



Quantum Chemical and Dynamical Tools for Solving Photochemical Problems



Workshop

Inés Corral

Institut für Chemie und Biochemie
FREIE UNIVERSITÄT BERLIN

18 June
2007



2.105430 3.413000 3.889592 9 H 3.413000 2.105430 1.099610 2.105430 3.413000 10 H
3.889592 3.413060 2.165430 1.099610 2.165430 11 H 3.413060 3.889592 3.413060 2.165430
1.099610 12 H 2.165430 3.413060 3.889592 3.413060 2.165430 6 7
2.165430 0.000000 7 H 2.165430 0.000000 8 H 3.413060 4.989202
4.320776 2.494601 0.000000 11 H 2.165430 4.320776 4.989202 4.320776 2.494601 12 H
1.099610 2.494601 4.320776 4.989202 4.320776 11 12 11 H 0.000000
12 H 2.494601 0.000000 Stoichiometry C6H6 Framework group D6H[3C2'(HC.CH)] Deg. of freedom 2
Full point group D6H NOp 24 Largest Abelian subgroup D2H NOp 8 Largest
concise Abelian subgroup D2 NOp 4 Standard orientation:
----- Center Atomic Atomic
Coordinates (Angstroms) Number Number Type X Y Z -----

1.394991 0.000000 2 6 0 1.208097 0.697495 0.000000 3 0.000000
0 1.208097 -0.697495 0.000000 4 0 0 0.000000 -1.394991
0.000000 5 20 09 6 6
0 -1.208097 0.697495 0.000000 7 1 0 0.000000 2.494601
0.000000 8 1 1.160388 1.247300 0.000000 9
0 2.160388 -1.247300 0.000000 10 0 0.000000 -2.160388
0.000000 0 -2.160388 -1.247300 0.000000 12
0 0.000000
----- Rotational c
12,C-12,C-12,H-1,H-1 at Tue Oct 25 16:23:29 2005, MaxMem= 125829120
0.1 (Enter /r1/g98/l standard (5) 31 symmetry adapted
functions of AG symmetry adapted basis functions of B1G symmetry. There
7 symmetry adapted basis functions of B2G symmetry. There are 11 symmetry adapted basis functions
B3G symmetry. There are 7 symmetry adapted basis functions of AU symmetry. There are 11
adapted basis functions of BU symmetry. There are 11 symmetry adapted basis functions of BU
There are 11 symmetry adapted basis functions of B3U symmetry. Crude estimate of orbital expansion
from reduced integrals=1.013. long. tti teg
format. 21 alpha electrons 21 beta electrons nuclear repulsion energy 20 5312 3 Har
Leave Link 302 at Tue Oct 25 16:23:29 2005, MaxMem= 125829120 cpu: 0.2 (Enter /r1/g98/l302.e
One-electron integrals computed using PRISM. One-electron integral symmetry used in NBas 14
RBF= 7 11 7 31 23 NBsUsed 3 23
Leave Link 302 at Tue Oct 25 16:23:29 2005, MaxMem= 125829120
/g98/l303.exe) DipDrv: MaxL=1. Leave Link 303 at Tue Oct 25 16:23:29 2005, MaxMem= 125829120
cpu: 3.8 (Enter /r1/g98/l401.exe) Projected INDO Guess orbital symmetry
Occupied (?A) (?A) (?A) (?A) (?A) (?A) (A1G) (E1U) (E1U)
(B1U) (E1U) (E1U) (E2G) (E2G) (E1G) (E1G) Virt (E1U) (E2U) (A1G) (E2G)
(E2G) (E1U) (E1U) (B2G) (E2G) (E2G) (E1U) (E1U) (B1U) (?B) (?B) (?B)

