

An Introduction into Multireference Theory

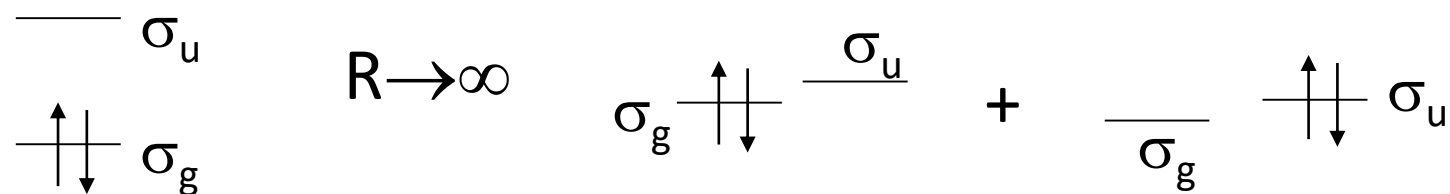
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Why do we need Multireference Methods?

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

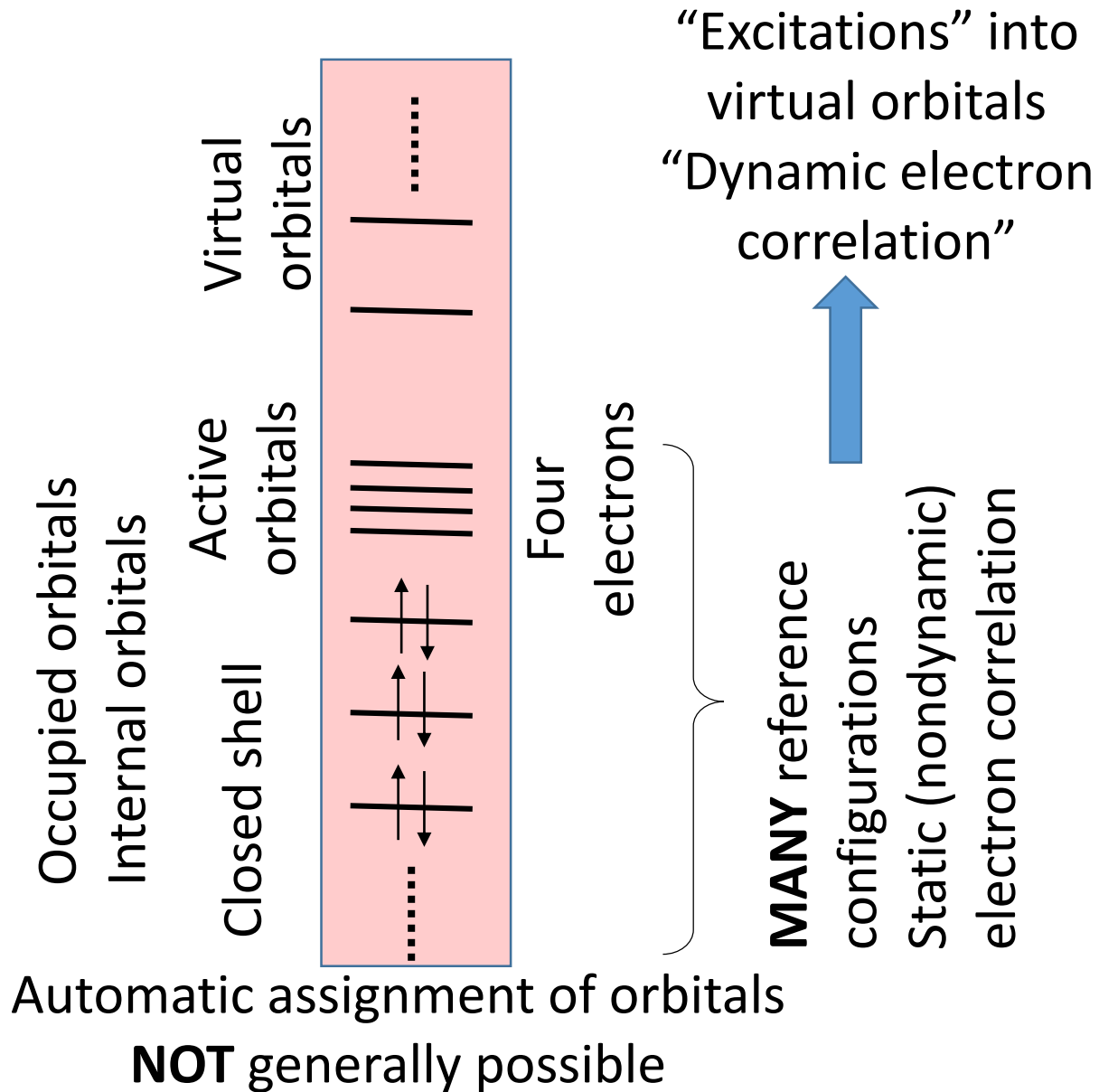
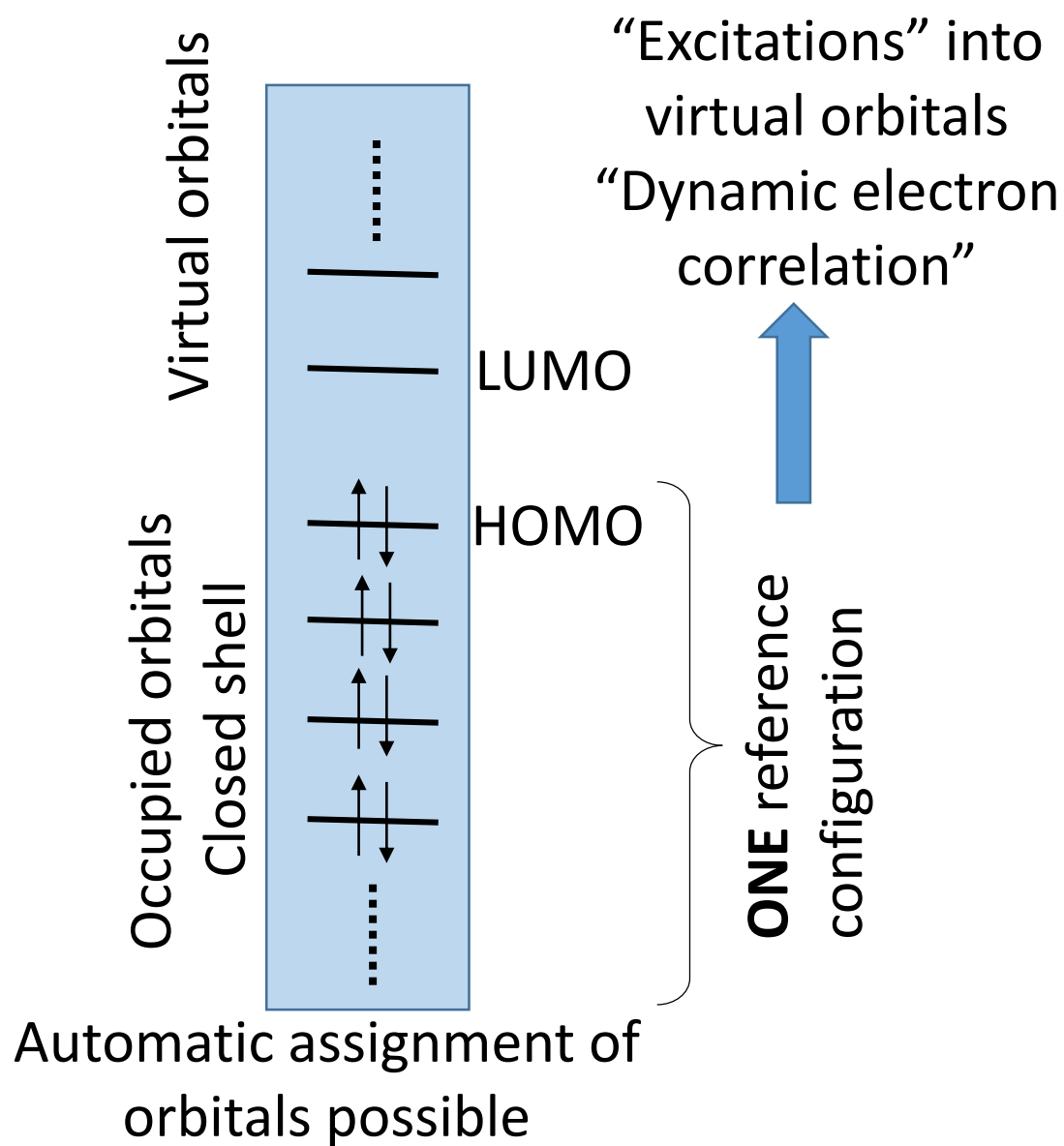
Simple Example: Bond Dissociation of H₂



