\mathbf{x}) = \varphi_i(\mathbf{x}) + \partial\varphi_i(\mathbf{x})$$

constraint

$$\langle \varphi_i(\mathbf{x}) | \varphi_k(\mathbf{x}) \rangle = \delta_{ik}$$

Langrange multipliers

# Hartree-Fock Theory for $n$ electrons

task: finding the best orbitals that minimize total energy

Lagrangian (adding a smart zero!)

$$\mathcal{L} = E - \sum_i \sum_k \epsilon_{ik} [\langle \varphi_i | \varphi_k \rangle - \delta_{ik}]$$

minimum

$$\partial \mathcal{L} = \partial E - \sum_i \sum_k \epsilon_{ik} [\langle \partial \varphi_i | \varphi_k \rangle + \langle \varphi_i | \partial \varphi_k \rangle] = 0$$

rearranging

$$\begin{aligned} \partial E &= \sum_i \langle \partial \varphi_i | \hat{h} | \varphi_i \rangle + \frac{1}{2} \sum_i \sum_k & & [\langle \partial \varphi_i | \varphi_k | \frac{1}{r_{12}} | \varphi_i | \varphi_k \rangle + \langle \varphi_i | \partial \varphi_k | \frac{1}{r_{12}} | \varphi_i | \varphi_k \rangle \\ &&& - \langle \partial \varphi_i | \varphi_k | \frac{1}{r_{12}} | \varphi_k | \varphi_i \rangle - \langle \varphi_i | \partial \varphi_k | \frac{1}{r_{12}} | \varphi_k | \varphi_i \rangle] \\ &+ \sum_i \langle \varphi_i | \hat{h} | \partial \varphi_i \rangle + \frac{1}{2} \sum_i \sum_k & & [\langle \varphi_i | \varphi_k | \frac{1}{r_{12}} | \partial \varphi_i | \varphi_k \rangle + \langle \varphi_i | \varphi_k | \frac{1}{r_{12}} | \varphi_i | \partial \varphi_k \rangle \\ &&& - \langle \varphi_i | \varphi_k | \frac{1}{r_{12}} | \partial \varphi_k | \varphi_i \rangle - \langle \varphi_i | \varphi_k | \frac{1}{r_{12}} | \varphi_k | \partial \varphi_i \rangle] \end{aligned}$$

# Hartree-Fock Theory for $n$ electrons

task: finding the best orbitals that minimize total energy

Lagrangian (adding a smart zero!)

$$\mathcal{L} = E - \sum_i \sum_k \epsilon_{ik} [\langle \varphi_i | \varphi_k \rangle - \delta_{ik}]$$

minimum

$$\partial \mathcal{L} = \partial E - \sum_i \sum_k \epsilon_{ik} [\langle \partial \varphi_i | \varphi_k \rangle + \langle \varphi_i | \partial \varphi_k \rangle] = 0$$

rearranging

$$\begin{aligned} \partial E = & \sum_i \langle \partial \varphi_i | \hat{h} | \varphi_i \rangle + \frac{1}{2} \sum_i \sum_k & [\langle \partial \varphi_i | \varphi_k | \frac{1}{r_{12}} | \varphi_i | \varphi_k \rangle + \langle \varphi_i | \partial \varphi_k | \frac{1}{r_{12}} | \varphi_i | \varphi_k \rangle \\ & & - \langle \partial \varphi_i | \varphi_k | \frac{1}{r_{12}} | \varphi_k | \varphi_i \rangle - \langle \varphi_i | \partial \varphi_k | \frac{1}{r_{12}} | \varphi_k | \varphi_i \rangle] \\ & + \sum_i \langle \varphi_i | \hat{h} | \partial \varphi_i \rangle + \frac{1}{2} \sum_i \sum_k & [\langle \varphi_i | \varphi_k | \frac{1}{r_{12}} | \partial \varphi_i | \varphi_k \rangle + \langle \varphi_i | \varphi_k | \frac{1}{r_{12}} | \varphi_i | \partial \varphi_k \rangle \\ & & - \langle \varphi_i | \varphi_k | \frac{1}{r_{12}} | \partial \varphi_k | \varphi_i \rangle - \langle \varphi_i | \varphi_k | \frac{1}{r_{12}} | \varphi_k | \partial \varphi_i \rangle] \end{aligned}$$

complex conjugate

# Hartree-Fock Theory for $n$ electrons

task: finding the best orbitals that minimize total energy

Lagrangian (adding a smart zero!)

$$\mathcal{L} = E - \sum_i \sum_k \epsilon_{ik} [\langle \varphi_i | \varphi_k \rangle - \delta_{ik}]$$

minimum

$$\partial \mathcal{L} = \partial E - \sum_i \sum_k \epsilon_{ik} [\langle \partial \varphi_i | \varphi_k \rangle + \langle \varphi_i | \partial \varphi_k \rangle] = 0$$

rearranging

$$\partial E = \sum_i \langle \partial \varphi_i | \hat{h} | \varphi_i \rangle + \frac{1}{2} \sum_i \sum_k$$

changing variables

$$[\langle \partial \varphi_i | \varphi_k | \frac{1}{r_{12}} | \varphi_i \varphi_k \rangle + \langle \varphi_i | \partial \varphi_k | \frac{1}{r_{12}} | \varphi_i \varphi_k \rangle \\ - \langle \partial \varphi_i | \varphi_k | \frac{1}{r_{12}} | \varphi_k \varphi_i \rangle - \langle \varphi_i | \partial \varphi_k | \frac{1}{r_{12}} | \varphi_k \varphi_i \rangle]$$

$$+ \sum_i \langle \varphi_i | \hat{h} | \partial \varphi_i \rangle + \frac{1}{2} \sum_i \sum_k [\langle \varphi_i \varphi_k | \frac{1}{r_{12}} | \partial \varphi_i \varphi_k \rangle + \langle \varphi_i \varphi_k | \frac{1}{r_{12}} | \varphi_i \partial \varphi_k \rangle \\ - \langle \varphi_i \varphi_k | \frac{1}{r_{12}} | \partial \varphi_k \varphi_i \rangle - \langle \varphi_i \varphi_k | \frac{1}{r_{12}} | \varphi_k \partial \varphi_i \rangle]$$

complex conjugate

# Hartree-Fock Theory for $n$ electrons

task: finding the best orbitals that minimize total energy

Lagrangian (adding a smart zero!)

$$\mathcal{L} = E - \sum_i \sum_k \epsilon_{ik} [\langle \varphi_i | \varphi_k \rangle - \delta_{ik}]$$

minimum

$$\partial \mathcal{L} = \partial E - \sum_i \sum_k \epsilon_{ik} [\langle \partial \varphi_i | \varphi_k \rangle + \langle \varphi_i | \partial \varphi_k \rangle] = 0$$

rearranging

$$\begin{aligned} \partial E &= \sum_i \langle \partial \varphi_i | \hat{h} | \varphi_i \rangle + \sum_i \sum_k [\langle \partial \varphi_i | \varphi_k | \frac{1}{r_{12}} | \varphi_i | \varphi_k \rangle - \langle \partial \varphi_i | \varphi_k | \frac{1}{r_{12}} | \varphi_k | \varphi_i \rangle] \\ &\quad + \text{c.c} \end{aligned}$$

# Hartree-Fock Theory for $n$ electrons

task: finding the best orbitals that minimize total energy

rearranging

$$\begin{aligned}\partial E = & \sum_i \langle \partial \varphi_i | \hat{h} | \varphi_i \rangle + \sum_i \sum_k \langle \partial \varphi_i \varphi_k | \frac{1}{r_{12}} | \varphi_i \varphi_k \rangle \\ & - \sum_i \sum_k \langle \partial \varphi_i \varphi_k | \frac{1}{r_{12}} | \varphi_k \varphi_i \rangle \\ & + \text{c.c.}\end{aligned}$$

coulomb  
exchange

for each orbital:

$$\langle \partial \varphi_i | \hat{h} | \varphi_i \rangle + \langle \partial \varphi_i | \sum_k \frac{|\varphi_k|^2}{r_{12}} | \varphi_i \rangle - \langle \partial \varphi_i | \sum_k \langle \varphi_k | \frac{1}{r_{12}} | \varphi_i \rangle \varphi_k \rangle$$

# Hartree-Fock Theory for $n$ electrons

task: finding the best orbitals that minimize total energy

rearranging a bit more

$$\langle \partial\varphi_i | \hat{h} | \varphi_i \rangle + \langle \partial\varphi_i | \sum_k \frac{|\varphi_k|^2}{r_{12}} | \varphi_i \rangle - \langle \partial\varphi_i | \sum_k \langle \varphi_k | \frac{1}{r_{12}} | \varphi_i \rangle \varphi_k \rangle$$

local coulomb operator

$$\hat{K}_k |\varphi_i(1)\rangle = \langle \varphi_k(2) | \frac{1}{r_{12}} | \varphi_i(2) \rangle | \varphi_k(1) \rangle$$

non-local exchange operator

$$\hat{J}_k |\varphi_i(1)\rangle = \frac{|\varphi_k|^2}{r_{12}} |\varphi_i(1)\rangle$$

Fock operator

$$\hat{f} = \hat{h} + \sum_k [\hat{J}_k - \hat{K}_k]$$

# Hartree-Fock Theory for $n$ electrons

task: finding the best orbitals that minimize total energy

going back the the lagrangian

$$\partial \mathcal{L} = \partial E - \sum_i \sum_k \epsilon_{ik} [\langle \partial \varphi_i | \varphi_k \rangle + \langle \varphi_i | \partial \varphi_k \rangle] = 0$$

thus

$$\sum_i \left[ \langle \partial \varphi_i | \hat{f} | \varphi_i \rangle - \sum_k \epsilon_{ik} \langle \partial \varphi_i | \varphi_k \rangle \right] = 0$$

$$\langle \partial \varphi_i | \left[ \hat{f} | \varphi_i \rangle - \sum_k \epsilon_{ik} | \varphi_k \rangle \right] = 0$$

system of  $n$  coupled non-linear equations

$$\hat{f} | \varphi_i \rangle = \sum_k \epsilon_{ik} | \varphi_k \rangle$$

let's try to uncouple them!

# Hartree-Fock Theory for $n$ electrons

task: finding the best orbitals that minimize total energy

system of  $n$  coupled non-linear equations

$$\hat{f}|\varphi_i\rangle = \sum_k \epsilon_{ik} |\varphi_k\rangle$$

matrix notation

$$\mathbf{F}|\varphi\rangle = \boldsymbol{\epsilon}|\varphi\rangle$$

unitary transformation

$$|\varphi'_i\rangle = \hat{U}|\varphi_i\rangle = \sum_k U_{ik} |\varphi_k\rangle \quad \hat{U}^\dagger \hat{U} = 1 \quad \hat{U}^\dagger = \hat{U}^{-1}$$

Fock equation

$$\mathbf{U}\mathbf{F}\mathbf{U}^\dagger\mathbf{U}|\varphi\rangle = \mathbf{U}\boldsymbol{\epsilon}\mathbf{U}^\dagger\mathbf{U}|\varphi\rangle$$

choose unitary transformation that diagonalizes  $\boldsymbol{\epsilon}$

$$\mathbf{F}'|\varphi'\rangle = \boldsymbol{\epsilon}'|\varphi'\rangle \quad \epsilon'_{ik} = \delta_{ik} \epsilon_k$$

# Hartree-Fock Theory for $n$ electrons

task: finding the best orbitals that minimize total energy

canonical Hartree-Fock orbitals

$$\hat{f}|\varphi'_i\rangle = \epsilon'_i |\varphi'_i\rangle$$

orbital energies (ionization energies and electron affinities)

$$\epsilon_i = \langle \varphi_i | \hat{h} | \varphi \rangle + \sum_k \int \frac{|\varphi_i(\mathbf{x})_1|^2 |\varphi_k(\mathbf{x}_2)|^2}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2$$

$$- \sum_k \int \frac{\varphi_i^*(\mathbf{x}_1) \varphi_k^*(\mathbf{x}_2) \varphi_k(\mathbf{x}_1) \varphi_i(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2$$

$$E = \sum_i h_{ii} + \sum_i \sum_k J_{ik} - \sum_i \sum_k K_{ik}$$

total energy (correct double counting, also first order energy in PT)

$$E = \sum_i h_{ii} + \frac{1}{2} \sum_i \sum_k J_{ik} - \frac{1}{2} \sum_i \sum_k K_{ik}$$

# Hartree-Fock Theory for $n$ electrons

task: finding the best orbitals that minimize total energy

canonical Hartree-Fock orbitals

$$\hat{f}|\varphi_i\rangle = \epsilon_i |\varphi_i\rangle$$

orbital energies (ionization energies and electron affinities)

$$\epsilon_i = \langle \varphi_i | \hat{h} | \varphi \rangle + \sum_k \int \frac{|\varphi_i(\mathbf{x})_1|^2 |\varphi_k(\mathbf{x}_2)|^2}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2$$

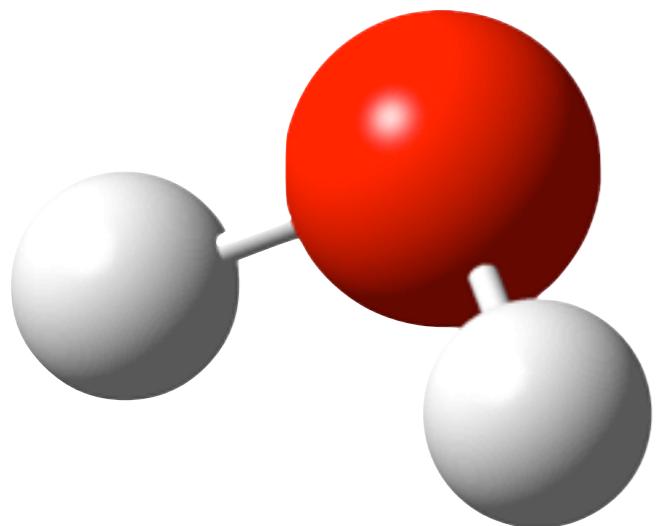
$$- \sum_k \int \frac{\varphi_i^*(\mathbf{x}_1) \varphi_k^*(\mathbf{x}_2) \varphi_k(\mathbf{x}_1) \varphi_i(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2$$

$$E = \sum_i h_{ii} + \sum_i \sum_k J_{ik} - \sum_i \sum_k K_{ik}$$

total energy (correct double counting)

$$E = \sum_i h_{ii} + \frac{1}{2} \sum_i \sum_k J_{ik} - \frac{1}{2} \sum_i \sum_k K_{ik}$$

# Wassermolekül



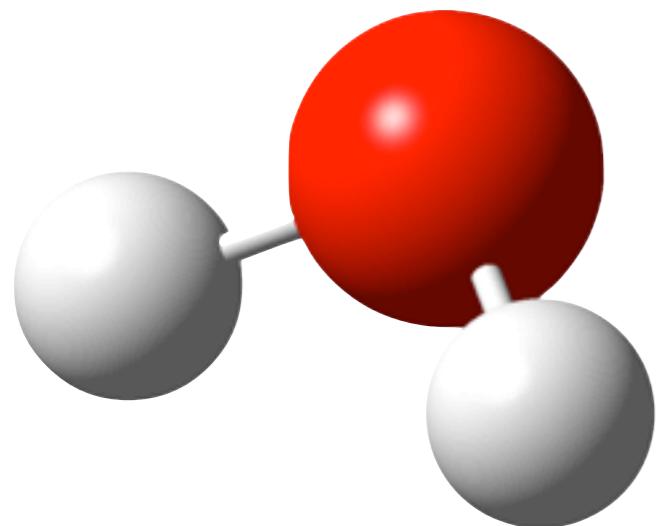
2 H<sup>+</sup>

1 O<sup>8+</sup>

10 Elektronen

10 Molekülorbitale

# Wassermolekül

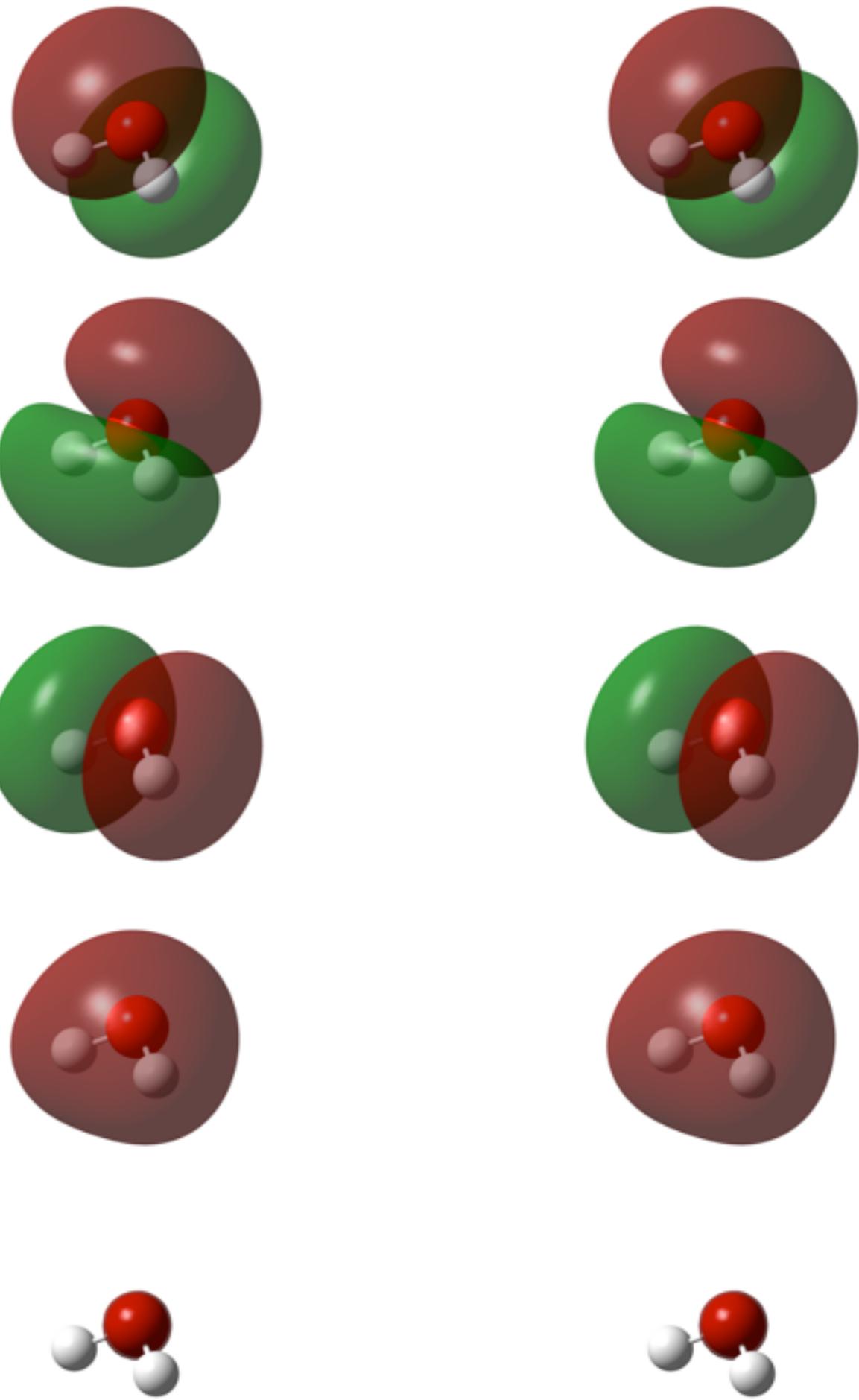


2 H<sup>+</sup>

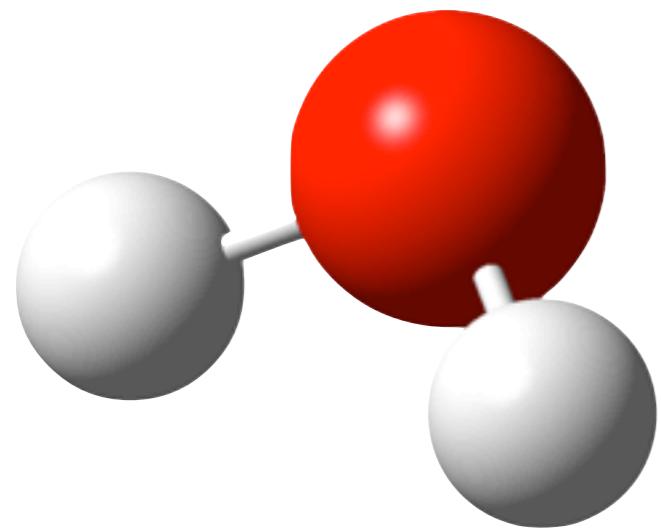
1 O<sup>8+</sup>

10 Elektronen

10 Molekülorbitale



# Wassermolekül



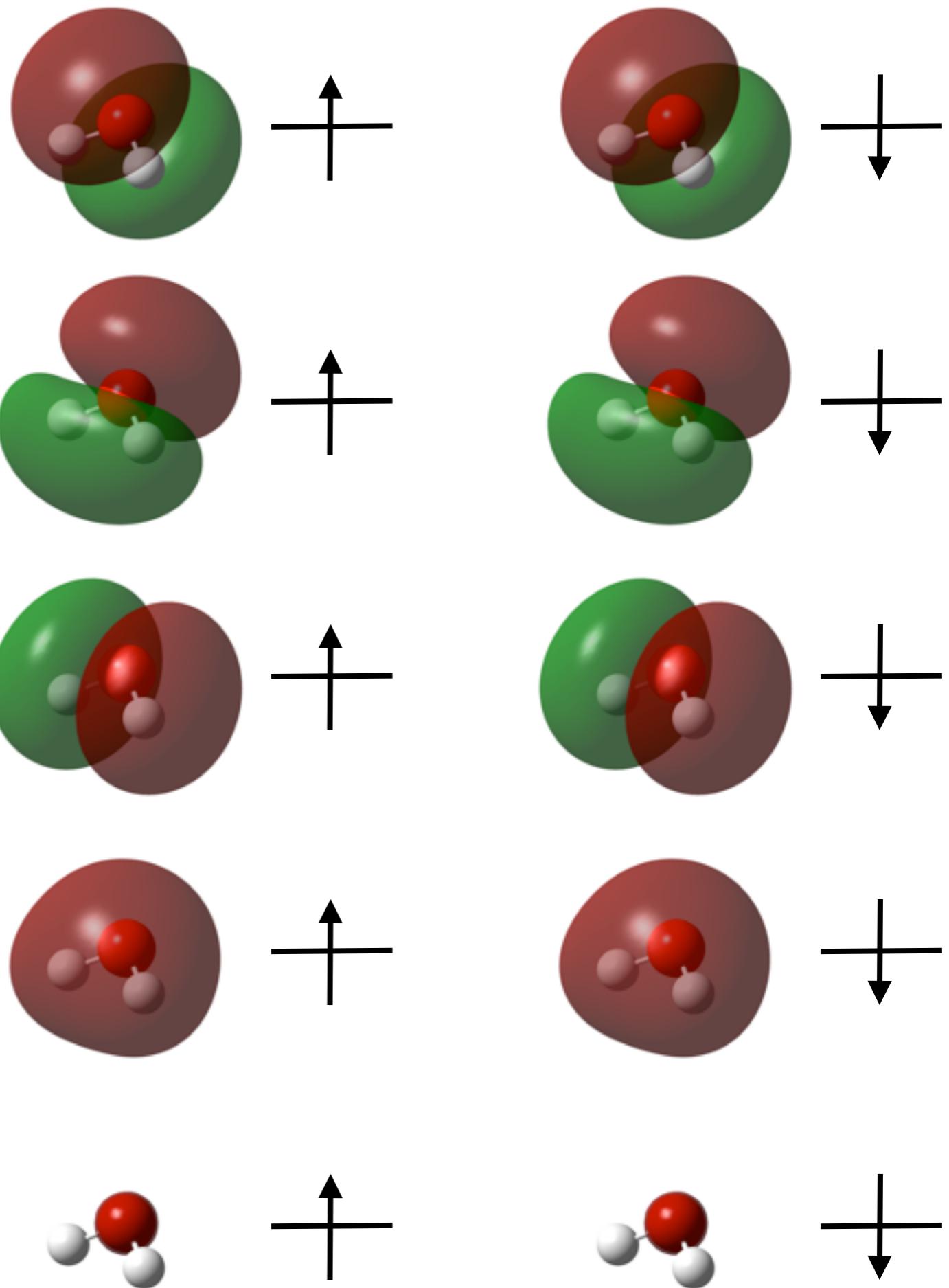
$2 \text{ H}^+$

$1 \text{ O}^{8+}$

10 Elektronen

10 Molekülorbitale

Energie ↑



# Hartree-Fock Theory for $n$ electrons

Hartree-Fock eigenvalue equations

$$\hat{f}(\mathbf{x}_1)\varphi_i(\mathbf{r}_1) = \epsilon_i\varphi(\mathbf{r}_1)$$

solving non-linear eigenvalues equations numerically

step 1: get rid of spin and express in real spatial orbitals

step 2: expand spatial orbitals in basis functions

restricted Hartree Fock

electron pair with opposite spin in same spatial orbital

$$\varphi_i(\mathbf{x}) = \phi_j(\mathbf{r})\alpha(s)$$

$$\varphi_{i+1}(\mathbf{x}) = \phi_j(\mathbf{r})\beta(s)$$

# Hartree-Fock Theory for $n$ electrons

solving non-linear eigenvalues equations numerically

step I: get rid of spin and express in real spatial orbitals

$$\begin{aligned}\hat{f}(\mathbf{x}_1)\phi_i(\mathbf{r}_1)\alpha(s_1) &= \hat{h}^0(\mathbf{r}_1)\phi_i(\mathbf{r}_1)\alpha(s_1) \\ &\quad + \sum_k^{n/2} \int \int \phi_k^*(\mathbf{r}_2)\alpha^*(s_2) \frac{1}{r_{12}} \phi_k(\mathbf{r}_2)\alpha(s_2)\phi_i(\mathbf{r}_1)\alpha(s_1) d\mathbf{r}_2 ds_2 \\ &\quad + \sum_k^{n/2} \int \int \phi_k^*(\mathbf{r}_2)\beta^*(s_2) \frac{1}{r_{12}} \phi_k(\mathbf{r}_2)\beta(s_2)\phi_i(\mathbf{r}_1)\alpha(s_1) d\mathbf{r}_2 ds_2 \\ &\quad - \sum_k^{n/2} \int \int \phi_k^*(\mathbf{r}_2)\alpha^*(s_2) \frac{1}{r_{12}} \phi_i(\mathbf{r}_2)\alpha(s_2)\phi_k(\mathbf{r}_1)\alpha(s_1) d\mathbf{r}_2 ds_2 \\ &\quad - \sum_k^{n/2} \int \int \phi_k^*(\mathbf{r}_2)\beta^*(s_2) \frac{1}{r_{12}} \phi_i(\mathbf{r}_2)\alpha(s_2)\phi_k(\mathbf{r}_1)\beta(s_1) d\mathbf{r}_2 ds_2\end{aligned}$$

# Hartree-Fock Theory for $n$ electrons

solving non-linear eigenvalues equations numerically

step I: get rid of spin and express in real spatial orbitals

$$\hat{f}(\mathbf{x}_1)\phi_i(\mathbf{r}_1)\alpha(s_1) = \hat{h}^0(\mathbf{r}_1)\phi_i(\mathbf{r}_1)\alpha(s_1)$$

$$+ \sum_k^{n/2} \int \int \phi_k^*(\mathbf{r}_2) \alpha^*(s_2) \frac{1}{r_{12}} \phi_k(\mathbf{r}_2) \alpha(s_2) \phi_i(\mathbf{r}_1) \alpha(s_1) d\mathbf{r}_2 ds_2$$

$$+ \sum_k^{n/2} \int \int \phi_k^*(\mathbf{r}_2) \beta^*(s_2) \frac{1}{r_{12}} \phi_k(\mathbf{r}_2) \beta(s_2) \phi_i(\mathbf{r}_1) \alpha(s_1) d\mathbf{r}_2 ds_2$$

$$- \sum_k^{n/2} \int \int \phi_k^*(\mathbf{r}_2) \alpha^*(s_2) \frac{1}{r_{12}} \phi_i(\mathbf{r}_2) \alpha(s_2) \phi_k(\mathbf{r}_1) \alpha(s_1) d\mathbf{r}_2 ds_2$$

$$- \sum_k^{n/2} \int \int \phi_k^*(\mathbf{r}_2) \beta^*(s_2) \frac{1}{r_{12}} \phi_i(\mathbf{r}_2) \alpha(s_2) \phi_k(\mathbf{r}_1) \beta(s_1) d\mathbf{r}_2 ds_2$$

# Hartree-Fock Theory for $n$ electrons

solving non-linear eigenvalues equations numerically

step I: get rid of spin and express in real spatial orbitals

$$\hat{f}(\mathbf{x}_1)\phi_i(\mathbf{r}_1)\alpha(s_1) = \hat{h}^0(\mathbf{r}_1)\phi_i(\mathbf{r}_1)\alpha(s_1)$$

$$+ \sum_k^{n/2} \int \phi_k^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_k(\mathbf{r}_2) \phi_i(\mathbf{r}_1) \alpha(s_1) d\mathbf{r}_2$$

$$+ \sum_k^{n/2} \int \phi_k^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_k(\mathbf{r}_2) \phi_i(\mathbf{r}_1) \alpha(s_1) d\mathbf{r}_2$$

$$- \sum_k^{n/2} \int \phi_k^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_i(\mathbf{r}_2) \phi_k(\mathbf{r}_1) \alpha(s_1) d\mathbf{r}_2$$

# Hartree-Fock Theory for $n$ electrons

solving non-linear eigenvalues equations numerically

step I: get rid of spin and express in real spatial orbitals

$$\begin{aligned} \int \alpha^*(s_1) \hat{f}(\mathbf{x}_1) \alpha(s_1) ds_1 \phi_i(\mathbf{r}_1) &= \int \alpha^*(s_1) \hat{h}^0(\mathbf{r}_1) \phi(\mathbf{r}_1) \alpha(s_1) ds_1 \\ &\quad + \sum_k^{n/2} \int \int \alpha^*(s_1) \phi_k^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_k(\mathbf{r}_2) \phi_i(\mathbf{r}_1) \alpha(s_1) d\mathbf{r}_2 ds_1 \\ &\quad + \sum_k^{n/2} \int \int \alpha^*(s_1) \phi_k^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_k(\mathbf{r}_2) \phi_i(\mathbf{r}_1) \alpha(s_1) d\mathbf{r}_2 ds_1 \\ &\quad - \sum_k^{n/2} \int \int \alpha^*(s_1) \phi_k^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_i(\mathbf{r}_2) \phi_k(\mathbf{r}_1) \alpha(s_1) d\mathbf{r}_2 ds_1 \end{aligned}$$

