Introduction to *ab-initio* methods
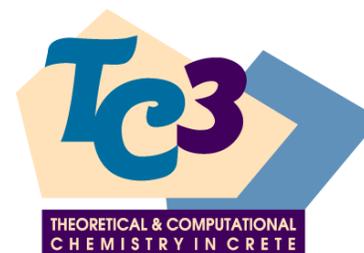# and relation to nanomaterials research

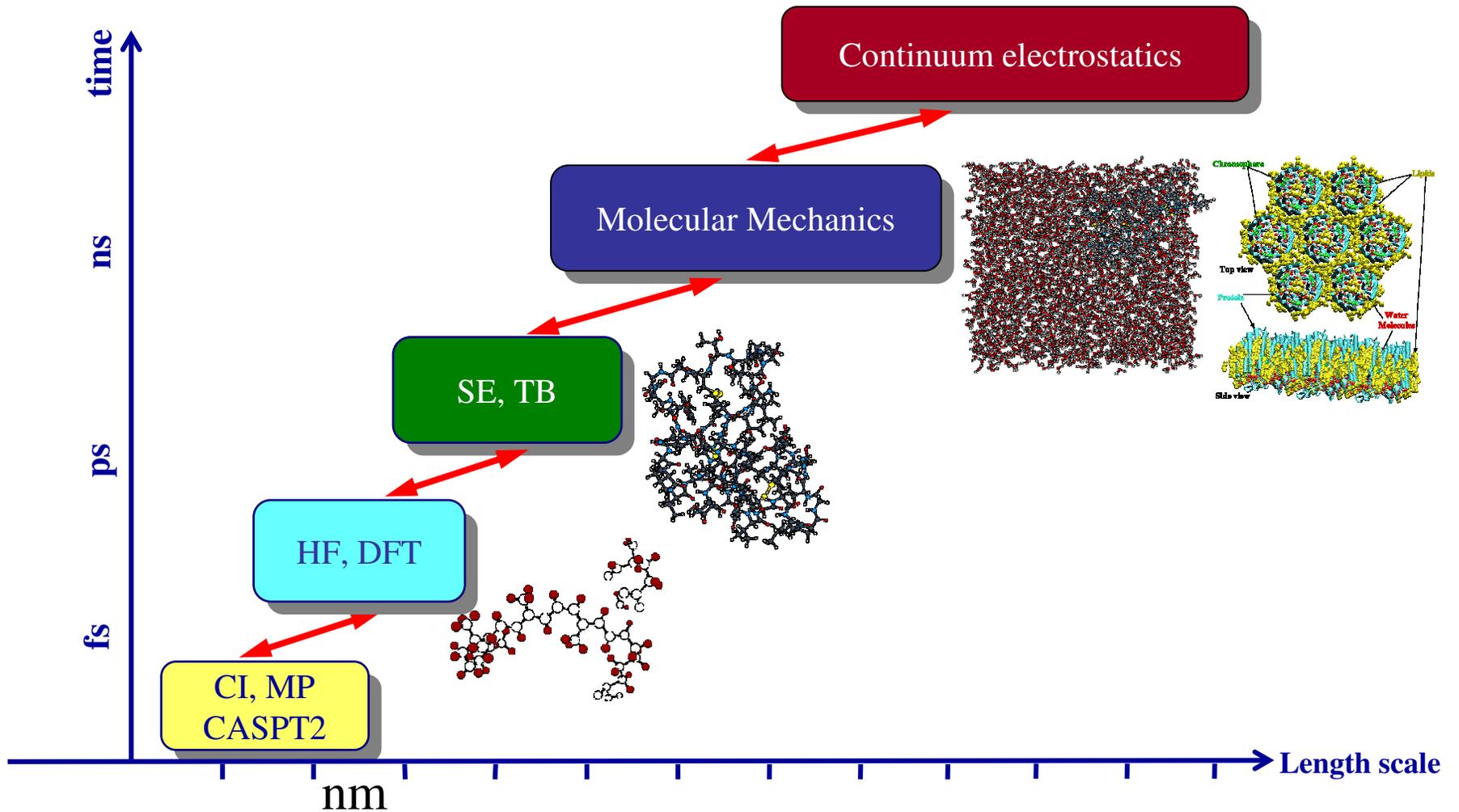**George E. Froudakis**

Associate Professor
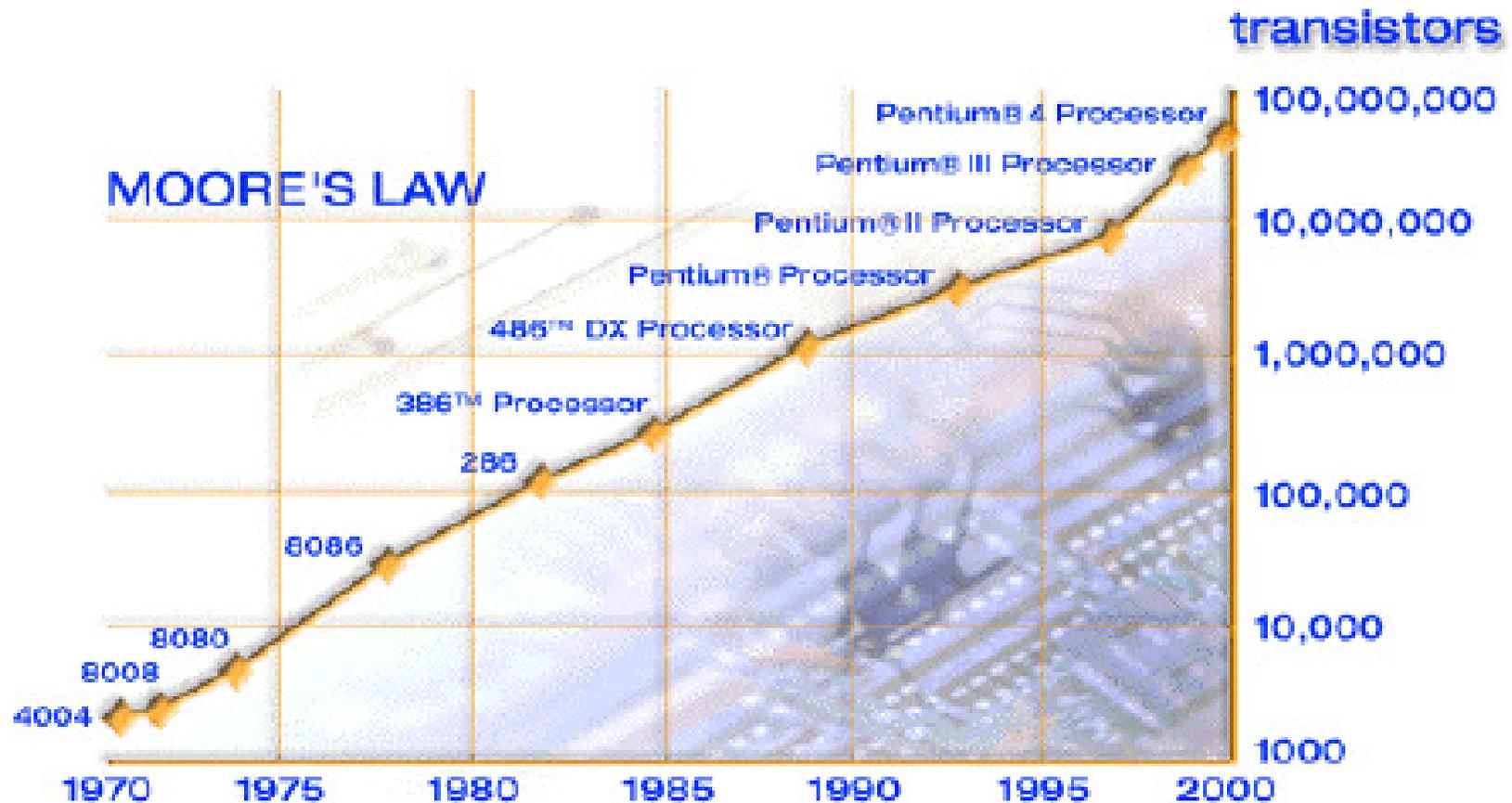
Dept. of Chemistry

Uni. of Crete - Greece

Why we need theory and modeling ?