Occupied and virtual orbitals are well separated

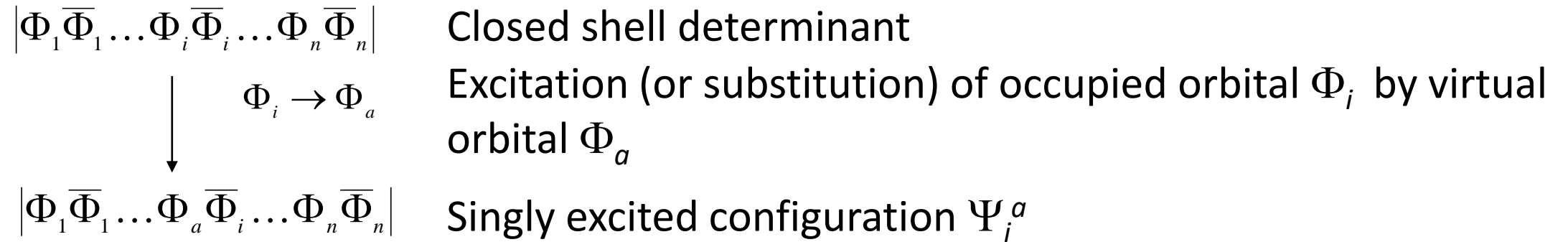
Occupied and virtual orbitals are quasi-degenerate

Generalization to Many Electrons



Single Reference Configuration Interaction (SRCI)

Excitation (substitution) of occupied orbitals by virtual ones



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

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

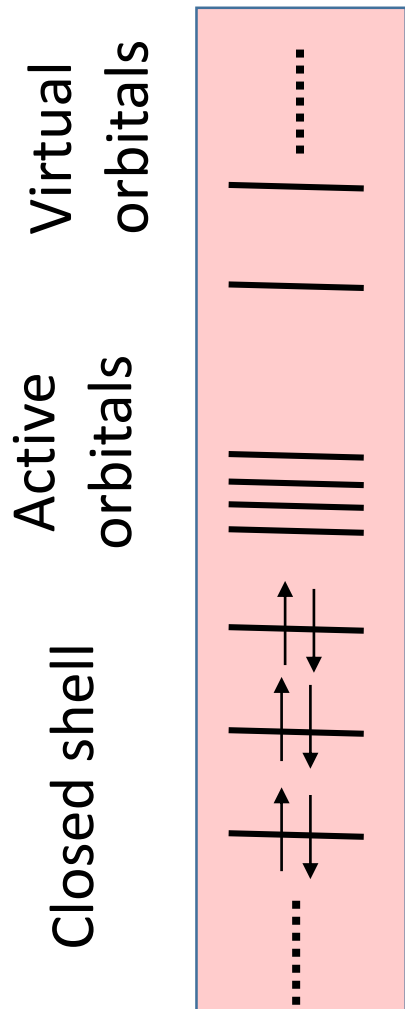
Method of configuration interaction (CI):

$$\Psi_{\text{SR-CI}} = c_0 \Psi_0 + \sum_{i,a} c_i^a \Psi_i^a + \sum_{i,j,a,b} c_{ij}^{ab} \Psi_{ij}^{ab} + \dots \quad \text{Variation principle (Ritz) is used to determine the coefficients and the energy}$$

Note: Orbitals are usually taken from SCF calculation

Multireference Configuration Interaction (MRCI)