Hartree-Fock eigenvalue equation for spatial orbitals

$$\begin{aligned} \hat{f}(\mathbf{r}_1) \phi_i(\mathbf{r}_1) &= \hat{h}^0(\mathbf{r}_1) \phi(\mathbf{r}_1) \\ &\quad + 2 \sum_k^{n/2} \int \phi_k^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_k(\mathbf{r}_2) \phi_i(\mathbf{r}_1) d\mathbf{r}_2 \\ &\quad - \sum_k^{n/2} \int \phi_k^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_i(\mathbf{r}_2) \phi_k(\mathbf{r}_1) d\mathbf{r}_2 \\ &= \epsilon_i \phi_i(\mathbf{r}_1) \end{aligned}$$

# Hartree-Fock Theory for $n$ electrons

solving non-linear eigenvalues equations numerically

step 1: get rid of spin and express in real spatial orbitals

$$\begin{aligned}\hat{f}(\mathbf{r}_1)\phi_i(\mathbf{r}_1) &= \hat{h}^0(\mathbf{r}_1)\phi_i(\mathbf{r}_1) \\ &\quad + 2 \sum_k^{n/2} \int \phi_k^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_k(\mathbf{r}_2) \phi_i(\mathbf{r}_1) d\mathbf{r}_2 \\ &\quad - \sum_k^{n/2} \int \phi_k^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_i(\mathbf{r}_2) \phi_k(\mathbf{r}_1) d\mathbf{r}_2 \\ &= \epsilon_i \phi_i(\mathbf{r}_1)\end{aligned}$$

step 2: expand spatial orbitals in basis functions (basisset)

$$\phi_i(\mathbf{r}) = \sum_j^k c_{ij} \gamma_j(\mathbf{r} - \mathbf{R}_j)$$

# Hartree-Fock Theory for $n$ electrons

linear combination of atomic orbitals

$$\phi_i(\mathbf{r}) = \sum_j^k c_{ij} \gamma_j(\mathbf{r} - \mathbf{R}_j)$$

hydrogen-like orbitals (one possibility out of many....)

$$\gamma_1 = \psi^{1s}(\zeta_1)$$

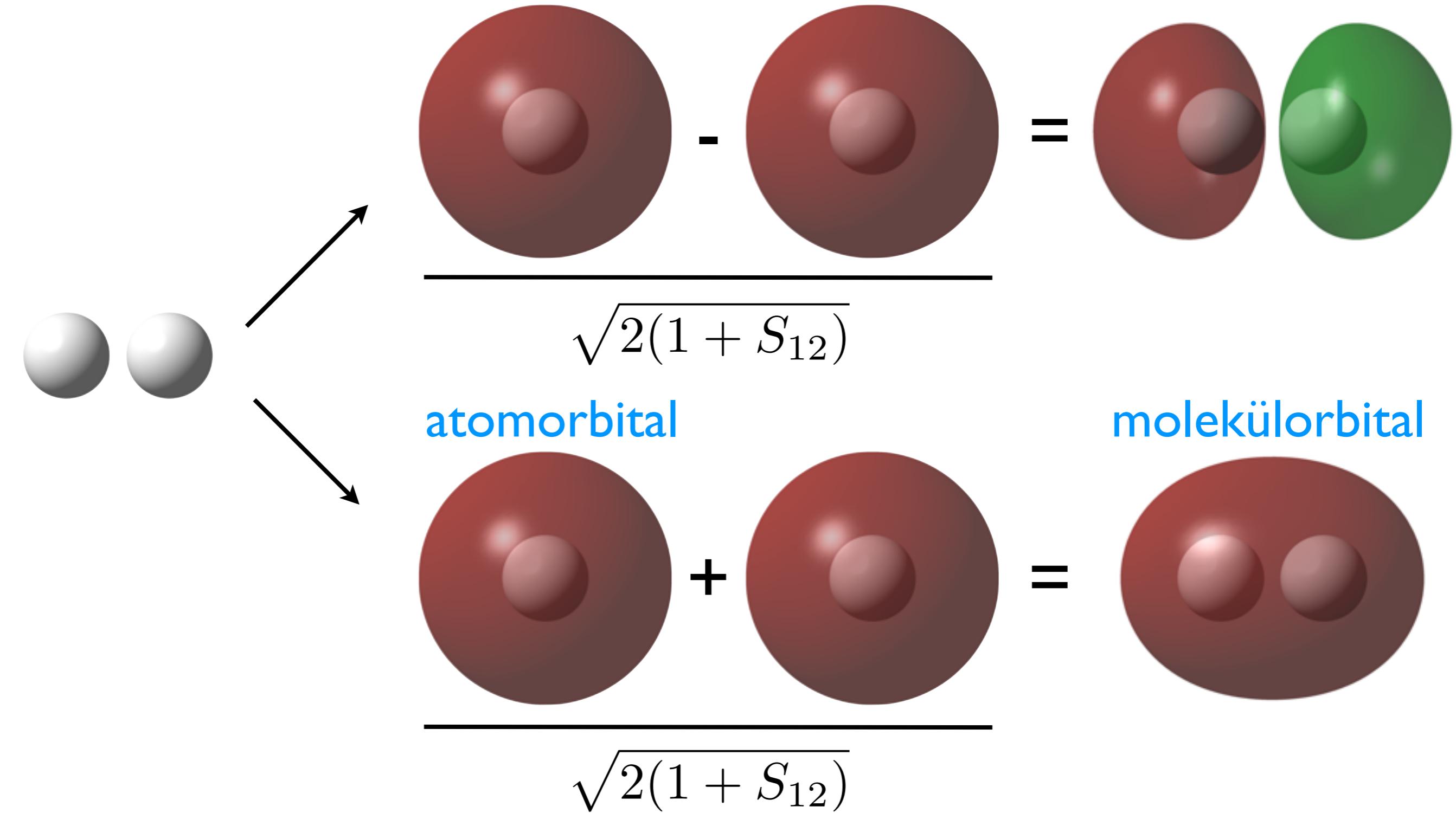
$$\gamma_2 = \psi^{2s}(\zeta_2)$$

$$\gamma_3 = \psi^{2p}(\zeta_3)$$

$$\gamma_4 = \dots$$

# Wasserstoffmolekül

Lineare Kombination von einzelne Wasserstoff-Orbitale



# Hartree-Fock Theory for $n$ electrons

solving non-linear eigenvalues equations numerically

step 2: expand spatial orbitals in basis functions

$$\hat{f}(\mathbf{r}_1)\phi_i(\mathbf{r}_1) = \epsilon_i\phi_i(\mathbf{r}_1)$$

$$\phi_i(\mathbf{r}) = \sum_j^k c_{ij}\gamma_j(\mathbf{r} - \mathbf{R}_j)$$

$$\hat{f}(\mathbf{r}_1) \sum_\nu c_{\nu i} \gamma_\nu(\mathbf{r}_1) = \epsilon_i \sum_\nu c_{\nu i} \gamma_\nu(\mathbf{r}_1)$$

$$\sum_\nu c_{\nu i} \int \gamma_\mu^*(\mathbf{r}_1) \hat{f}(\mathbf{r}_1) \gamma_\nu(\mathbf{r}_1) d\mathbf{r}_1 = \epsilon_i \sum_\nu c_{\nu i} \int \gamma_\mu(\mathbf{r}_1) \gamma_\nu(\mathbf{r}_1) d\mathbf{r}_1$$

# Hartree-Fock Theory for $n$ electrons

solving non-linear eigenvalues equations numerically

step 2: expand spatial orbitals in basis functions (basisset)

$$\sum_{\nu} c_{\nu i} \int \gamma_{\mu}^{*}(\mathbf{r}_1) \hat{f}(\mathbf{r}_1) \gamma_{\nu}(\mathbf{r}_1) d\mathbf{r}_1 = \epsilon_i \sum_{\nu} c_{\nu i} \int \gamma_{\mu}(\mathbf{r}_1) \gamma_{\nu}(\mathbf{r}_1) d\mathbf{r}_1$$

express in terms of matrices

$$\sum_{\nu} F_{\mu\nu} c_{\nu i} = \epsilon_i \sum_{\nu} S_{\mu\nu} c_{\nu i}$$

$$\mathbf{F}\mathbf{C} = \mathbf{S}\mathbf{C}\boldsymbol{\epsilon}$$

solution if, and only if

$$|\mathbf{F} - \epsilon_i \mathbf{S}| = 0$$

# Hartree-Fock Theory for $n$ electrons

solving non-linear eigenvalues equations numerically

non-linear:  $\mathbf{F}$  depends on  $\mathbf{C}$

$$F_{\mu\nu} = \int \gamma_\mu^*(\mathbf{r}_1) \hat{h}^0(\mathbf{r}_1) \gamma_\nu(\mathbf{r}_1) d\mathbf{r}_1$$

$$+ 2 \sum_a \int \int \gamma_\mu^*(\mathbf{r}_1) \phi_a^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_a(\mathbf{r}_2) \gamma_\nu(\mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}$$

$$- \sum_a \int \int \gamma_\mu^*(\mathbf{r}_1) \phi_a^*(\mathbf{r}_2) \frac{1}{r_{12}} \gamma_\nu(\mathbf{r}_2) \phi_a(\mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}$$

$$F_{\mu\nu} = h_{\mu\nu}^0$$

$$+ 2 \sum_a \sum_\kappa \sum_\lambda c_{\kappa a}^* c_{\lambda a}^* \int \int \gamma_\mu^*(\mathbf{r}_1) \gamma_\kappa^*(\mathbf{r}_2) \frac{1}{r_{12}} \gamma_\lambda(\mathbf{r}_2) \gamma_\nu(\mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}$$

$$- \sum_a \sum_\kappa \sum_\lambda c_{\kappa a}^* c_{\lambda a}^* \int \int \gamma_\mu^*(\mathbf{r}_1) \gamma_\kappa^*(\mathbf{r}_2) \frac{1}{r_{12}} \gamma_\nu(\mathbf{r}_2) \gamma_a(\mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}$$

# Hartree-Fock

## Roothaan-Hall equations

non-linear eigenvalue problem

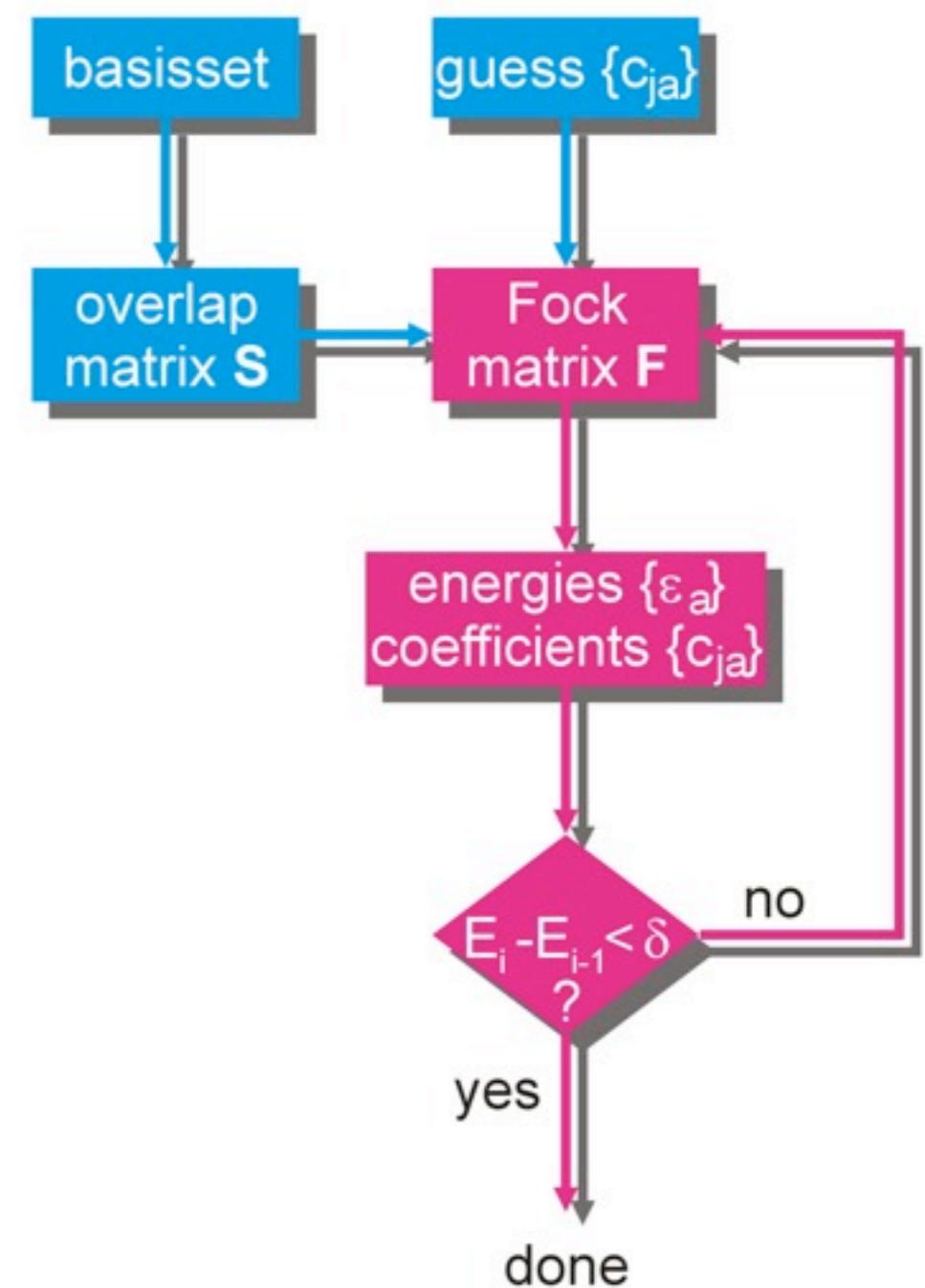
$$Fc = \epsilon_i Sc$$

practical algorithm

iterate until self-consistency

pre-compute integrals of basisset

$$S_{\mu\nu} = \langle \gamma_\mu | \gamma_\nu \rangle$$



# Basissets

minimal basis (1 function per shell)

H-He: 1s (1)

Li-Ne: 1s, 2s, 2p<sub>x</sub>, 2p<sub>y</sub>, 2p<sub>z</sub> (5)

Na-Ar: 1s, 2s, 2p<sub>x</sub>, 2p<sub>y</sub>, 2p<sub>z</sub>, 3s, 3p<sub>x</sub>, 3p<sub>y</sub>, 3p<sub>z</sub> (9)

Slater-type orbitals

computationally demanding

$$f_{1s}(\zeta, \mathbf{r}) = \exp[-\zeta r]$$

Gaussian-type orbitals

computationally convenient

$$g_{1s}(\alpha, \mathbf{r}) = (8\alpha^3/\pi^3)^{1/4} \exp[-\alpha r^2]$$

$$g_{2p_x}(\alpha, \mathbf{r}) = (128\alpha^5/\pi^3)^{1/4} x \exp[-\alpha r^2]$$

$$g_{3d_{xy}}(\alpha, \mathbf{r}) = (2048\alpha^7/\pi^3)^{1/4} xy \exp[-\alpha r^2]$$

# Basissets

## Gaussian-type orbitals

computationally convenient, but not as accurate as Slater-type orbitals

linear combination (contraction) of several gaussians (primitives)

### STO-3G

$$\phi_{1s}^{\text{CGF}} = \sum_i^3 d_{i,1s} g_{1s}(\alpha_{i,1s})$$

$$\phi_{2s}^{\text{CGF}} = \sum_i^3 d_{i,2s} g_{1s}(\alpha_{i,2sp})$$

$$\phi_{2p}^{\text{CGF}} = \sum_i^3 d_{i,2p} g_{2p}(\alpha_{i,2sp})$$

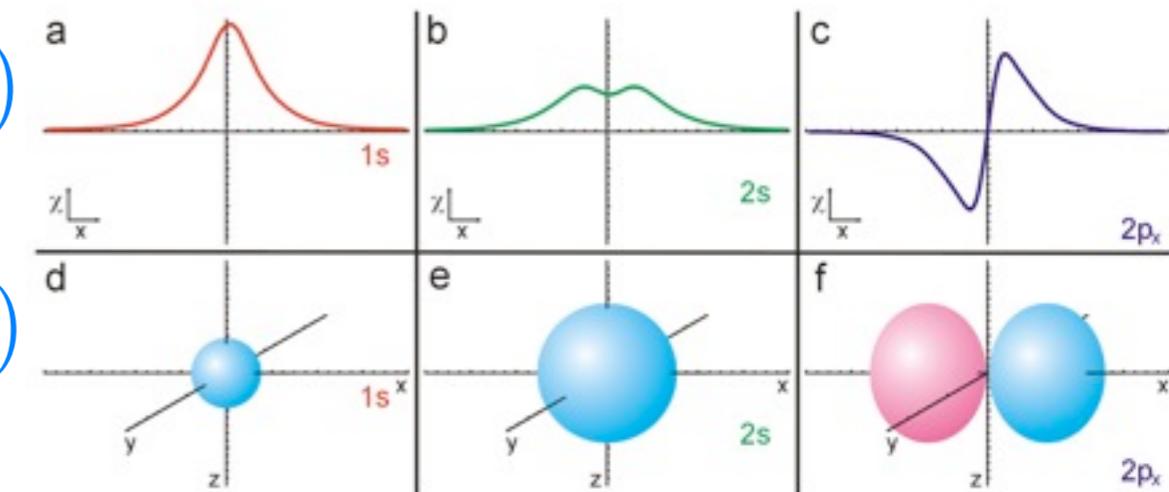
least-square fit to Slater orbitals

$$\min \left[ \int (\phi_{1s}^{\text{SF}}(\mathbf{r}) - \phi_{1s}^{\text{CGF}}(\mathbf{r})) d\mathbf{r} \right]^2$$

$$\min \left[ \int (\phi_{2s}^{\text{SF}}(\mathbf{r}) - \phi_{2s}^{\text{CGF}}(\mathbf{r})) d\mathbf{r} - \int (\phi_{2p}^{\text{SF}}(\mathbf{r}) - \phi_{2p}^{\text{CGF}}(\mathbf{r})) d\mathbf{r} \right]^2$$

notation (for 1st row elements)

$$(6s3p/3s)[2s1p/1s]$$



# Basissets

## Double-Zeta basis

two basisfunctions (contractions) per valence orbital

3-21G

$$(6s3p/3s)[3s2p/2s]$$

H-He:

$$\phi'_{1s} = \sum_i^2 d_{i,1s} g_{1s}(\alpha'_{i,1s})$$

$$\phi''_{1s} = g_{1s}(\alpha''_{i,1s})$$

Li-Ne:

$$\phi_{1s} = \sum_i^3 d_{i,1s} g_{1s}(\alpha_{i,1s})$$

$$\phi'_{2s} = \sum_i^2 d'_{i,2s} g_{1s}(\alpha'_{i,2sp})$$

$$\phi''_{2s} = g_{1s}(\alpha''_{i,2sp})$$

$$\phi'_{2p} = \sum_i^2 d'_{i,2p} g_{2p}(\alpha'_{i,2sp})$$

$$\phi''_{2p} = g_{2p}(\alpha''_{i,2sp})$$

# Basissets

## Double-Zeta basis

two basisfunctions (contractions) per valence orbital

4-31G

$$(8s4p/4s)[3s2p/2s]$$

H-He:

$$\phi'_{1s} = \sum_i^3 d_{i,1s} g_{1s}(\alpha'_{i,1s})$$

$$\phi''_{1s} = g_{1s}(\alpha''_{i,1s})$$

Li-Ne:

$$\phi_{1s} = \sum_i^4 d_{i,1s} g_{1s}(\alpha_{i,1s})$$

$$\phi'_{2s} = \sum_i^3 d'_{i,2s} g_{1s}(\alpha'_{i,2sp})$$

$$\phi''_{2s} = g_{1s}(\alpha''_{i,2sp})$$

$$\phi'_{2p} = \sum_i^3 d'_{i,2p} g_{2p}(\alpha'_{i,2sp})$$

$$\phi''_{2p} = g_{2p}(\alpha''_{i,2sp})$$

# Basissets

## Double-Zeta basis

two basisfunctions (contractions) per valence orbital

6-31G

(10s4p/4s)[3s2p/2s]

H-He:

$$\phi'_{1s} = \sum_i^3 d_{i,1s} g_{1s}(\alpha'_{i,1s})$$

$$\phi''_{1s} = g_{1s}(\alpha''_{i,1s})$$

Li-Ne:

$$\phi_{1s} = \sum_i^6 d_{i,1s} g_{1s}(\alpha_{i,1s})$$

$$\phi'_{2s} = \sum_i^3 d'_{i,2s} g_{1s}(\alpha'_{i,2sp})$$

$$\phi''_{2s} = g_{1s}(\alpha''_{i,2sp})$$

$$\phi'_{2p} = \sum_i^3 d'_{i,2p} g_{2p}(\alpha'_{i,2sp})$$

$$\phi''_{2p} = g_{2p}(\alpha''_{i,2sp})$$

# Basissets

## Double-Zeta basis with polarization functions

two basisfunctions (contractions) per valence orbital

Li-Ne: 3d functions (\*)

H-He: 2p functions (\*\*)

3-21G\*, 4-31G\*, 6-31G\*, 6-31G\*\*

note 6 d-functions (i.e. 5 3d functions + 3s)

$3d_{xx}, 3d_{yy}, 3d_{zz}, 3d_{xy}, 3d_{yz}, 3d_{zx}$

linear combinations of 5 pure 3d functions + 3s:

$3d_{xy}, 3d_{x^2-y^2}, 3d_{yz}, 3d_{zx}, 3d_{z^2}, 3s_{x^2+y^2+z^2}$

contractions

6-31G\*:  $(11s4p1d/4s)[4s2p1d/2s]$

6-31G\*\*:  $(11s4p1d/4s1p)[4s2p1d/2s1p]$

# Molecular Quantum Mechanics

## molecular orbitals

linear combination of atomic orbitals (hydrogen)

$$\phi_i(r) = \sum_j c_{ji} \chi_j(r)$$

example: hydrogen molecule, minimal basis

$$\phi_1(r) = \chi_1(r) + \chi_2(r)$$

$$\phi_2(r) = \chi_1(r) - \chi_2(r)$$



# Molecular Quantum Mechanics

## molecular orbitals

linear combination of atomic orbitals (hydrogen)

$$\phi_i(r) = \sum_j c_{ji} \chi_j(r)$$

example: hydrogen molecule, minimal basis

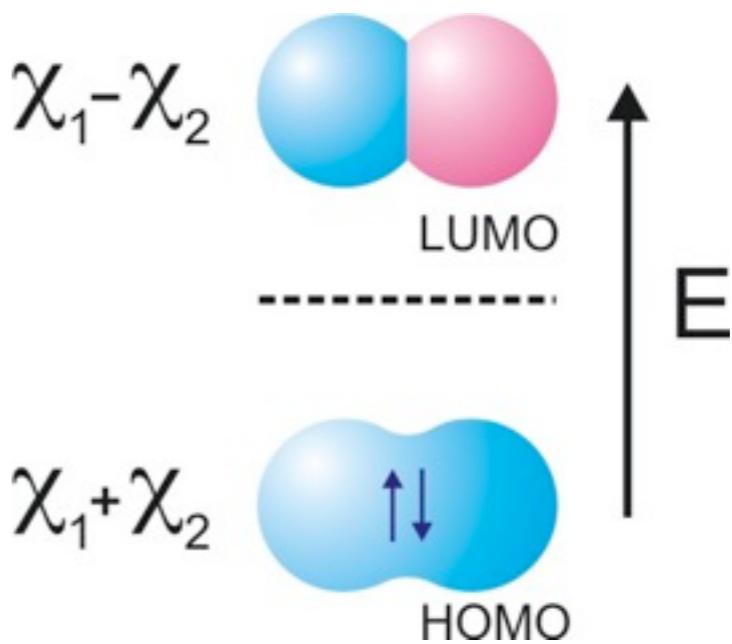
$$\phi_1(r) = \chi_1(r) + \chi_2(r)$$

$$\Psi(r_1, r_2) = |\phi_1(r_1)\bar{\phi}_1(r_2)|$$

$$\phi_2(r) = \chi_1(r) - \chi_2(r)$$



dissociation!!!



# Molecular Quantum Mechanics

## limitations of Hartree-Fock theory

- ▶ mean-field: no electron correlation

## beyond Hartree-Fock

- ▶ configuration interaction (ci)

$$\begin{aligned}\Psi = & C_0 |\phi_a(r_1)\phi_b(r_2) \dots \phi_k(r_{n-1})\phi_l(r_{n-1})| + \\ & C_1 |\phi_k(r_1)\phi_b(r_2) \dots \phi_k(r_{n-1})\phi_l(r_{n-1})| + \\ & C_2 |\phi_k(r_1)\phi_l(r_2) \dots \phi_k(r_{n-1})\phi_l(r_{n-1})| + \dots\end{aligned}$$

- ▶ multiconfiguration self-consistent field (mcscf)

# Electron correlation

## definition

$$E^{\text{corr.}} = E^{\text{exact}} - E^{\text{HF}}$$

## Configuration Interaction

sum over all possible Slater determinants/spin adapted-configuration state functions)

general expression for correlation energy (not so useful...)

truncated CI

MCSCF/CASSCF

size consistency

## Perturbation theory

Slater determinants, single, double, triple, ... excitations

## Combinations of CI and PT

MCSCF with  $x$ th order perturbation ( $x=2$ )

Concludes the ab initio, next is density functional theory

# Configuration interaction

## restricted Hartree Fock in nutshell

### one particle, mean field theory

# Configuration interaction

restricted Hartree Fock in nutshell

one particle, mean field theory

Slater determinant (Pauli principle)

$$\psi_0(\mathbf{r}) = \det [\phi_1(\mathbf{r}_1)\bar{\phi}_1(\mathbf{r}_2)\phi_2(\mathbf{r}_3)\bar{\phi}_2(\mathbf{r}_4)....\phi_{n/2}(\mathbf{r}_{n-1})\bar{\phi}_{n/2}(\mathbf{r}_n)]$$

# Configuration interaction

restricted Hartree Fock in nutshell

one particle, mean field theory

Slater determinant (Pauli principle)

$$\psi_0(\mathbf{r}) = \det [\phi_1(\mathbf{r}_1)\bar{\phi}_1(\mathbf{r}_2)\phi_2(\mathbf{r}_3)\bar{\phi}_2(\mathbf{r}_4)....\phi_{n/2}(\mathbf{r}_{n-1})\bar{\phi}_{n/2}(\mathbf{r}_n)]$$

molecular orbitals

$$\hat{f}\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

# Configuration interaction

## restricted Hartree Fock in nutshell

one particle, mean field theory

Slater determinant (Pauli principle)

$$\psi_0(\mathbf{r}) = \det [\phi_1(\mathbf{r}_1) \bar{\phi}_1(\mathbf{r}_2) \phi_2(\mathbf{r}_3) \bar{\phi}_2(\mathbf{r}_4) \dots \phi_{n/2}(\mathbf{r}_{n-1}) \bar{\phi}_{n/2}(\mathbf{r}_n)]$$

molecular orbitals

$$\hat{f}\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

Fock operator

$$f_{ij} = \langle \phi_i(\mathbf{r}_1) | h(\mathbf{r}_1) | \phi_j(\mathbf{r}_1) \rangle + \sum_k \left\langle \phi_i(\mathbf{r}_1) \phi_k(\mathbf{r}_2) \left| \frac{2 - \hat{p}_{12}}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \phi_k(\mathbf{r}_1) \phi_j(\mathbf{r}_2) \right\rangle$$

# Configuration interaction

restricted Hartree Fock in nutshell

one particle, mean field theory

Slater determinant (Pauli principle)

$$\psi_0(\mathbf{r}) = \det [\phi_1(\mathbf{r}_1) \bar{\phi}_1(\mathbf{r}_2) \phi_2(\mathbf{r}_3) \bar{\phi}_2(\mathbf{r}_4) \dots \phi_{n/2}(\mathbf{r}_{n-1}) \bar{\phi}_{n/2}(\mathbf{r}_n)]$$

molecular orbitals

$$\hat{f}\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

Fock operator

$$f_{ij} = \langle \phi_i(\mathbf{r}_1) | h(\mathbf{r}_1) | \phi_j(\mathbf{r}_1) \rangle + \sum_k \left\langle \phi_i(\mathbf{r}_1) \phi_k(\mathbf{r}_2) \left| \frac{2 - \hat{p}_{12}}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \phi_k(\mathbf{r}_1) \phi_j(\mathbf{r}_2) \right\rangle$$

basisset

$$\phi_i(\mathbf{r}_1) = \sum_{\alpha} c_{i\alpha} \chi_{\alpha}(\mathbf{r}_1)$$

density matrix

$$\hat{f} = h + \frac{1}{2} \sum_{\lambda} \sum_{\sigma} P_{\lambda\sigma} \left\langle \chi_{\sigma} \left| \frac{2 - \hat{p}_{12}}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \chi_{\lambda} \right\rangle$$

$$P_{\mu\nu} = 2 \sum_a^{\frac{1}{2} n_e} c_{\mu a} c_{\nu a}^*$$

# Configuration interaction

## restricted Hartree Fock in nutshell

one particle, mean field theory

Slater determinant (Pauli principle)

$$\psi_0(\mathbf{r}) = \det [\phi_1(\mathbf{r}_1) \bar{\phi}_1(\mathbf{r}_2) \phi_2(\mathbf{r}_3) \bar{\phi}_2(\mathbf{r}_4) \dots \phi_{n/2}(\mathbf{r}_{n-1}) \bar{\phi}_{n/2}(\mathbf{r}_n)]$$

molecular orbitals

$$\hat{f}\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

Fock operator

$$f_{ij} = \langle \phi_i(\mathbf{r}_1) | h(\mathbf{r}_1) | \phi_j(\mathbf{r}_1) \rangle + \sum_k \left\langle \phi_i(\mathbf{r}_1) \phi_k(\mathbf{r}_2) \left| \frac{2 - \hat{p}_{12}}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \phi_k(\mathbf{r}_1) \phi_j(\mathbf{r}_2) \right\rangle$$

basisset

$$\phi_i(\mathbf{r}_1) = \sum_{\alpha} c_{i\alpha} \chi_{\alpha}(\mathbf{r}_1)$$

density matrix

$$\hat{f} = h + \frac{1}{2} \sum_{\lambda} \sum_{\sigma} P_{\lambda\sigma} \left\langle \chi_{\sigma} \left| \frac{2 - \hat{p}_{12}}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \chi_{\lambda} \right\rangle$$

$$P_{\mu\nu} = 2 \sum_a^{\frac{1}{2} n_e} c_{\mu a} c_{\nu a}^*$$

iterative self-consistent solution procedure

# Configuration interaction

restricted Hartree Fock in nutshell

one particle, mean field theory, no e-e correlation

Slater determinant

$$\psi_0(\mathbf{r}) = \det [\phi_1(\mathbf{r}_1)\bar{\phi}_1(\mathbf{r}_2)\phi_2(\mathbf{r}_3)\bar{\phi}_2(\mathbf{r}_4)....\phi_{n/2}(\mathbf{r}_{n-1})\bar{\phi}_{n/2}(\mathbf{r}_n)]$$