OUTLINE

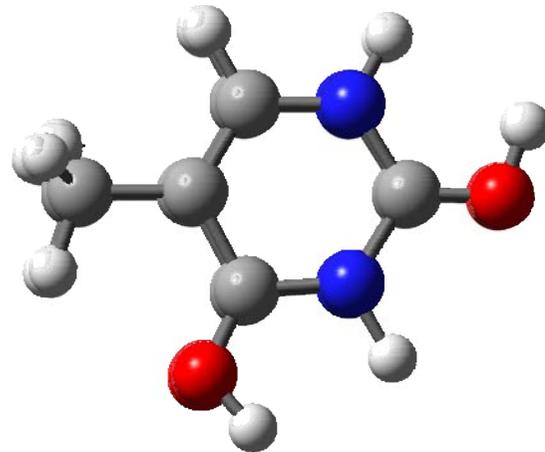
1. Quantum Chemistry

2. Quantum Dynamics

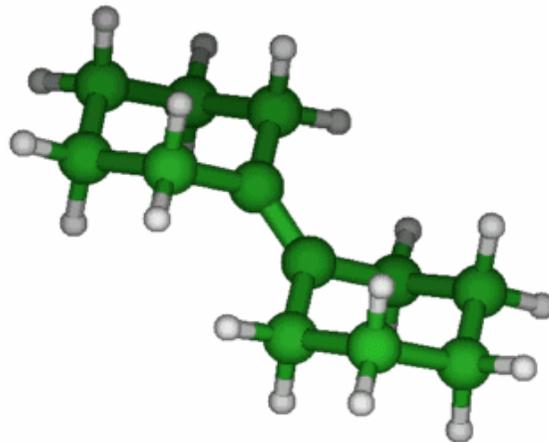
3. Quantum Control

18 June
20
07

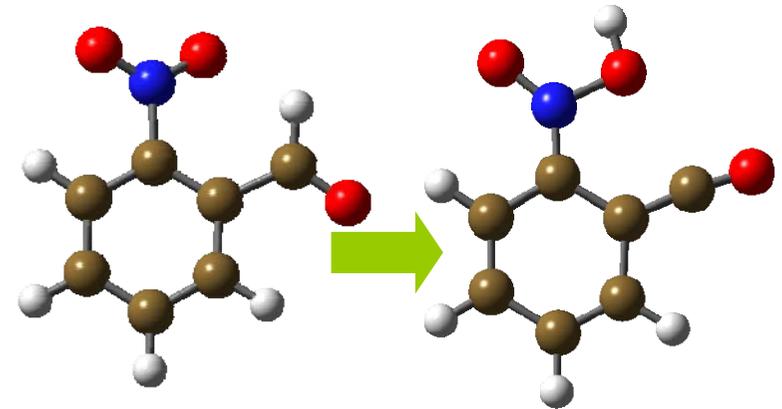
DNA isomerization



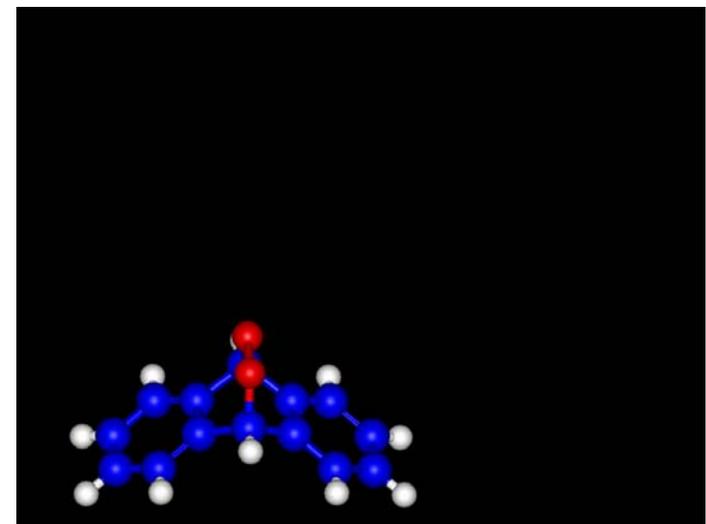
Molecular rotors



Proton transfer



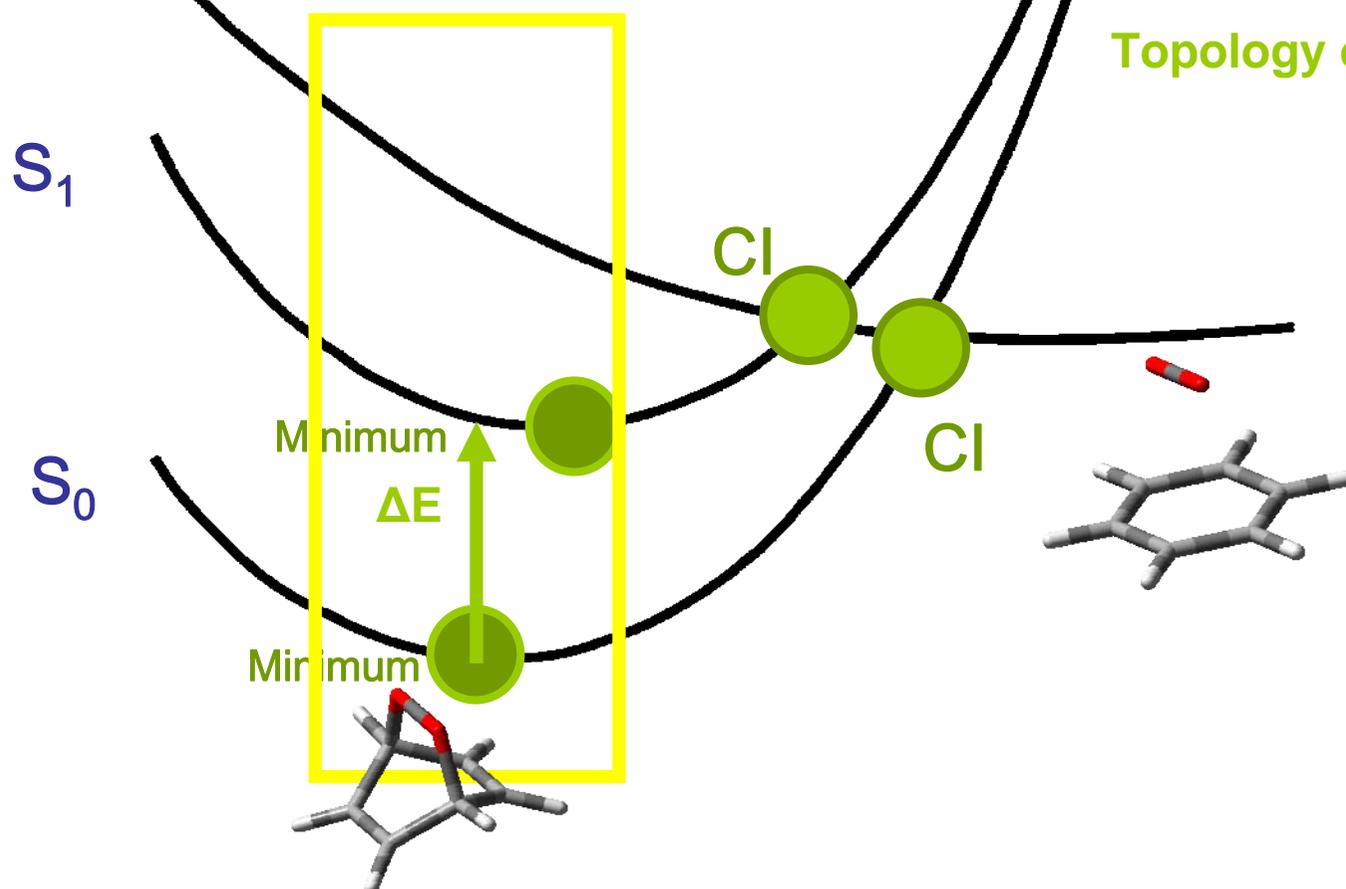
Singlet Oxygen Generators



18 June
20
07

INFORMATION

Quantum Chemistry



Vertical Excited Spectrum

Structure of Stationary Points

Conical Intersections

Topology of the PES

18 June
20
07

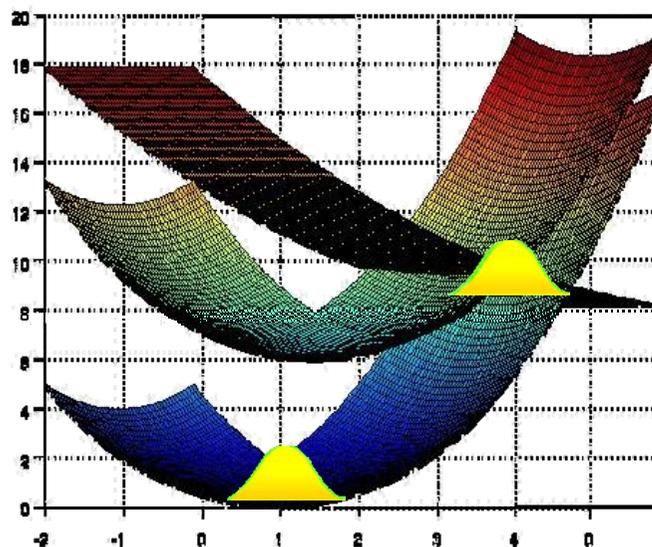
INFORMATION

Quantum Dynamics Time-scale of the elementary processes

Evolution of the molecular system in time

Branching ratio and product distribution

Absorption spectra

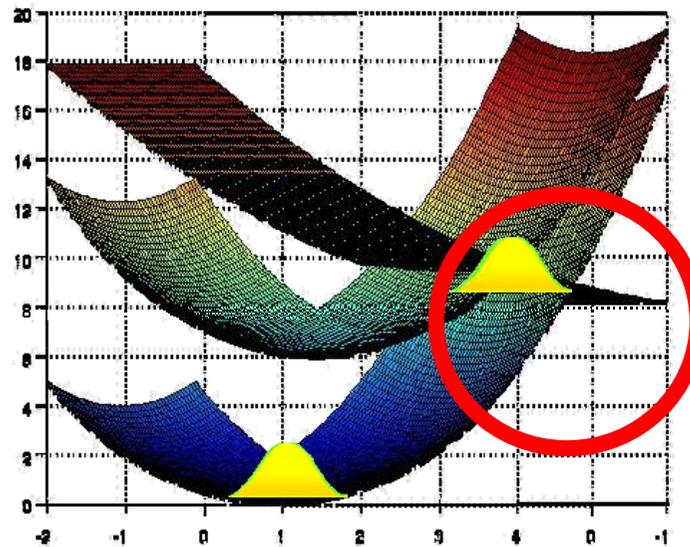


18 June
20
07

INFORMATION

Quantum Control

Designing laser strategies for maximizing the production of $^1\text{O}_2$



18 June
20
07

1. Quantum Chemistry

$$\mathbf{H}_{\text{el}} \Psi_{\text{el}} = E_{\text{el}} \Psi_{\text{el}}$$

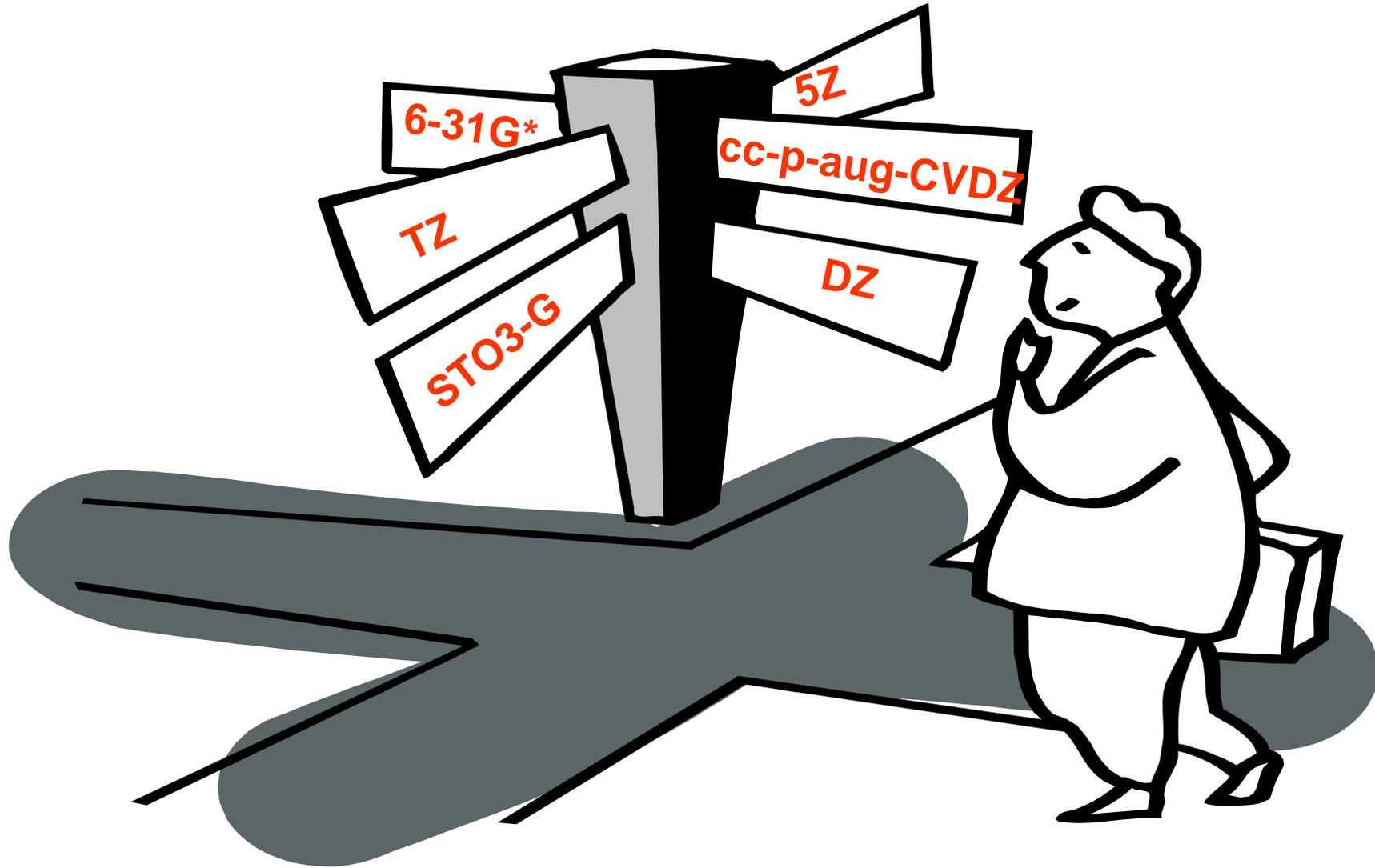
Method

$$H_{el} \Psi_{el} = E_{el} \Psi_{el}$$

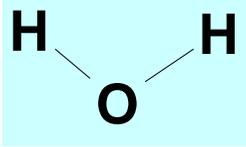


Basis set

$$H_{el} \Psi_{el} = E_{el} \Psi_{el}$$



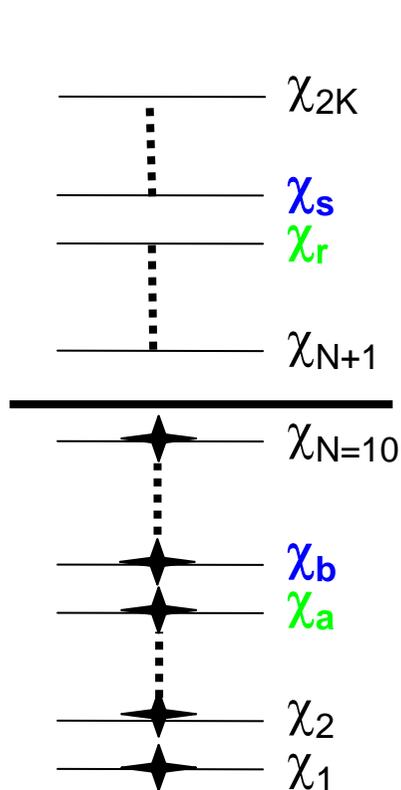