Orbital scheme



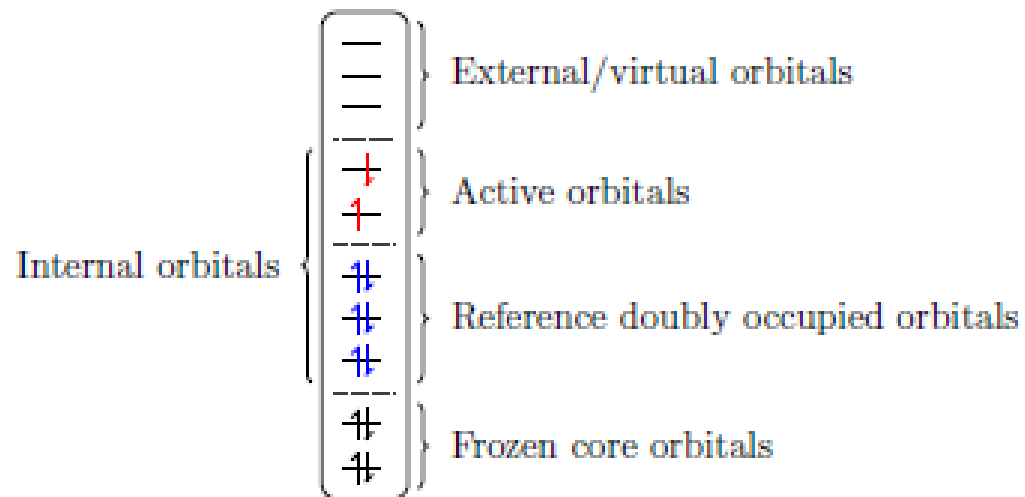
Reference wave function $\Psi_0: \Psi_1 \dots \Psi_{N_{ref}}$
 m-tuple excitations from $\Psi_i, i = 1 \dots N_{ref}$
 into the virtual orbitals creates a set of
 configurations $\{\Psi_I\}$

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

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

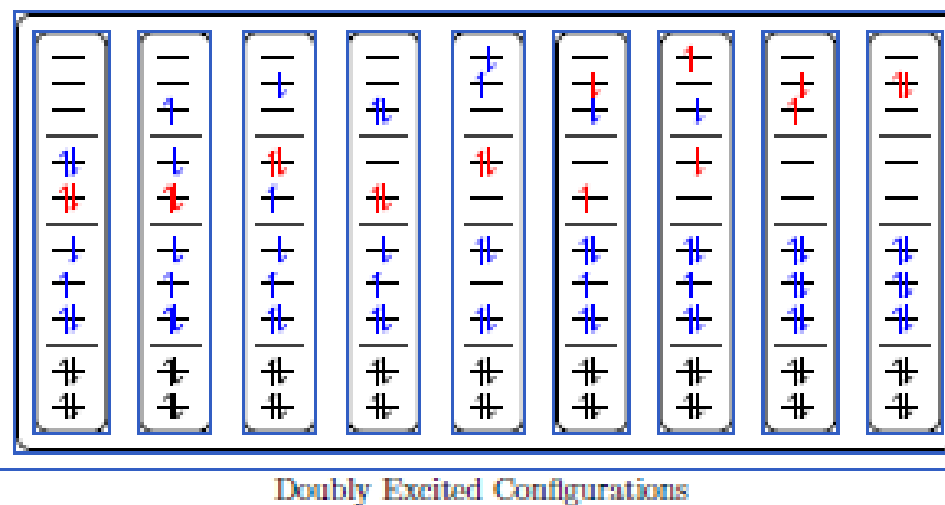
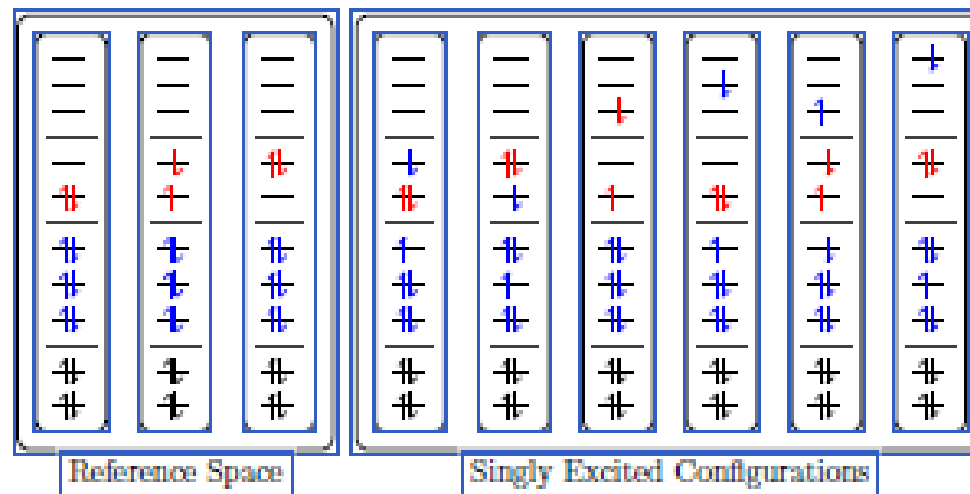
Standard approach: inclusion of single (S) and double (D) excitations