# Configuration interaction

restricted Hartree Fock in nutshell

one particle, mean field theory

Slater determinant

$$\psi_0(\mathbf{r}) = \det [\phi_1(\mathbf{r}_1)\bar{\phi}_1(\mathbf{r}_2)\phi_2(\mathbf{r}_3)\bar{\phi}_2(\mathbf{r}_4)....\phi_{n/2}(\mathbf{r}_{n-1})\bar{\phi}_{n/2}(\mathbf{r}_n)]$$

electron-electron correlation

static correlation

large separation of electrons in pair

near degeneracies: different spatial wavefunctions

multi-configuration SCF

# Configuration interaction

restricted Hartree Fock in nutshell

one particle, mean field theory

Slater determinant

$$\psi_0(\mathbf{r}) = \det [\phi_1(\mathbf{r}_1)\bar{\phi}_1(\mathbf{r}_2)\phi_2(\mathbf{r}_3)\bar{\phi}_2(\mathbf{r}_4)....\phi_{n/2}(\mathbf{r}_{n-1})\bar{\phi}_{n/2}(\mathbf{r}_n)]$$

electron-electron correlation

static correlation

large separation of electrons in pair

near degeneracies: different spatial wavefunctions

multi-configuration SCF

dynamic correlation

short distance: cusp

not so dependent on orbitals/density

perturbation theory

# Configuration interaction

restricted Hartree Fock in nutshell

one particle, mean field theory

Slater determinant

$$\psi_0(\mathbf{r}) = \det [\phi_1(\mathbf{r}_1)\bar{\phi}_1(\mathbf{r}_2)\phi_2(\mathbf{r}_3)\bar{\phi}_2(\mathbf{r}_4)....\phi_{n/2}(\mathbf{r}_{n-1})\bar{\phi}_{n/2}(\mathbf{r}_n)]$$

electron-electron correlation

static correlation

large separation of electrons in pair

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multi-configuration SCF

dynamic correlation

short distance: cusp

not so dependent on orbitals/density

perturbation theory

simple distinction not always possible

# Beyond Hartree-Fock: Configuration Interaction

one-electron basisset

$$\Phi(\mathbf{x}_1) = \sum_i a_i \phi_i(\mathbf{x}_1)$$

two-electron basisset

$$\Phi(\mathbf{x}_1, \mathbf{x}_2) = \sum_i a_i(\mathbf{x}_2) \phi_i(\mathbf{x}_1)$$

$$\Phi(\mathbf{x}_1, \mathbf{x}_2) = \sum_i \sum_j b_{ij} \phi_i(\mathbf{x}_1) \phi_j(\mathbf{x}_2)$$

# excited state electronic structure

## configuration interaction

functions of one electron

expansion in one-electron functions

$$\phi(x_1) = \sum_i a_i \chi_i(x_1)$$

functions of two electrons

# excited state electronic structure

## configuration interaction

functions of one electron

expansion in one-electron functions

$$\phi(x_1) = \sum_i a_i \chi_i(x_1)$$

functions of two electrons

expansion in one-electron functions, keeping second electron fixed

$$\phi(x_1, x_2) = \sum_i a_i(x_2) \chi_i(x_1)$$

# excited state electronic structure

## configuration interaction

functions of one electron

expansion in one-electron functions

$$\phi(x_1) = \sum_i a_i \chi_i(x_1)$$

functions of two electrons

expansion in one-electron functions, keeping second electron fixed

$$\phi(x_1, x_2) = \sum_i a_i(x_2) \chi_i(x_1)$$

expansion of coefficients in one-electron functions

$$a(x_2) = \sum_j b_{ij} \chi_j(x_2)$$

# excited state electronic structure

## configuration interaction

functions of one electron

expansion in one-electron functions

$$\phi(x_1) = \sum_i a_i \chi_i(x_1)$$

functions of two electrons

expansion in one-electron functions, keeping second electron fixed

$$\phi(x_1, x_2) = \sum_i a_i(x_2) \chi_i(x_1)$$

expansion of coefficients in one-electron functions

$$a(x_2) = \sum_j b_{ij} \chi_j(x_2)$$

so that

$$\phi(x_1, x_2) = \sum_i \sum_j b_{ij} \chi_i(x_1) \chi_j(x_2)$$

# excited state electronic structure

## configuration interaction

### functions of two electrons

Pauli principle

$$\phi(x_1, x_2) = -\phi(x_2, x_1)$$

# excited state electronic structure

## configuration interaction

### functions of two electrons

Pauli principle

$$\phi(x_1, x_2) = -\phi(x_2, x_1)$$

antisymmetric superposition

$$\phi(x_1, x_2) = \sum_i \sum_{j>i} b_{ij} [\chi_i(x_1)\chi_j(x_2) - \chi_j(x_1)\chi_i(x_2)]$$

# excited state electronic structure

## configuration interaction

### functions of two electrons

Pauli principle

$$\phi(x_1, x_2) = -\phi(x_2, x_1)$$

antisymmetric superposition

$$\phi(x_1, x_2) = \sum_i \sum_{j>i} b_{ij} [\chi_i(x_1)\chi_j(x_2) - \chi_j(x_1)\chi_i(x_2)]$$

in determinants

$$\phi(x_1, x_2) = \sum_i \sum_j \frac{1}{\sqrt{2}} b_{ij} \det [\chi_i(x_1)\chi_j(x_2)]$$

# excited state electronic structure

## configuration interaction

### functions of two electrons

Pauli principle

$$\phi(x_1, x_2) = -\phi(x_2, x_1)$$

antisymmetric superposition

$$\phi(x_1, x_2) = \sum_i \sum_{j>i} b_{ij} [\chi_i(x_1)\chi_j(x_2) - \chi_j(x_1)\chi_i(x_2)]$$

in determinants

$$\phi(x_1, x_2) = \sum_i \sum_j \frac{1}{\sqrt{2}} b_{ij} \det [\chi_i(x_1)\chi_j(x_2)]$$

in general

n-electron wavefunction

$$\Psi_i = \sum_j C_{ij} \psi_j = C_{i0} \psi_0 + \sum_{ra} C_{ia}^r \psi_a^r + \sum_{\substack{a < b \\ r < s}} C_{iab}^{rs} \psi_{ab}^{rs} + \dots$$

# excited state electronic structure

## full configuration interaction

exact solution (within finite basisset)

$$\Psi_i = \sum_j C_{ij} \psi_j = C_{i0} \psi_0 + \sum_{ra} C_{ia}^r \psi_a^r + \sum_{\substack{a < b \\ r < s}} C_{iab}^{rs} \psi_{ab}^{rs} + \dots$$

# excited state electronic structure

## full configuration interaction

exact solution (within finite basisset)

$$\Psi_i = \sum_j C_{ij} \psi_j = C_{i0} \psi_0 + \sum_{ra} C_{ia}^r \psi_a^r + \sum_{\substack{a < b \\ r < s}} C_{iab}^{rs} \psi_{ab}^{rs} + \dots$$

## truncated configuration interaction

**CISingles**

excited states (higher roots)

no correlation in ground state

**CISinglesDoubles**

stronger correlation in ground state

**CISinglesDoublesTriples**

stronger correlation in excited states than in ground state

...

too expensive: number of configurations blows up

# excited state electronic structure

## truncated configuration interaction

CI Singles, Double, Triples ...

systematic

number of configurations blows up

# excited state electronic structure

truncated configuration interaction

CI Singles, Double, Triples ...

systematic

number of configurations blows up

multi-configuration SCF

multiple configurations

free to choose, not black box!

optimize both CI and MO coefficients

$$\Psi_i = \sum_j^M C_{ij} \psi_j.$$

Slater

# excited state electronic structure

truncated configuration interaction

CI Singles, Double, Triples ...

systematic

number of configurations blows up

multi-configuration SCF

multiple configurations

free to choose, not black box!

optimize both CI and MO coefficients

basis for higher level methods

MultiReferenceCI

$$\Phi = \sum_I (K_I \Psi_I + \sum_{i,a} K_{Iia} \Psi_{Iia} + \sum_{i,a,j,b} K_{Iiajb} \Psi_{Iiajb} + \dots)$$

a root in MCSCF

single excitations

double excitations

of Slaters in each configuration in root

$$\Psi_i = \sum_j^M C_{ij} \psi_j.$$

Slater



# excited state electronic structure

truncated configuration interaction

CI Singles, Double, Triples ...

systematic

number of configurations blows up

multi-configuration SCF

multiple configurations

free to choose, not black box!

optimize both CI and MO coefficients

basis for higher level methods

MultiReferenceCI

$$\Phi = \sum_I (K_I \Psi_I + \sum_{i,a} K_{Iia} \Psi_{Iia} + \sum_{i,a,j,b} K_{Iiajb} \Psi_{Iiajb} + \dots)$$

perturbation theory: CASPT2

$$\Psi_i = \sum_j^M C_{ij} \psi_j.$$

# excited state electronic structure

## multi-configuration SCF

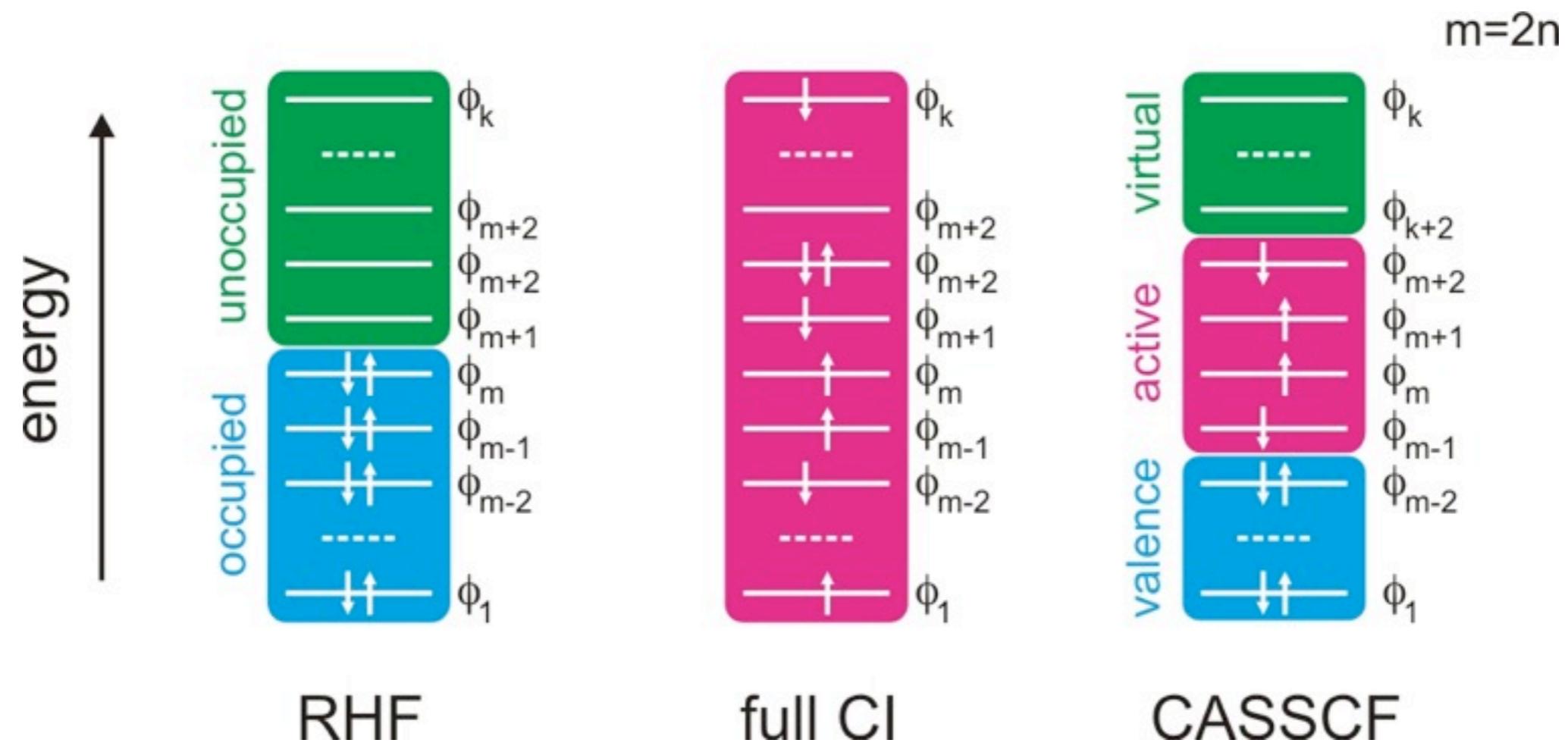
### multiple configurations

free to choose

not black box

### Complete Active Space SCF

select orbitals for full CI



# excited state electronic structure

## multi-configuration SCF

### Complete Active Space SCF

select electrons and orbitals for full CI (HF, NBO)

knowledge/intuition/luck

# excited state electronic structure

## multi-configuration SCF

### Complete Active Space SCF

select electrons and orbitals for full CI (HF, NBO)

knowledge/intuition/luck/

# excited state electronic structure

## multi-configuration SCF

### Complete Active Space SCF

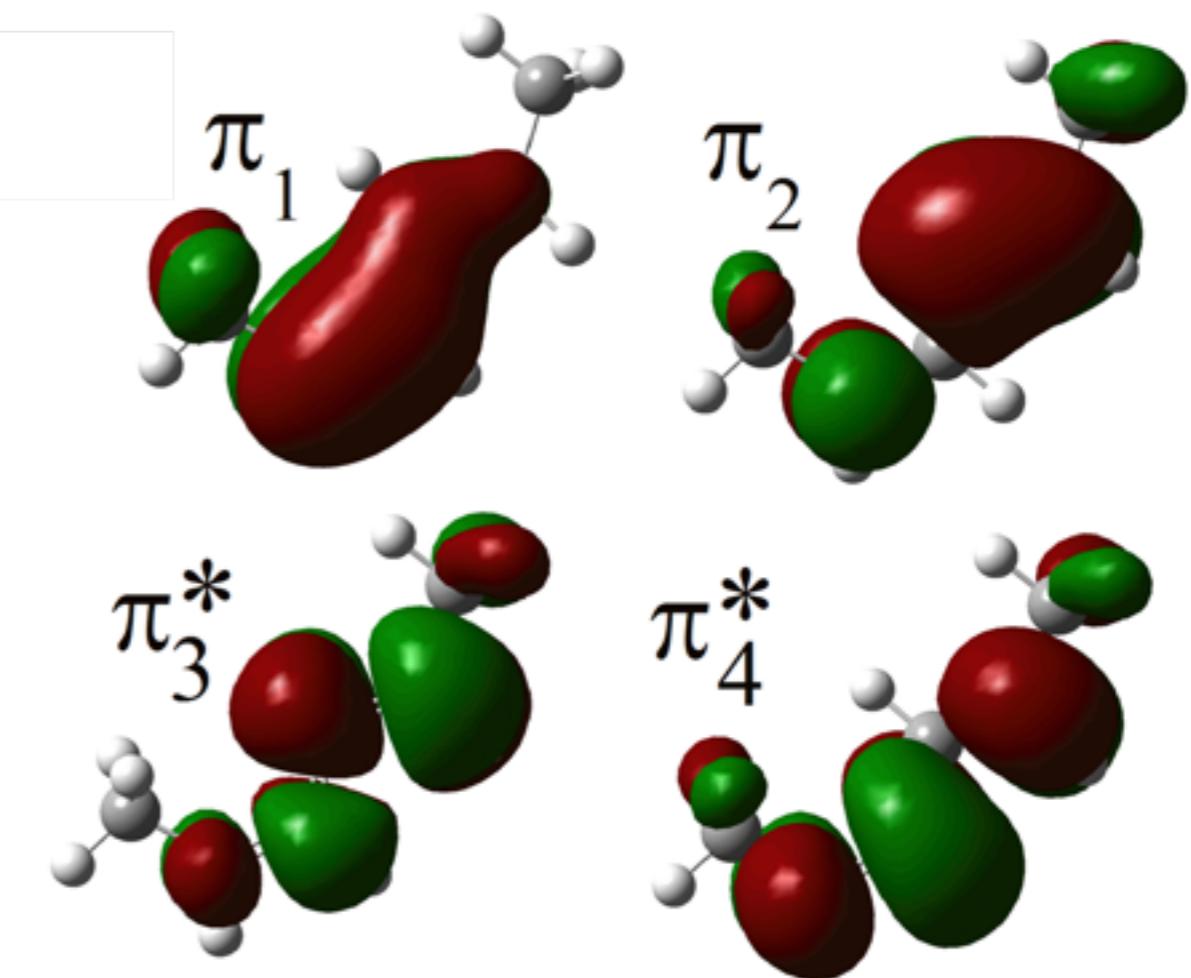
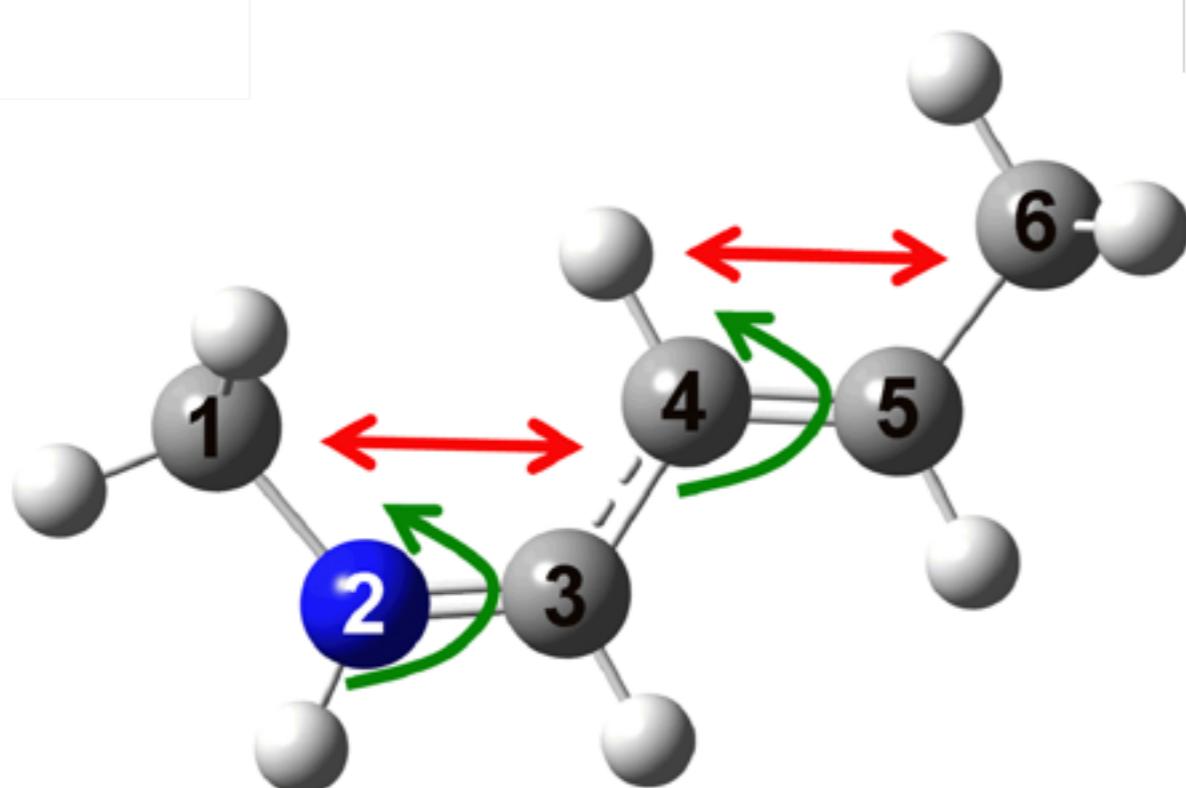
select electrons and orbitals for full CI (HF, NBO)

knowledge/intuition/luck

### example

protonated schiff base

CAS(4,4) with all  $\pi$  orbitals



# excited state electronic structure

## CASSCF

recovers static correlation

near degeneracy

# excited state electronic structure

## CASSCF

recovers static correlation

near degeneracy

excited states

optimize second root in CI

# excited state electronic structure

## CASSCF

recovers static correlation

near degeneracy

excited states

optimize second root in CI

problem: need expectation values involving both states

$$\langle \psi_{S_0} | \nabla_{\mathbf{R}} H | \psi_{S_1} \rangle$$

# excited state electronic structure

## CASSCF

recovers static correlation

near degeneracy

excited states

optimize second root in CI

problem: need expectation values involving both states

$$\langle \psi_{S_0} | \nabla_{\mathbf{R}} H | \psi_{S_1} \rangle$$

problem: root flipping

# excited state electronic structure

## CASSCF

recovers static correlation

near degeneracy

excited states

optimize second root in CI

problem: need expectation values involving both states

$$\langle \psi_{S_0} | \nabla_{\mathbf{R}} H | \psi_{S_1} \rangle$$

problem: root flipping

state average CASSCF

same molecular orbitals for all states

optimize the weighted average energy

$$E^{\text{SA}} = \sum_i \omega_i E_i$$

average density matrix

# excited state electronic structure

## SA-CASSCF

same molecular orbitals for all states

sometimes orbitals change drastically upon excitation

wavefunction is not variational minimum

$$\nabla_{\mathbf{R}} E = \nabla_{\mathbf{R}} \langle \psi | H | \psi \rangle$$

$$= \langle \nabla_{\mathbf{R}} \psi | H | \psi \rangle + \langle \psi | \nabla_{\mathbf{R}} H | \psi \rangle + \langle \psi | H | \nabla_{\mathbf{R}} \psi \rangle$$

# excited state electronic structure

## SA-CASSCF

same molecular orbitals for all states

sometimes orbitals change drastically upon excitation

wavefunction is not variational minimum

$$\nabla_{\mathbf{R}} E = \nabla_{\mathbf{R}} \langle \psi | H | \psi \rangle$$

$$= \langle \nabla_{\mathbf{R}} \psi | H | \psi \rangle + \langle \psi | \nabla_{\mathbf{R}} H | \psi \rangle + \langle \psi | H | \nabla_{\mathbf{R}} \psi \rangle$$

$$\langle \nabla_{\mathbf{R}} \psi | H | \psi \rangle = \langle \nabla_{\mathbf{c}_{\text{MO}}} \psi | H | \psi \rangle \nabla_{\mathbf{R}} \mathbf{c}_{\text{MO}} +$$

$$\langle \nabla_{\mathbf{c}_{\text{CI}}} \psi | H | \psi \rangle \nabla_{\mathbf{R}} \mathbf{c}_{\text{CI}} +$$

# excited state electronic structure

## SA-CASSCF

quantities for surface hopping

expression for non-adiabatic coupling

$$F_{ij}(\mathbf{R}) = \frac{\mathbf{h}_{ij}(\mathbf{R})}{V_i - V_j} + \sum_{a,b} c_{ia}^*(\mathbf{R}) c_{jb}(\mathbf{R}) \langle \psi_a | \nabla_{\mathbf{R}} \psi_b \rangle$$

$$\mathbf{h}_{ij}(\mathbf{R}) = \mathbf{C}_i^\dagger(\mathbf{R}) \nabla_{\mathbf{R}} H^{\text{cf}} \mathbf{C}_j(\mathbf{R})$$

$$\nabla_{\mathbf{R}} H_{ab}^{\text{cf}}(\mathbf{R}) = \nabla_{\mathbf{R}} \langle \psi_a | H^e(\mathbf{r}, \mathbf{R}) | \psi_b \rangle$$

expression for diabatic hop

$$\langle \psi_1(t) | \psi_2(t + \Delta t) \rangle = \mathbf{C}_1^t \cdot \mathbf{C}_2^{t+\Delta t}$$

# beyond Hartree Fock

## Configuration Interaction

linear combination of Slater determinants

$$\begin{aligned}\Psi = & |\psi_0\rangle + \sum_a^r c_a^r |\psi_a^r\rangle + \sum_a^r \sum_{b>a}^{s>r} c_{ab}^{rs} |\psi_{ab}^{rs}\rangle \\ & + \sum_a^r \sum_{b>a}^{s>r} \sum_{c>b}^{t>s} c_{abc}^{rst} |\psi_{abc}^{rst}\rangle \\ & + \sum_a^r \sum_{b>a}^{s>r} \sum_{c>b}^{t>s} \sum_{d>c}^{u>t} c_{abcd}^{rstu} |\psi_{abcd}^{rstu}\rangle + \dots\end{aligned}$$

intermediate normalization

$$\langle \Psi | \psi_0 \rangle = 1$$

size consistent, if all determinants are included

variational in  $c$

# beyond Hartree Fock

## Configuration Interaction

linear combination of Slater determinants

$$\begin{aligned}\Psi = & |\psi_0\rangle + \sum_a^r c_a^r \hat{X}_a^r |\psi_0\rangle + \sum_a^r \sum_{b>a}^{s>r} c_{ab}^{rs} \hat{X}_{ab}^{rs} |\psi_0\rangle \\ & + \sum_a^r \sum_{b>a}^{s>r} \sum_{c>b}^{t>s} c_{abc}^{rst} \hat{X}_{abc}^{rst} |\psi_0\rangle \\ & + \sum_a^r \sum_{b>a}^{s>r} \sum_{c>b}^{t>s} \sum_{d>c}^{u>t} c_{abcd}^{rstu} \hat{X}_{abcd}^{rstu} |\psi_0\rangle + \dots\end{aligned}$$

truncation of full CI to limit computational effort

CISD, CISDT, CISDTQ, ...

not size consistent because not all determinants are included

# beyond Hartree Fock

• •  
| 2

## Full Configuration Interaction expansion

all determinants included

example H<sub>2</sub> and 2 H<sub>2</sub>

$$1 \text{ H}_2: \Psi^1 = |\phi_1^1 \alpha \phi_1^1 \beta\rangle + c_{1_1 \bar{1}_1}^{2_1 \bar{2}_1} |\phi_2^1 \alpha \phi_2^1 \beta\rangle$$

$$= |1_1 \bar{1}_1\rangle + c_{1_1 \bar{1}_1}^{2_1 \bar{2}_1} |2_1 \bar{2}_1\rangle$$

$$2 \text{ H}_2: \Psi^{12} = |1_1 \bar{1}_1 1_2 \bar{1}_2\rangle + c_{1_1 \bar{1}_1}^{2_1 \bar{2}_1} |2_1 \bar{2}_1 1_2 \bar{1}_2\rangle + c_{1_2 \bar{1}_2}^{2_2 \bar{2}_2} |1_1 \bar{1}_1 2_2 \bar{2}_2\rangle$$

$$+ c_{1_1 \bar{1}_1 1_2 \bar{1}_2}^{2_1 \bar{2}_1 2_2 \bar{2}_2} |2_1 \bar{2}_1 2_2 \bar{2}_2\rangle$$

## Truncated Configuration Interaction expansion

only include HF, single and doubly excited determinants

$$2 \text{ H}_2: \Psi^{12} = |1_1 \bar{1}_1 1_2 \bar{1}_2\rangle + c_{1_1 \bar{1}_1}^{2_1 \bar{2}_1} |2_1 \bar{2}_1 1_2 \bar{1}_2\rangle + c_{1_2 \bar{1}_2}^{2_2 \bar{2}_2} |1_1 \bar{1}_1 2_2 \bar{2}_2\rangle$$

# beyond Hartree Fock

## Full CI

all determinants included

$$\Psi^{12} = |1_1\bar{1}_11_2\bar{1}_2\rangle + c_{1_1\bar{1}_1}^{2_1\bar{2}_1}|2_1\bar{2}_11_2\bar{1}_2\rangle + c_{1_2\bar{1}_2}^{2_2\bar{2}_2}|1_1\bar{1}_12_2\bar{2}_2\rangle$$

$$+c_{1_1\bar{1}_11_2\bar{1}_2}^{2_1\bar{2}_12_2\bar{2}_2}|2_1\bar{2}_12_2\bar{2}_2\rangle$$

at large separation: independent molecules!

$$\Psi^{12} = \Psi^1 \Psi^2$$

$$= \left( |1_1\bar{1}_1\rangle + c_{1_1\bar{1}_1}^{2_1\bar{2}_1}|2_1\bar{2}_1\rangle \right) \left( |1_2\bar{1}_2\rangle + c_{1_2\bar{1}_2}^{2_2\bar{2}_2}|2_2\bar{2}_2\rangle \right)$$

$$= |1_1\bar{1}_1\rangle|1_2\bar{1}_2\rangle + c_{1_1\bar{1}_1}^{2_1\bar{2}_1}|2_1\bar{2}_1\rangle|1_2\bar{1}_2\rangle + c_{1_2\bar{1}_2}^{2_2\bar{2}_2}|1_1\bar{1}_1\rangle|2_2\bar{2}_2\rangle$$

$$+c_{1_1\bar{1}_1}^{2_1\bar{2}_1}c_{1_2\bar{1}_2}^{2_2\bar{2}_2}|2_1\bar{2}_1\rangle|2_2\bar{2}_2\rangle$$

# Coupled Clusters

idea

approximate the quadruples coefficients by doubles...

$$c_{abcd}^{rstu} \approx c_{ab}^{rs} * c_{cd}^{tu}$$

due to anti-symmetry there are 18 such terms:

$$c_{abcd}^{rstu} \approx c_{ab}^{rs} c_{cd}^{tu} - c_{ac}^{rs} c_{bd}^{tu} + c_{ad}^{rs} c_{bc}^{tu} + \dots$$

coupled-clusters doubles wavefunction

$$\Psi^{CCD} = \prod_{ab,rs} (1 + c_{ab}^{rs} X_{ab}^{rs}) |\psi_0\rangle$$

non-linear expansion in coefficients

all (2n)-tuply excited determinants included: size consistent!

only uses doubles coefficients

non-variational

# Coupled Clusters

idea

approximate the n-tuply coefficients by singles, doubles, ..

$$c_{abcd}^{rstu} \approx c_{ab}^{rs} * c_{cd}^{tu}$$

$$c_{abcde}^{rstuv} \approx c_{ab}^{rs} * c_{cd}^{tu} * c_e^v$$

$$c_{abcdef}^{rstuvw} \approx c_{ab}^{rs} * c_{cd}^{tu} * c_{ef}^{vw}$$

general case

non-linear expansion in coefficients and excitations

$$\Psi^{CC} = [\Pi_{a,r}(1 + c_a^r X_a^r)] [\Pi_{a,r}(1 + c_{ab}^{rs} X_{ab}^{rs})] \dots |\psi_0\rangle$$

identical to full CI if all possible excitation levels are considered

# Coupled Clusters

general case

non-linear expansion in coefficients and excitations

$$\Psi^{CC} = [\Pi_{a,r}(1 + c_a^r X_a^r)] [\Pi_{a,r}(1 + c_{ab}^{rs} X_{ab}^{rs})] \dots |\psi_0\rangle$$

identical to full CI if all possible excitation levels are considered

restrict excitation level to doubles: CCSD

$$\Psi^{CCSD} = [\Pi_{a,r}(1 + c_a^r X_a^r)] [\Pi_{a,r}(1 + c_{ab}^{rs} X_{ab}^{rs})] |\psi_0\rangle$$

all n-tuply excited determinants included: size consistent!

only singles and doubles coefficients needed

optimization of coefficients

# Coupled Clusters

general case

non-linear expansion in coefficients and excitations

$$\Psi^{CC} = [\Pi_{a,r}(1 + c_a^r X_a^r)] [\Pi_{a,r}(1 + c_{ab}^{rs} X_{ab}^{rs})] \dots |\psi_0\rangle$$

exponential ansatz

since

$$\hat{X}_{ab}^{rs} \hat{X}_{ab}^{rs} = 0$$

we can use the Taylor series

$$1 + c_{ab}^{rs} \hat{X}_{ab}^{rs} = 1 + c_{ab}^{rs} \hat{X}_{ab}^{rs} + \frac{1}{2} (c_{ab}^{rs})^2 \hat{X}_{ab}^{rs} \hat{X}_{ab}^{rs} + \dots = \exp(c_{ab}^{rs} \hat{X}_{ab}^{rs})$$

to recast the coupled clusters expansion

$$\Psi^{CC} = \Pi_{a,r} \exp(c_a^r \hat{X}_a^r) \Pi_{ab,rs} \exp(c_{ab}^{rs} \hat{X}_{ab}^{rs}) \dots |\psi_0\rangle$$

$$\Psi^{CC} = \exp \left( \sum_{a,r} c_a^r \hat{X}_a^r + \sum_{ab,rs} c_{ab}^{rs} \hat{X}_{ab}^{rs} + \dots \right) |\psi_0\rangle$$

# Coupled Clusters

exponential ansatz of CC

$$\Psi^{CC} = \exp \left( \sum_{a,r} c_a^r \hat{x}_a^r + \sum_{ab,rs} c_{ab}^{rs} \hat{X}_{ab}^{rs} + \dots \right) |\psi_0\rangle$$

restrict excitation level up to doubles: CCSD

$$\Psi^{CCSD} = \exp \left( \sum_{a,r} c_a^r \hat{x}_a^r + \sum_{ab,rs} c_{ab}^{rs} \hat{X}_{ab}^{rs} \right) |\psi_0\rangle$$

includes all excited determinants: size consistent!

only uses singles and doubles coefficients

single reference methods

works only if HF is reasonable approximation

fails if ground state has multi-configurational character: dissociation!

