Columbus in João Pessoa

COLUMBUS
IN JOÃO PESSOA
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João Pessoa - Paraíba
ONDE O SOL
NASCE PRIMEIRO!

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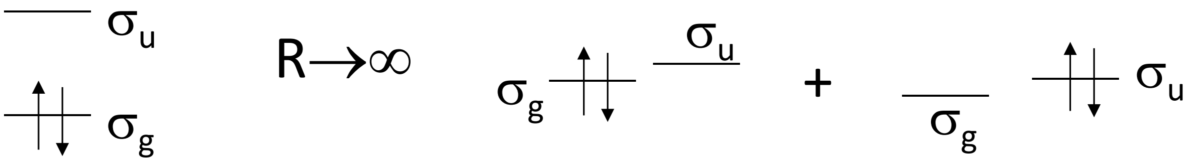
Why do we need Multireference Methods?

- Density functional theory (DFT)
- Møller-Plesset perturbation theory (MP2)
- Coupled cluster theory (CCSD(T))
- Semiempirical methods
- Why more???

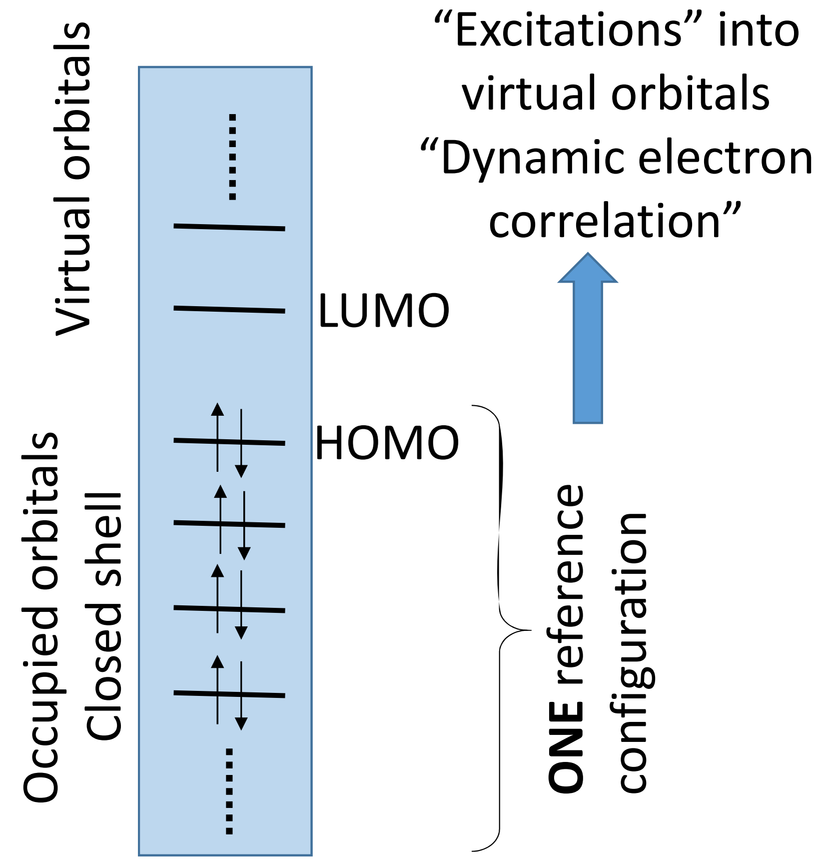
Simple Example: Bond Dissociation of H_2