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



Excitation scheme:

- refdocc \rightarrow active
- active \rightarrow virtual
- refdocc \rightarrow virtual
- active \rightarrow active



Multiconfiguration SCF (MCSCF)

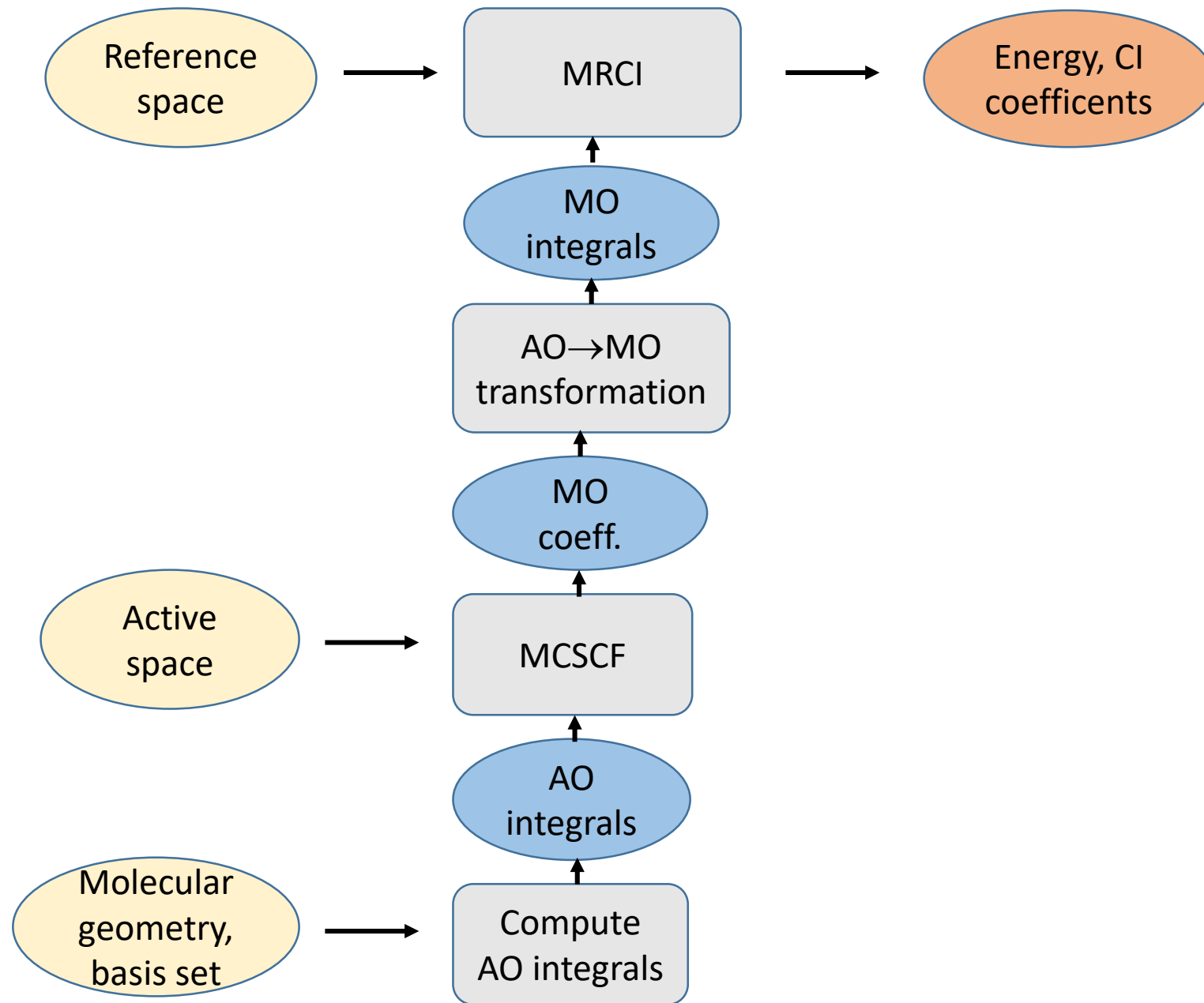
- Approach used to compute molecular orbitals (MOs) for MRCI
- Independent calculations
- Wavefunction as in MRCI:

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

- 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)

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

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



Types of MRCI: uncontracted or contracted

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

- 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 (MR-AQCC) method: size extensivity corrections

Ritz Variational Principle

$$H|\Psi^\alpha\rangle = E^\alpha|\Psi^\alpha\rangle \quad \text{Schrödinger equation}$$

$$|\Psi^\alpha\rangle = \sum_{k=1}^{N_{\text{CI}}} c_k^\alpha |\psi_k\rangle \quad \text{CI expansion}$$

$$\sum_{k=1}^{N_{\text{CI}}} c_k^\alpha H|\psi_k\rangle = \sum_{k=1}^{N_{\text{CI}}} c_k^\alpha E^\alpha |\psi_k\rangle \quad \text{Multiply from the left with } \psi_l \text{ and integrate}$$

$$\sum_{k=1}^{N_{\text{CI}}} c_k^\alpha \langle \psi_l | H | \psi_k \rangle = \sum_{k=1}^{N_{\text{CI}}} c_k^\alpha E^\alpha \langle \psi_l | \psi_k \rangle \quad \text{using } \langle \psi_l | \psi_k \rangle = \delta_{kl} \\ \text{and } H_{kl} = \langle \psi_l | H | \psi_k \rangle$$

$$\sum_{k=1}^{N_{\text{CI}}} H_{lk} c_k^\alpha = E^\alpha c_l^\alpha \quad \Rightarrow \quad \mathbf{H}\mathbf{c}^\alpha = E^\alpha \mathbf{c}^\alpha$$

Strategy for Multibillion CI calculations

Solving for individual eigenstates: “Davidson subspace method”¹⁾

Projection of the Hamiltonian matrix \mathbf{H} into a set of an increasing number of subspace expansion vectors \mathbf{v}_i leading to smaller matrices $\tilde{\mathbf{H}}$ and solve the smaller eigenvalue problems until convergence is achieved.

$$\tilde{H}_{st} = \mathbf{v}_s^t \mathbf{H} \mathbf{v}_t$$

The main computational step is the matrix-vector product $\mathbf{w}_j = \mathbf{H} \mathbf{v}_j$.

Direct CI (Roos): “on-the-fly” calculation of the contributions to the matrix-vector product

¹⁾ E. R. Davidson, J. Comp. Physics **17**, 87, 1975

Classification and Organization of Different Terms

$$H_{st} = \langle \psi_s | H | \psi_t \rangle = \sum_{ij} a_{ij}^{st} h_{ij} + \sum_{ijkl} b_{ijkl}^{st} g_{ijkl}$$

Indices i, j, k, l run over the number of orbitals.

$h_{ij} = \langle \phi_i | h | \phi_j \rangle$ and $g_{ijkl} = \langle \phi_i \phi_k | 1 / r_{12} | \phi_j \phi_l \rangle$ are the one- and two-electron integrals and a_{ij}^{st} and b_{ijkl}^{st} are coupling coefficients.

The matrix-vector product can be written as

$$w_s = \sum_t \sum_{ij} a_{ij}^{st} h_{ij} v_t + \sum_t \sum_{ijkl} b_{ijkl}^{st} g_{ijkl} v_t$$

Calculation of coupling coefficient using the **Graphical Unitary Group Approach (GUGA)**^{1,2)}

Graphical representation of a **Distinct Row Table (DRT)**

Reference configurations in red

Inactive (reference doubly occupied)