UHF reference

# Beyond Hartree-Fock: Perturbation Theory

## Møller-Plesset

zeroth order Hamiltonian

$$\hat{H}^0 = \sum_i^{n_e} \hat{f}(\mathbf{r}_i) = \sum_i^{n_e} \left( \hat{h}^0(\mathbf{r}_i) + \hat{v}^{\text{mf}}(\mathbf{r}_i) \right)$$

zeroth order wavefunction

$$\Psi(\mathbf{x}_1, \mathbf{x}_1, \dots, \mathbf{x}_n) = \det[\varphi_1(\mathbf{x}_1) \varphi_2(\mathbf{x}_2) \dots \varphi_n(\mathbf{x}_n)]$$

zeroth order energy (!!)

$$E^0 = \sum_i^{n_e} \epsilon_i$$

true Hamiltonian

$$\hat{H} = \hat{H}^0 + \hat{V}$$

perturbation

$$\hat{H} = \sum_i^{n_e} \hat{h}^0(\mathbf{r}_i) + \frac{1}{2} \sum_i^{n_e} \sum_j^{n_e} \frac{1}{r_{ij}}$$

# Beyond Hartree-Fock: Perturbation Theory

## Møller-Plesset

zeroth order Hamiltonian

$$\hat{H}^0 = \sum_i^{n_e} \hat{f}(\mathbf{r}_i) = \sum_i^{n_e} \left( \hat{h}^0(\mathbf{r}_i) + \hat{v}^{\text{mf}}(\mathbf{r}_i) \right)$$

true Hamiltonian

$$\hat{H} = \sum_i^{n_e} \hat{h}^0(\mathbf{r}_i) + \frac{1}{2} \sum_i^{n_e} \sum_j^{n_e} \frac{1}{r_{ij}}$$

perturbation

$$\hat{V} = \hat{H} - \hat{H}^0$$

$$\hat{V} = \frac{1}{2} \sum_i^{n_e} \sum_j^{n_e} \frac{1}{r_{ij}} - \sum_i^{n_e} v^{\text{mf}}$$

# Beyond Hartree-Fock: Perturbation Theory

## Møller-Plesset

perturbation

$$\hat{V} = \frac{1}{2} \sum_i^{n_e} \sum_j^{n_e} \frac{1}{r_{ij}} - \sum_i^{n_e} \hat{v}^{\text{mf}}$$

first order correction to energy

$$E_0^{(1)} = -\frac{1}{2} \sum_i^{n_e} \sum_j^{n_e} \int \int \varphi_i^*(\mathbf{x}_1) \varphi_j^*(\mathbf{x}_2) \frac{1 - \hat{P}_{12}}{r_{ij}} \varphi_j(\mathbf{x}_2) \varphi_i(\mathbf{x}_1) d\mathbf{x}_1 d\mathbf{x}_2$$

second order correction to energy

$$E_0^{(2)} = \sum_{j \neq 0} \frac{|\langle \Psi_0 | \hat{V} | \Psi_j \rangle|^2}{E_0^{(0)} - E_j^{(0)}}$$

$$E_0^{(2)} = \frac{1}{4} \sum_a^{n_{\text{occ}}} \sum_b^{n_{\text{occ}}} \sum_r^{n_{\text{virt}}} \sum_s^{n_{\text{virt}}} \frac{|\langle \Psi_0 | \hat{V} | \Psi_{ab}^{rs} \rangle|^2}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}$$

$$E_0^{(2)} = \frac{1}{4} \sum_a^{n_{\text{occ}}} \sum_b^{n_{\text{occ}}} \sum_r^{n_{\text{virt}}} \sum_s^{n_{\text{virt}}} \frac{|\int \int \varphi_a^*(\mathbf{x}_1) \varphi_b^*(\mathbf{x}_2) \frac{1 - \hat{P}_{12}}{r_{12}} \varphi_r(\mathbf{x}_1) \varphi_s(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2|^2}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}$$

# Semi-empirical quantum chemistry

## Fock Matrix elements

basisfunctions ( $N^5$  operations)

$$F_{\mu\nu} = h_{\mu\nu}^0$$

$$+ 2 \sum_a \sum_{\kappa} \sum_{\lambda} c_{\kappa a}^* c_{\lambda a}^* \int \int \gamma_{\mu}^*(\mathbf{r}_1) \gamma_{\kappa}^*(\mathbf{r}_2) \frac{1}{r_{12}} \gamma_{\lambda}(\mathbf{r}_2) \gamma_{\nu}(\mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2$$
$$- \sum_a \sum_{\kappa} \sum_{\lambda} c_{\kappa a}^* c_{\lambda a}^* \int \int \gamma_{\mu}^*(\mathbf{r}_1) \gamma_{\kappa}^*(\mathbf{r}_2) \frac{1}{r_{12}} \gamma_{\nu}(\mathbf{r}_2) \gamma_a(\mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2$$

## speeding up the calculation of Fock matrix

only valence electrons (2s,2p)

minimal basis, one function per electron

zero differential overlap

$$S_{\mu\nu} = \langle \gamma_{\mu} | \gamma_{\nu} \rangle = \delta_{\mu\nu}$$

replace remaining integral by parameters fitted to experimental data (NIST)

NDDO, MNDO, MNDO/d, AM1, PM3

# Density functional theory

## Hohenberg-Kohn theorems

exact mapping between non-interacting and interacting electronic systems

$$\Psi^{\text{real}} \leftarrow V^{\text{eff}}[\rho(\mathbf{r})] \rightarrow \Psi^{\text{non-int.}}$$

effective potential exists, so that densities are the same (ground-state only!!)

$$H^{\text{non-int.}} = \sum_i^N \left( -\frac{1}{2} \nabla^2 + V^{\text{eff}} \right)$$

one-electron wavefunctions: Kohn-Sham orbitals

$$\left( -\frac{1}{2} \nabla^2 + V^{\text{eff}} \right) \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

density of both systems

$$\rho(\mathbf{r}) = \sum_i^n |\phi_i(\mathbf{r})|^2$$

with exact effective potential

$$\rho(\mathbf{r}) = \rho^{\text{real}}(\mathbf{r})$$

# Density functional theory

## Hohenberg-Kohn theorems

exact mapping between non-interacting and interacting electronic systems

$$\Psi^{\text{real}} \xleftarrow{V^{\text{eff}}[\rho(\mathbf{r})]} \rightarrow \Psi^{\text{non-int.}}$$

ground-state only

energy functional

$$E[\rho] = T[\rho] + E_{ee}[\rho] + E_{ne}[\rho] + E_{XC}[\rho]$$

variational principle

$$E[\rho(\mathbf{r})] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{H} | \Psi \rangle \geq E_0$$

# Density functional theory

energy functional

$$E[\rho] = T[\rho] + E_{ee}[\rho] + E_{ne}[\rho] + E_{XC}[\rho]$$

electron-electron repulsion

$$E_{ee}[\rho] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

electron-nuclei attraction

$$E_{en}[\rho] = \int \sum_A^N \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} \rho(\mathbf{r}) d\mathbf{r} = \int V_{en}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}$$

exchange-correlation energy (uniform electron gas)

$$E_{XC}^{\text{LDA}}[\rho] = \int \epsilon_{XC}(\rho(\mathbf{r})) \rho(\mathbf{r}) d\mathbf{r}$$

kinetic energy of non-interacting systems

$$T[\rho(\mathbf{r})] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T}^{\text{non-int.}} | \Psi \rangle$$

# Density functional theory

minimize functional with respect to density

$$\partial E = \int \left( \frac{\partial}{\partial \rho} T + V_{ee} + E_{ne} + V_{XC} \right) \partial \rho d\mathbf{r} = 0$$

electron-electron repulsion

$$V_{ee}([\rho], r) = \frac{1}{2} \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

electron-nuclei attraction

$$V_{en}([\rho], \mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|}$$

exchange-correlation energy (uniform electron gas)

$$V_{XC}^{\text{LDA}}([\rho], \mathbf{r}) = \frac{\partial}{\partial \rho} E_{XC}^{\text{LDA}} = \rho(\mathbf{r}) \frac{\partial \epsilon_{XC}(\rho(\mathbf{r}))}{\partial \rho} \Big|_{\rho=\rho(r)} + \epsilon_{XC}(\rho(\mathbf{r}))$$

# Density functional theory

energy functional of non-interacting system

$$E^{\text{non-int.}}[\rho] = T[\rho] + \int V^{\text{eff}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$$

minimize functional of non-interacting system

$$\partial E^{\text{non-int.}}[\rho] = \int \left( \frac{\partial}{\partial \rho} T[\rho] + V^{\text{eff}}(\mathbf{r}) \right) \partial \rho(\mathbf{r}) d\mathbf{r} = 0$$

kinetic energy functional

$$\frac{\partial}{\partial \rho} T[\rho] = -V^{\text{eff}}(\mathbf{r})$$

effective potential function of true potentials

$$V^{\text{eff}}(\mathbf{r}) = V_{en}(\mathbf{r}) + V_{ee}([\rho], \mathbf{r}) + V_{XC}([\rho], \mathbf{r})$$

# Density functional theory

## Practical DFT scheme

Step 1: guess density  $\rho(\mathbf{r})$

Step 2: construct effective potential

$$V^{\text{eff}}(\mathbf{r}) = V_{en}(\mathbf{r}) + V_{ee}([\rho], \mathbf{r}) + V_{XC}([\rho], \mathbf{r})$$

Step 3a: solve the Schrödinger equation for non-interacting electrons

$$\left(-\frac{1}{2}\nabla^2 + V^{\text{eff}}\right)\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

Step 3b: compute new density & kinetic energy

$$\rho(\mathbf{r}) = \sum_i^n |\phi_i(\mathbf{r})|^2$$

$$T[\rho] = \sum_i^n \langle \phi_i | -\frac{1}{2}\nabla^2 | \phi_i \rangle = \sum_i^n \epsilon_i - \int V^{\text{eff}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$$

Step 4: goto step 2, until convergence is reached

final energy:

$$E[\rho_0] = \sum_i^n \epsilon_i - \int V^{\text{eff}}(\mathbf{r})\rho_0(\mathbf{r})d\mathbf{r} + E_{en}[\rho_0] + E_{ee}[\rho_0] + E_{XC}[\rho_0]$$

# Quantum Monte Carlo

## Variational Monte Carlo

expectation value of energy

$$\frac{\int \Psi_T^*(\mathbf{r}, \{\alpha\}) \hat{H} \Psi_T(\mathbf{r}, \{\alpha\}) d\mathbf{r}}{\int \Psi_T^*(\mathbf{r}, \{\alpha\}) \Psi_T(\mathbf{r}, \{\alpha\}) d\mathbf{r}} = E(\{\alpha\}) \geq E_0$$

importance sampling (Monte Carlo)

$$p(\mathbf{r}) = \frac{|\Psi(\mathbf{r})|}{\int |\Psi(\mathbf{r}')| d\mathbf{r}'}$$

local energy

$$E_L(\mathbf{r}) = \frac{\hat{H} \Psi_T(\mathbf{r})}{\Psi_T(\mathbf{r})}$$

Sampling of energy, optimize coefficients in wavefunction

$$\langle \hat{H} \rangle = \int p(\mathbf{r}) E_L(\mathbf{r}) d\mathbf{r}$$

$$\langle \hat{H} \rangle = \frac{1}{M} \sum_{i=1}^M E_L(\mathbf{r}_i) = \frac{1}{M} \sum_{i=1}^M \frac{\hat{H} \Psi_T(\mathbf{r})}{\Psi_T(\mathbf{r})}$$

# Quantum Monte Carlo

## Variational Monte Carlo

wavefunction

$$\Psi_T(\mathbf{x}) = \exp[J(\mathbf{x})] \sum_i c_i D_i(\mathbf{x})$$

determinant (antisymmetric)

$$D_i(\mathbf{x}) = \begin{vmatrix} \varphi_1(\mathbf{x}_1) & \varphi_1(\mathbf{x}_2) & \dots & \varphi_1(\mathbf{x}_n) \\ \varphi_2(\mathbf{x}_1) & \varphi_2(\mathbf{x}_2) & \dots & \varphi_2(\mathbf{x}_n) \\ \dots & \dots & \dots & \dots \\ \varphi_n(\mathbf{x}_1) & \varphi_n(\mathbf{x}_2) & \dots & \varphi_n(\mathbf{x}_n) \end{vmatrix}$$

Jastrow factor

$$J(\mathbf{r}) = \sum_{i>j}^N u(r_{ij}) + \sum_{i=1}^N \sum_{I=1}^{N_I} \chi_I(r_{iI}) + \sum_{i>j}^N \sum_{I=1}^{N_I} f_I(r_{ij}, r_{iI}, r_{jI})$$

# Quantum Monte Carlo

## Diffusion Monte Carlo

propagate Schrödinger equation in imaginary time

$$i \frac{\partial \Psi(\mathbf{r}, t)}{\partial t} = -\frac{1}{2} \nabla^2 \Psi(\mathbf{r}, t) + V(\mathbf{r}, t) \Psi(\mathbf{r}, t)$$

$$\tau = it$$

diffusion equation of electronic positions

$$-\frac{\partial \Psi^{\text{DMC}}(\mathbf{R}, t)}{\partial \tau} = -\frac{1}{2} \nabla^2 \Psi(\mathbf{r}, \tau) + (V(\mathbf{r}) - E_T) \Psi(\mathbf{r}, t)$$

project out ground state

# Quantum Monte Carlo

## Diffusion Monte Carlo

propagate Schrödinger equation in imaginary time

$$-\frac{\partial \Psi^{\text{DMC}}(\mathbf{R}, t)}{\partial \tau} = -\frac{1}{2} \nabla^2 \Psi(\mathbf{r}, \tau) + (V(\mathbf{r}) - E_T) \Psi(\mathbf{r}, t)$$

expansion in (unknown) eigenstates

$$\Psi(\mathbf{r}, t) = \sum_{n=0}^{\infty} c_n \psi_n(\mathbf{r}) e^{-i(E_n - E_t)t}$$

$$\Psi(\mathbf{r}, \tau) = \sum_{n=0}^{\infty} c_n \psi_n(\mathbf{r}) e^{-(E_n - E_t)\tau}$$

with  $E_T = E_0$  we can single out ground state in diffusion process

$$\Psi(\mathbf{r}, \tau) = c_0 \psi_0(\mathbf{r}) + \sum_{n=1}^{\infty} c_n \psi_n(\mathbf{r}) e^{-(E_n - E_0)\tau}$$

# Some practical guidelines

## Basissets

STO-3G too small

6-31G\* & 6-31G\*\* reasonable results

DFT often less sensitive to basisset

often better than cc-pVDZ

higher accuracy with cc-pVTZ, better than 6-311G\*\*, etc.

diffuse functions (aug- or +)

anions

excited states

dispersion bound complexes

# Some practical guidelines

## Methods

prefer DFT over HF

HF < DFT ~ MP2 < CCSD < CCSD(T)

MPn may not converge with n

beyond MP2, use CC

CASSCF/CASPT2

bond breaking, diradicals, excited states, transition metals

DFT can be dangerous

HF, semi-empirical and DFT fail for VDW complexes

MP2, CC, dispersion corrected DFT

# Some practical guidelines

Always do!

check if SCF converged!

check for multiconfigurational character (MPn/CC:T2)

check if geometry converged

NMA analysis

minimum: all positive frequencies

transition state: one negative frequency.

non-covalent complexes: flat surface, difficult, go by hand

think of symmetry

optimization cannot break symmetry

know what to expect: think first

never thrust the computer

CASSCF/CASPT2

check final natural orbital density matrix

check for large orbital rotations

# Gradients

## Analytical derivatives

$$\frac{\partial E}{\partial X_A} = \frac{\partial \tilde{E}}{\partial X_A} + \sum_{\mu a} \frac{\partial E}{\partial C_{\mu a}} \frac{\partial C_{\mu a}}{\partial X_A}$$

Hartree Fock solution

$$\frac{\partial E}{\partial X_A} = \frac{\partial \tilde{E}}{\partial X_A}$$

Hartree-Fock energy

$$E = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu}^{\text{core}} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} \langle \mu\nu | \frac{1 - \frac{1}{2}\hat{p}_{12}}{r_{12}} | \lambda\sigma \rangle + V_{NN}$$

$$P_{\mu\nu} = 2 \sum_a^{n/2} C_{\mu a}^* C_{\nu a}$$

# Gradients

## Analytical derivatives

Hartree Fock energy

$$E = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu}^{\text{core}} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} \langle \mu\nu | \frac{1 - \frac{1}{2}\hat{p}_{12}}{r_{12}} | \lambda\sigma \rangle + V_{NN}$$

gradient

$$\frac{\partial E}{\partial X_A} = \sum_{\mu\nu} P_{\mu\nu} \frac{\partial H_{\mu\nu}^{\text{core}}}{\partial X_A}$$

$$+ \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} \frac{\partial}{\partial X_A} \langle \mu\nu | \frac{1 - \frac{1}{2}\hat{p}_{12}}{r_{12}} | \lambda\sigma \rangle + \frac{\partial V_{NN}}{\partial X_A}$$

$$+ \sum_{\mu\nu} \frac{\partial P_{\mu\nu}}{\partial X_A} H_{\mu\nu}^{\text{core}} + \sum_{\mu\nu\lambda\sigma} \frac{\partial P_{\mu\nu}}{\partial X_A} P_{\lambda\sigma} \langle \mu\nu | \frac{1 - \frac{1}{2}\hat{p}_{12}}{r_{12}} | \lambda\sigma \rangle$$

# Gradients

## Analytical derivatives

orthogonality of RHF molecular orbitals

$$\sum_{\mu\nu} C_{\mu a} S_{\mu\nu} C_{\nu b} = \delta_{ab}$$

$$2 \sum_{\mu\nu} \frac{\partial C_{\mu a}}{\partial X_A} S_{\mu\nu\nu b} = - \sum_{\mu\nu} C_{\mu a} C_{\nu a} \frac{\partial S_{\mu\nu}}{\partial X_A}$$

gradient

$$\frac{\partial E}{\partial X_A} = \sum_{\mu\nu} P_{\mu\nu} \frac{\partial H_{\mu\nu}^{\text{core}}}{\partial X_A}$$

$$+ \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} \frac{\partial}{\partial X_A} \langle \mu\nu | \frac{1 - \frac{1}{2}\hat{p}_{12}}{r_{12}} | \lambda\sigma \rangle + \frac{V_{NN}}{\partial X_A}$$

$$- \sum_{\mu\nu} Q_{\mu\nu} \frac{\partial S_{\mu\nu}}{\partial X_A}$$

with

$$Q_{\mu\nu} = 2 \sum_{a=1}^{n/2} \epsilon_a C_{\mu a} C_{\nu a}$$

# Gradients

## Analytical derivatives

Configuration interaction

$$|\Psi\rangle = \sum_I c_I |\psi_I\rangle$$

general gradient

$$\frac{\partial E}{\partial X_A} = \frac{\partial \tilde{E}}{\partial X_A} + \sum_{\mu a} \frac{\partial E}{\partial C_{\mu i}} \frac{\partial C_{\mu i}}{\partial X_A} + \sum_I \frac{\partial E}{\partial c_I} \frac{\partial c_I}{\partial X_A}$$

MCSCF gradient

$$\frac{\partial E}{\partial X_A} = \frac{\partial \tilde{E}}{\partial X_A}$$

CI gradient

$$\frac{\partial E}{\partial X_A} = \frac{\partial \tilde{E}}{\partial X_A} + \sum_{\mu a} \frac{\partial E}{\partial C_{\mu i}} \frac{\partial C_{\mu i}}{\partial X_A}$$

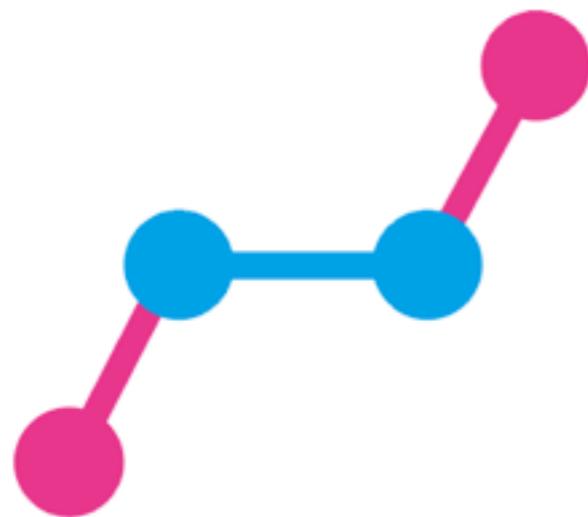
# Molecular Mechanics

**throw away the electrons!!!**

**low-dimensional functions, empirical parameters**

$$V^{\text{MM}}(R_1, R_2, \dots, R_N) = \sum_k v_k(R_i, R_j, R_k, R_l; \{p_k\})$$

**bonded interaction functions:**



$$v_b = \frac{1}{2} k_b (r_{ij} - r_0)^2$$

$$v_a = \frac{1}{2} k_a (\theta_{ijk} - \theta_0)^2$$



$$v_d = \sum_n^5 C_n (\cos(\varphi_{ijkl}))^n$$

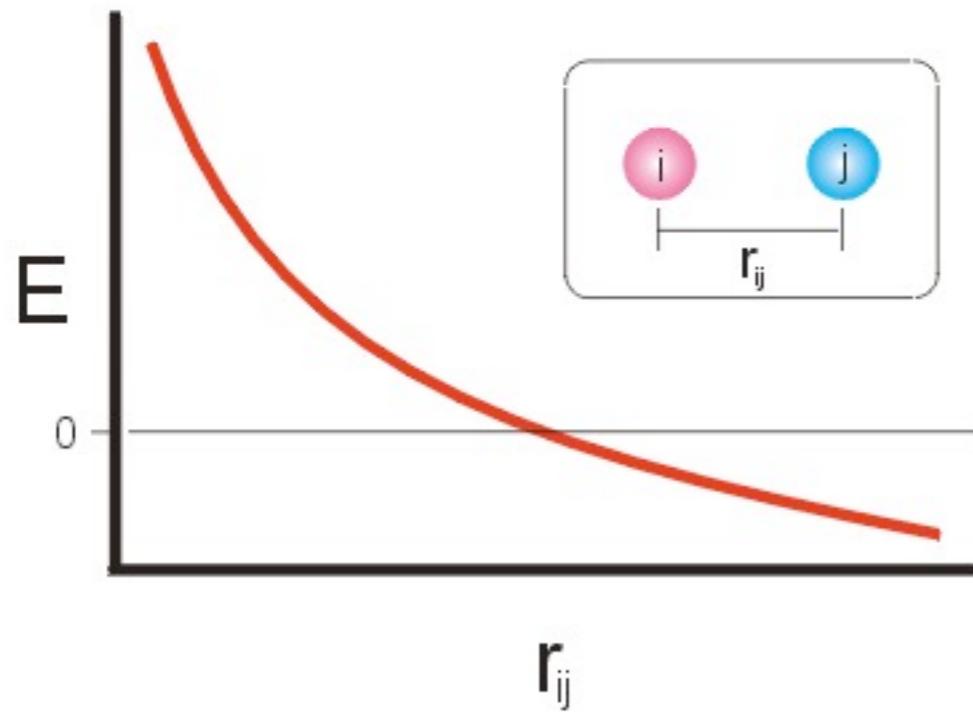
# Molecular Mechanics

throw away the electrons!!!