Occupied and virtual orbitals are well separated

Occupied and virtual orbitals are quasi-degenerate

Generalization to Many Electrons



Virtual orbitals

LUMO

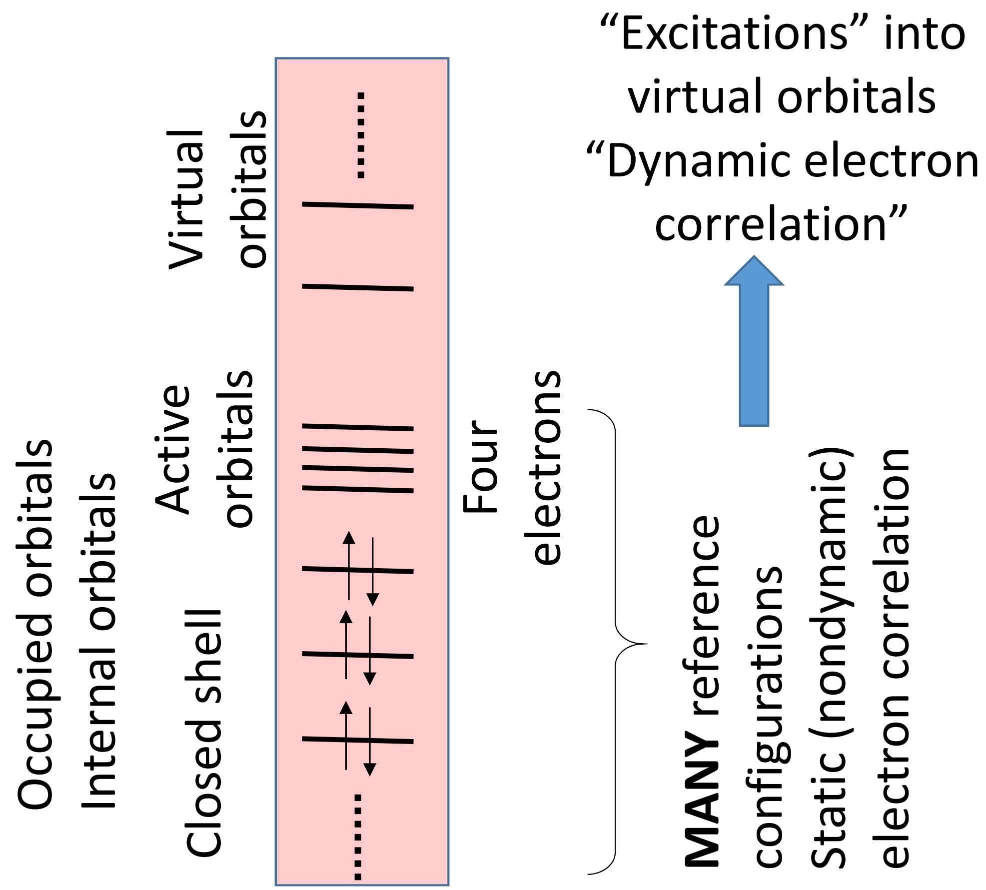
HOMO

Occupied orbitals
Closed shell

“Excitations” into virtual orbitals “Dynamic electron correlation”

ONE reference configuration

Automatic assignment of orbitals possible



Virtual orbitals

Active orbitals

Four electrons

Occupied orbitals
Internal orbitals

Closed shell

“Excitations” into virtual orbitals “Dynamic electron correlation”

MANY reference configurations
Static (nondynamic) electron correlation

Automatic assignment of orbitals **NOT** generally possible

Single Reference Configuration Interaction (SRCI)

Excitation (substitution) of occupied orbitals by virtual ones

$\left\|\Phi_1\overline{\Phi}_1\ldots\Phi_i\overline{\Phi}_i\ldots\Phi_n\overline{\Phi}_n\right\|$	Closed shell determinant
$\Big\downarrow \quad \Phi_i \rightarrow \Phi_a$	Excitation (or substitution) of occupied orbital Φ_i by virtual orbital Φ_a
$\left\|\Phi_1\overline{\Phi}_1\ldots\Phi_a\overline{\Phi}_i\ldots\Phi_n\overline{\Phi}_n\right\|$	Singly excited configuration Ψ_i^a

Single-, double-, triple- … m-tuple excitations

$$\Psi_i^a, \Psi_{ij}^{ab}, \Psi_{ijk}^{abc} \ldots$$

Method of configuration interaction (CI):