- Explanation of experimental results

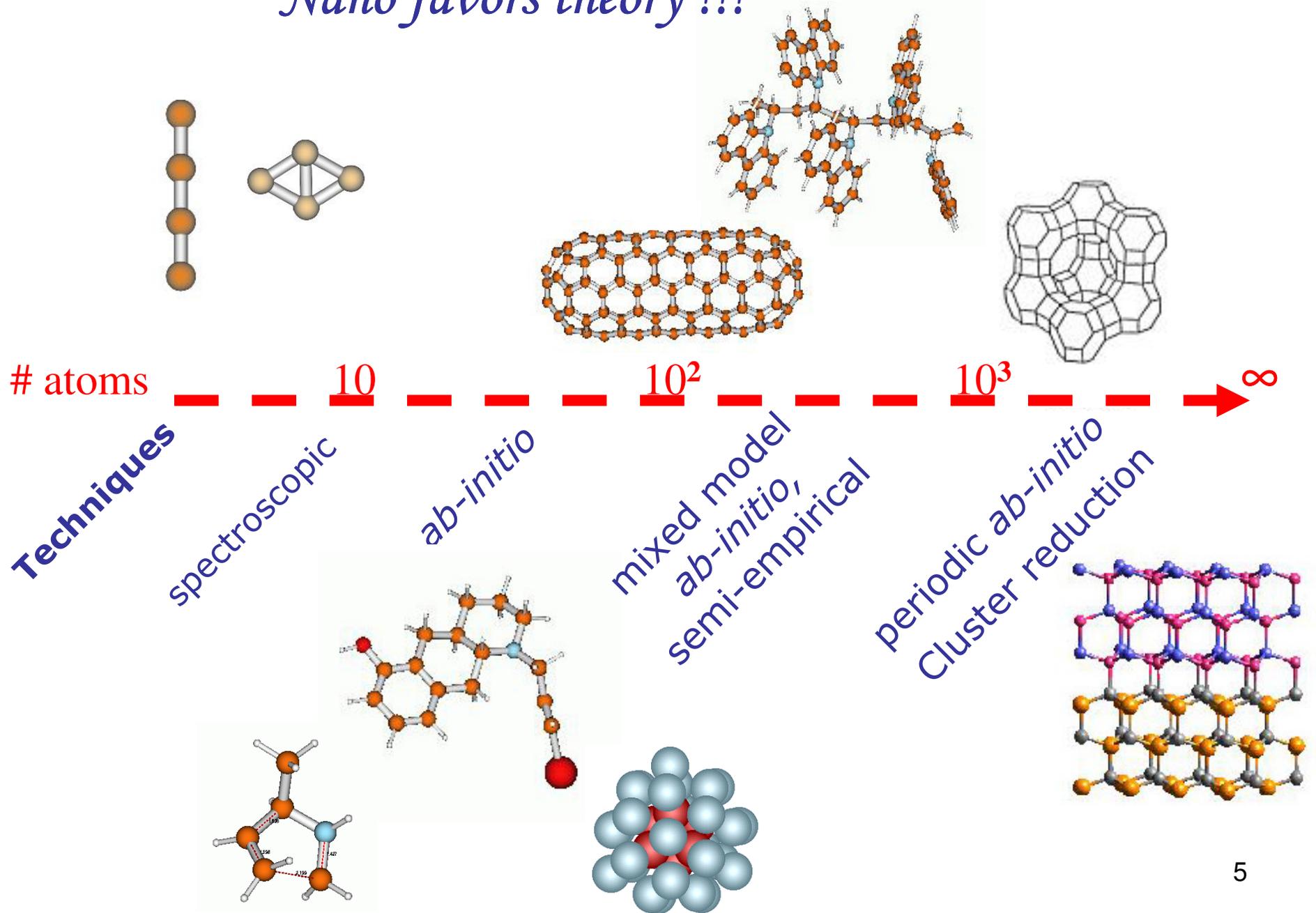- Material testing *in silico*

- Designing novel materials

Hierarchy of methods

time

ns

ps

fs

Continuum electrostatics

Molecular Mechanics

SE, TB

HF, DFT

CI, MP
CASPT2

Length scale

nm

In past 30 years, computational power
(driven by Moore's Law) has increased
by over 5 orders of magnitude

transistors

MOORE'S LAW

Pentium® 4 Processor   100,000,000

Pentium® III Processor

Pentium® II Processor   10,000,000

Pentium® Processor

486™ DX Processor   1,000,000

386™ Processor

286   100,000

8086

10,000

8080

8008

4004   1000

1970   1975   1980   1985   1990   1995   2000

Nano favors theory !!!