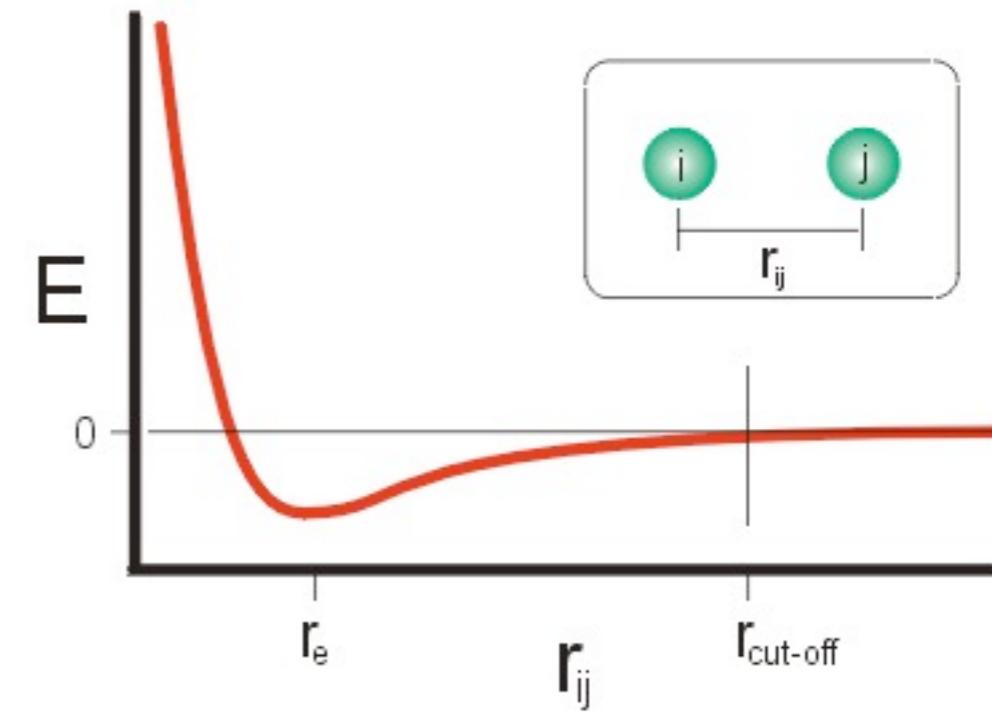
low-dimensional functions, empirical parameters

$$V^{\text{MM}}(R_1, R_2, \dots, R_N) = \sum_k v_k(R_i, R_j, R_k, R_l; \{p_k\})$$

non-bonded interaction functions:



$$v_{\text{Coul}}(r_{ij}) = \frac{e^2 q_i q_j}{4\pi\epsilon_0 r_{ij}}$$



$$v_{\text{LJ}}(r_{ij}) = \frac{C_{ij}^{(12)}}{r_{ij}^{12}} - \frac{C_{ij}^{(6)}}{r_{ij}^6}$$

# Molecular Modeling

## Hartree-Fock

mean-field: no electron-electron correlation

## post Hartree-Fock methods

configuration interaction

coupled clusters

perturbation theory

## density functional theory

$$E [\rho(\mathbf{r})] = T [\rho(\mathbf{r})] + V_{\text{coul}} [\rho(\mathbf{r})] + V_{\text{xc}} [\rho(\mathbf{r})]$$

empirical exchange-correlation functionals

Kohn-Sham orbitals

## semi-empirical methods

partial neglect of orbital overlap (interactions)

empirical parameters

## molecular mechanics forcefield

# Molecular Dynamics

nuclei are classical particles

$$F_n = m_n \ddot{x}_n = -\nabla_{x_n} V(x_1, x_2, \dots, x_N)$$

$$x_n(t) = x_n(t_0) + \dot{x}_n(t_0)(t - t_0) + \frac{1}{2} \ddot{x}_n^2 (t - t_0)^2$$

potential energy and forces

molecular quantum mechanics

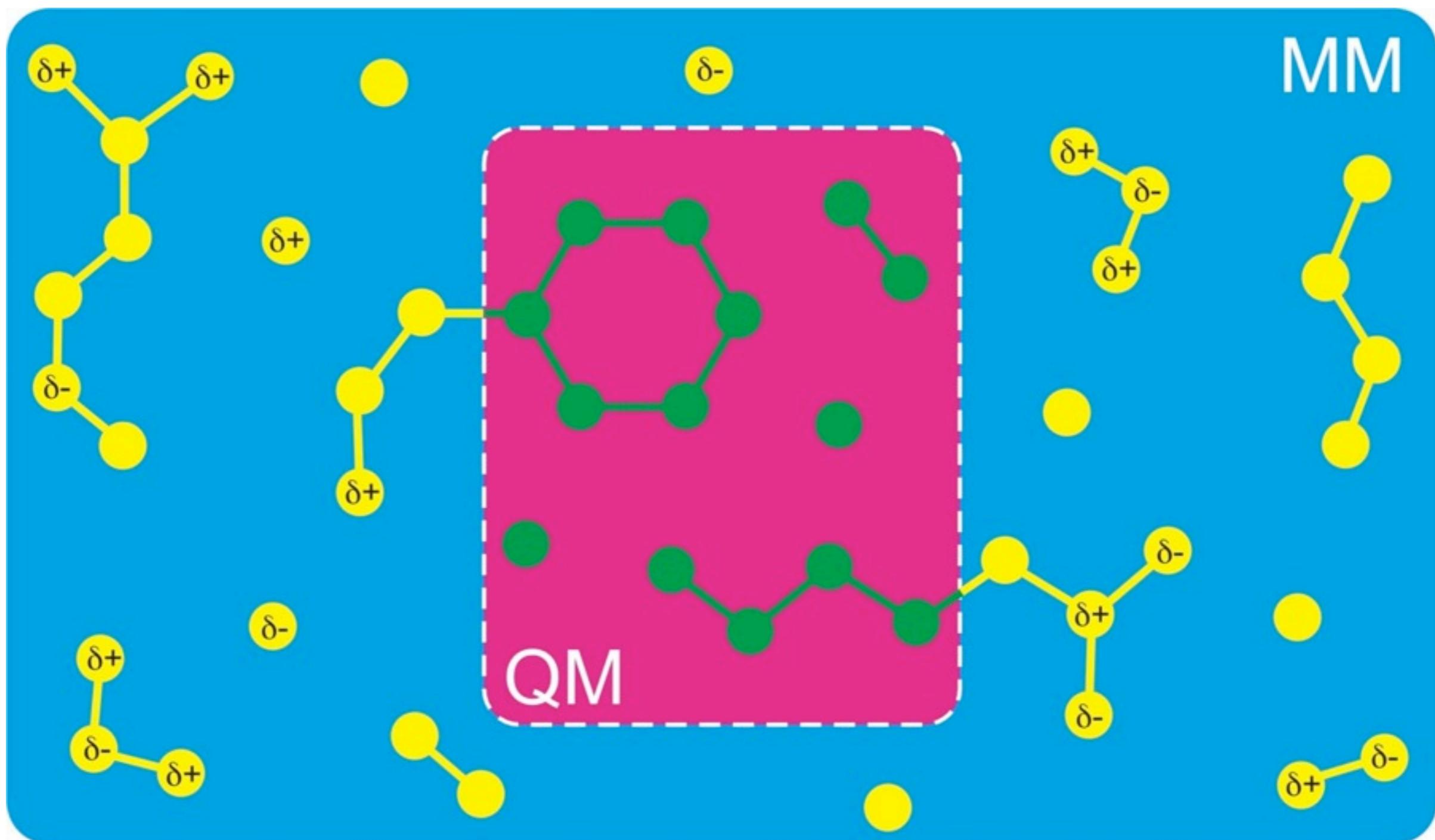
$$V(x_1, x_2, \dots, x_N) = \langle \Psi_e | \hat{H}(x_1, x_2, \dots, x_N) | \Psi_e \rangle$$

molecular mechanics forcefield

$$V(x_1, x_2, \dots, x_N) = \sum_k v_k(x; p_k)$$

# Quantum Mechanics/Molecular Mechanics

electrons treated explicitly in small subsystem  
molecular mechanics forcefield for remainder

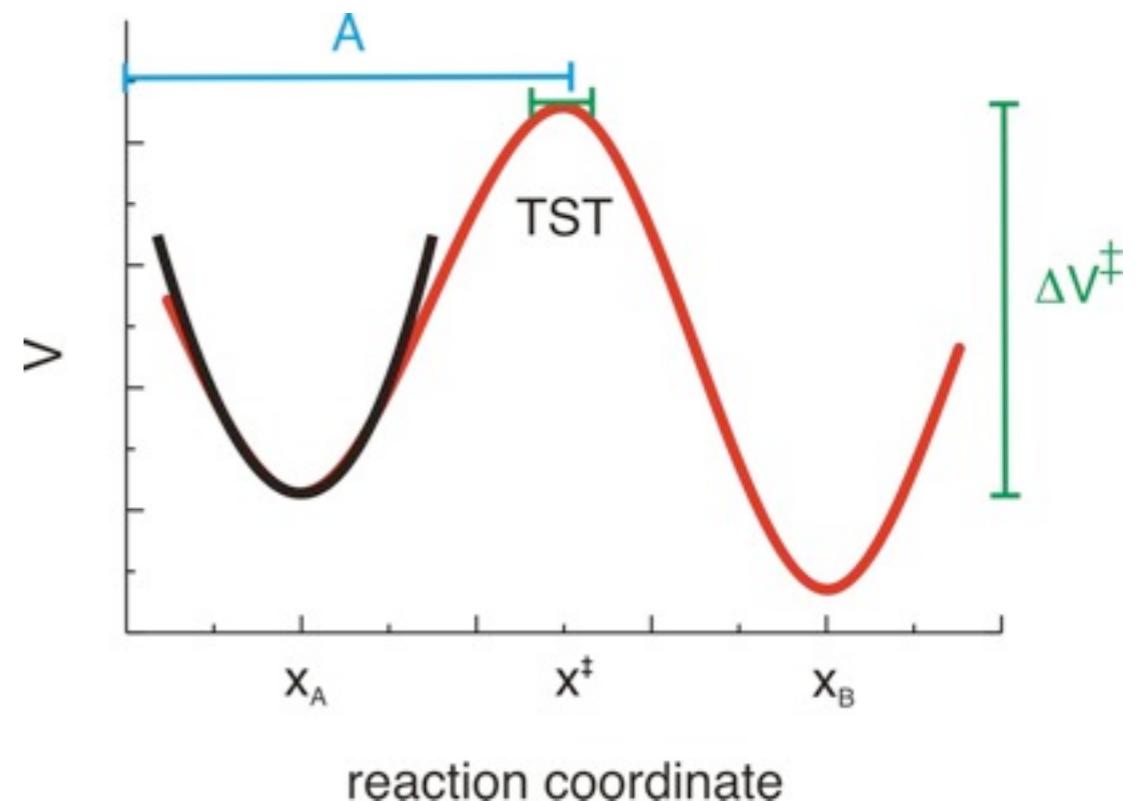


# rate theory (summary)

Eyring TST equation

one-dimensional systems

$$k = \frac{k_B T}{h q_{RS}} \exp \left[ -\frac{V(x^\ddagger)}{k_B T} \right]$$



# rate theory (summary)

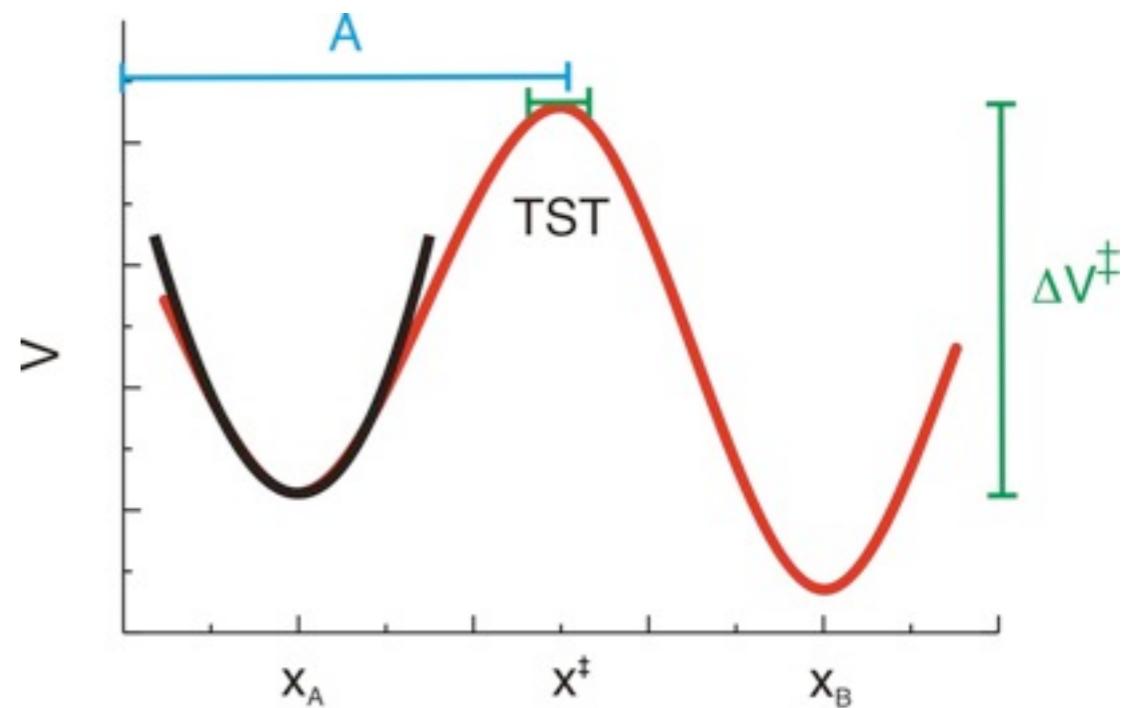
Eyring TST equation

one-dimensional systems

$$k = \frac{k_B T}{h q_{RS}} \exp \left[ -\frac{V(x^\ddagger)}{k_B T} \right]$$

high-dimensional systems

$$k = \frac{k_B T}{h q_{RS}} \exp \left[ -\frac{V^{\text{PMF}}(\mathbf{x}^\ddagger)}{k_B T} \right] = \frac{k_B T}{h q_{RS}} \exp \left[ -\frac{\Delta g^\ddagger}{k_B T} \right]$$



# rate theory (summary)

Eyring TST equation

one-dimensional systems

$$k = \frac{k_B T}{h q_{\text{RS}}} \exp \left[ -\frac{V(x^\ddagger)}{k_B T} \right]$$

high-dimensional systems

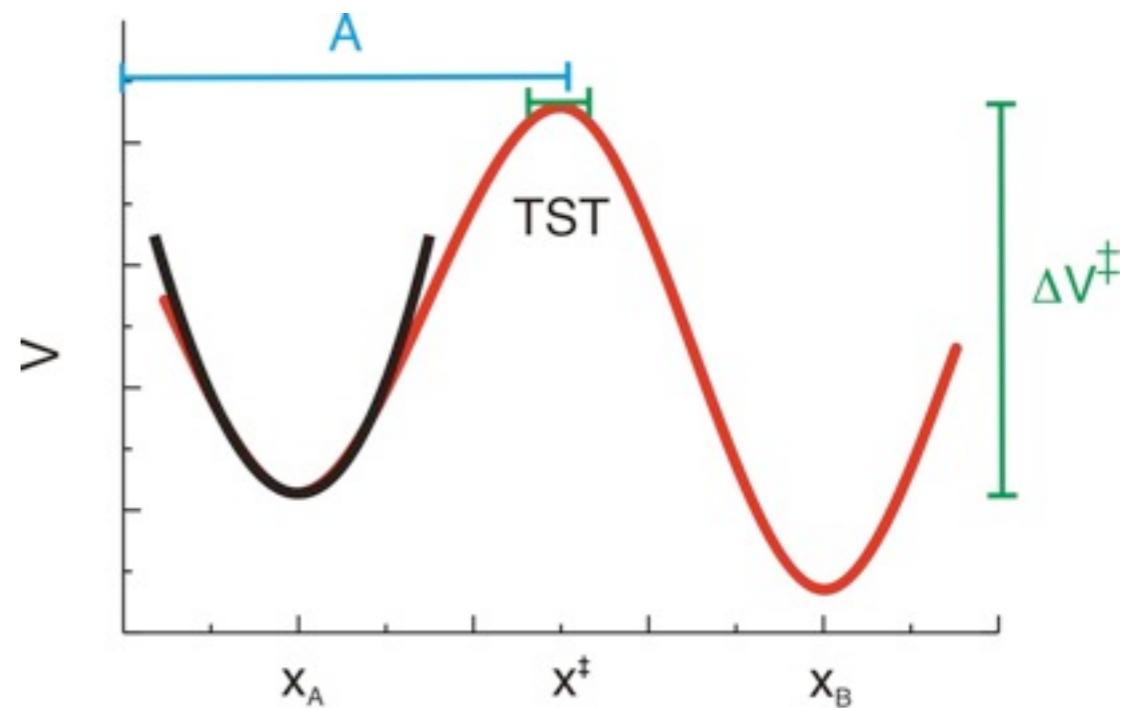
$$k = \frac{k_B T}{h q_{\text{RS}}} \exp \left[ -\frac{V^{\text{PMF}}(\mathbf{x}^\ddagger)}{k_B T} \right] = \frac{k_B T}{h q_{\text{RS}}} \exp \left[ -\frac{\Delta g^\ddagger}{k_B T} \right]$$

reaction coordinate

partition function of RS within harmonic approximation

one-dimensional systems

$$q_{\text{RS}} = \frac{1}{h} 2\pi k_B T \frac{1}{\omega_{\text{RS}}}$$



# rate theory (summary)

Eyring TST equation

one-dimensional systems

$$k = \frac{k_B T}{h q_{\text{RS}}} \exp \left[ -\frac{V(x^\ddagger)}{k_B T} \right]$$

high-dimensional systems

$$k = \frac{k_B T}{h q_{\text{RS}}} \exp \left[ -\frac{V^{\text{PMF}}(\mathbf{x}^\ddagger)}{k_B T} \right] = \frac{k_B T}{h q_{\text{RS}}} \exp \left[ -\frac{\Delta g^\ddagger}{k_B T} \right] \quad \text{reaction coordinate}$$

partition function of RS within harmonic approximation

one-dimensional systems

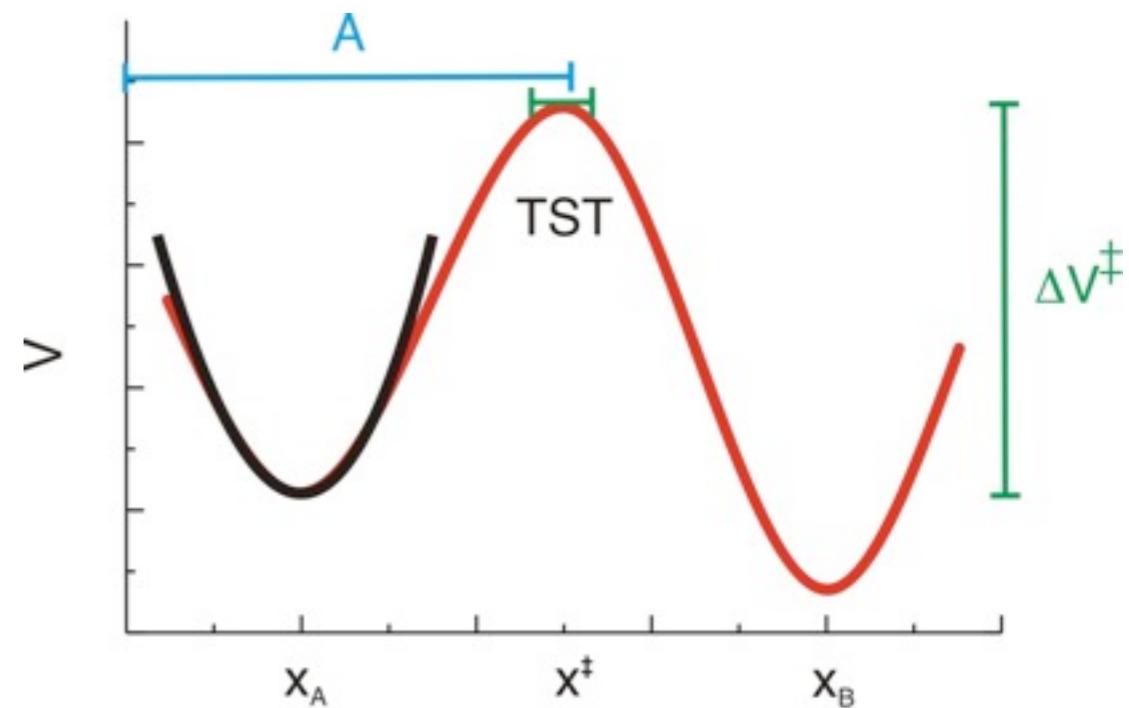
$$q_{\text{RS}} = \frac{1}{h} 2\pi k_B T \frac{1}{\omega_{\text{RS}}}$$

high-dimensional systems

$$q_{\text{RS}} = \frac{1}{h} 2\pi k_B T \frac{1}{\bar{\omega}_{\text{RS}}}$$

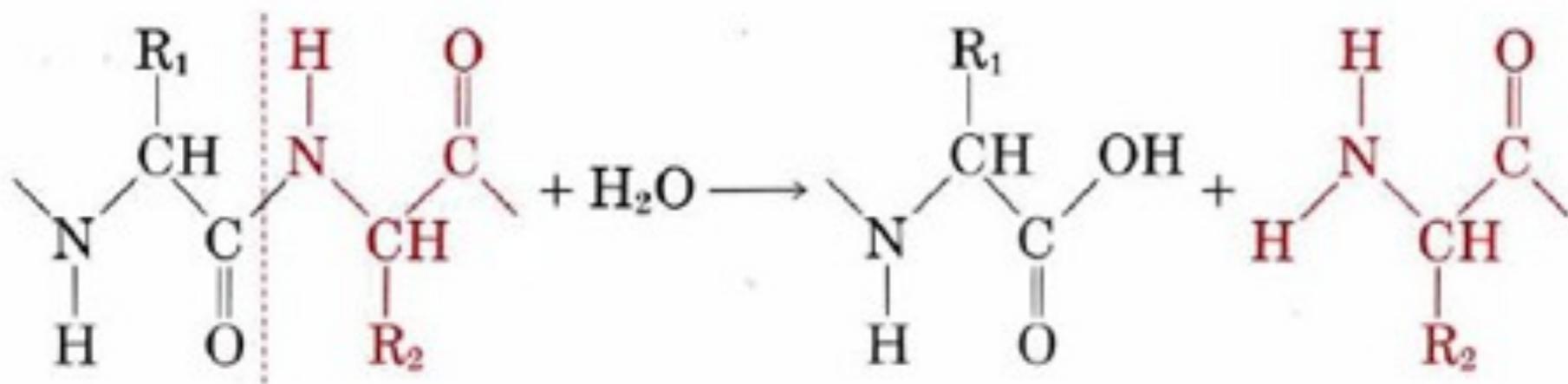
equipartition:  $h\bar{\omega}_{\text{RS}}/2\pi = k_B T \rightarrow q_{\text{RS}} = 1$

$$k = \frac{k_B T}{h} \exp \left[ -\frac{\Delta g^\ddagger}{k_B T} \right]$$



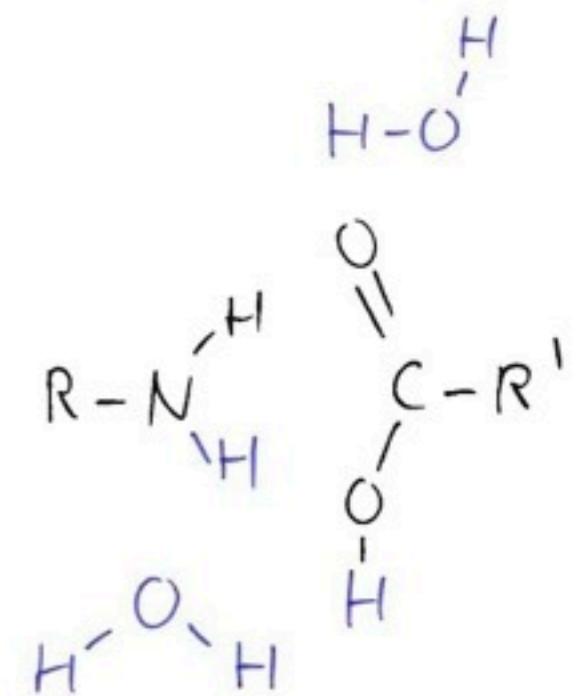
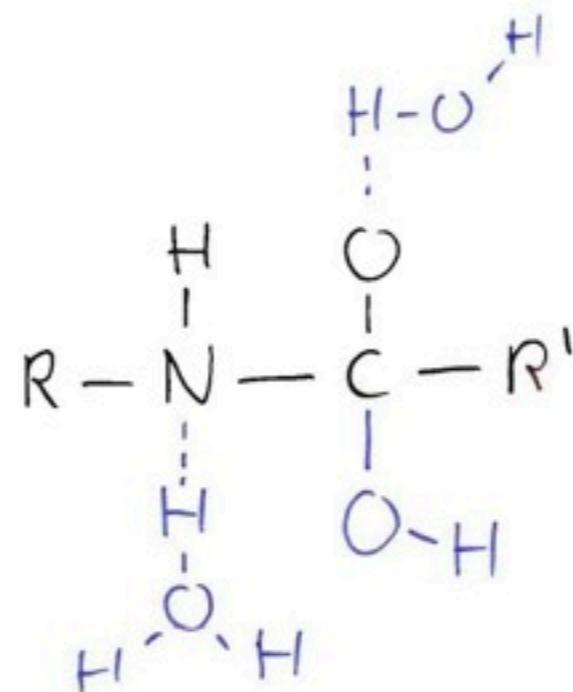
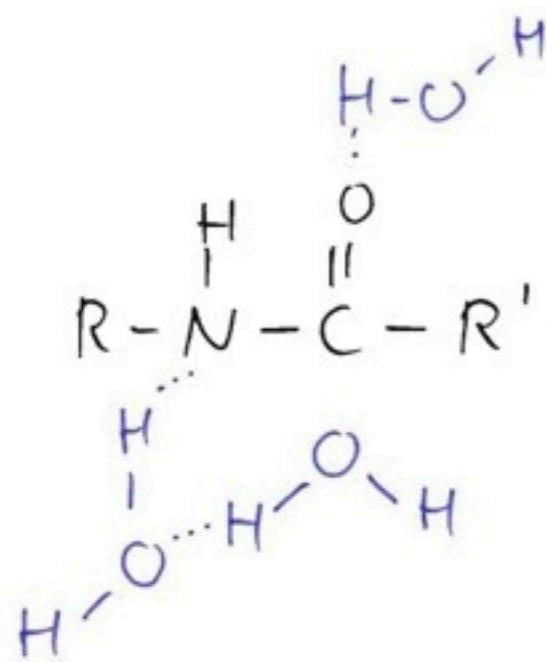
# Chemical reactions