Hartree-Fock approximation



Electronic configuration:

$$10 e^- \rightarrow (1s_O)^2(\sigma_{OH})^2(\sigma_{OH})^2(\eta_O)^2(\eta_O)^2(\sigma_{OH}^*)^0(\sigma_{OH}^*)^0$$

Equivalent to the MO approximation



$$\chi_i(\bar{x}) = \begin{cases} \psi_i(\bar{r}) \cdot \alpha(\omega) \\ \psi_i(\bar{r}) \cdot \beta(\omega) \end{cases} \quad k \{ \psi_i \}_{i=1 \dots k} \Rightarrow 2k \{ \chi_i \}_{i=1 \dots 2k}$$

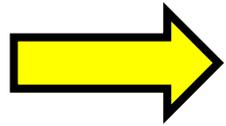
SPIN
ORBITALS SPATIAL
ORBITALS

$$\psi(\chi_1 \dots \chi_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_i(x_1) \chi_j(x_1) \dots \chi_k(x_1) \\ \chi_i(x_2) \chi_j(x_2) \dots \chi_k(x_2) \\ \vdots \\ \chi_i(x_N) \chi_j(x_N) \dots \chi_k(x_N) \end{vmatrix} =$$

SLATER
DETERMINANT

$$= | \chi_1 \chi_2 \dots \chi_i \chi_j \dots \chi_N \rangle$$

Molecular orbital model

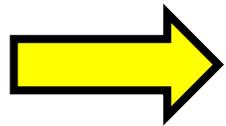


In practice:

the unknown spatial orbitals (MO) are described as a linear combination of a set of known basis functions

$$\psi_i = \sum_{\mu=1}^N c_{\mu i} \phi_{\mu} \quad \phi_{\mu} \equiv \text{one-electron basis function}$$

If the basis function contains the atomic orbitals → MO=LCAO



Next problem:

How do we determine the unknown coefficients $c_{\mu i}$?