atoms — — — 10 — — — — 10^2 — — — — 10^3 — — — ∞

Techniques

spectroscopic

ab-initio

mixed model
ab-initio,
semi-empirical

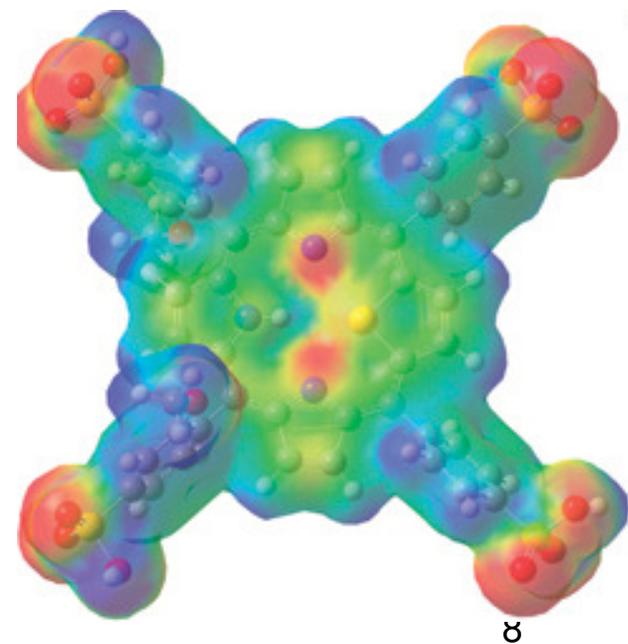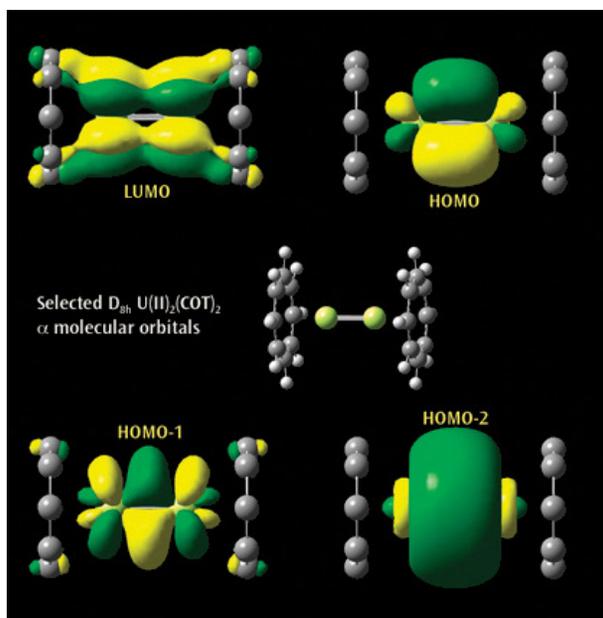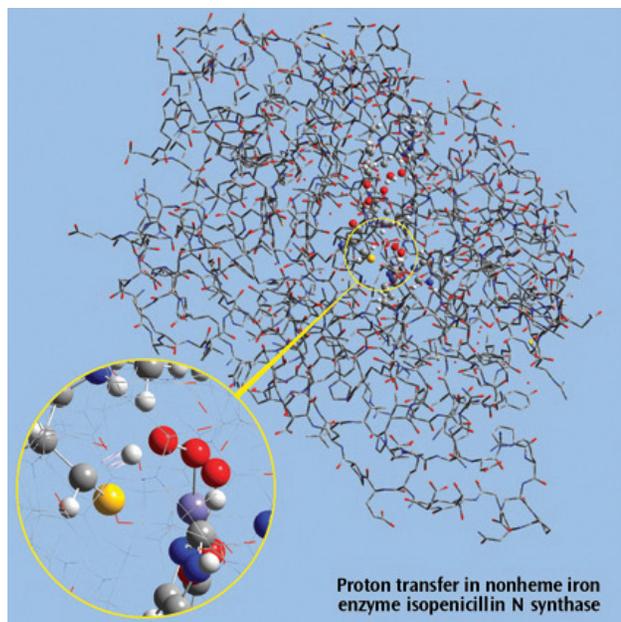periodic *ab-initio*
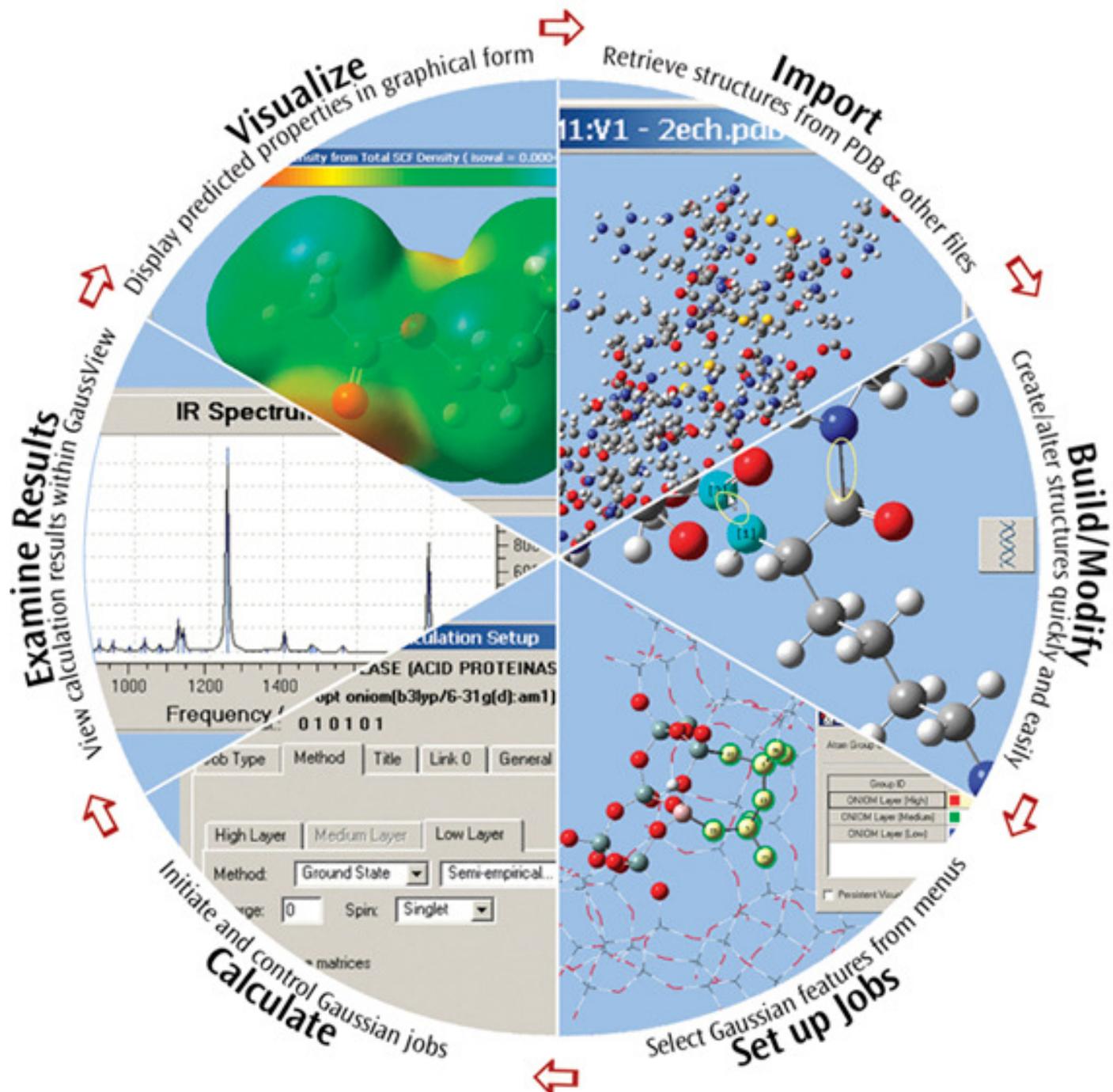Cluster reduction

5

What is Quantum Chemistry?

- Quantum Mechanics applied to Atoms and Molecules

- Aim: Understanding of Electronic Structure

- Solution of the electronic Schrödinger equation

- Derived: Properties of Atoms and Molecules

Molecular
Properties

Transition States
Reaction Paths.

Ab initio electronic structure theory
Hartree-Fock (HF)
Electron Correlation (MP2, CI, CC, etc.)

Spectroscopic
Observables

Geometry
Prediction

Benchmarks for
Parameterization

Electronic
Structure
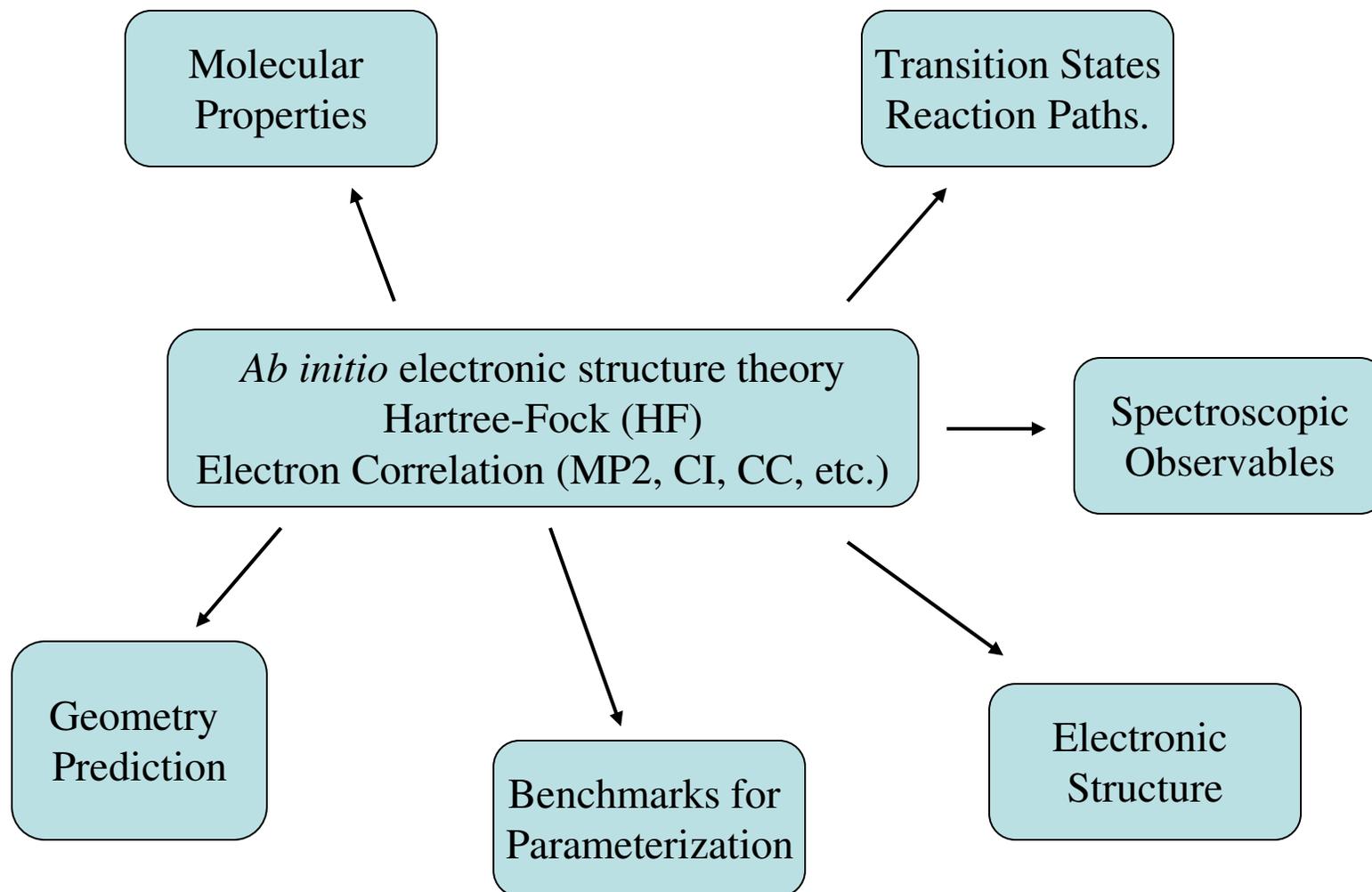
Goal: Insight into chemical phenomena.