## protein hydrolysis

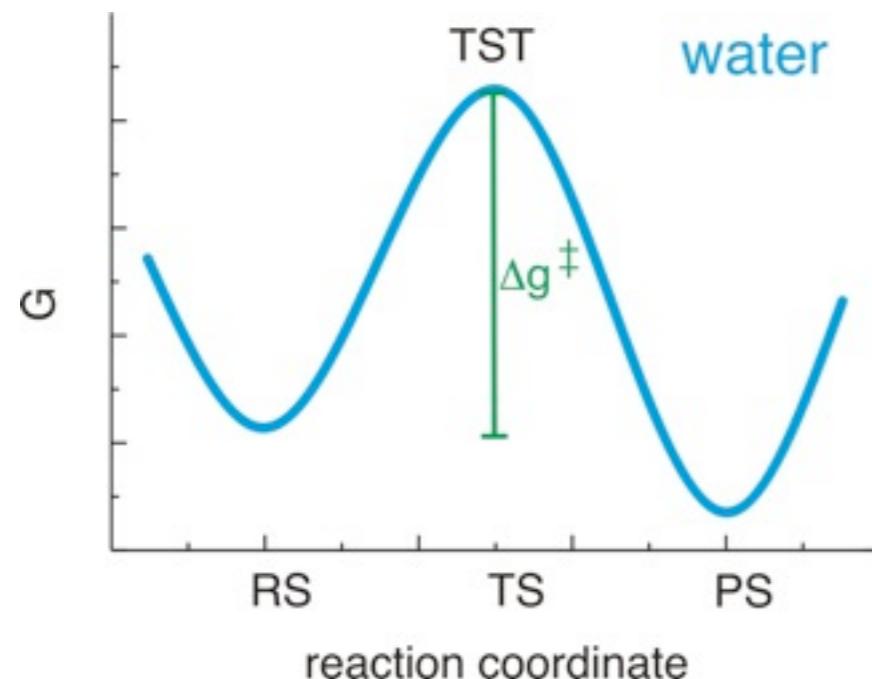


# Chemical reactions

protein hydrolysis in water



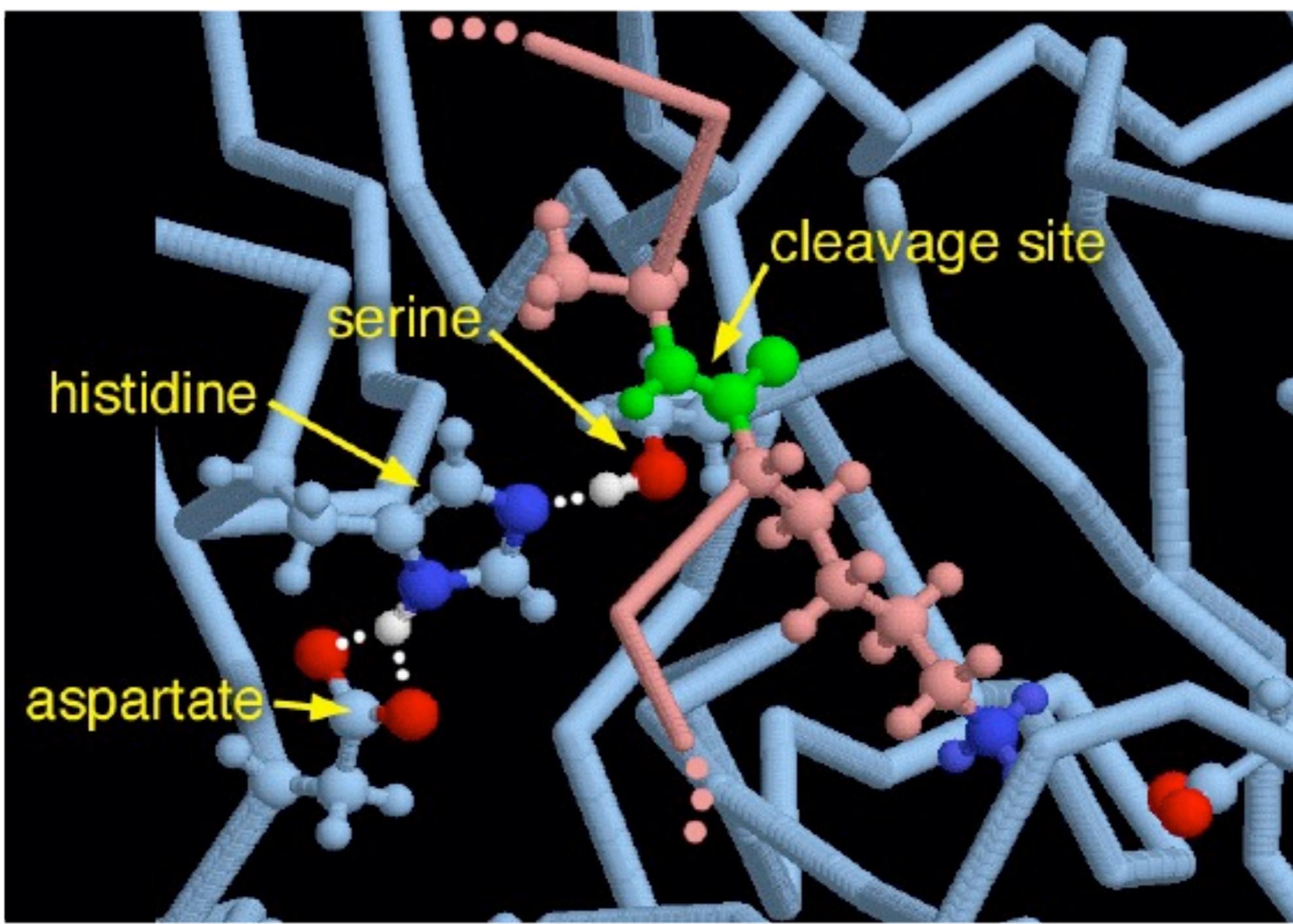
slow process



# Chemical reactions

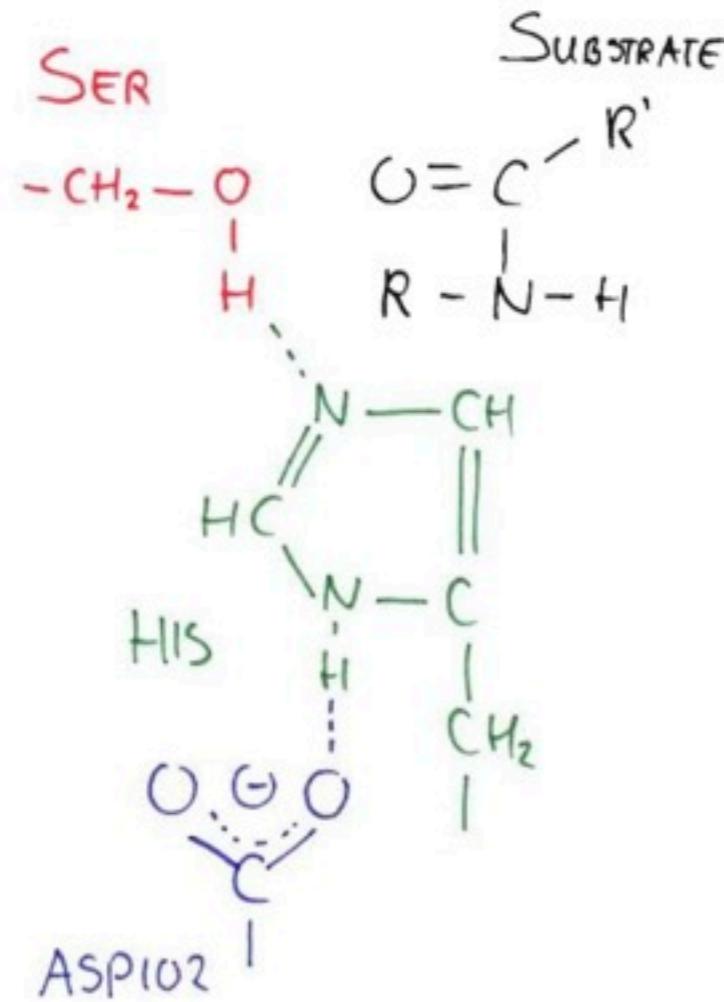
protein hydrolysis in water

protein hydrolysis in trypsin

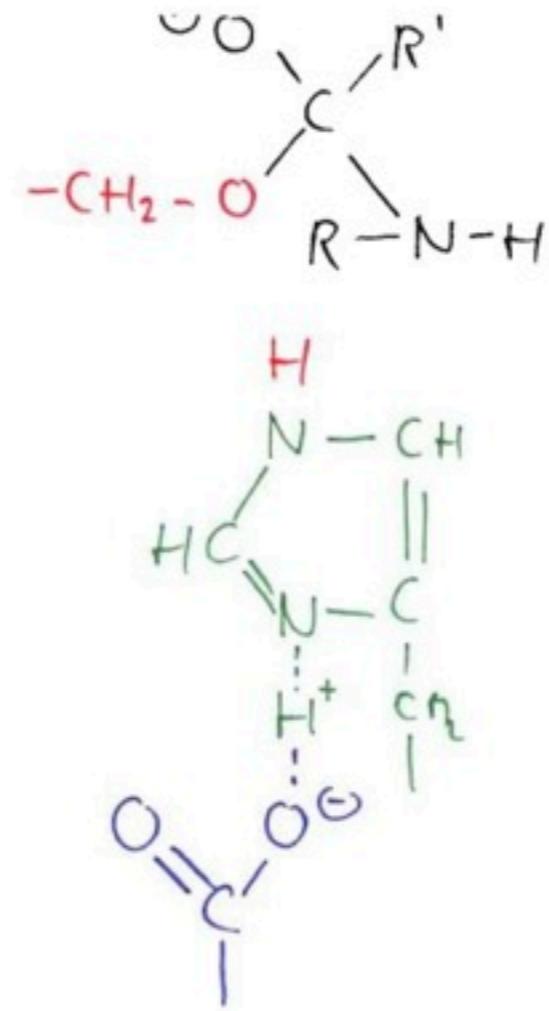


# Chemical reactions

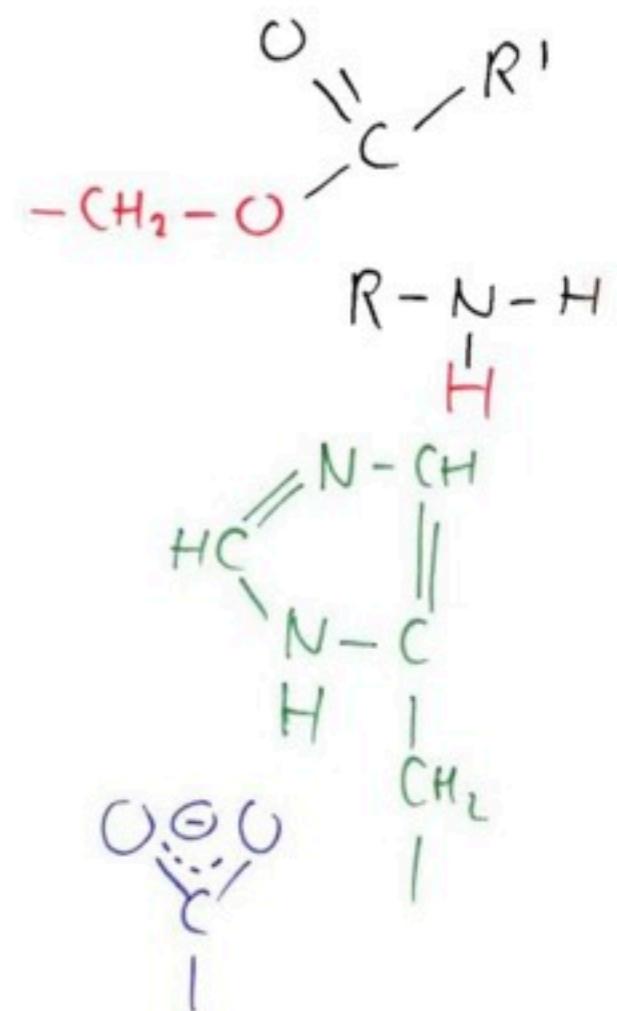
## protein hydrolysis in water



reactant state



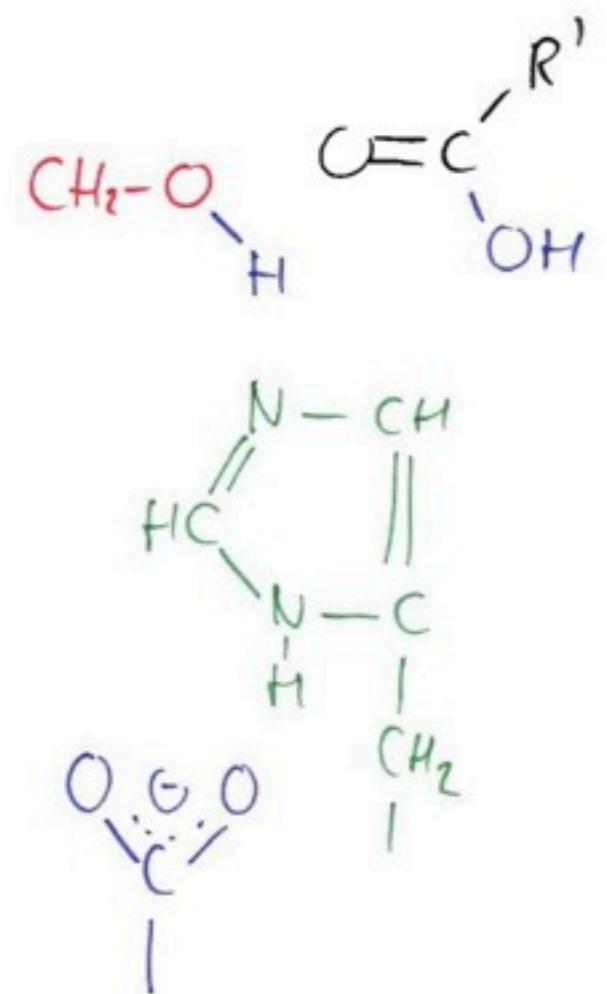
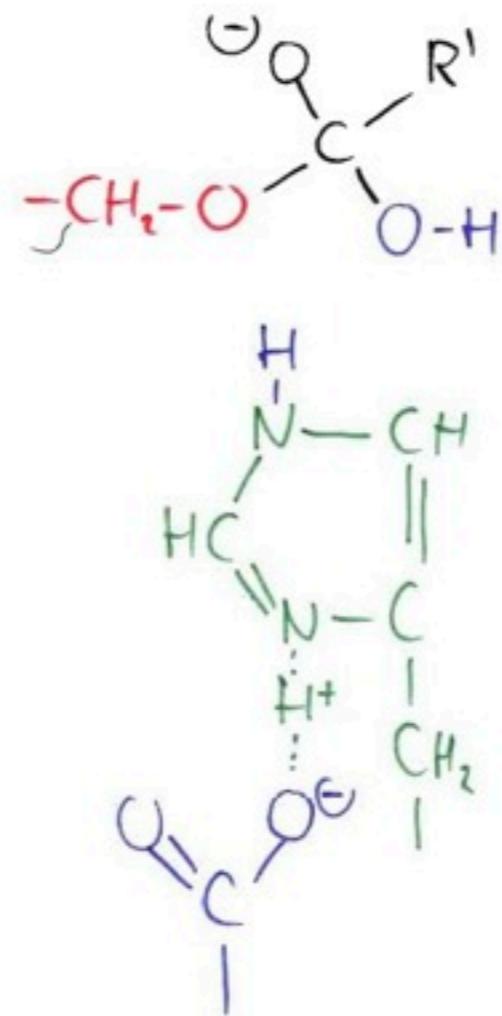
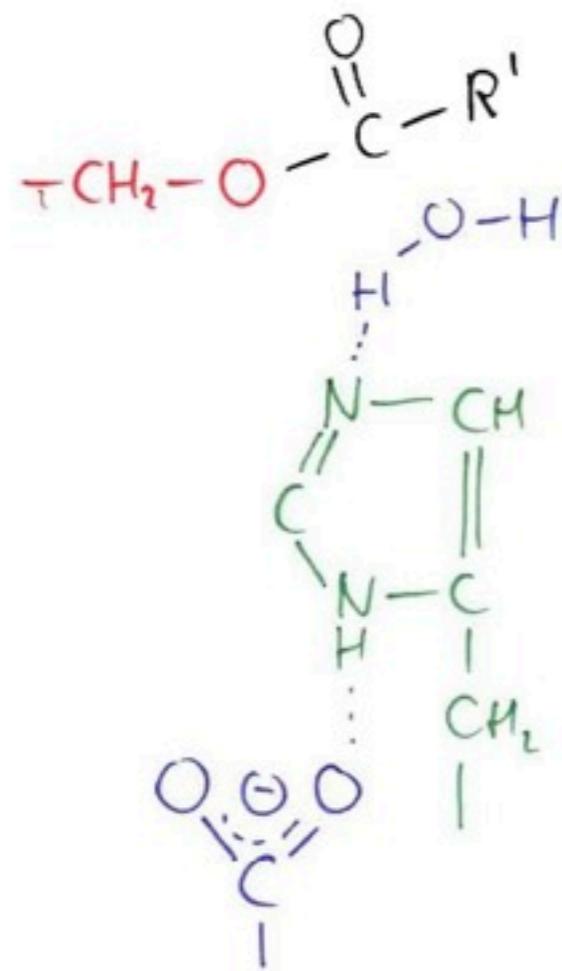
transition state I



intermediate

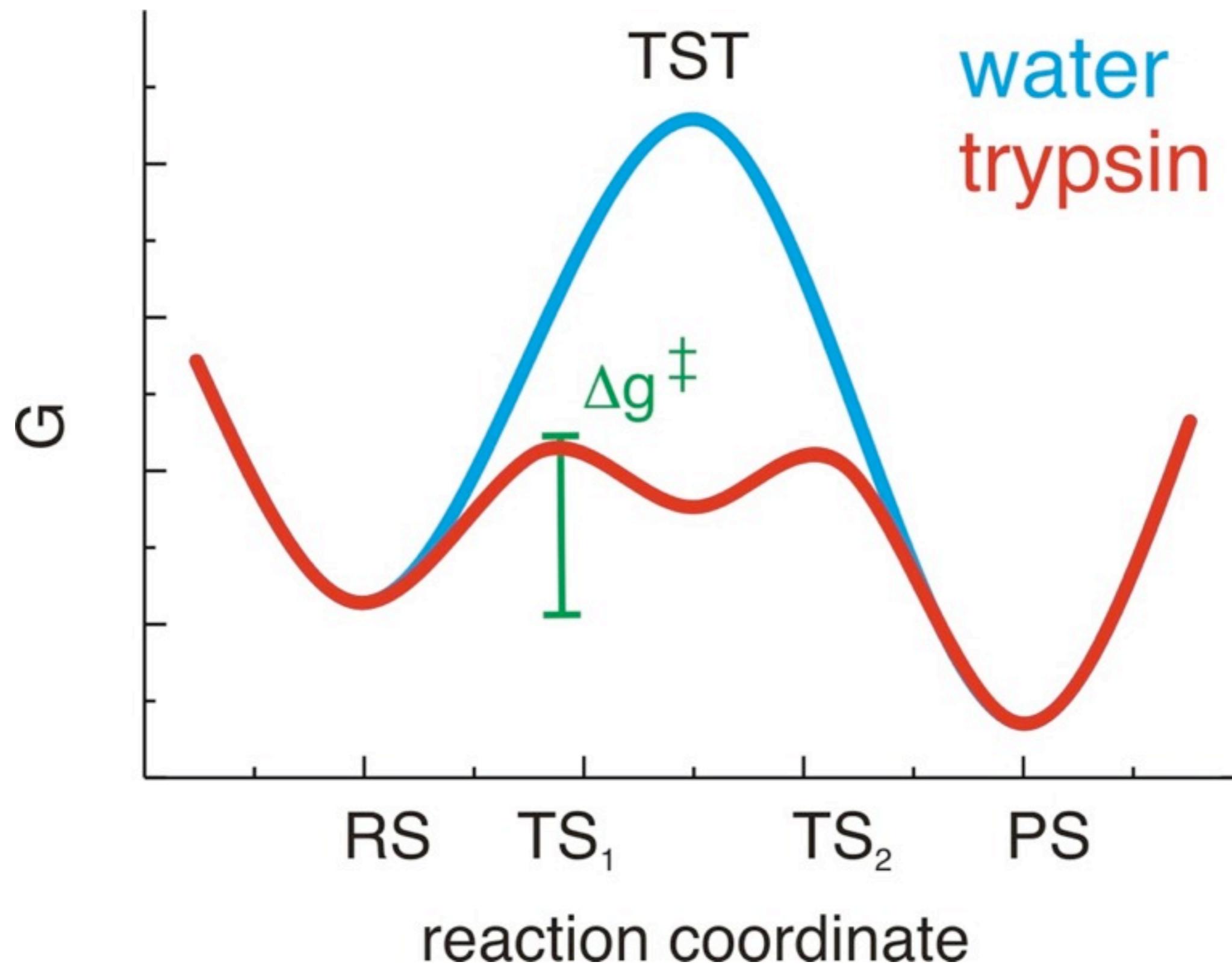
# Chemical reactions

protein hydrolysis in water



# Chemical reactions

protein hydrolysis in trypsin vs. in water

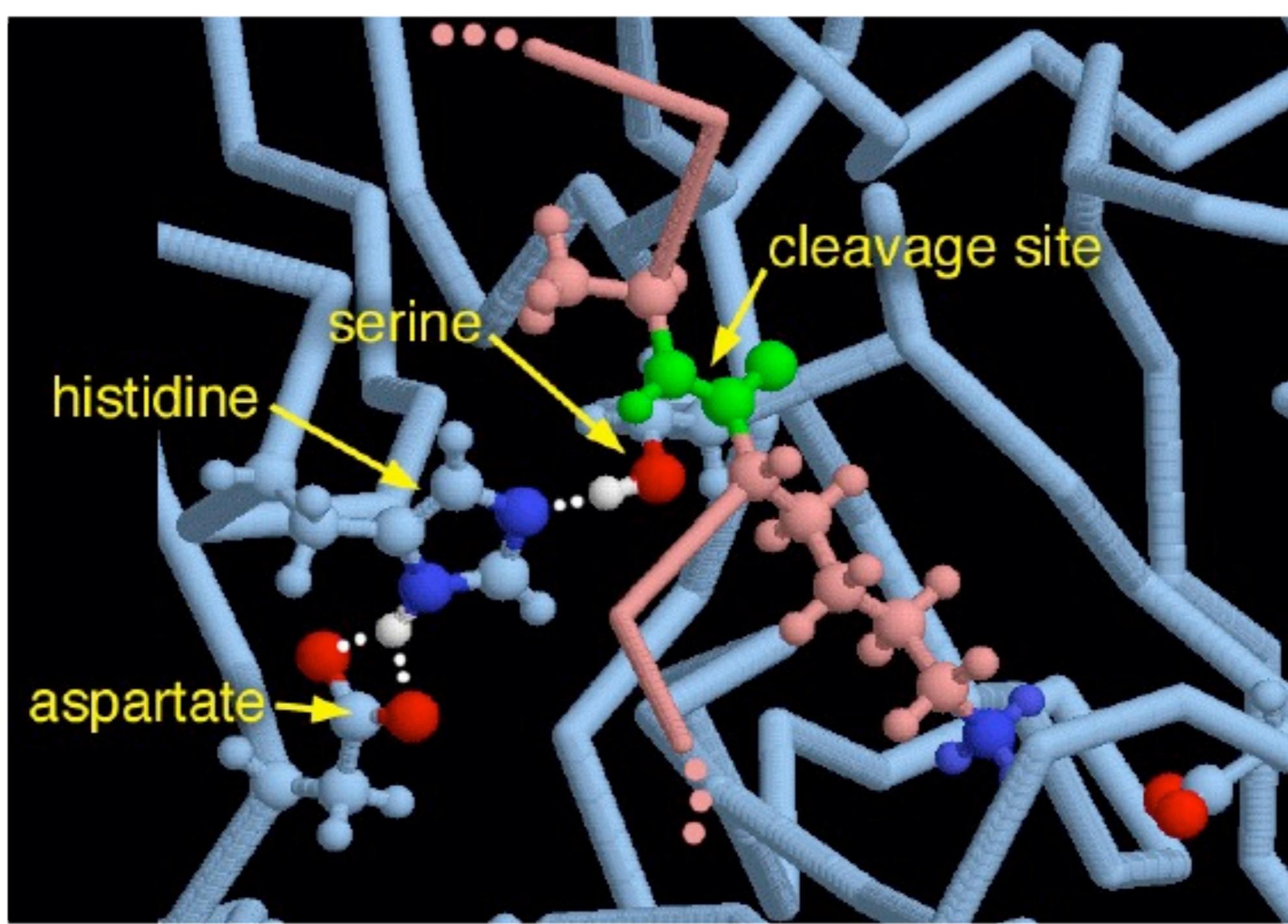
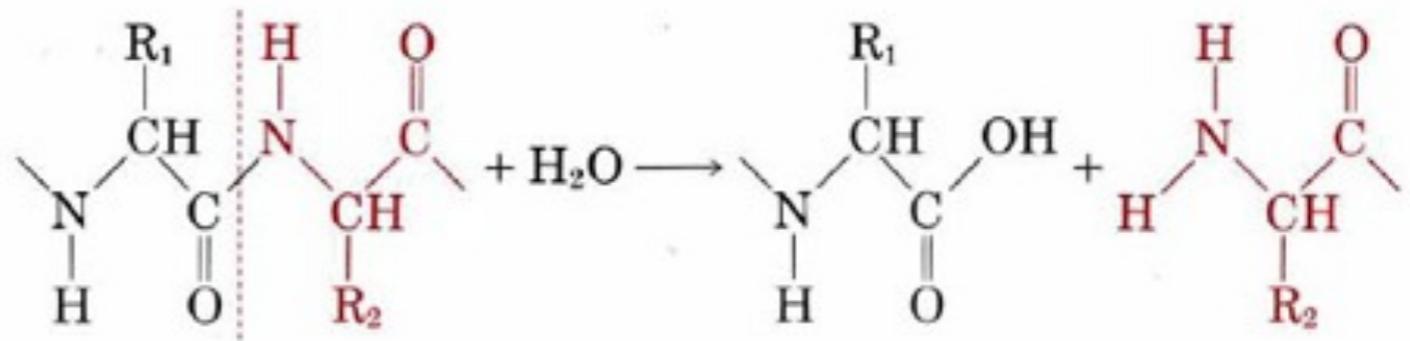


# Chemical reactions

specificity

Trypsin: R<sub>1</sub>=Arg/Lys

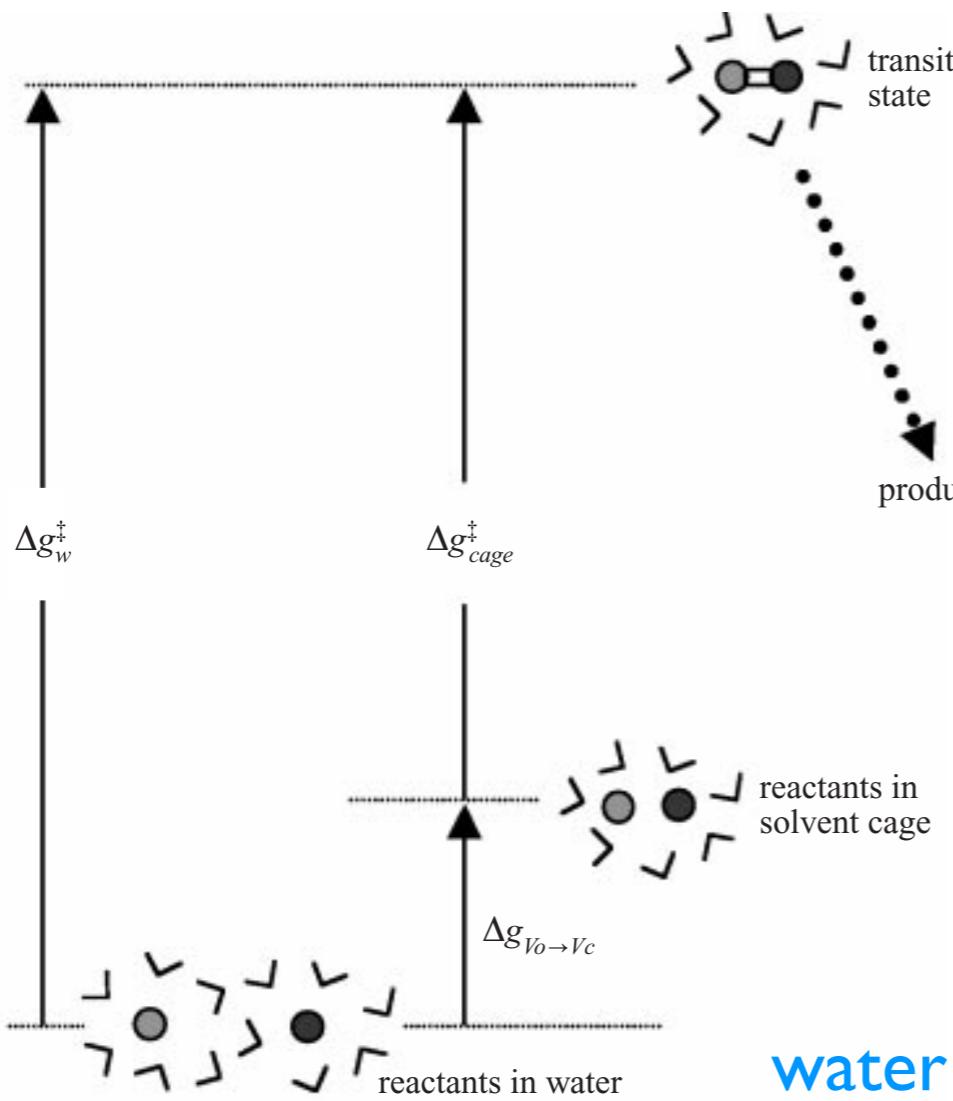
Thrombin: R<sub>1</sub>=Arg, R<sub>2</sub>=Gly



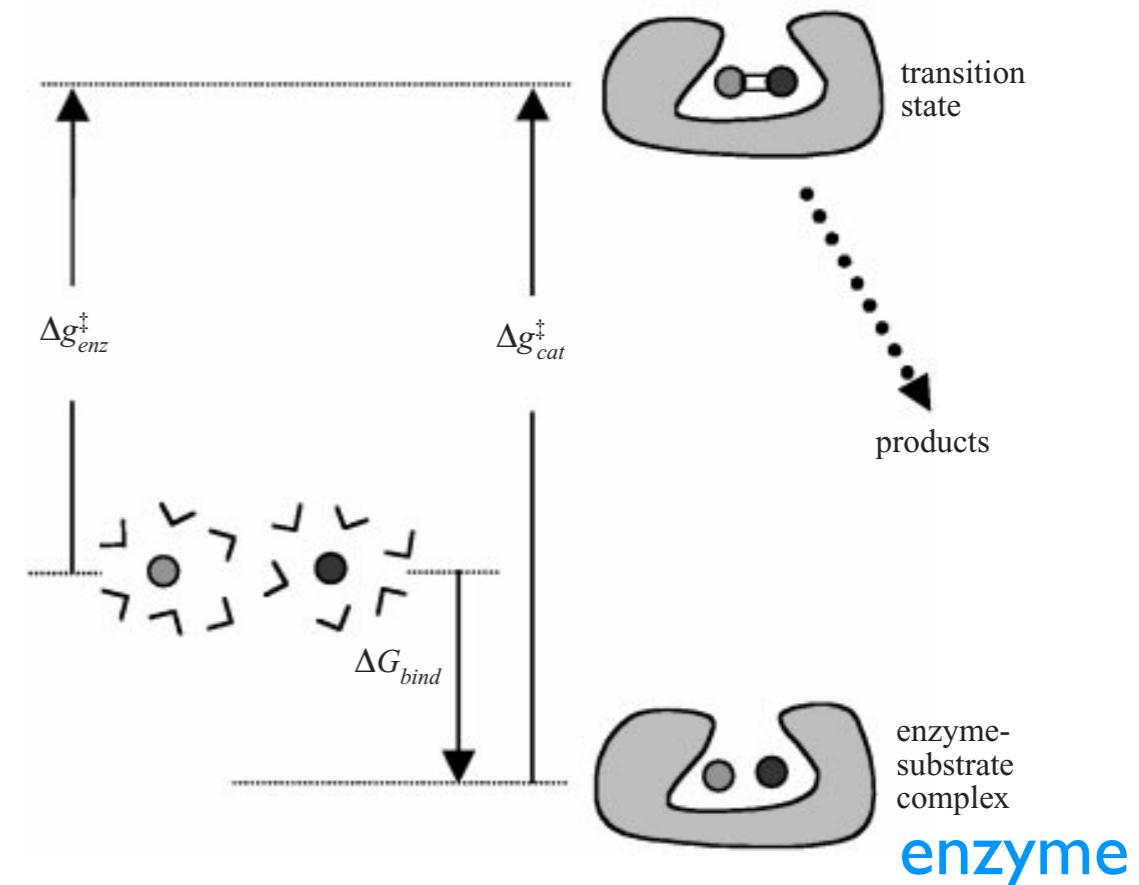
# Enzymes

accelerate reaction with respect to water

$$k = \frac{h}{k_B T} \exp \left[ -\frac{\Delta g^\ddagger}{k_B T} \right]$$



water

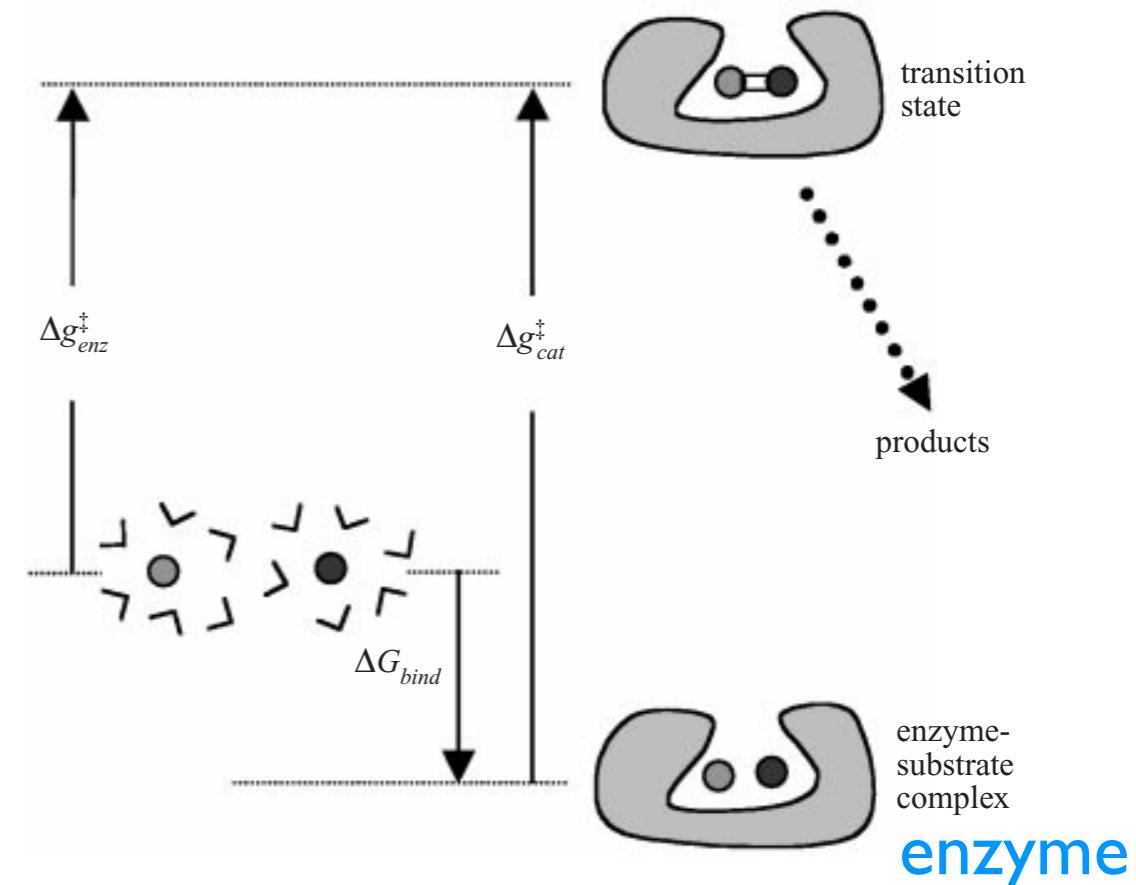
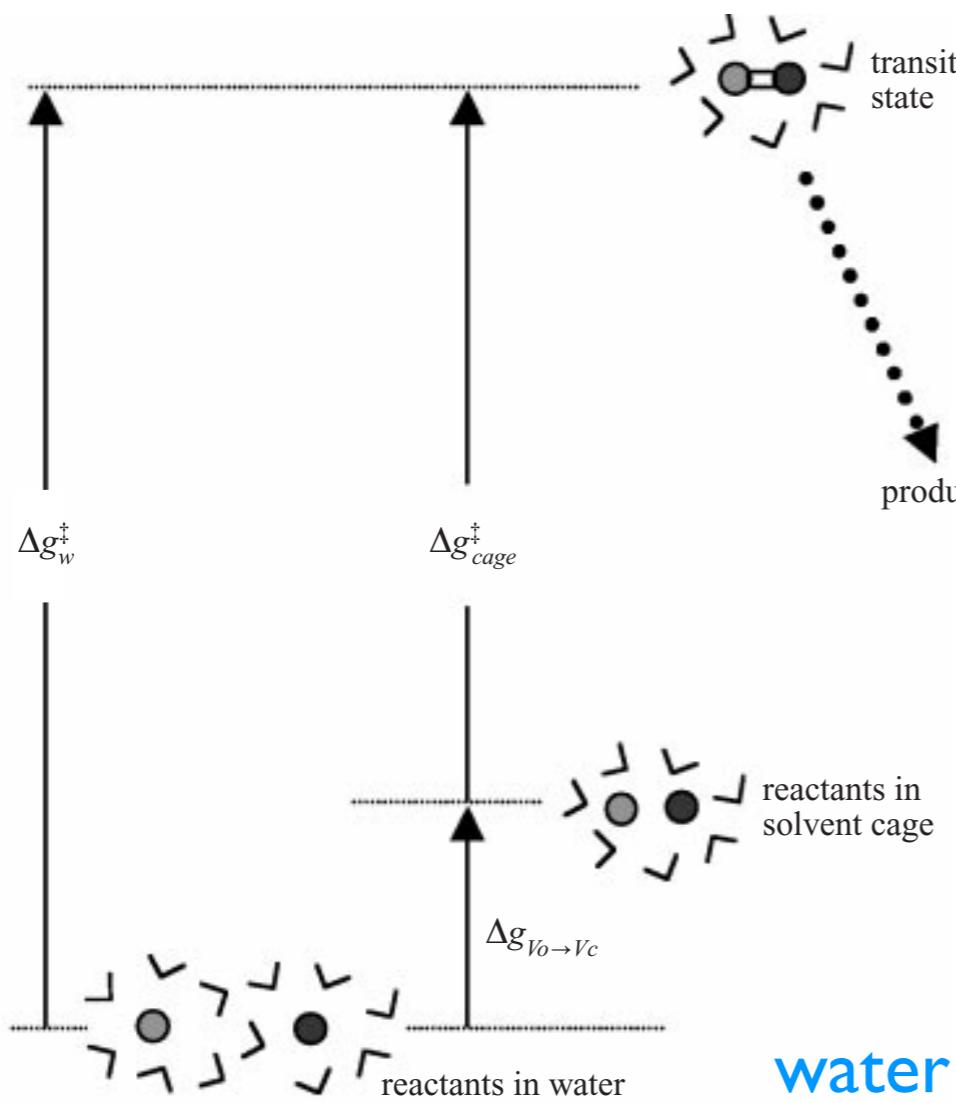