Variational principle = an approximate wavefunction has an energy which is above or equal to the exact energy, and the unknown coefficients are determined so that the total energy calculated from the many-electron wavefunction is minimized.

Basis sets

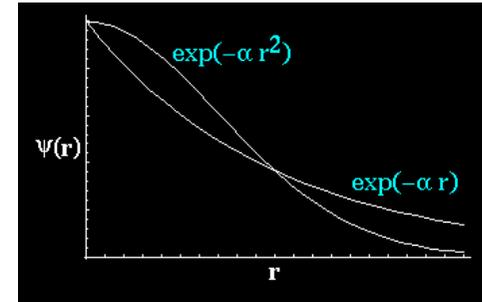
- ① Slater-type orbitals

$$\phi_{STO} \propto e^{-\xi \cdot r} \longrightarrow \text{Closest to H atom solutions}$$

- ② Gaussian-type orbitals

$$\phi_{GTO} \propto e^{-\xi \cdot r^2}$$

Less accurate than STO
Fast integral calculation!!



- ③ **SOLUTION**: Linear combination of Gaussians

$$\phi_{CGTO} = \sum_{p=1}^L d_{p\mu} \phi_p^{GTO}$$

contraction $p=1$ **primitives** L=length of contraction

Number of basis sets used

1s

Minimal basis set: using the minimum number of basis functions

1s,1s'

1s,1s',1s''

The periodic table shows the following highlighted regions:

- Yellow box:** Hydrogen (H) and Helium (He).
- Red box:** Lithium (Li) and Beryllium (Be).
- Blue box:** The transition metal block from Scandium (Sc) to Zinc (Zn).

1s, 2s, 2p_{x,y,z}

1s, 2s, 2p_{x,y,z}

1s, 2s', 2p'_{x,y,z}

1s, 2s, 2p_{x,y,z}

1s', 2s', 2p'_{x,y,z}

1s'', 2s'', 2p''_{x,y,z}

DZ: doubling all basis functions

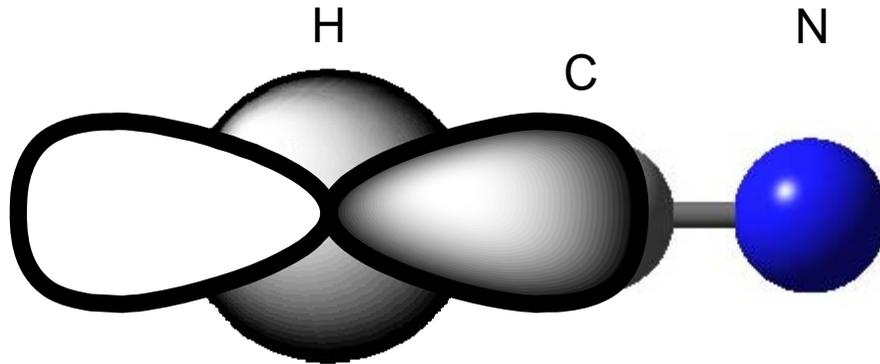
TZ: contains 3 times as many basis functions as the minimal basis set

Any Extras....?

Polarization functions: higher angular momentum functions * or (d,p)

p orbitals are used for the polarization of s orbitals
d orbitals are used for the polarization of p orbitals

....



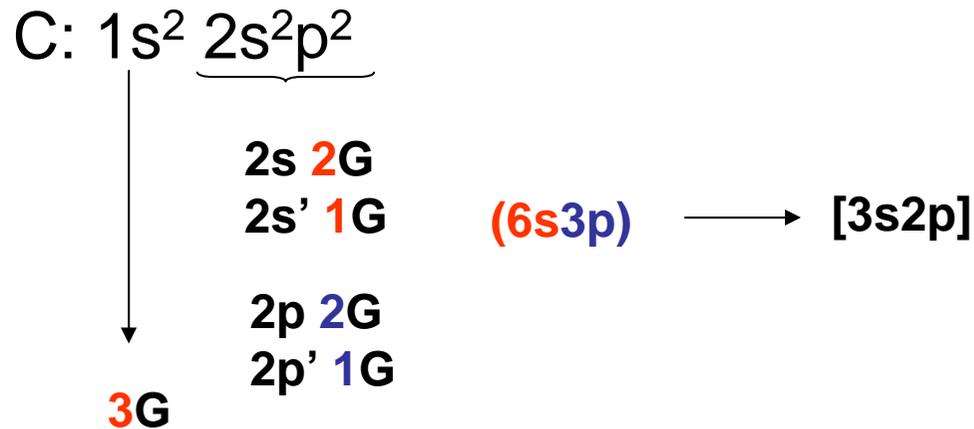
Diffuse functions: small exponents to describe weakly bound electrons +

Examples: anions, Hydrogen bonds

Type of basis sets

Pople basis sets

Split-valence: 3-21G, 6-31G, 6-311G,...



Dunning basis sets, ANO basis sets, Core correlated...

Electronic correlation

TWO APPROXIMATIONS:

- Our wavefunction consists on one single slater determinant
- Use of limited basis set in the orbital expansion

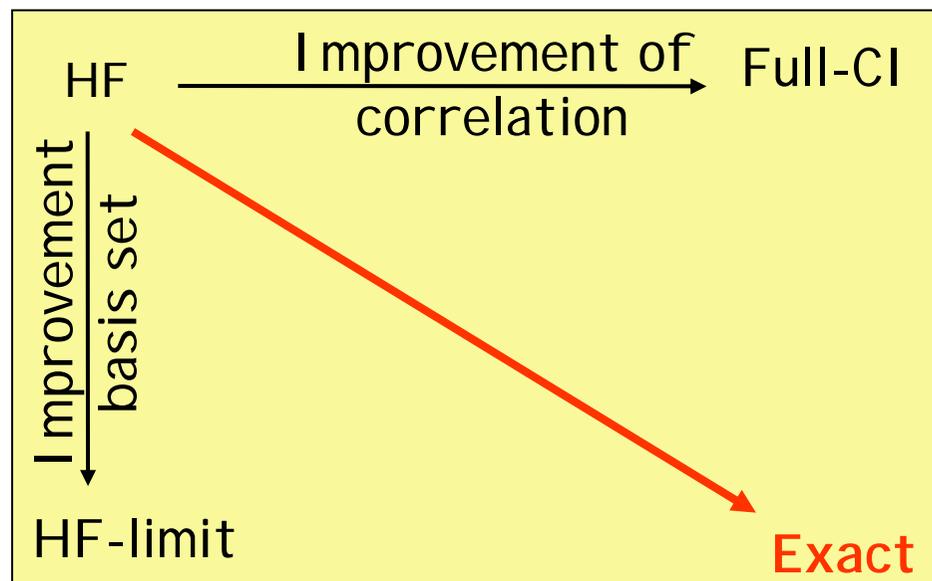
MAIN DEFICIENCY:

lack of correlation between motion of the electrons

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

SOLUTION:

*more than a
single
configuration!!*



Perturbation theory

$$H = H_0 + \lambda V$$

perturbation is assumed to be small

can be solved exactly

$$E = E_0 + \lambda E_1 + \lambda^2 E_2 + \lambda^3 E_3 + \dots$$

$$\Psi = \Psi_0 + \lambda \Psi_1 + \lambda^2 \Psi_2 + \lambda^3 \Psi_3 + \dots$$

$$\Psi_1 = \sum_t \left(\frac{\langle \Psi_t | V | \Psi_0 \rangle}{E_0 - E_t} \right) \quad H_0 = \sum_i F_i \quad H_0 \Psi_s = E_s \Psi_s$$

- **MP2, MP3, MP4.....**
- *In principle*, leads to good results, but perturbation must be small

Configuration interaction

$$\Psi = c_o |\psi_o\rangle + \sum_{ra} c_a^r |\psi_a^r\rangle + \sum_{\substack{a < b \\ r < s}} c_{ab}^{rs} |\psi_{ab}^{rs}\rangle + \dots$$

single, **S**

$a \rightarrow r$

double, **D**

$a \rightarrow r$

$b \rightarrow s$

- Orbitals not re-optimized
- Complete expansion: **FullCI**

H₂O 6-31G*
10 electrons
38 spinorbitals

4.7 · 10⁹ SD!!!!!!

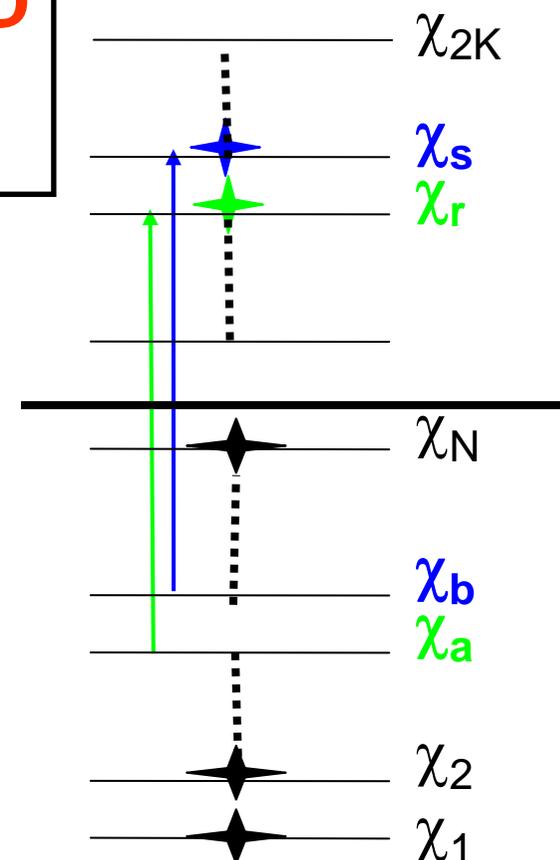
Truncated CI: **CIS, CISD, CISDT, ...**



Size-consistency problem !

Quadratic CI: **QCISD, QCISDT...**

Coupled Cluster: **CCSD, CCSDT...**



Multiconfigurational methods

When a single Lewis structure is not enough.....

- excited states
- diradicals
- often transition states

Coefficients in front of the determinants are optimized

MOs used for the construction of the determinants are also optimized

CASSCF (Complete Active Space Self Consistent Field)

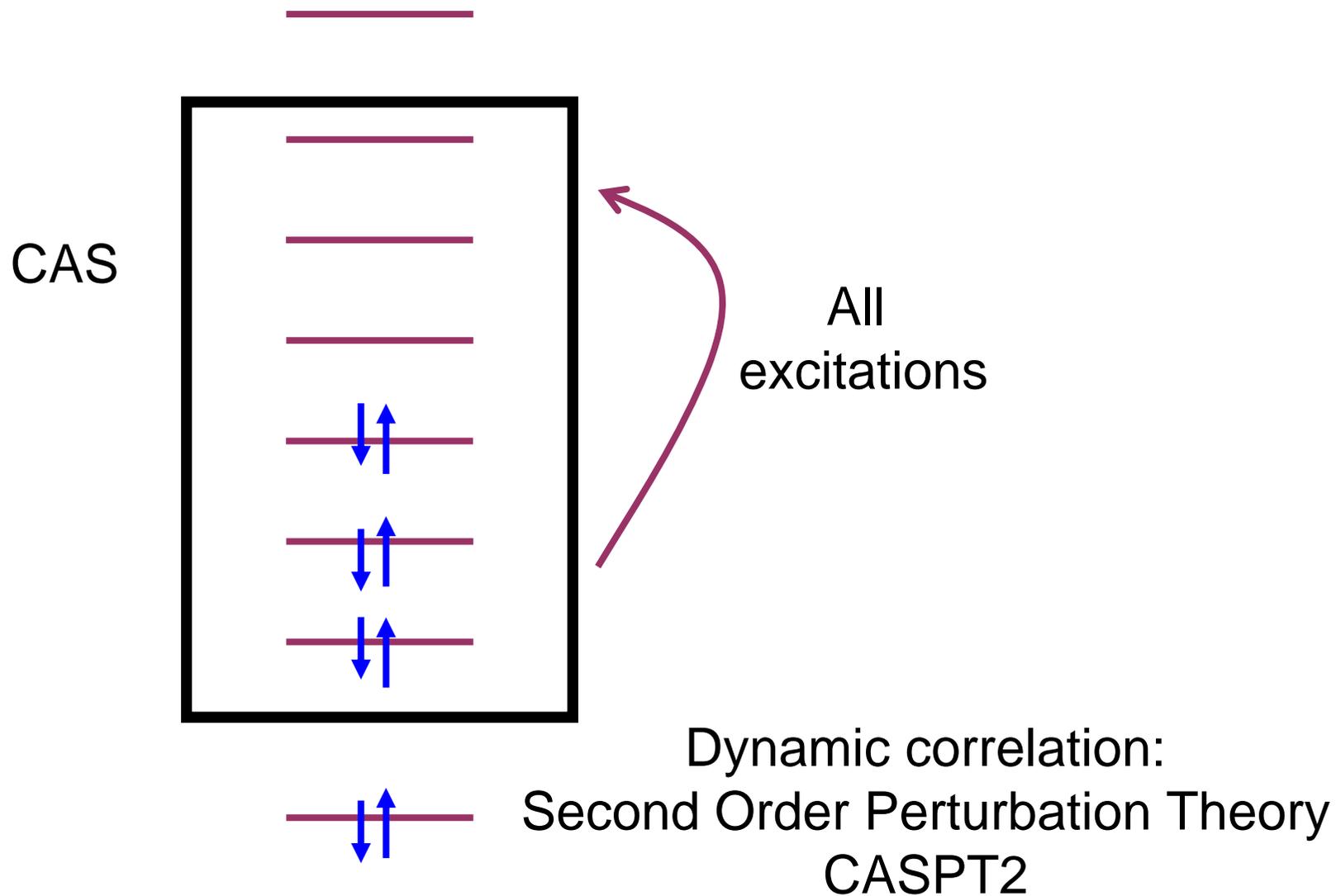
- Select electrons and orbitals involved in the chemical process

CASSCF(n, m)

n number of electrons

m is the number of orbitals

CASSCF (Complete Active Space Self Consistent Field)



Density functional Theory (DFT)

In Hartree-Fock  $\Psi(x_1, x_2, \dots, x_N)$

Exact Hamiltonian, but approx. wavefunction.