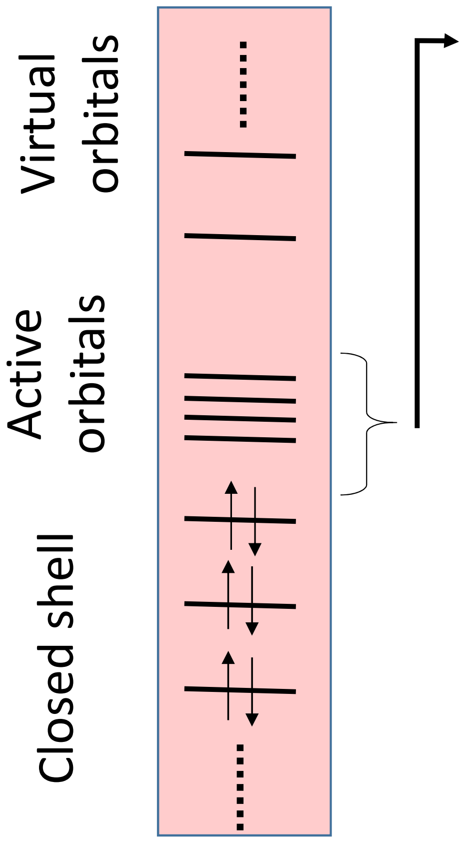
$$\Psi_{\mathrm{SR-C}I} = c_0\Psi_0 + \sum_{i,a} c_i^a \Psi_i^a + \sum_{i,j,a,b} c_{ij}^{ab}\Psi_{ij}^{ab} + \ldots$$

Variation principle (Ritz) is used to determine the coefficients and the energy

Note: Orbitals are usually taken from SCF calculation

Multireference Configuration Interaction (MRCI)

Orbital scheme



Reference wave function Ψ_0: $\Psi_1 \ldots \Psi_{N_{ref}}$

m-tuple excitations from $\Psi_i, i = 1 \ldots N_{ref}$

into the virtual orbitals creates a set of

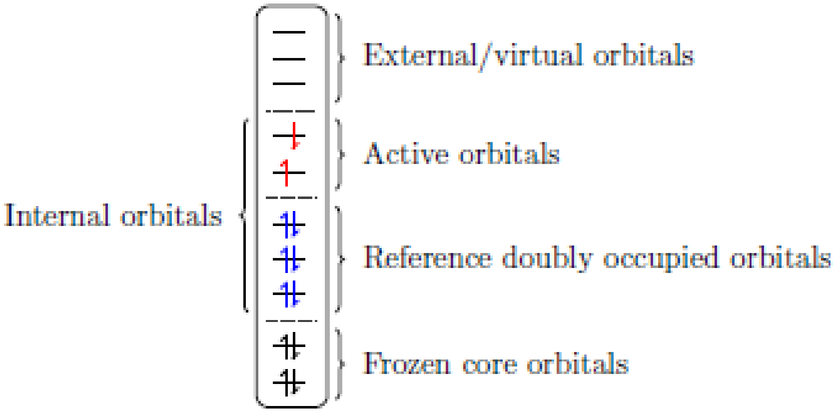
configurations $\{\Psi_I\}$

$$\Psi_{\mathrm{MR-CI}} = \sum c_I \Psi_I$$

Application of the Ritz variation principle leads to the MR-CI method.