enzyme

# Enzymes

accelerate reaction with respect to water

$$k = \frac{h}{k_B T} \exp \left[ -\frac{\Delta g^\ddagger}{k_B T} \right]$$

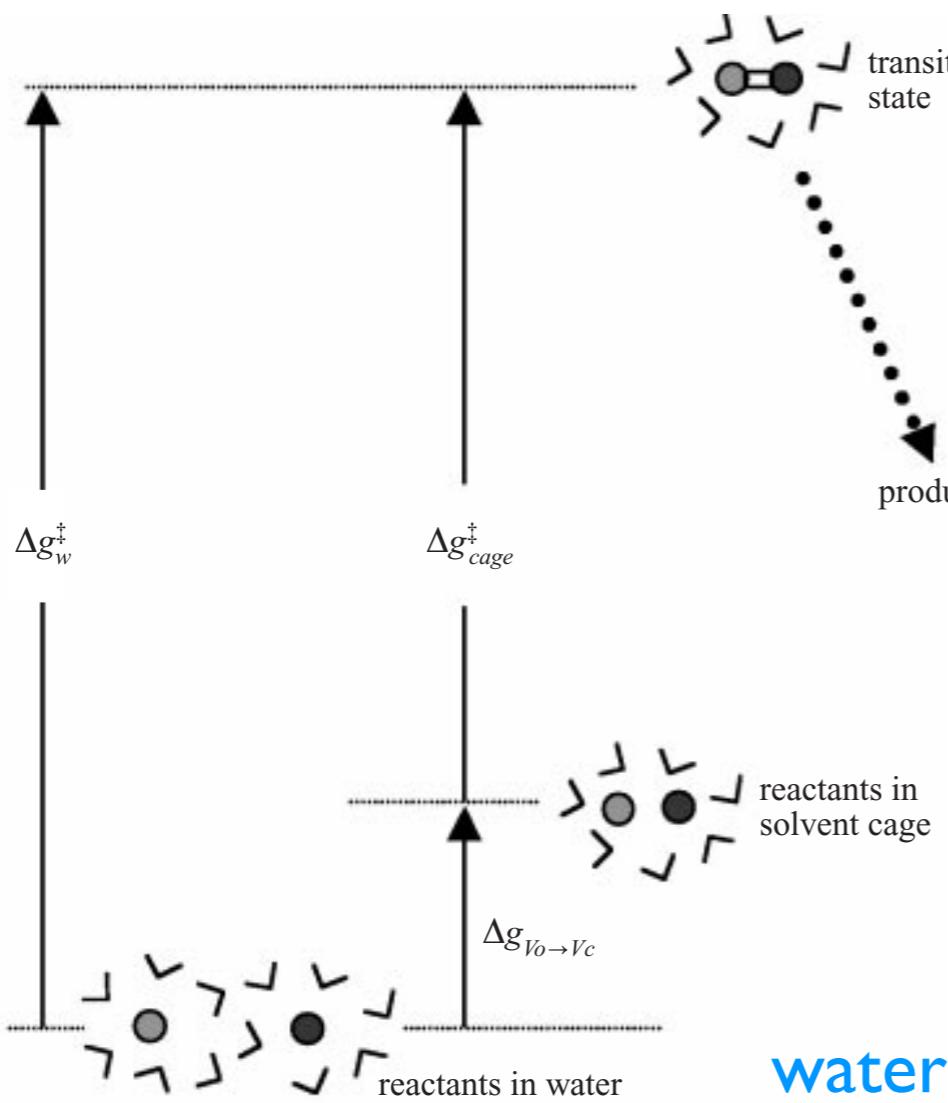


$$\Delta g_{V_0 \rightarrow V_c} \approx -T \Delta S_{V_0 \rightarrow V_c} \approx k_B T \ln [V_c/V_o]$$

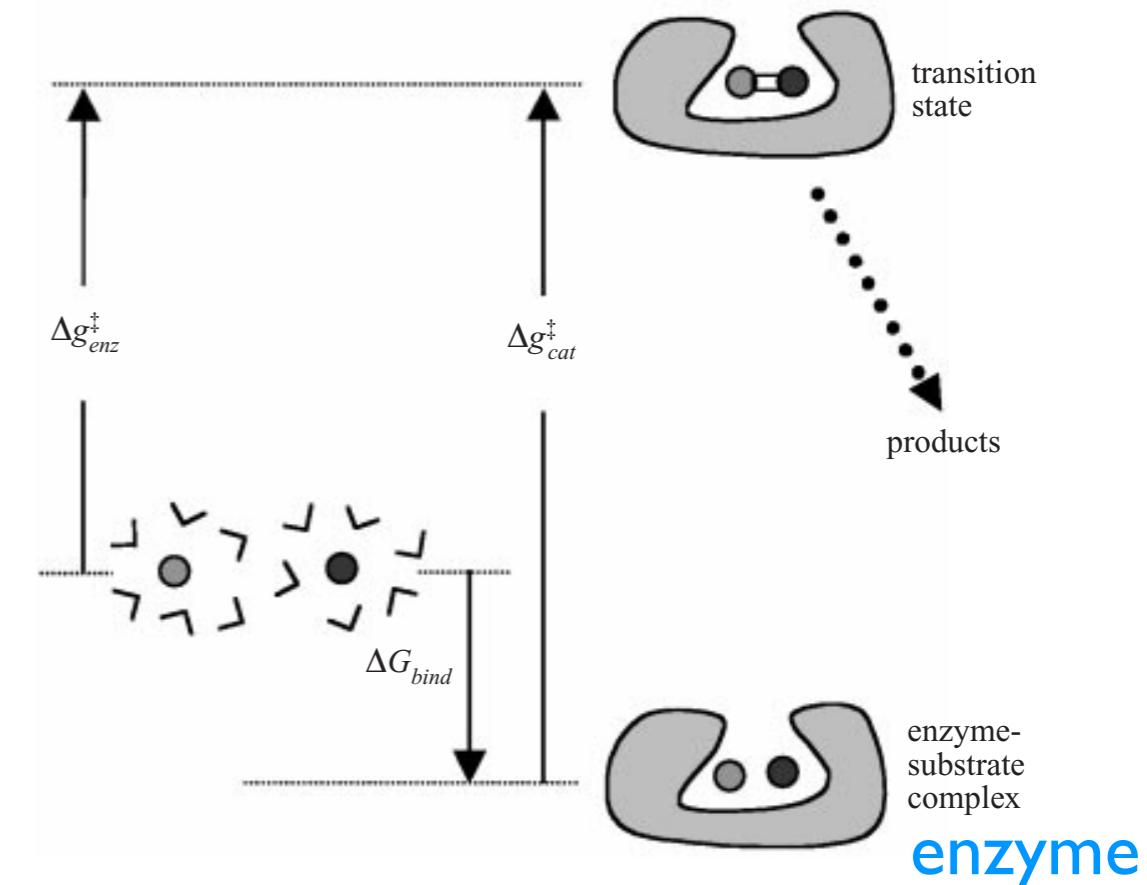
# Enzymes

accelerate reaction with respect to water

$$k = \frac{h}{k_B T} \exp \left[ -\frac{\Delta g^\ddagger}{k_B T} \right]$$



water



enzyme

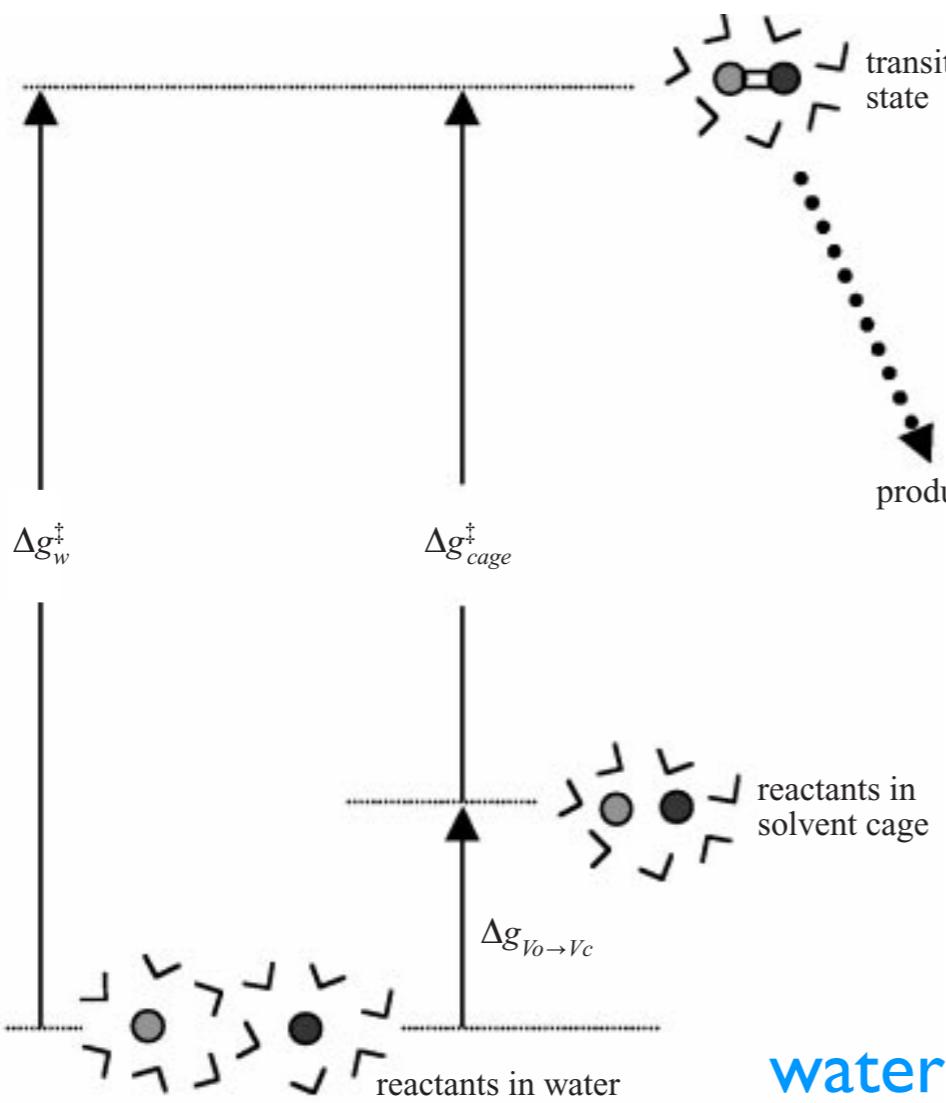
reversible!

forward and backward acceleration by same factor (often forgotten)

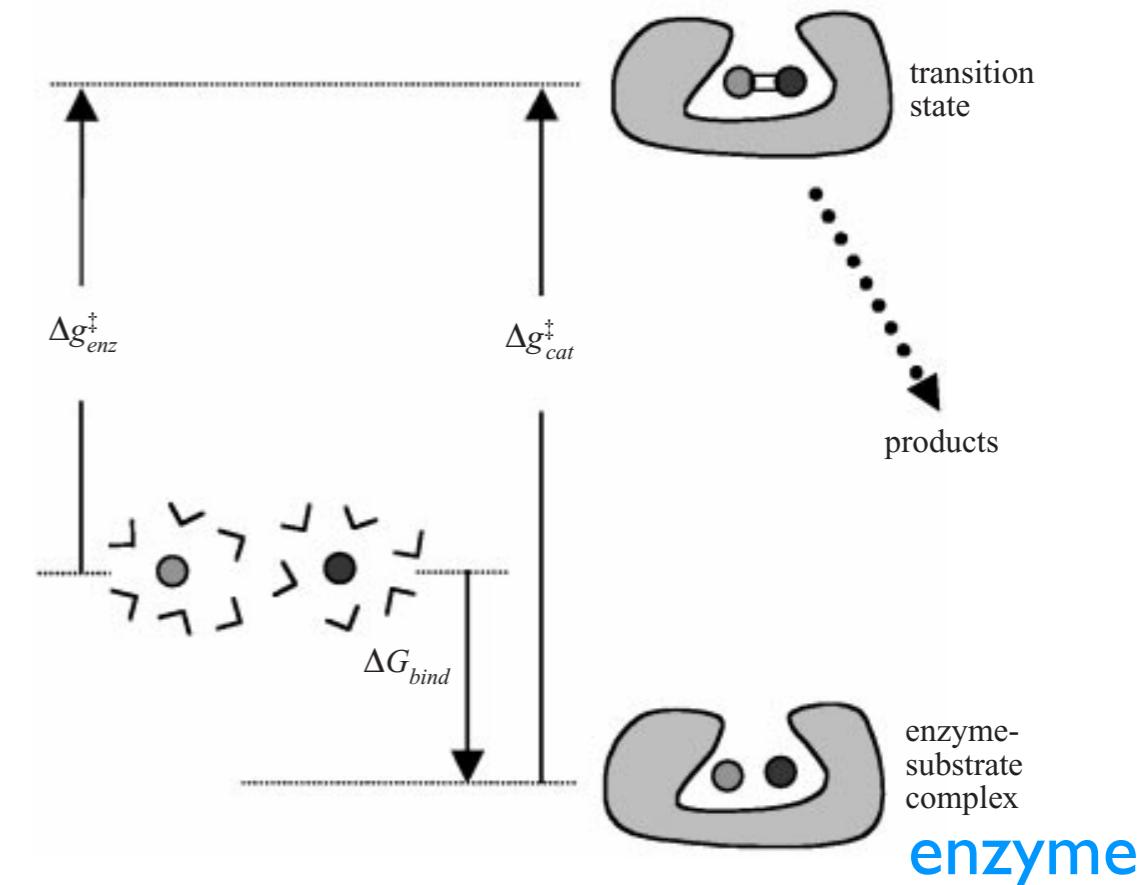
# Enzymes

accelerate reaction with respect to water

$$k = \frac{h}{k_B T} \exp \left[ -\frac{\Delta g^\ddagger}{k_B T} \right]$$



water



enzyme

highly specific  
substrate and product

# Enzymes

accelerate reaction with respect to water

$$k = \frac{h}{k_B T} \exp\left[-\frac{\Delta g^\ddagger}{k_B T}\right]$$

dramatic speedups:

| Enzyme                     | Nonenzymatic half-life | Uncatalyzed rate ( $k_{un}$ , s <sup>-1</sup> ) | Catalyzed rate ( $k_{cat}$ , s <sup>-1</sup> ) | Rate enhancement ( $k_{cat}/k_{un}$ ) |
|----------------------------|------------------------|-------------------------------------------------|------------------------------------------------|---------------------------------------|
| OMP decarboxylase          | 78,000,000 years       | $2.8 \times 10^{-16}$                           | 39                                             | $1.4 \times 10^{17}$                  |
| Staphylococcal nuclease    | 130,000 years          | $1.7 \times 10^{-13}$                           | 95                                             | $5.6 \times 10^{14}$                  |
| AMP nucleosidase           | 69,000 years           | $1.0 \times 10^{-11}$                           | 60                                             | $6.0 \times 10^{12}$                  |
| Carboxypeptidase A         | 7.3 years              | $3.0 \times 10^{-9}$                            | 578                                            | $1.9 \times 10^{11}$                  |
| Ketosteroid isomerase      | 7 weeks                | $1.7 \times 10^{-7}$                            | 66,000                                         | $3.9 \times 10^{11}$                  |
| Triose phosphate isomerase | 1.9 days               | $4.3 \times 10^{-6}$                            | 4,300                                          | $1.0 \times 10^9$                     |
| Chorismate mutase          | 7.4 hours              | $2.6 \times 10^{-5}$                            | 50                                             | $1.9 \times 10^6$                     |
| Carbonic anhydrase         | 5 seconds              | $1.3 \times 10^{-1}$                            | $1 \times 10^6$                                | $7.7 \times 10^6$                     |

# Enzymes

accelerate reaction with respect to water

$$k = \frac{h}{k_B T} \exp\left[-\frac{\Delta g^\ddagger}{k_B T}\right]$$

observation for many enzymes (Wolfenden *et al.*<sup>1</sup>, Bruice & Benkovic<sup>2</sup>)

$$\Delta G_{\text{cat}}^\ddagger \approx 40 \text{ kJ/mol}$$

typical reaction timescales

$$\tau \approx 10^{-3} - 10^{-1} \text{ s}$$

evolutionary pressure to reduce rate to the diffusion limit ?

key question: how do enzymes decrease  $\Delta G^\ddagger$

experiments (x-ray, mutations)

computer simulations

<sup>1</sup> JACS 121 (1999) 7419-7420

<sup>2</sup> Biochem. 39 (2000) 6267-6274

# Transition state stabilization

electrostatic (dipoles)

solvent

re-arrangement of dipoles (high free energy)

protein

pre-arrangement of dipoles (low free energy)

price paid in folding process

enzyme structure: tradeoff between stability and catalysis

steric

complementarity of TS, or RS

dynamic effects

functional modes

unlikely for slow state reactions

maybe for fast reactions

photo-induced processes

# computer simulations of enzyme activity

challenges

bond breaking & formation

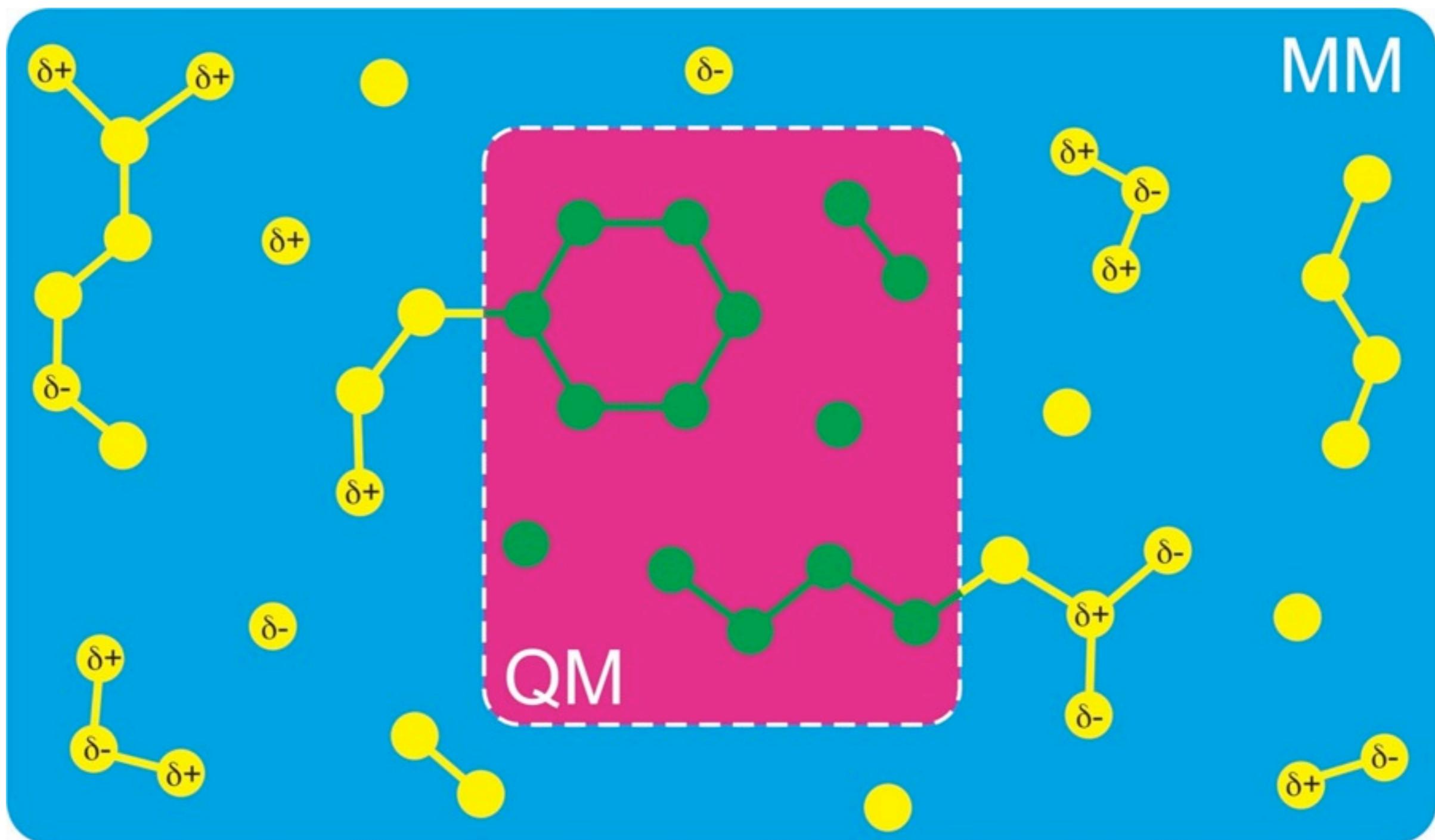
quantum mechanics for electrons (QM)

large systems (many atoms)

hybrid quantum mechanics/molecular mechanics (QM/MM)

# Quantum Mechanics/Molecular Mechanics

electrons treated explicitly in small subsystem  
molecular mechanics forcefield for remainder



# computer simulations of enzyme activity

## challenges

bond breaking & formation

quantum mechanics for electrons (QM)

large systems (many atoms)

hybrid quantum mechanics/molecular mechanics (QM/MM)

slow process

mapping potential

umbrella sampling

thermodynamic integration

free energy perturbation

# computer simulations of enzyme activity

## challenges

bond breaking & formation

quantum mechanics for electrons (QM)

large systems (many atoms)

hybrid quantum mechanics/molecular mechanics (QM/MM)

slow process

mapping potential

umbrella sampling

thermodynamic integration

free energy perturbation

reaction coordinate

intuition/experience/luck/divine intervention/...

black-box

all are waiting for that, but haven't seen one yet...

# computer simulations of enzyme activity

## mapping potential

### I. thermodynamic integration at MM level

$$V(\mathbf{r}, \lambda) = (1 - \lambda)V^{\text{RS}}(\mathbf{r}, \mathbf{q}^{\text{RS}}, b^{\text{RS}}) + \lambda V^{\text{TS}}(\mathbf{r}, \mathbf{q}^{\text{TS}}, b^{\text{TS}})$$



# computer simulations of enzyme activity

## mapping potential

### I. thermodynamic integration at MM level

$$V(\mathbf{r}, \lambda) = (1 - \lambda)V^{\text{RS}}(\mathbf{r}, \mathbf{q}^{\text{RS}}, b^{\text{RS}}) + \lambda V^{\text{TS}}(\mathbf{r}, \mathbf{q}^{\text{TS}}, b^{\text{TS}})$$

#### MM activation free energy

$$Z(\lambda) = \int \exp[-V(\lambda)/k_B T] d\mathbf{r}$$

$$G(\lambda) = -k_B T \ln(Z)$$

$$\frac{\partial G}{\partial \lambda} = -k_B T \frac{\partial Z}{\partial \lambda} / Z$$

$$= \frac{\int \frac{\partial V}{\partial \lambda} \exp[-V(\lambda)/k_B T] d\mathbf{r}}{\int \exp[-V(\lambda)/k_B T] d\mathbf{r}}$$

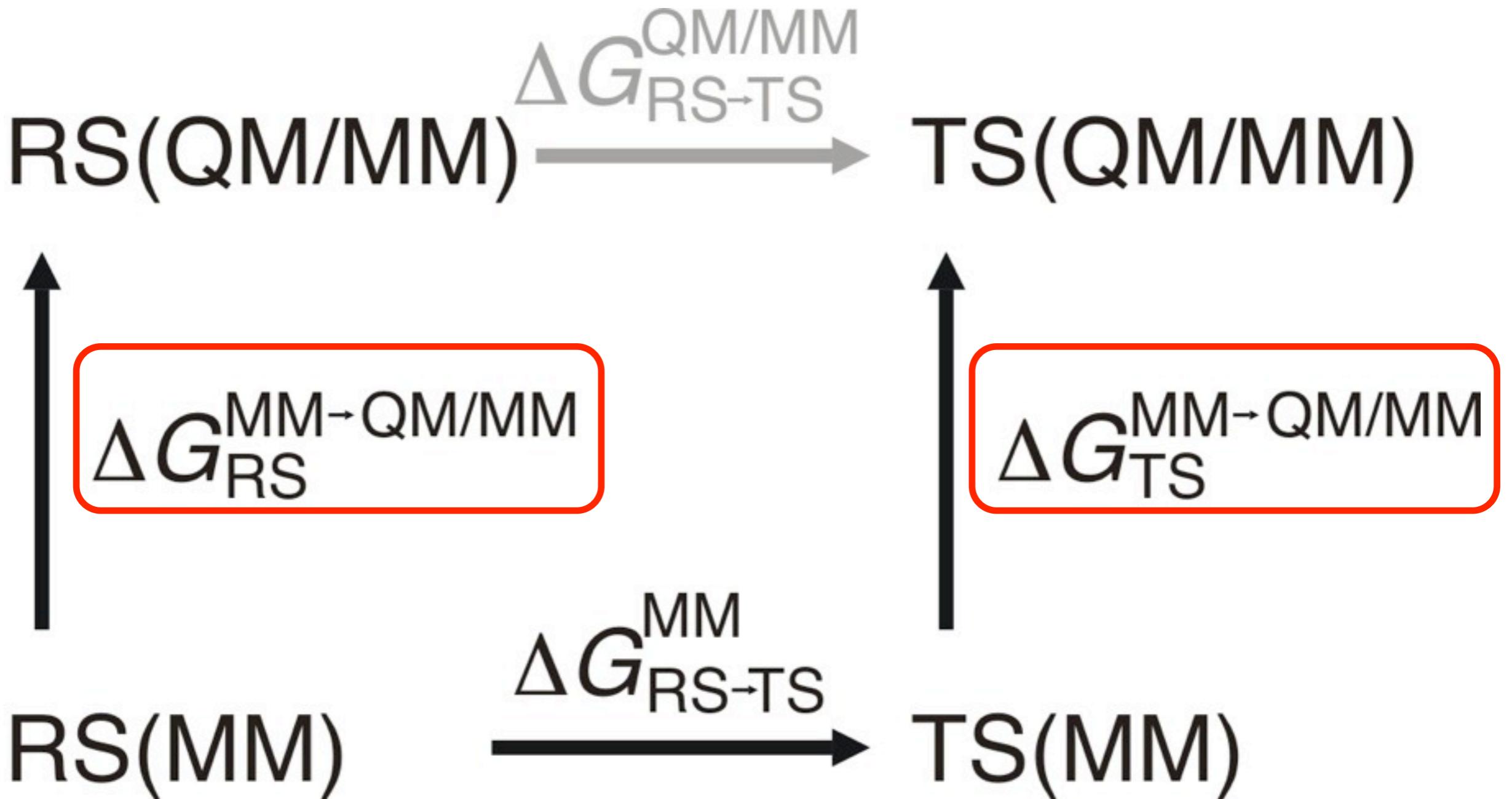
$$= \left\langle \frac{\partial V}{\partial \lambda} \right\rangle_\lambda$$

$$\Delta G^\ddagger = G(\lambda = 1) - G(\lambda = 0) = \int_0^1 \left\langle \frac{\partial V}{\partial \lambda} \right\rangle_\lambda d\lambda \approx \sum_{\lambda=0}^{\lambda=1} \left\langle \frac{\partial V}{\partial \lambda} \right\rangle_\lambda \Delta \lambda$$

# computer simulations of enzyme activity

## mapping potential

1. thermodynamic integration at MM level
2. free energy perturbation at RS and TS points



# computer simulations of enzyme activity

## mapping potential

1. thermodynamic integration at MM level

2. free energy perturbation at RS and TS points

$$\begin{aligned}\Delta G_{AB} &= G_B - G_A = -k_B T \ln[Z_B/Z_A] \\ &= -k_B T \ln \frac{\int \exp[-V_B/k_B T] d\mathbf{r}}{\int \exp[-V_A/k_B T] d\mathbf{r}} \\ &= -k_B T \ln \frac{\int \exp[-(V_B - V_A)/k_B T] \exp[-V_A/k_B T] d\mathbf{r}}{\int \exp[-V_A/k_B T] d\mathbf{r}}\end{aligned}$$

with  $1 = \exp(-(V_A - V_A)/k_B T) = \exp(V_A/k_B T) \exp(-V_A/k_B T)$  inserted