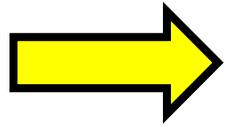
ELECTRON DENSITY

Important Saving: The wavefunction depends on $3N$ spatial coordinates + Spin
The electron density depends just on 3 spatial variables

Principles of DFT

The ground state density of the system is enough to obtain the energy and other properties.

Variational principle: for any trial density ρ the energy will represent an upper bound to the ground state energy E_0



Exact wavefunction, but...unknown Hamiltonian!!!

Looking for an approximate Exchange Correlation functional

$$F_{XC} = f_X + f_C \quad \text{Exchange + Correlation}$$

LDA

VWN (Vosko, Wilk and Nusair)

GGA

B-P86 (Becke88 and Perdew86)

Hybrid Functionals

$$f^{XC} = C_{HF} f^X_{HF} + C_{GGA} f^{XC}_{GGA}$$

B3-LYP (Becke 3 parameter functional-Lee Yang Paar)

Excited States Time-Dependent Density Functional theory

2. Quantum Dynamics

18 June
20
07

Goal: Follow the evolution molecular system in real time

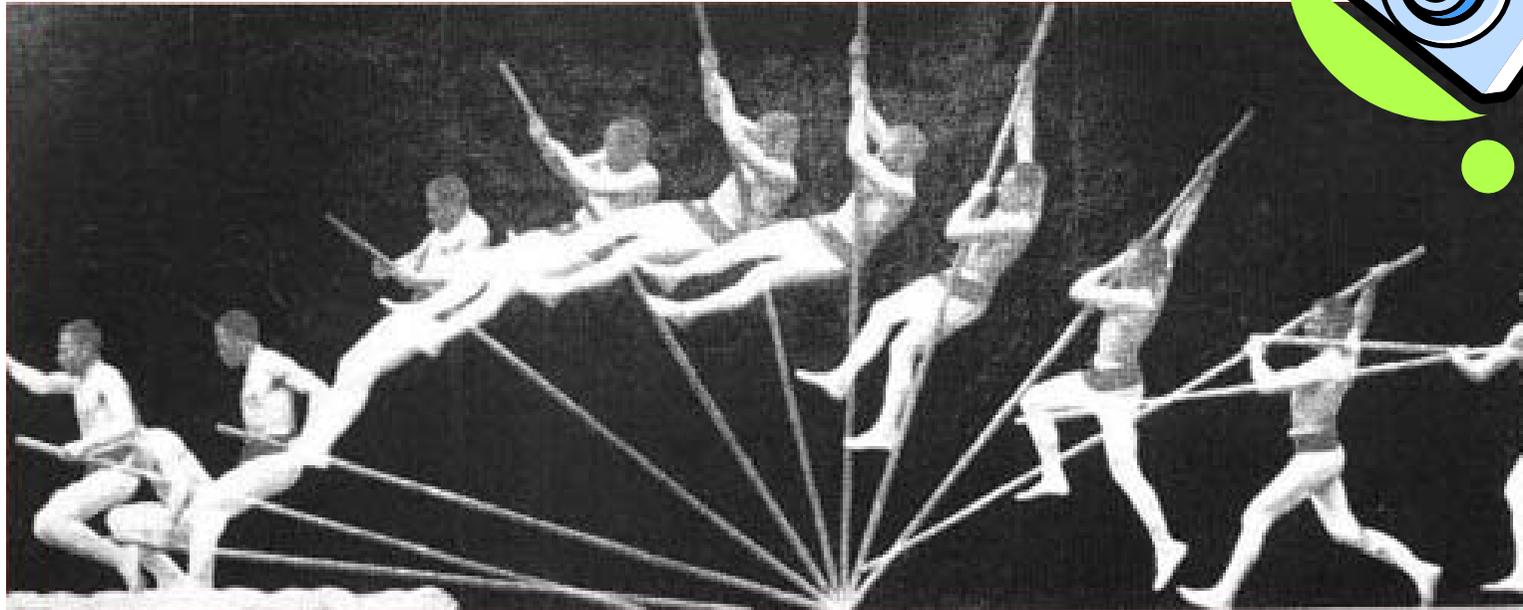
The speed of atomic motion: 1000m/s

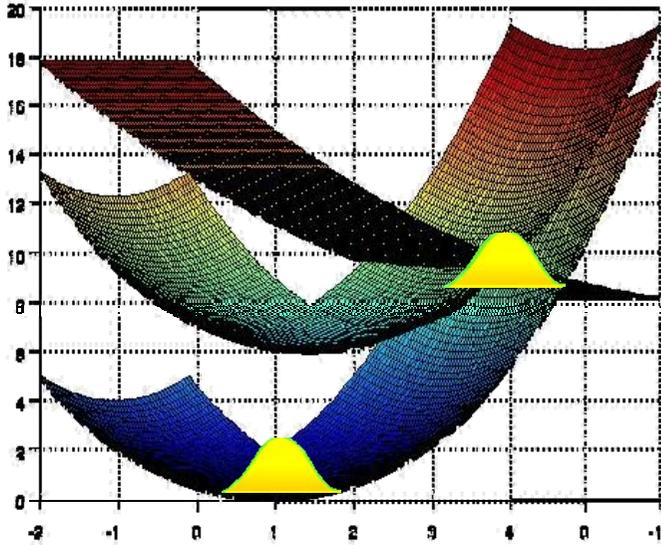


$$t = 10^{-13}\text{s} = 100 \text{ fs}$$

Chemical changes involve distances of Angstroms

Femtosecond laser camera





Time dependent Schrödinger equation

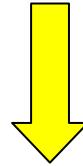
$$i\hbar \frac{\partial}{\partial t} |\Psi_{tot}(t)\rangle = \hat{H}(t) |\Psi_{tot}(t)\rangle$$

$$\Psi_{tot}(\{\vec{r}_i\}, \{\vec{R}_A\}, t) = \sum_{el} \psi_{el}(\{\vec{r}_i\}; \{\vec{R}_A\}) \psi_{nuc}^{el}(\{\vec{R}_A\}, t)$$