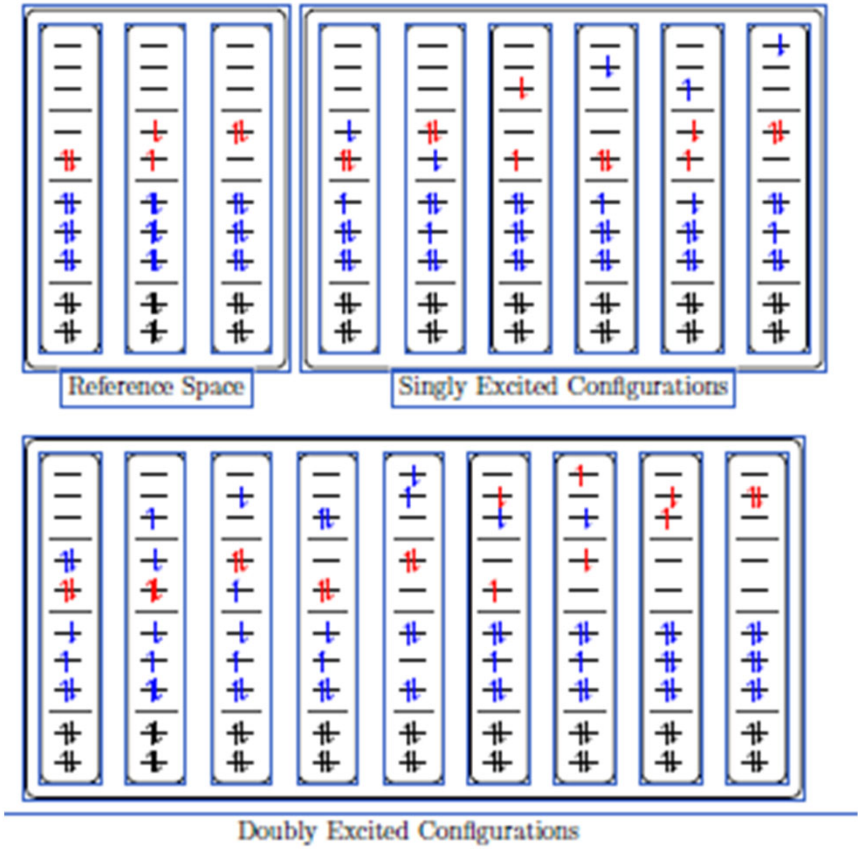
Standard approach: inclusion of single (S) and double (D) excitations

$$\Psi_{\mathrm{MRCI}} = \sum_{k=1}^{N_{\mathrm{ref}}} c_k^{\mathrm{ref}} \left| \Psi_k^{\mathrm{ref}} \right\rangle + \sum_l c_l^S \left| \Psi_l^S \right\rangle + \sum_m c_m^D \left| \Psi_m^D \right\rangle$$



Excitation scheme:

- refdocc →active
- active → virtual
- refdocc → virtual
- active → active



Multiconfiguration SCF (MCSCF)