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Proton transfer in nonheme iron enzyme isopenicillin N synthase

LUMO

HOMO

Selected D_{8h} U(II)$_2$(COT)$_2$ α molecular orbitals

HOMO-1

HOMO-2

Visualize
Display predicted properties in graphical form

Import
Retrieve structures from PDB & other files

Build/Modify
Create/alter structures quickly and easily

Set up Jobs
Select Gaussian features from menus

Calculate
Initiate and control Gaussian jobs

Examine Results
View calculation results within GaussView

11:V1 - 2ech.pdb

Density from Total SCF Density (isoval = 0.000-

IR Spectrum

1000   1200   1400

Frequency

Calculation Setup

EASE (ACID PROTEINAS

opt oniom(b3lyp/6-31g(d):am1

0 1 0 1 0 1

Job Type   Method   Title   Link 0   General

High Layer   Medium Layer   Low Layer

Method: Ground State   Semi-empirical...

arge: 0   Spin: Singlet

matrices

Group ID
ONIOM Layer [High]
ONIOM Layer [Medium]
ONIOM Layer [Low]

9

Exploring Chemistry with Electronic Structure Methods

Second Edition

James B. Foresman

Æleen Frisch

Gaussian, Inc.
Pittsburgh, PA

Part 1: Essential Concepts & Techniques

Appendices

1

Hamiltonian for a system with N-particles

$$\hat{H}(r)\Psi(r) = E\Psi(r)$$

Time-Independent Schrödinger Equation

$$\hat{H} = \hat{T} + \hat{V}$$

Sum of kinetic (T) and potential (V) energy

$$\hat{T} = \sum_{i=1}^{N}\hat{T}_i = -\sum_{i=1}^{N}\frac{\hbar^2}{2m_i}\nabla_i^2 = -\sum_{i=1}^{N}\frac{\hbar^2}{2m_i}\left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}\right)$$

Kinetic energy

$$\nabla_i^2 = \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}\right)$$

Laplacian operator

$$\hat{V} = \sum_{i=1}^{N}\sum_{j>1}^{N}V_{ij} = \sum_{i=1}^{N}\sum_{j>1}^{N}\frac{q_i q_j}{r_{ij}}$$

Potential energy

$$\psi = \psi(\vec{R_1}, \vec{R_2}, ..., \vec{R_m}, \vec{r_1}, \vec{r_2}, ..., \vec{r_n})$$

$$H = T_n + T_e + V_{ee} + V_{nn} + V_{en}$$

$$T_n = -\sum_{I=1}^{m} \frac{1}{2M_I} \nabla_I^2$$

$$T_e = -\sum_{i=1}^{n} \frac{1}{2} \nabla_i^2$$

$$V_{ee} = \sum_{i=1}^{n} \sum_{j<i} \frac{1}{\left| \vec{r_i} - \vec{r_j} \right|}$$

$$V_{nn} = \sum_{I=1}^{m} \sum_{J<I} \frac{Z_I Z_J}{\left| \vec{R_I} - \vec{R_J} \right|}$$

$$V_{en} = -\sum_{i=1}^{n} \sum_{I=1}^{m} = -\frac{1}{\left| \vec{r_i} - \vec{R_i} \right|} - \frac{1}{\left| \vec{r_J} - \vec{R_J} \right|}$$

Born-Oppenheimer Approximation (1927)

- So far, the Hamiltonian contains the following terms:

$$\hat{H} = \hat{T}_n + \hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee} + \hat{V}_{nn}$$

- Since nuclei are much heaver than electrons (m_n/m_e=1836), their velocities are much smaller.
- To a good approximation (error <1/1000*), the Schrödinger equation can be separated into two parts:

  - One part describes the electronic wavefunction for a fixed nuclear geometry.
  - The second describes the nuclear wavefunction, where the electronic energy plays the role of a potential energy.

$$H\psi = E\psi$$

$$H = H_e + T_n$$

$$\psi = \psi_i^e \psi_j^n$$

$$e : H_e \psi_i^e = E_i^e \psi_i^e \Rightarrow$$

$$n : (T_n + E_i^e)\psi_j^n$$

E

0

$H^\bullet + H^\bullet$

H—H
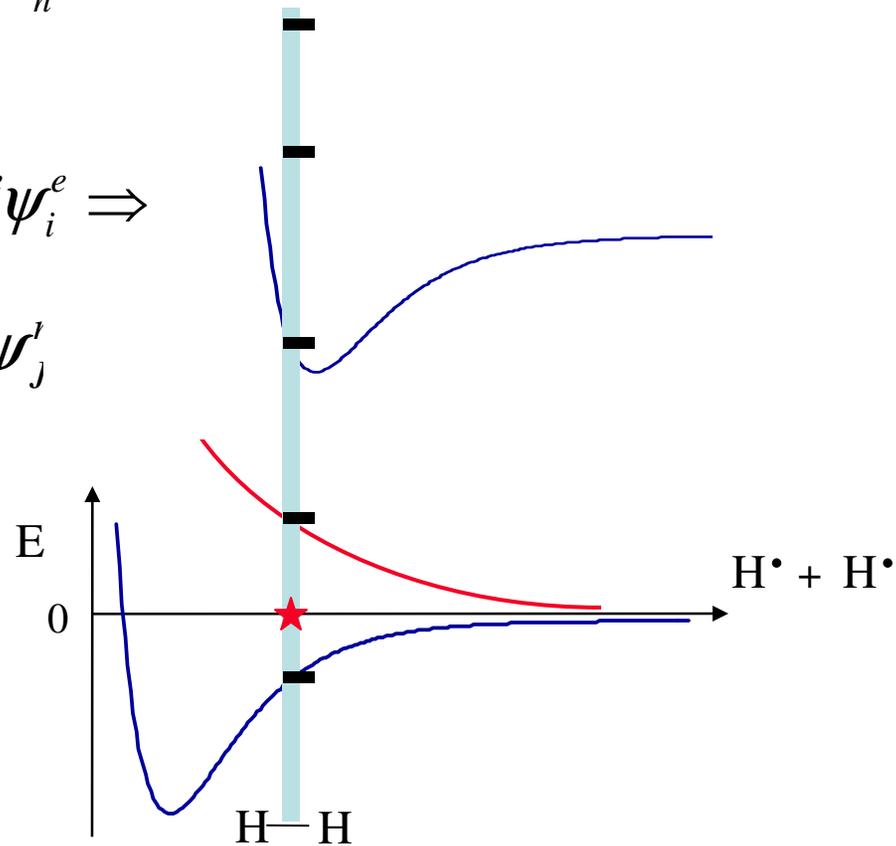
Limitations of the Born-Oppenheimer approximation

- The BO approx. is usually very good, but breaks down when two (or more) electronic states are close in energy at particular nuclear geometries. In such situations, a " non-adiabatic" wavefunction - a product of nuclear and electronic wavefunctions - must be used.

E

Cl-
Na+

Cl
Na

0
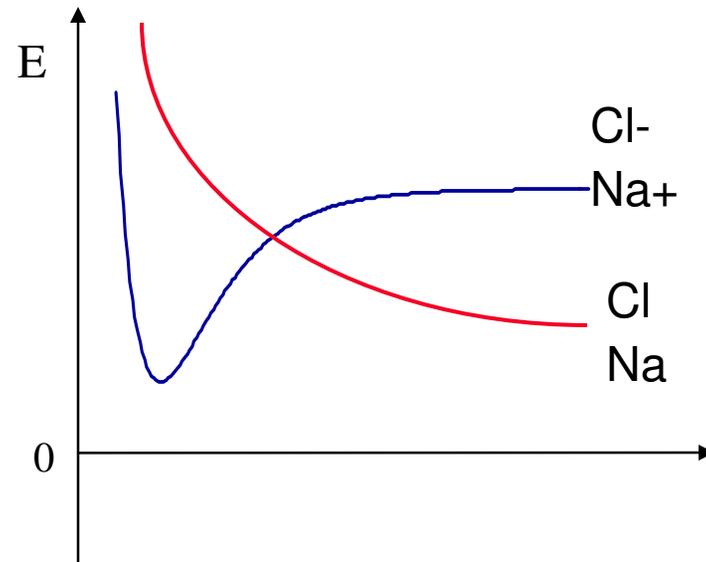
Hartree-Fock Theory

Electron-electron interaction:

$$V(r_1, r_i) = \frac{e^2}{4\pi\varepsilon_0}\left[-\frac{Z}{r_1} + \sum_{i+1}\frac{1}{r_{1i}}\right]$$