$$\hat{H}(t) = \hat{H} - \vec{\mu} \cdot \vec{E}(t)$$

1. Obtention of an initial wavefunction

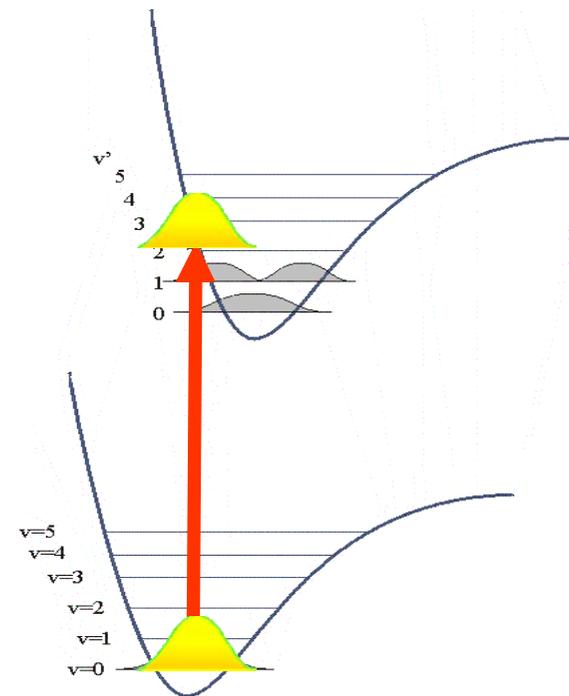
Solution of the time independent nuclear Schrödinger equation



Numerically: FGH (Fourrier Grid Hamiltonian)

2. Propagation: solution of the TDSE

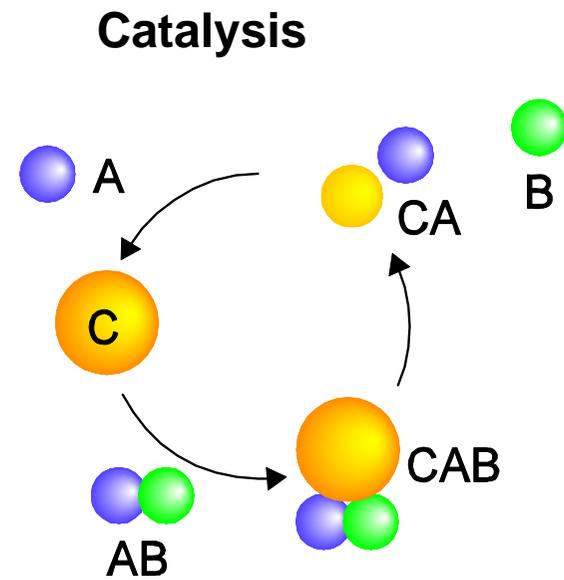
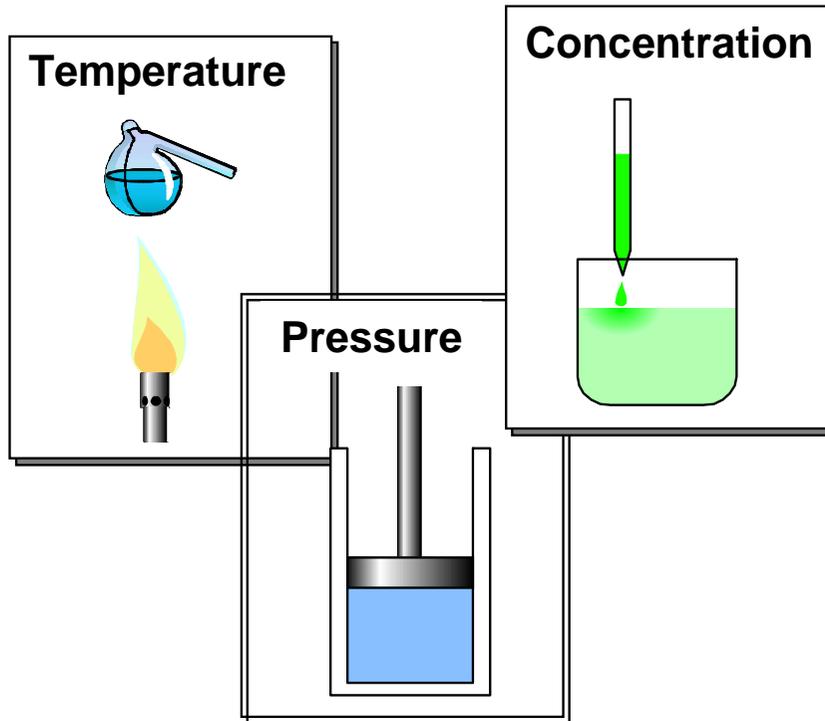
Wavepacket:
coherent superposition of stationary states