# computer simulations of enzyme activity

## mapping potential

1. thermodynamic integration at MM level

2. free energy perturbation at RS and TS points

$$\begin{aligned}\Delta G_{AB} &= G_B - G_A = -k_B T \ln[Z_B/Z_A] \\ &= -k_B T \ln \frac{\int \exp[-V_B/k_B T] d\mathbf{r}}{\int \exp[-V_A/k_B T] d\mathbf{r}} \\ &= -k_B T \ln \frac{\int \exp[-(V_B - V_A)/k_B T] \exp[-V_A/k_B T] d\mathbf{r}}{\int \exp[-V_A/k_B T] d\mathbf{r}} \\ &= -k_B T \ln \langle \exp[-(V_B - V_A)/k_B T] \rangle_A\end{aligned}$$

with

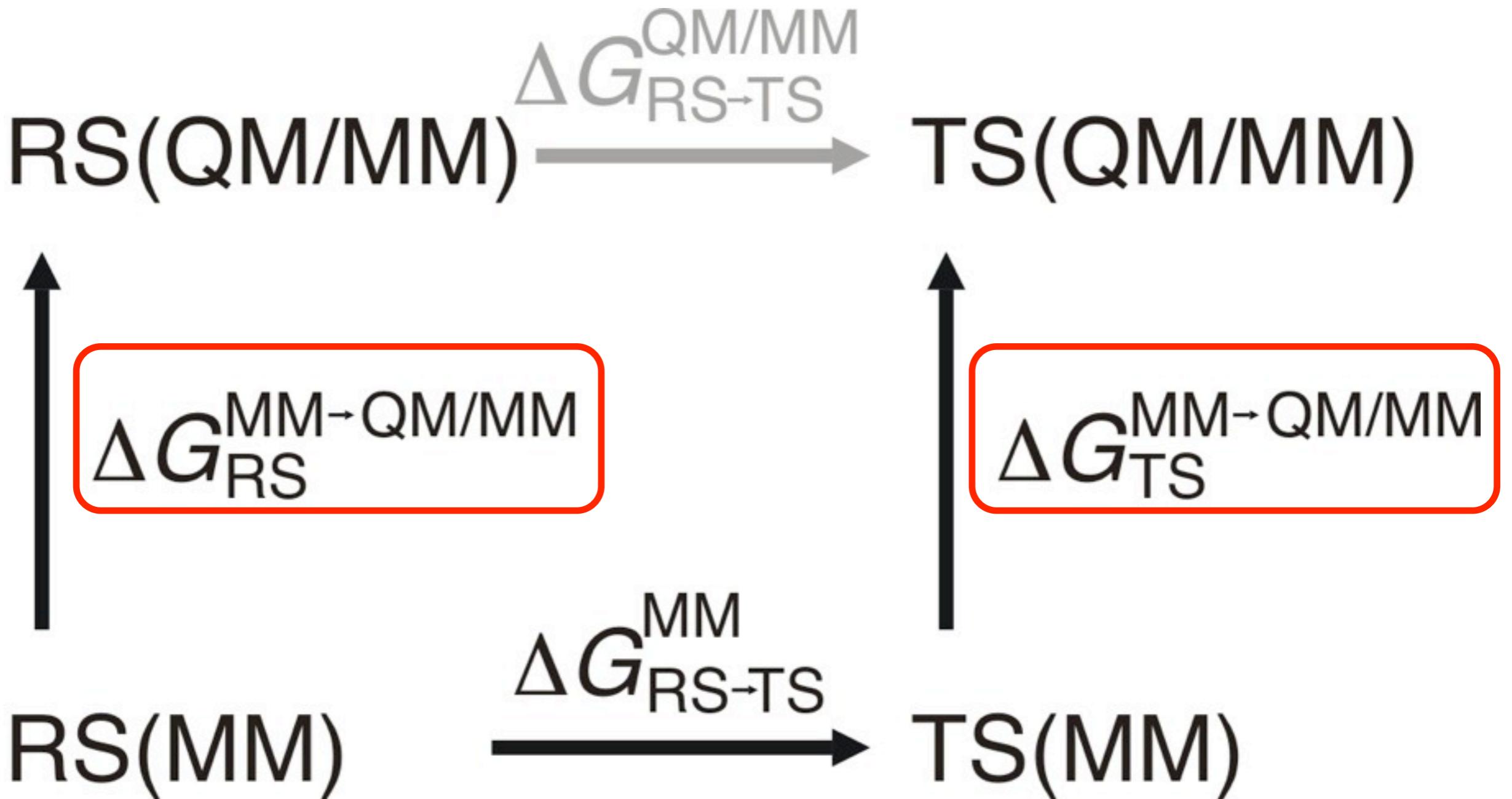
$$V_B = V^{\text{QM/MM}} \quad V_A = V^{\text{MM}}$$

$$\Delta G^{\text{MM} \rightarrow \text{QM/MM}} = -k_B T \ln \left\langle \exp[-(V^{\text{QM/MM}} - V^{\text{MM}})/k_B T] \right\rangle_{\text{MM}}$$

# computer simulations of enzyme activity

## mapping potential

1. thermodynamic integration at MM level
2. free energy perturbation at RS and TS points

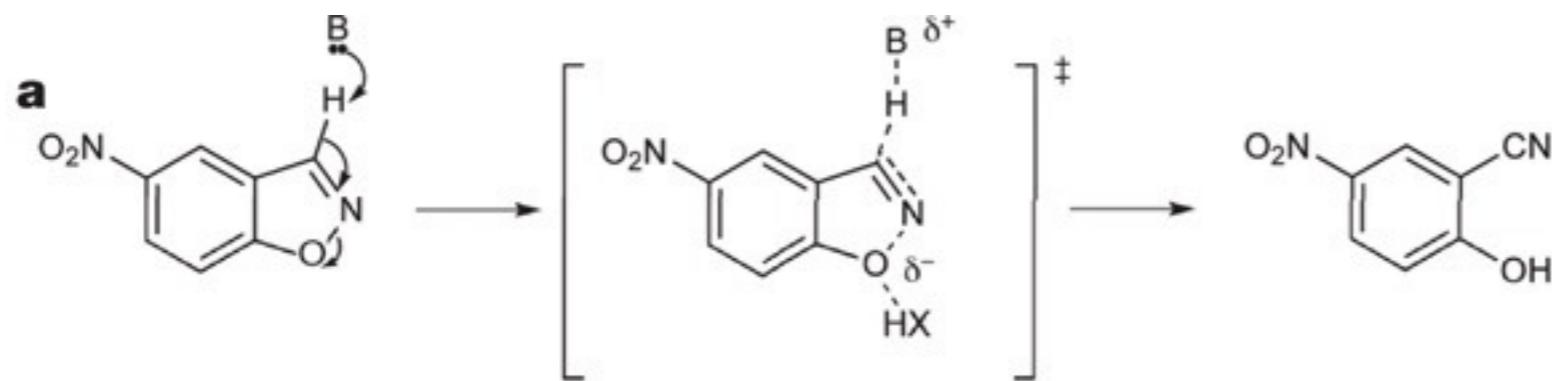


# Computational design of new enzymes

## design procedure

### I. choose catalytic mechanism

#### Kemp elimination

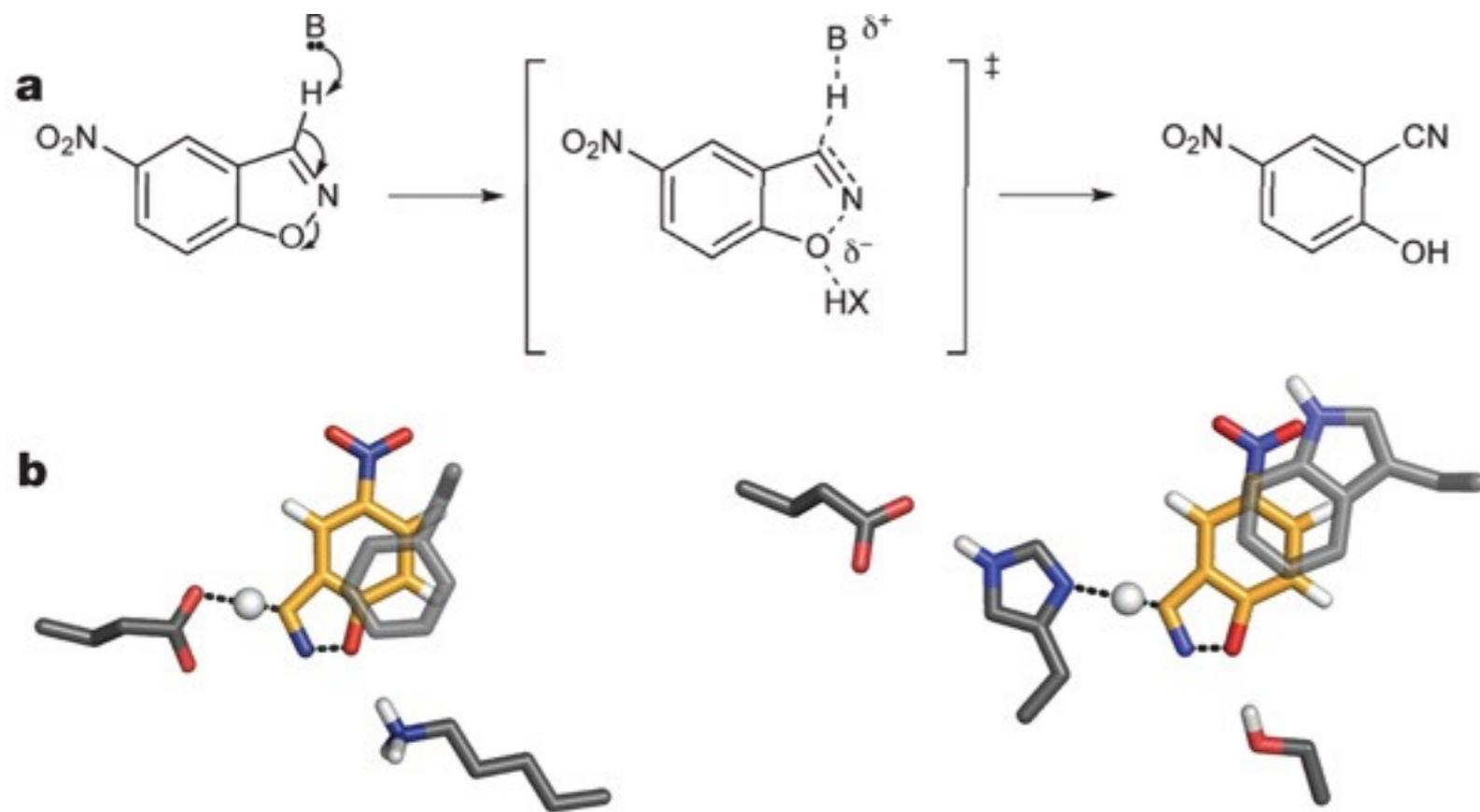


# Computational design of new enzymes

## design procedure

1. choose catalytic mechanism

2. design small active active site at QM level

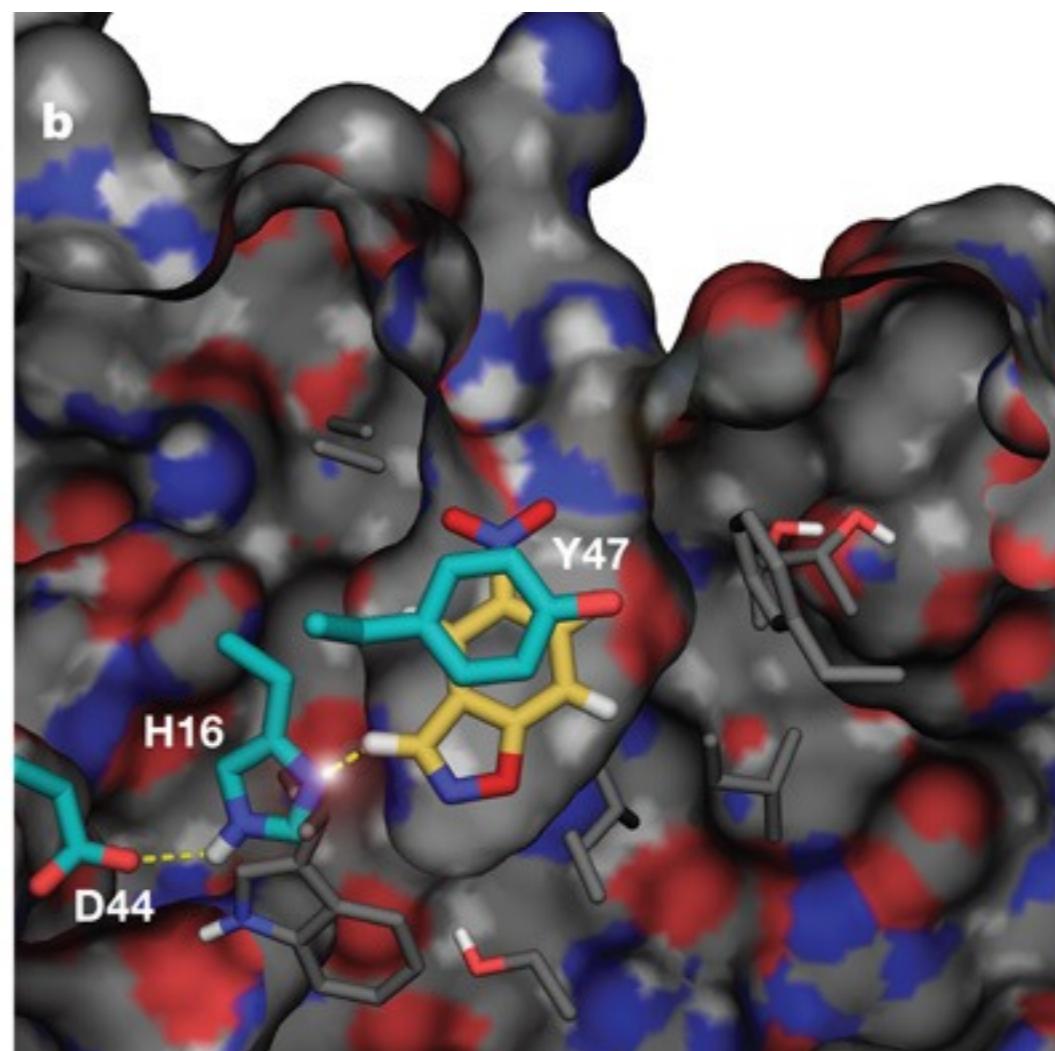
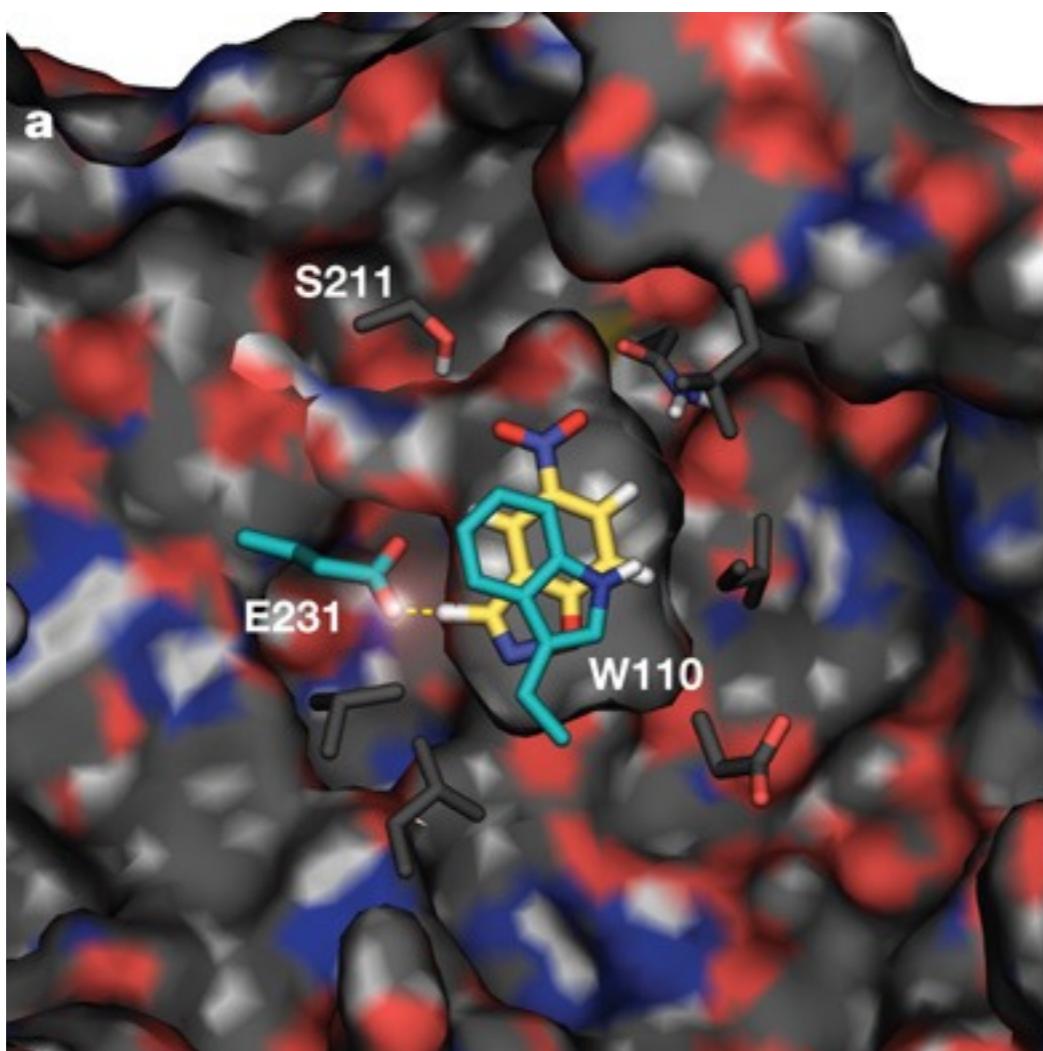


# Computational design of new enzymes

## design procedure

1. choose catalytic mechanism
2. design small active active site at QM level
3. search for protein scaffolds that can accomodate active site

### RosettaMatch

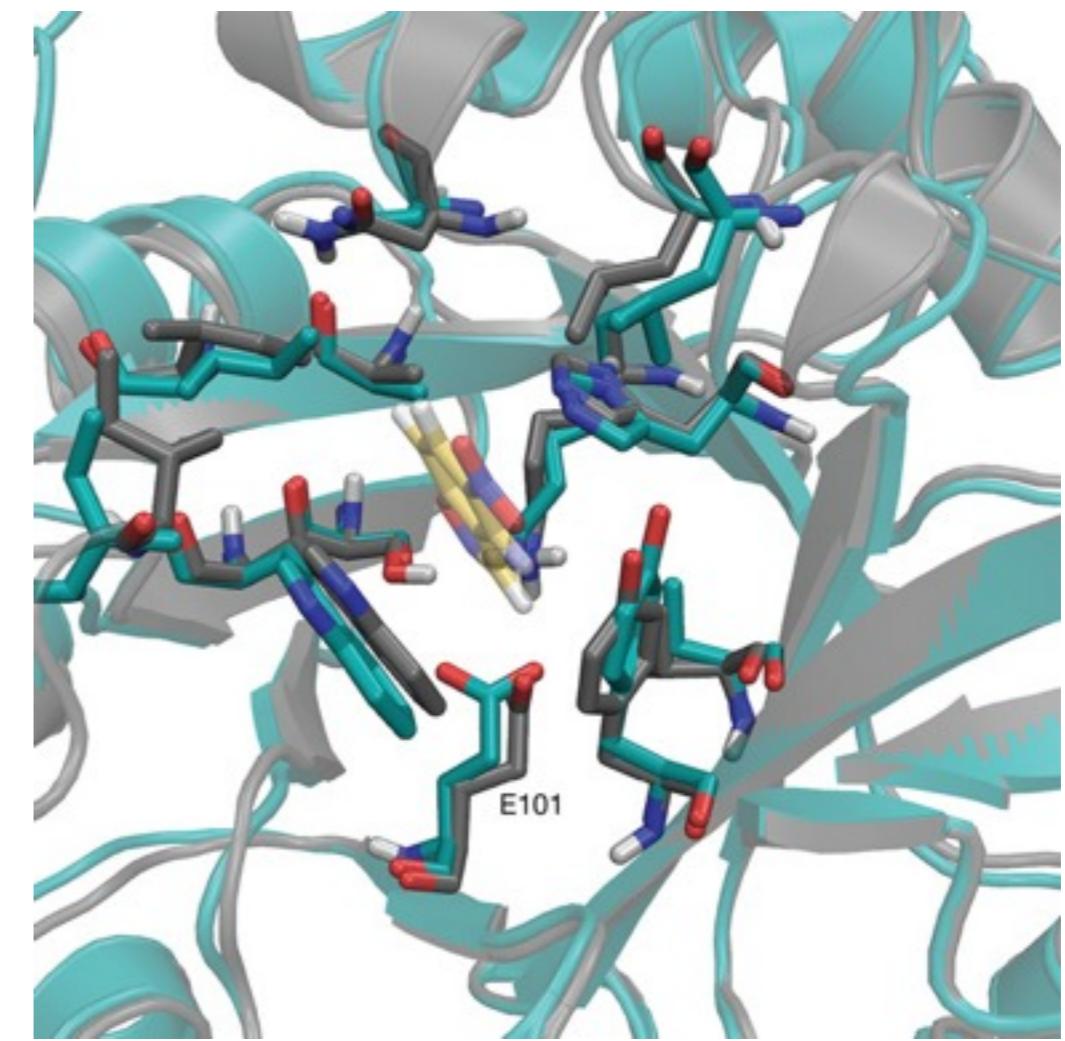
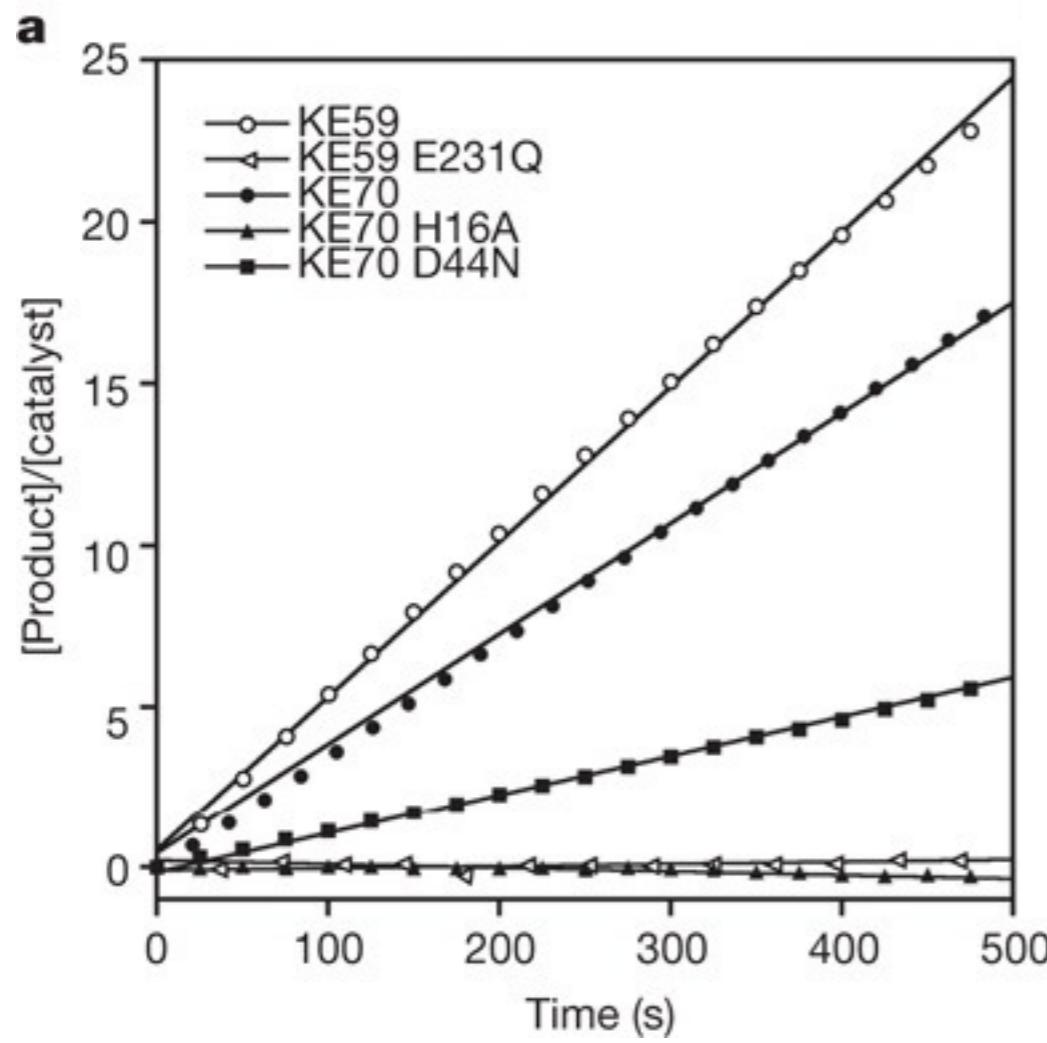


Nature 438 2008 190-195

# Computational design of new enzymes

## design procedure

1. choose catalytic mechanism
2. design small active active site at QM level
3. search for protein scaffolds that can accomodate active site
4. characterize new enzymes experimentally



Nature 438 2008 190-195

# Beyond Hartree-Fock: Configuration Interaction

one-electron basisset

$$\Phi(\mathbf{x}_1) = \sum_i a_i \phi_i(\mathbf{x}_1)$$

two-electron basisset

$$\Phi(\mathbf{x}_1, \mathbf{x}_2) = \sum_i a_i(\mathbf{x}_2) \phi_i(\mathbf{x}_1)$$

$$\Phi(\mathbf{x}_1, \mathbf{x}_2) = \sum_i \sum_j b_{ij} \phi_i(\mathbf{x}_1) \phi_j(\mathbf{x}_2)$$

$n$ -electron basisset

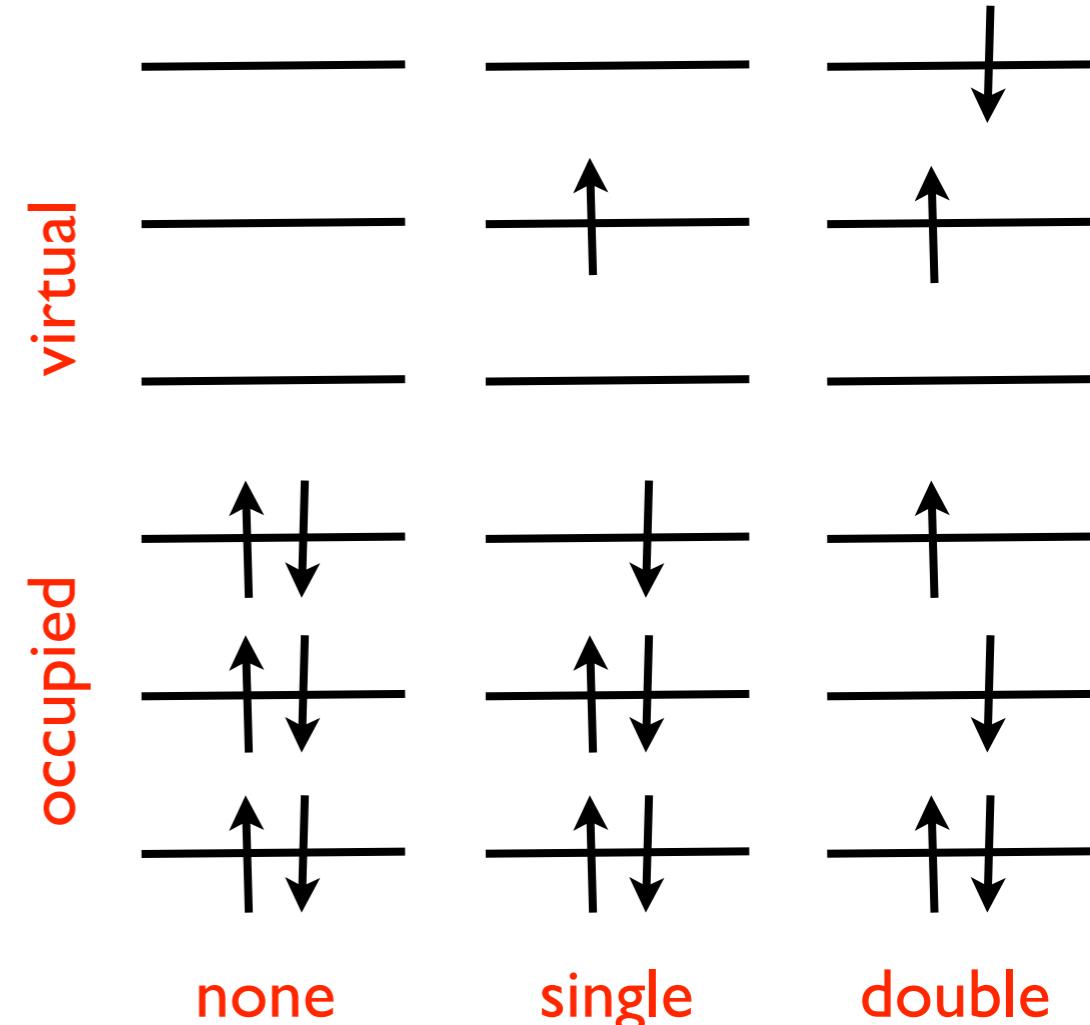
slater determinants, single, double, triple, ... excitations

$$\Phi = |\Psi_0\rangle + \sum_a^{\text{n_occ}} \sum_r^{\text{n_virt}} c_a^r |\Psi_a^r\rangle + \sum_a^{\text{n_occ}} \sum_b^{\text{n_occ}} \sum_r^{\text{n_virt}} \sum_s^{\text{n_virt}} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \dots$$

Brillouin's theorem

$$\langle \Psi_0 | \hat{H} | \Psi_a^r \rangle = 0$$

truncate: CIS, CISD, CISDT, CISDTQ, ... (size inconsistent!!)



# excited state electronic structure

## configuration interaction

functions of one electron

expansion in one-electron functions

$$\phi(x_1) = \sum_i a_i \chi_i(x_1)$$