$$V(r_1) \approx \frac{e^2}{4\pi\varepsilon_0}\left[-\frac{Z}{r_1} + \sum_{i+1}\frac{1}{r_{1i}}\right]$$
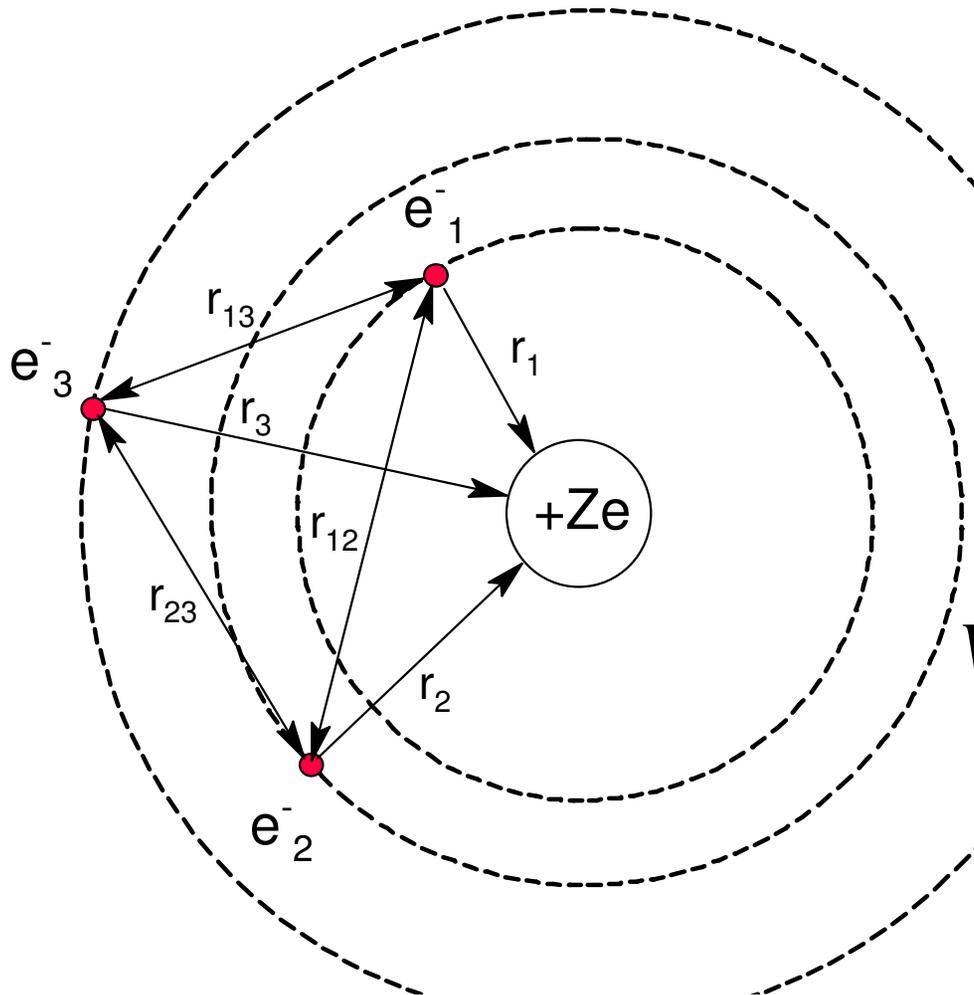
$$V^{HF}(r_1) \approx \frac{e^2}{4\pi\varepsilon_0}\left[-\frac{Z}{r_1} + \sum_{i+1}\frac{1}{r_{1i}}\right]$$

+Ze

e⁻₁ e⁻₂ e⁻₃

r_{13} r_1 r_3 r_{12} r_{23} r_2

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Self- **C**onsistent-**F**ield

Initial Guess for the orbitals

$$V^{HF}(r_1)$$

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2\psi}{\partial x_1^2}+\frac{\partial^2\psi}{\partial y_1^2}+\frac{\partial^2\psi}{\partial z_1^2}\right]+V^{HF}(r_1)\psi = E\psi$$

$$E^{HF}, \Psi^{HF} \Rightarrow \textit{new orbitals}$$

Self consistency

20
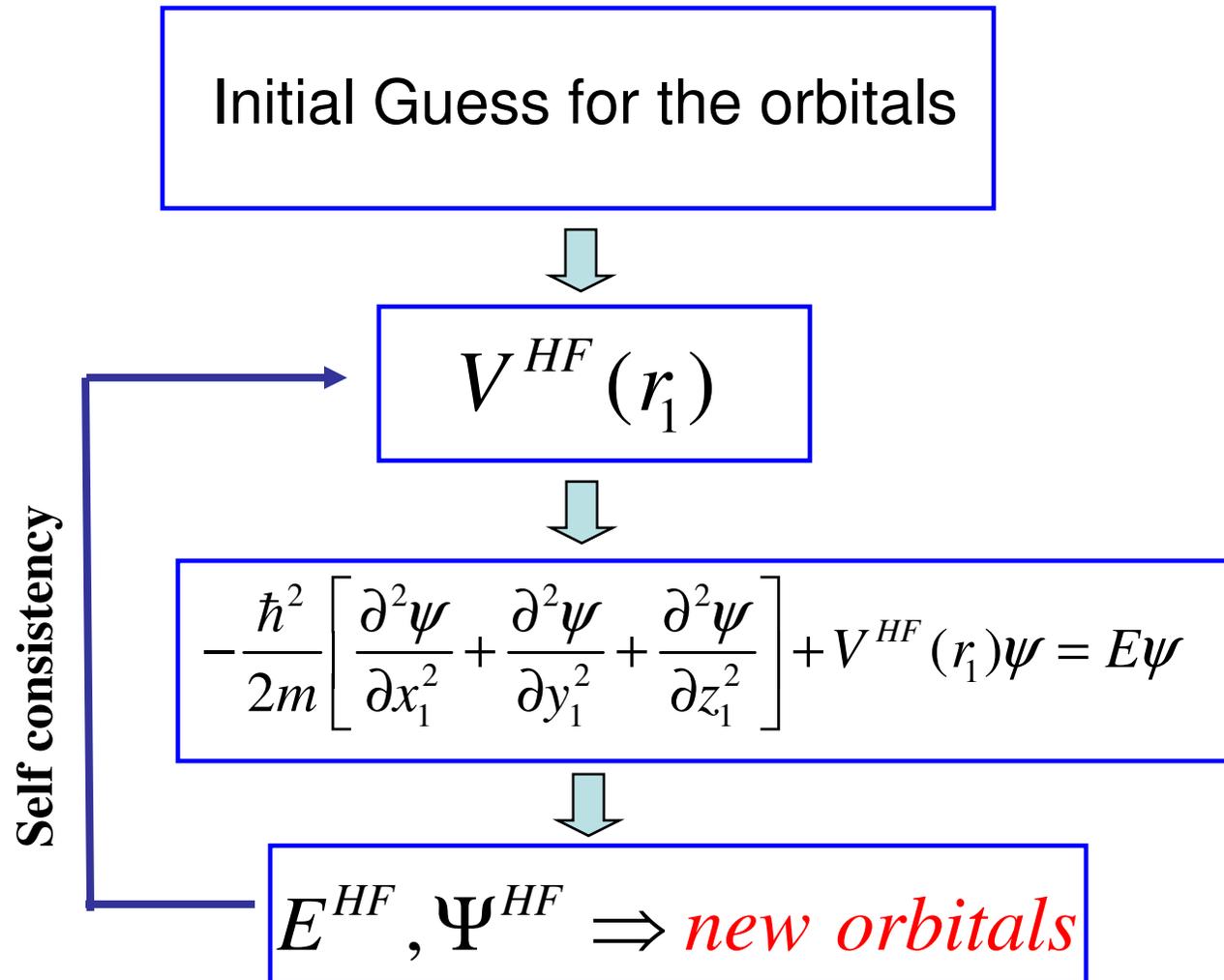
Restricted and Unrestricted Hartree-Fock