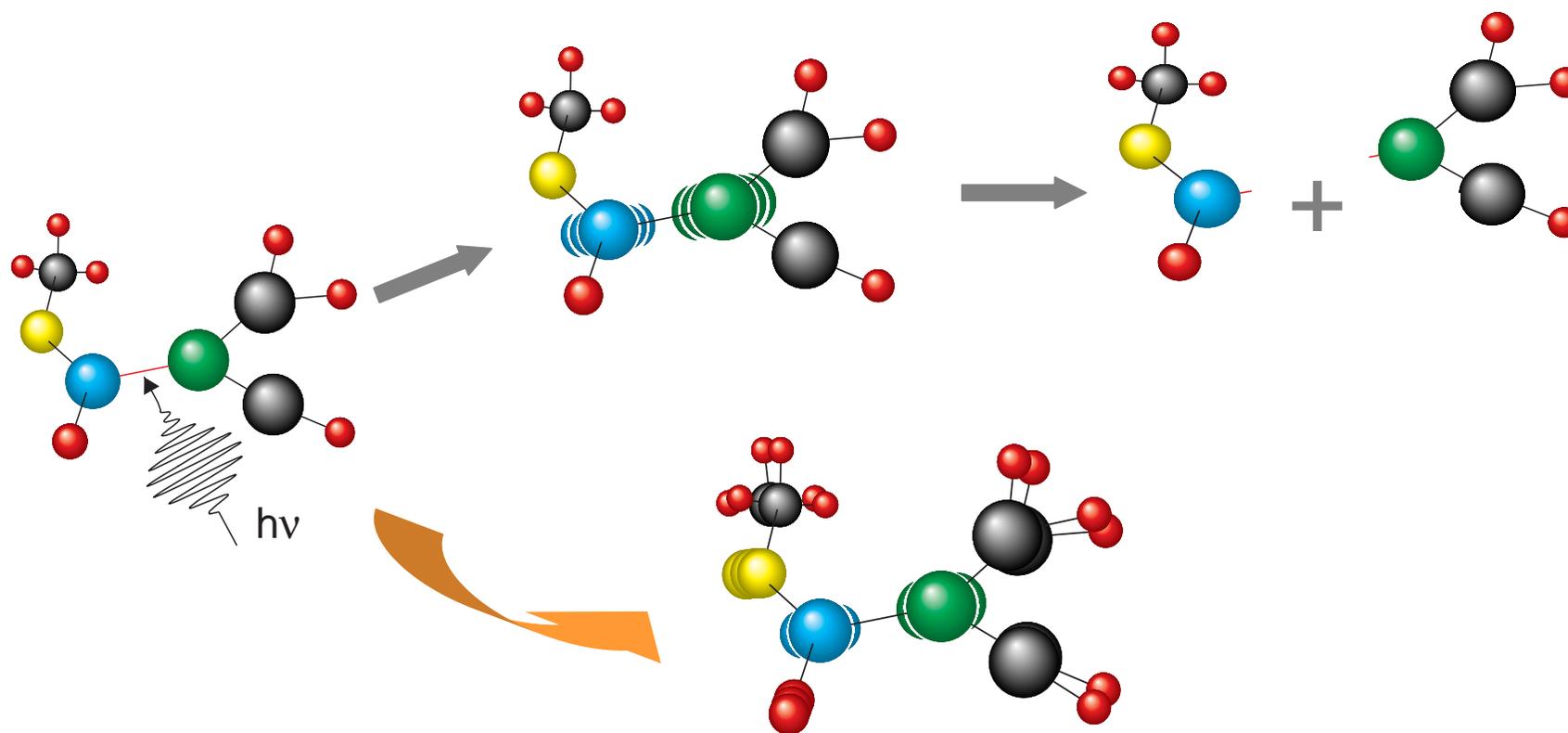
3. Quantum Control

18 June
20
07

Conventional chemical control



Mode-selective chemistry

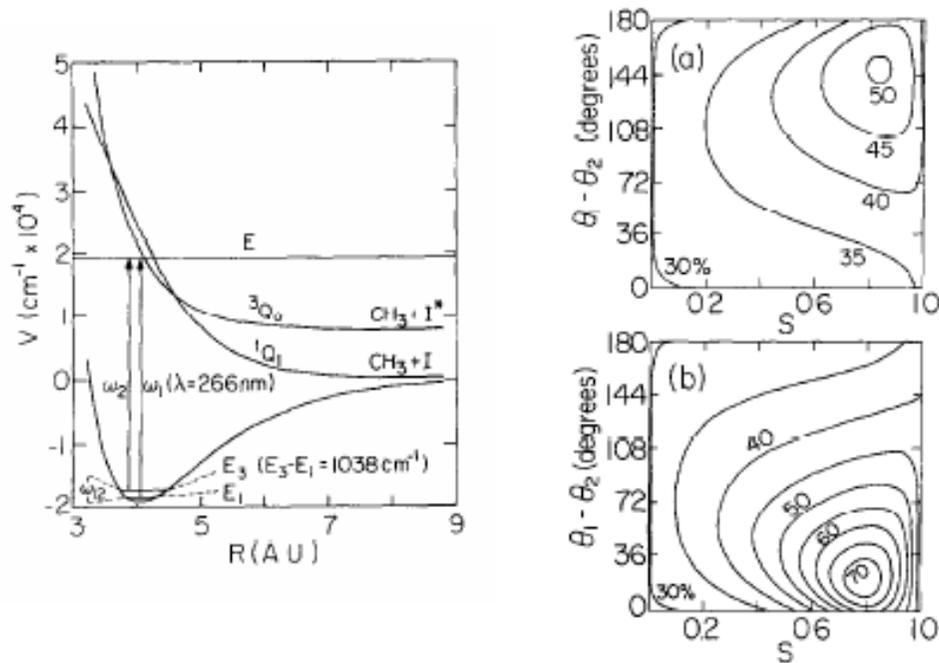


Fails in many cases since bonds are not independent!!

energy flows between them: IVR

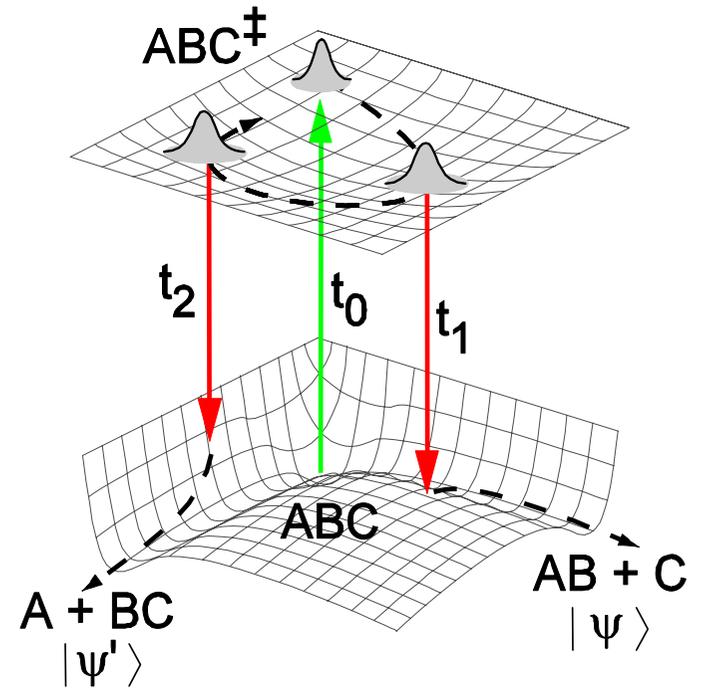
Brumer-Shapiro
“phase control”

Control through the manipulation
of the amplitude and
the phase parameters



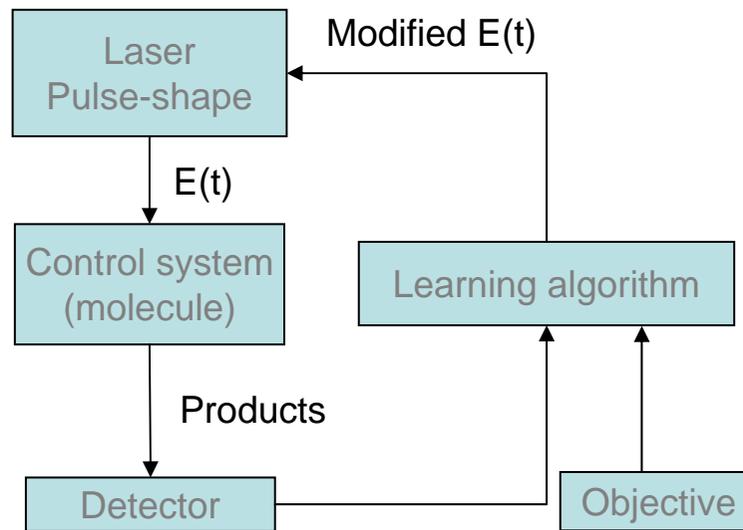
CPL 126 (1986) 541.

Tannor-Kosloff-Rice
“pump-dump control”



JCP 85 (1986) 5805.

Judson-Rabitz Optimal Control Theory



“ Teaching laser to control molecules ”

Rabitz, PRL 68 (1992) 1500.

Bibliography

Introduction to computational chemistry. Frank Jensen. Wiley

Modern Quantum Chemistry. Szabo and Ostlund. Dover

Introduction to quantum mechanics. A time dependent perspective. Tannor. University Science Books.