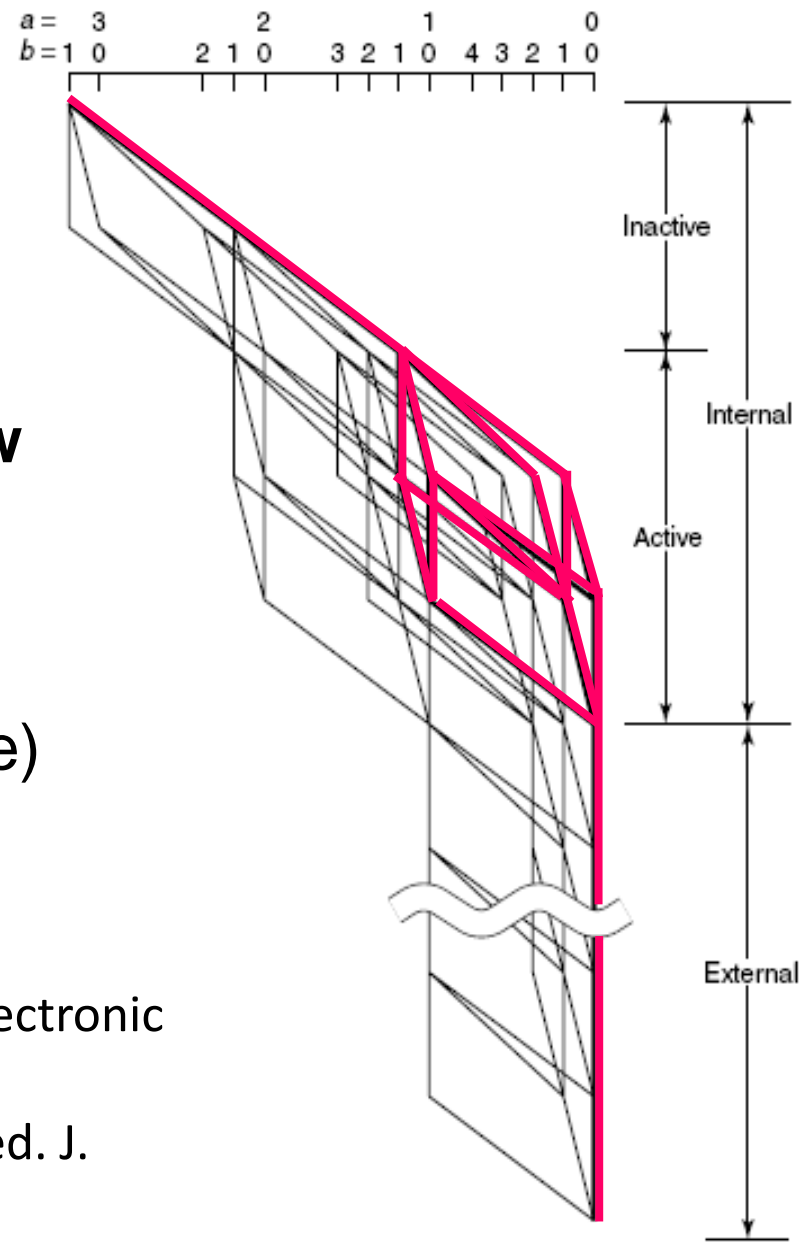
Active (variable occupation in the reference)

External (virtual) orbitals: only singles and doubles

¹⁾Paldus, J., J. Chem. Phys. **61**, 5321-5330, 1974

Shavitt, I., in: The Unitary Group for the Evaluation of Electronic Energy

²⁾Matrix Elements, Lecture Notes in Chemistry, vol. 22 (ed. J. Hinze), 51–99. Berlin: Springer, 1981



Step Vector

$d_i = 0 \Rightarrow$ orbital i is unoccupied (uo)

$d_i = 1,2 \Rightarrow$ orbital i is singly occupied (so)

$d_i = 3 \Rightarrow$ orbital i is doubly occupied (do)

Example:

Orbital 1 2 3 4 5 6

Step vector **1** **0** **3** **1** **0** **2**

so uo do so uo so

- The internal (active + closed shell) part of the graph is complicated, but relatively small in comparison to the virtual (external) space.
- The graph for the external space is very simple due to the fact that we allow only double excitations. Moreover, its structure is independent of the internal part. Respective loops (coupling elements) can be computed once and for all.
- The interface between internal and external space is given by the vertices Z (0-excitations), Y (single-excitations), X (double excitations, triplet coupling) and W (double excitations, singlet coupling)

- The loops are split into an internal part and into an external one. The internal part is computed explicitly and either stored on a file (formula file) or recomputed every Davidson iteration. The external part is added “on-the-fly” when the total coupling elements are computed.
- The two-electron integrals are sorted according to the number of internal indices: all (four)-internal, three-internal, two-internal, one internal and all-external.