Restricted Hartree-Fock (RHF)
For even electron, closed-shell singlet states, electrons in a given MO
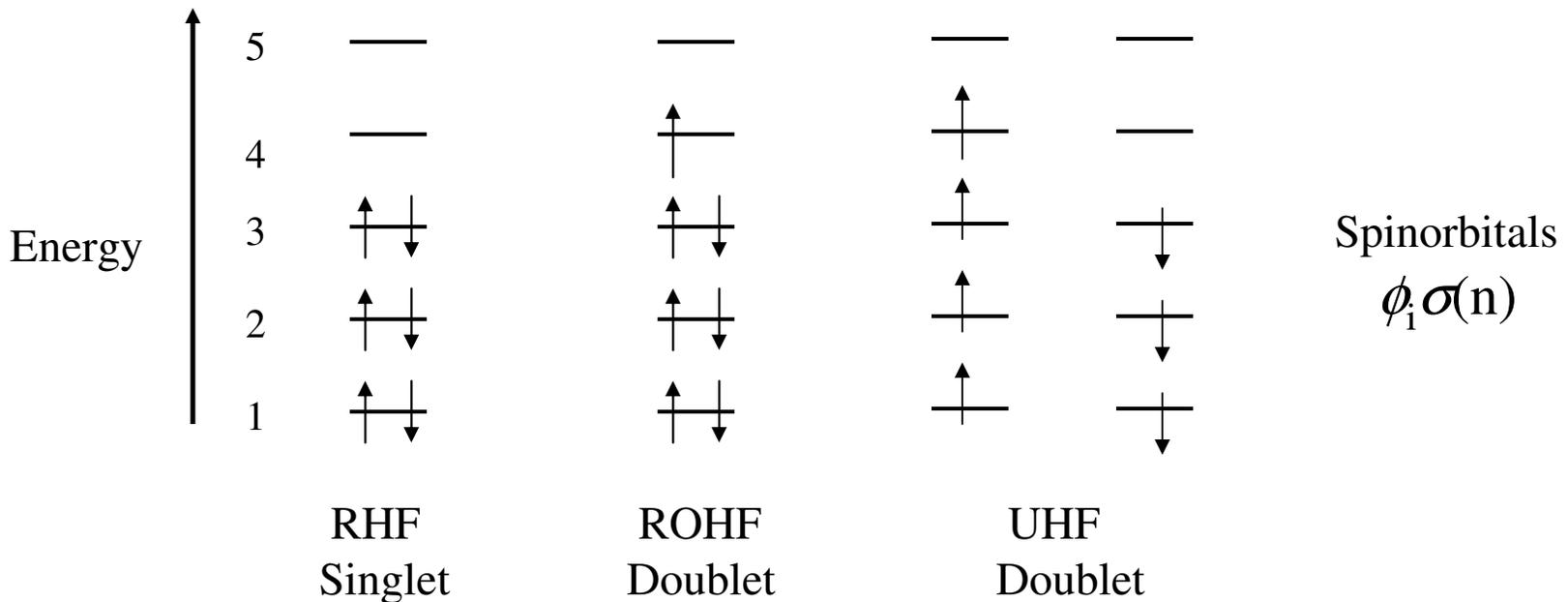with α and β spin are constrained to have the same spatial dependence.

Restricted Open-shell Hartree-Fock (ROHF)
The spatial part of the doubly occupied orbitals are restricted to be the same.

Unrestricted Hartree-fock (UHF)
α and β spinorbitals have different spatial parts.

Energy

5

4

3

2

1

α β

RHF
Singlet

ROHF
Doublet

UHF
Doublet

Spinorbitals
$\phi_i \sigma(n)$

Potential energy curves

Figure 4.3 6-31G** potential energy curves for H_2.
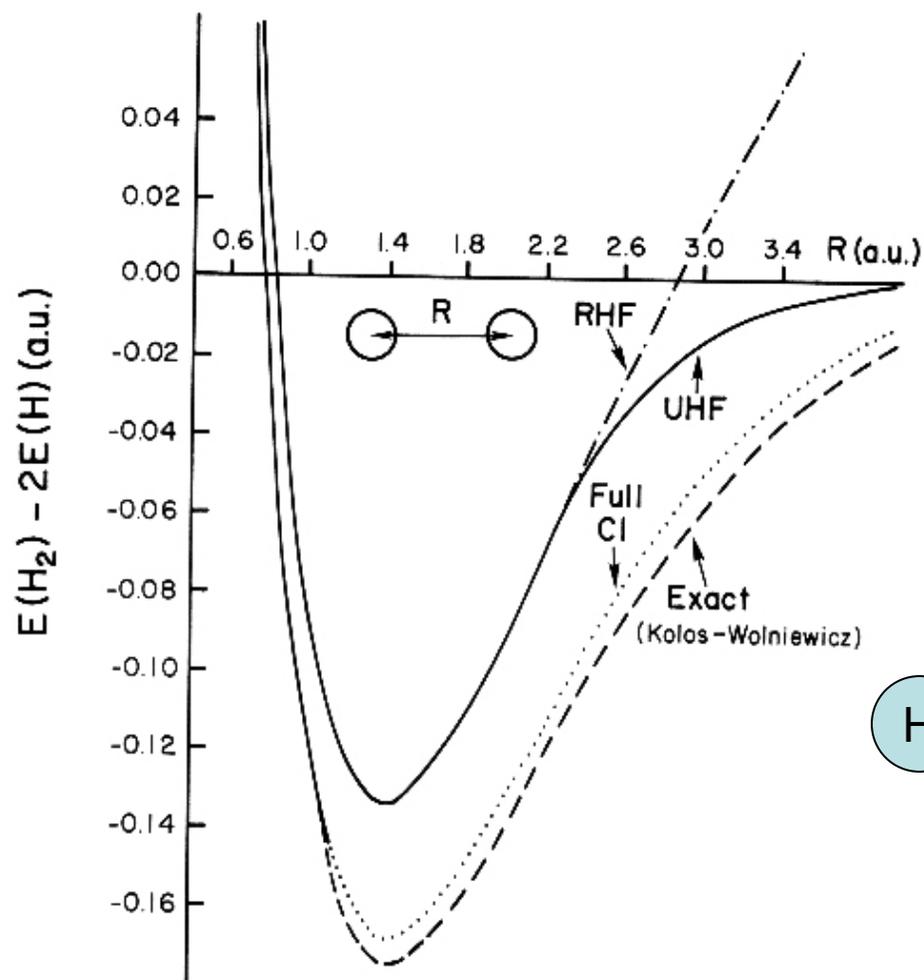
Restricted HF does not 'dissociate' correctly

Basis sets

$$\psi(x, y, z) = \sum_n c_n \Phi_n(x, y, z)$$

- **Mathematical trick** : Instead of looking for an unknown functions (ψ) we are searching for coefficients (c).
- "**Atoms-in-Molecule**" approach: Atomic electron density is only weakly perturbed in formation of molecule
- Hydrogen-like functions centered at atoms in molecule
- Additional functions for specific purposes (polarization, correlation, bonding etc.)