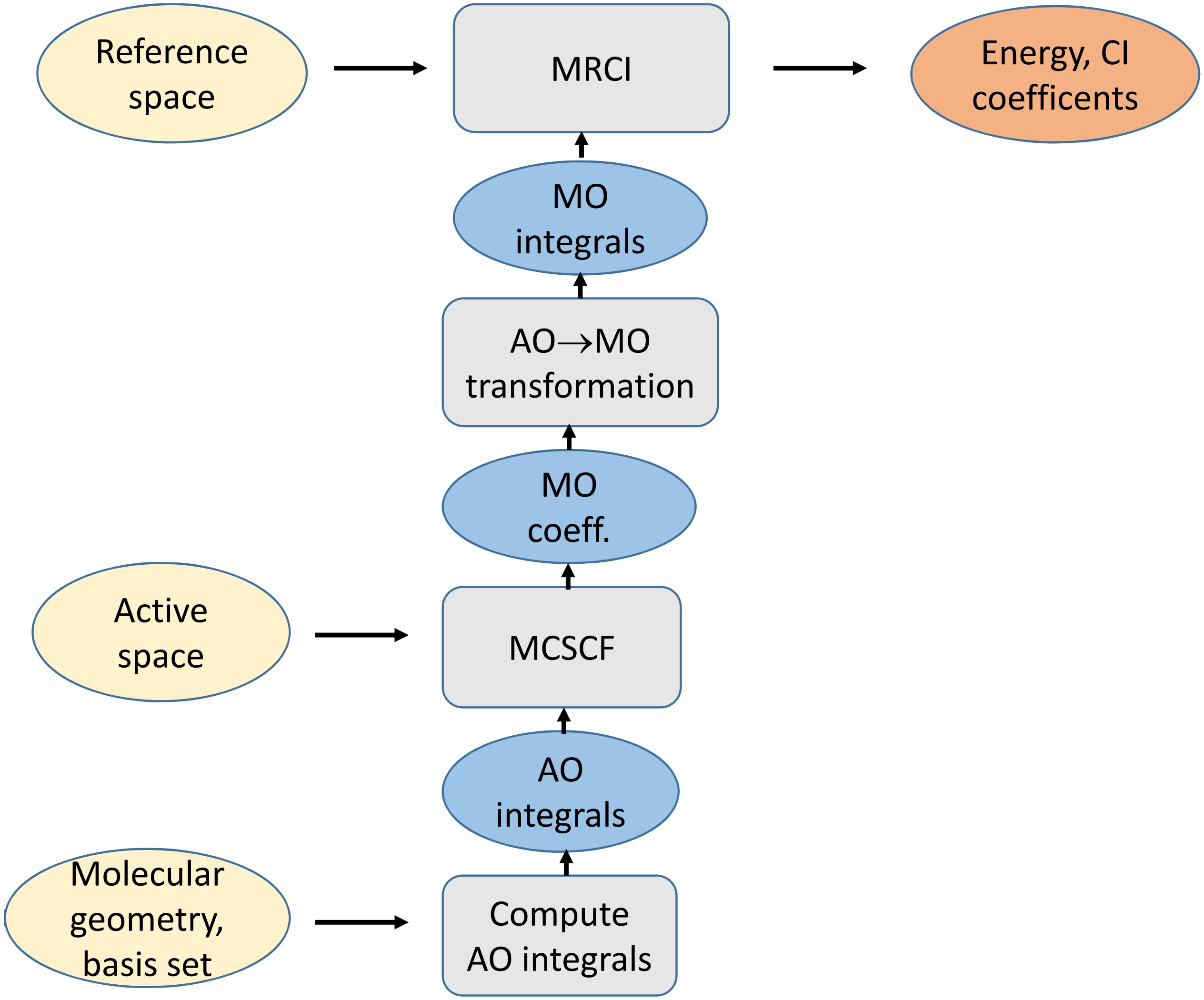
- Approach used to compute molecular orbitals (MOs) for MRCI
- Independent calculations
- Wavefunction as in MRCI:

$$\Psi_{\mathrm{MCSCF}} = \sum_{k=1}^{N_{\mathrm{MCSCF}}} c_k^{\mathrm{MCSCF}} \left| \Psi_k^{\mathrm{MCSCF}} \right\rangle$$

- In many cases the MCSCF expansion will be identical to the reference space of MRCI
- Important: the configurations are constructed from MOs, the MOs are expanded in a basis set (like SCF MOs)

$$\Phi_i = \sum_{\mu=1}^{N_{\mathrm{bas}}} d_{\mu i} \chi_\mu$$

Simultaneous optimization of the wavefunction expansion coefficients c_k^{MCSCF} and MO coefficients $d_{\mu i}$



Reference space

MRCI

Energy, CI coefficents

MO integrals

AO→MO transformation

MO coeff.

Active space

MCSCF

AO integrals

Molecular geometry, basis set

Compute AO integrals

Types of MRCI: uncontracted or contracted

$$\Psi_{\text{MRCI}} = \sum_{k=1}^{N_{\text{ref}}} \underset{\big\uparrow}{c_k^{\text{ref}}} \left|\Psi_k^{\text{ref}}\right\rangle + \sum_{l} c_l^{S} \left|\Psi_l^{S}\right\rangle + \sum_{m} c_m^{D} \left|\Psi_m^{D}\right\rangle$$

- Free variation, more flexible, more expensive
- Contraction, computationally faster

Truncation of MRCI leads to size extensivity errors: correlation energy does not scale correctly with size of the system

MR averaged quadratic coupled cluster method: size extensivity corrections

References

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  To be published soon