Basis sets: STOs and GTOs

STO $\approx e^{-\alpha r}$

GTO $\approx e^{-\alpha r^2}$
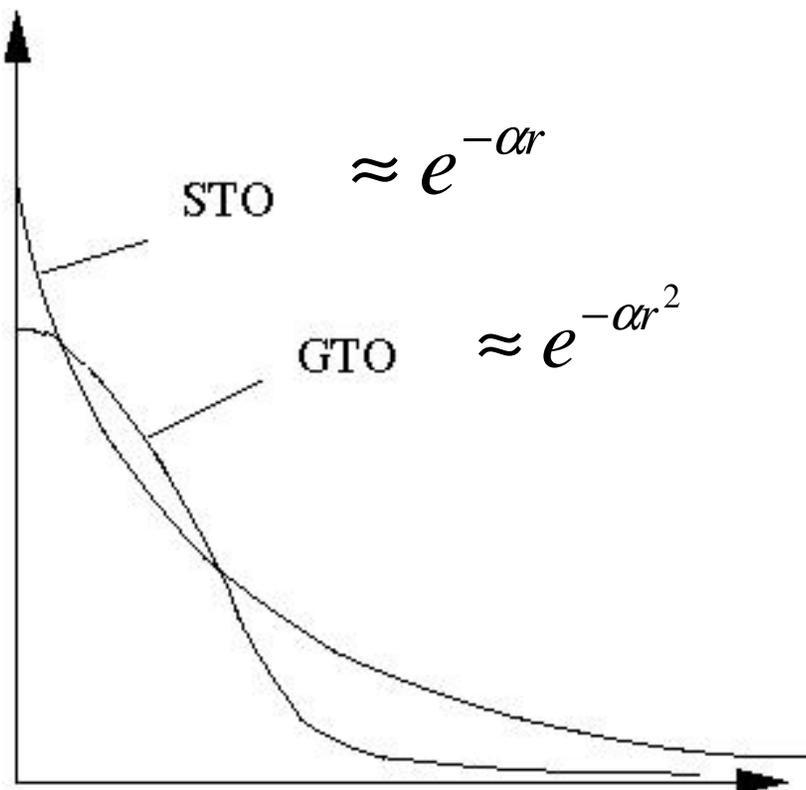
- Slater-Type Orbitals are H like
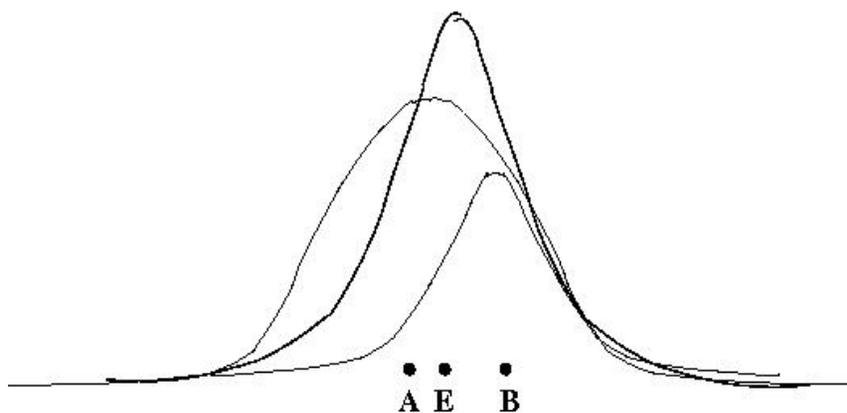- Gaussian Type Orbitals
- α: 'exponent'

Basis sets: Why GTOs ?

Situation in molecules:

Atomic centers A,B

- Use of atom-centered GTOs
- Products of two GTOs at centers A, B gives GTO at center E
- Hence: Ease of integration!
- Much faster than with STOs, despite increased number

Standard basis sets: Overview

- STO-NG: N GTO per STO

- Split-valence 6-31+G(*) sets:
  SZ (core)/DZ(valence),
  +: diffuse functions
  *: polarization functions
  Z(zeta): Number of contracted functions

- (aug)-cc-(p)VXZ: Correlation-consistent basis sets

Basis sets: Polarization functions

1s $1s+p_z$ atom   atom   atom   z
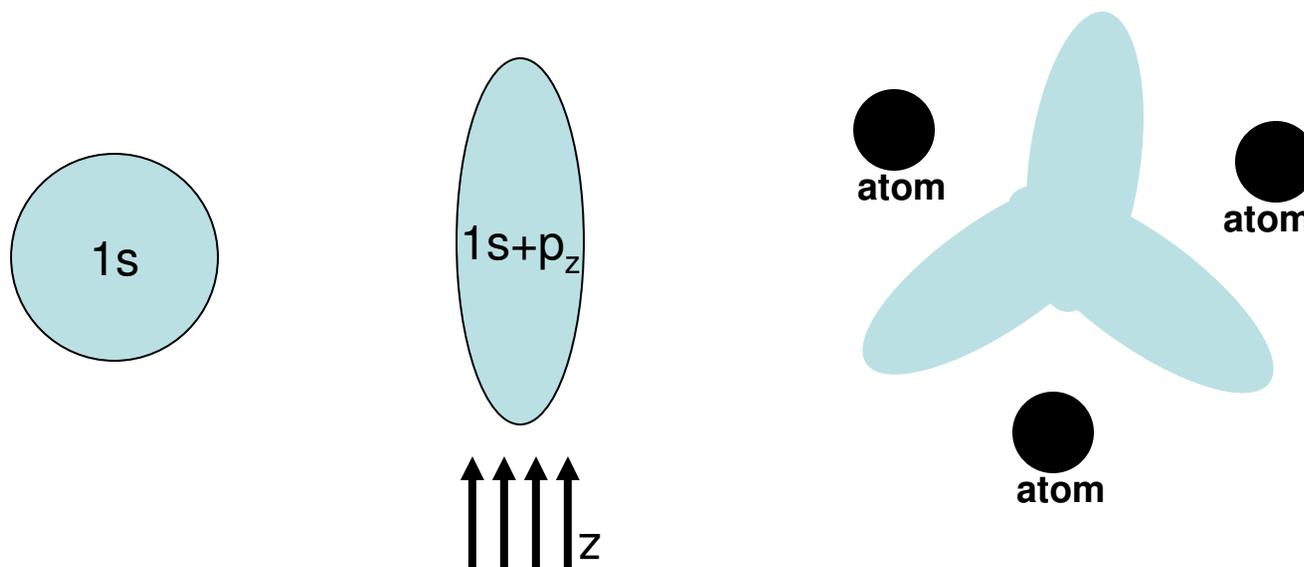
- Polarization of atomic density upon formation of chemical bond
- Molecular field breaks atomic symmetry !
- Use of higher angular-momentum functions
  E.g. p-functions for H , d-functions for C, etc.
- **Allows orbitals to change shape**

Complete **B**asis **S**et limit
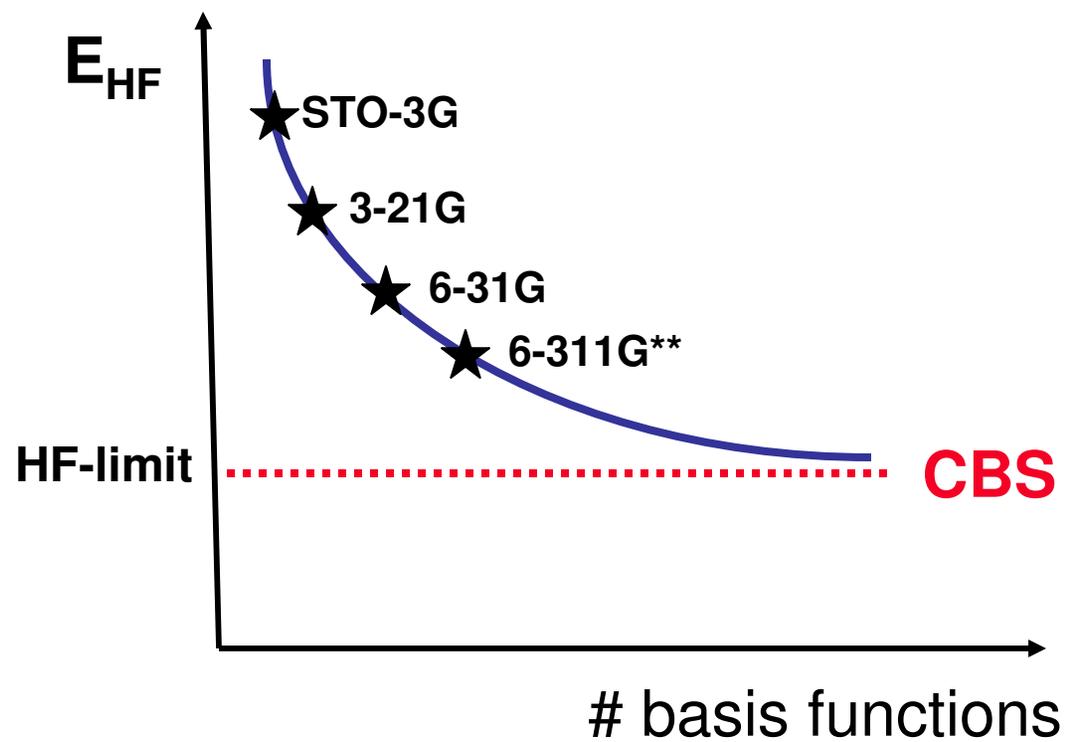
Configuration Interaction (CI)

- Principles:

  Based on HF (or MCSCF) wave function (orbitals)

  Linear expansion of many-particle wave function:

$$\Psi_{CI} = c_0\psi_0 + \sum_{ar} c_a^r \psi_a^r + \sum_{\substack{a<b \\ r<s}} c_{ab}^{rs} \psi_{ab}^{rs} + \sum_{\substack{a<b<c \\ r<s<t}} c_{abc}^{rst} \psi_{abc}^{rst} + ...$$

c: expansion coefficients ($c_0 > 90\%$)

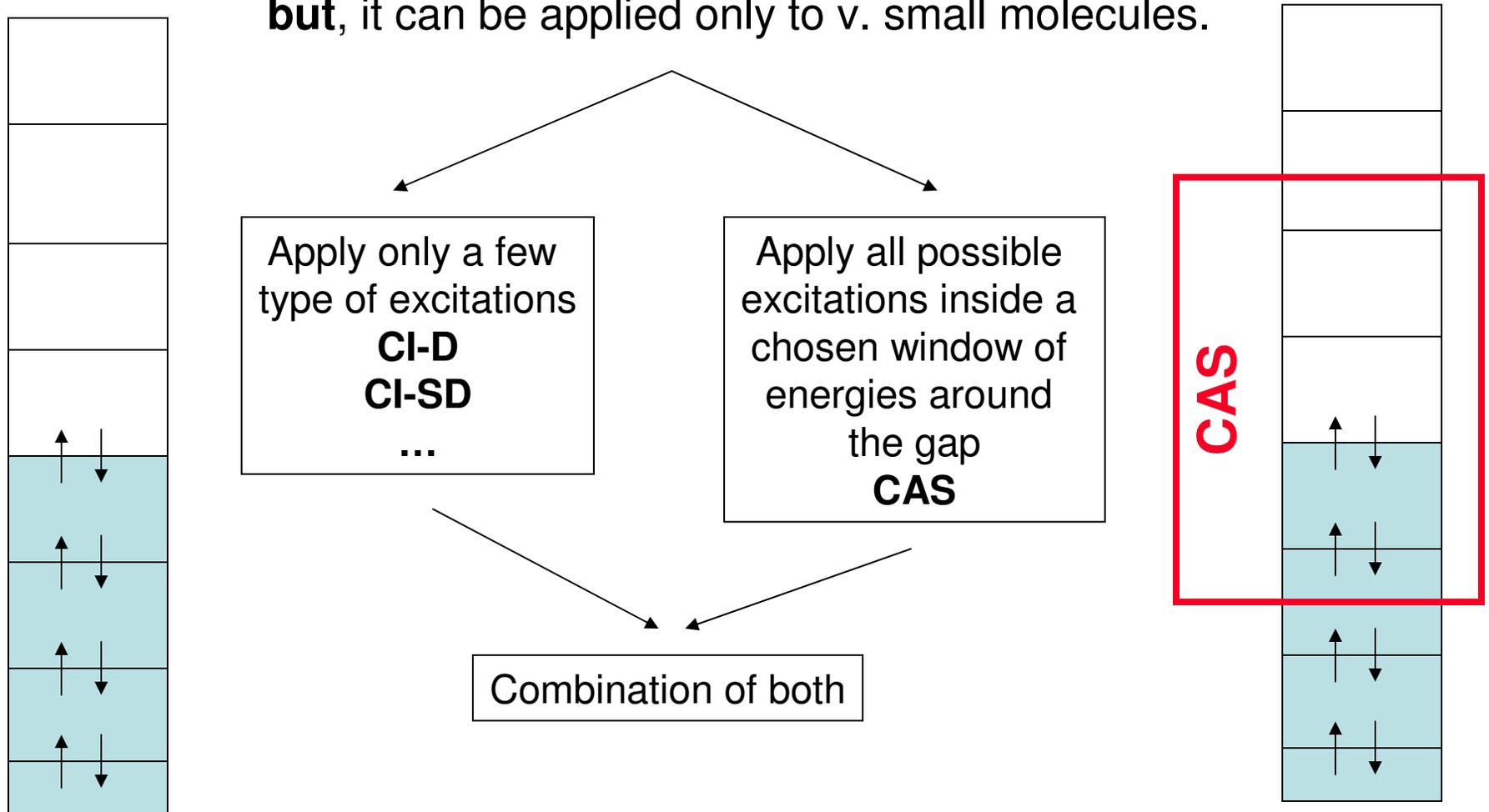Ψ: Slater determinants, ground and excited

CI: Excitation Level

The Hamiltonian matrix in determinant basis

Anregung	$|\Psi_0\rangle$	$|S\rangle$	$|D\rangle$	$|T\rangle$	$|Q\rangle$	$\dots$
$\langle\Psi_0|$	$\langle\Psi_0|\hat{H}|\Psi_0\rangle$	0	$\langle\Psi_0|\hat{H}|D\rangle$	0	0	$\dots$
$\langle S|$		$\langle S|\hat{H}|S\rangle$	$\langle S|\hat{H}|D\rangle$	$\langle S|\hat{H}|T\rangle$	0	$\dots$
$\langle D|$			$\langle D|\hat{H}|D\rangle$	$\langle D|\hat{H}|T\rangle$	$\langle D|\hat{H}|Q\rangle$	$\dots$
$\langle T|$				$\langle T|\hat{H}|T\rangle$	$\langle T|\hat{H}|Q\rangle$	$\dots$
$\langle Q|$					$\langle Q|\hat{H}|Q\rangle$	$\dots$
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$

- Double excitations couple directly to reference state
- All others couple indirectly (coupled linear equations)
- Strategy: Select important higher excitations !

Full-CI: the computational limitation

Full CI is the **most accurate** method for a define basis set
but, it can be applied only to v. small molecules.

Apply only a few type of excitations
CI-D
CI-SD
…

Apply all possible excitations inside a chosen window of energies around the gap
CAS

CAS

Combination of both

Moller-Plesset Perturbation Theory

Electron correlation:

$$V = \sum_{i<j} \frac{1}{r_{ij}} - \sum_{i} v^{HF}$$

- Principles:

  Idea: Electron correlation is a perturbation

  (<1% of total energy)

  Based on Rayleigh-Schrödinger PT

  Single-reference method !

  Size-consistent.

MPPT: Procedure

- Assume solution of zero-order problem (HF problem):

$$H_0 \Psi_0 = \sum_i f(i) \Psi_0 = E_0^{(0)} \Psi_0$$

- Definition of a perturbing potential :

$$V = \sum_{i<j} \frac{1}{r_{ij}} - \sum_i v^{HF}$$

- Total electronic Hamiltonian:

$$H = H_0 + V$$

- Apply Rayleigh-Schrödinger PT

$$E_i^{(2)} = \sum_{n \neq i} \frac{\left| \left\langle \Psi_i^{(0)} \left| \hat{V} \right| \Psi_n^{(0)} \right\rangle \right|^2}{E_i^{(0)} - E_n^{(0)}}$$

Density Functional Theory

- Total energy as functional of the electron density:
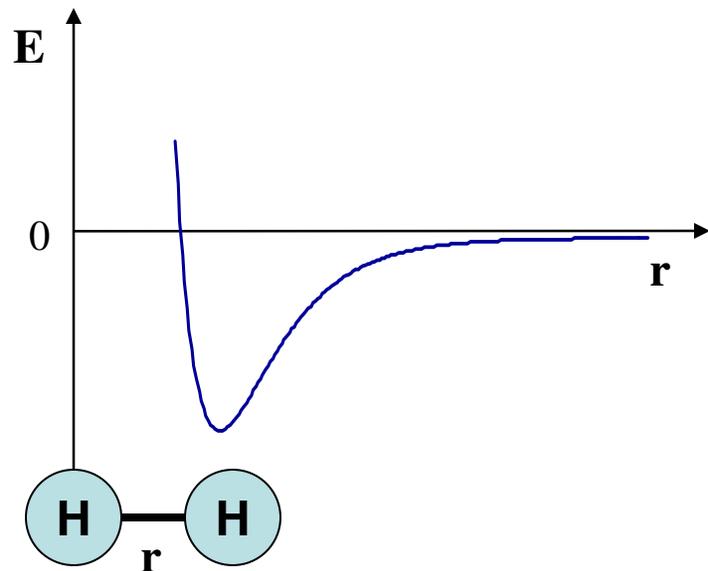
$$E[\rho] = T[\rho] + U[\rho] + E_{xc}[\rho]$$

$$p(r) = \sum_i \left| \varphi_i(r) \right| \qquad :\Phi = \text{occupied MOs}$$

- T: Kinetic Energy
- U: Coulomb interactions
- xc: Exchange & correlation interactions

* Nobel price 1998

DFT: XC functionals

- **Local Density Approximation** (LDA)

  No gradient of electron density in E_{xc}

  Like a uniform electron gas !

- **Generalized Gradient Approximation** (GGA)

  Gradient corrected density

- **Hybrid Functionals**

  Becke (B) LYP, B3LYP functionals

  Contain a contribution of HF exchange interaction

Geometry optimization