Analytic MRCI energy Gradients

Basic formalism:

R. Shepard, H. Lischka, P. G. Szalay, T. Kovar and M. Ernzerhof, J. Chem. Phys. **96**, 2085, 1992

Applicable to general MR wavefunctions

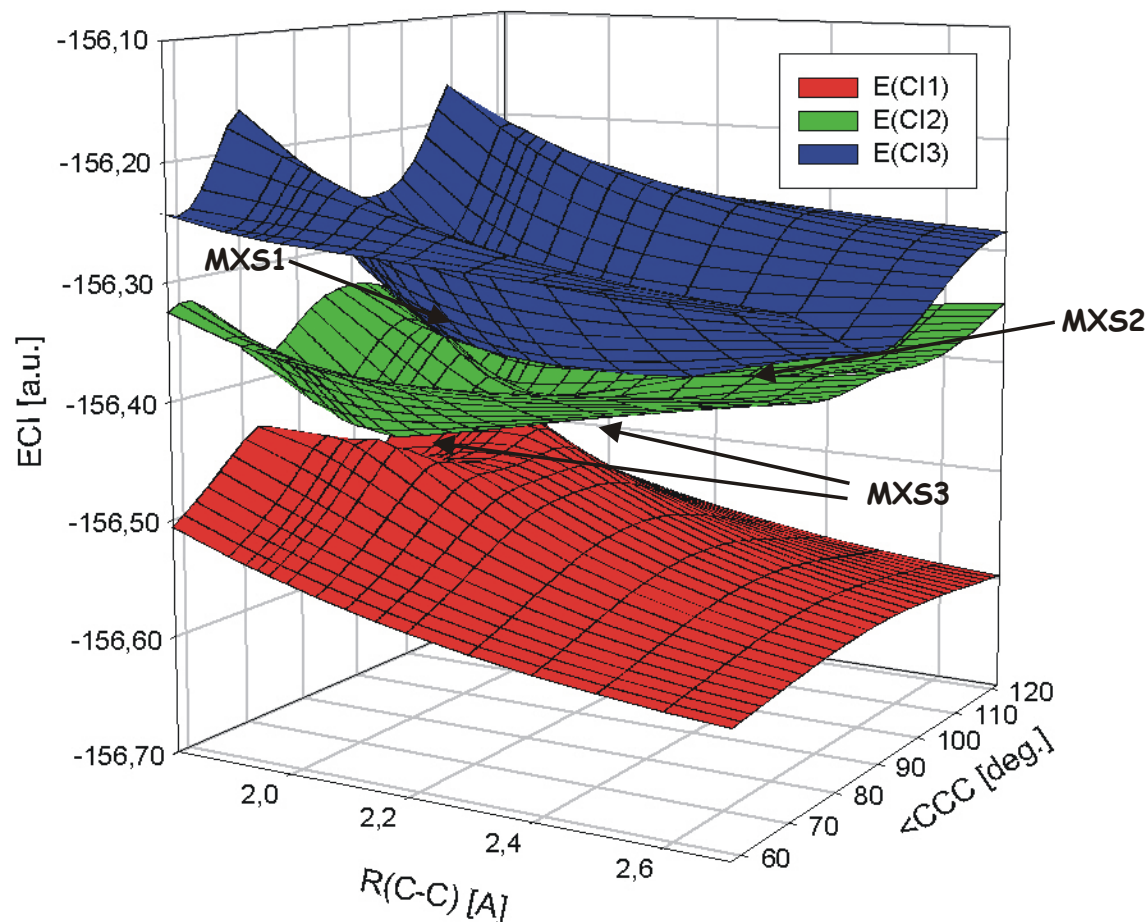
Extension to excited states

H. Lischka, M. Dallos and R. Shepard

Mol. Phys. **100**, 1647, 2002

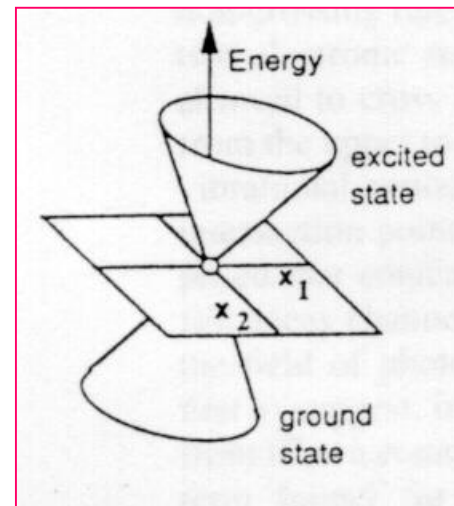
Based on state-averaged MCSCF calculation

Conical Intersection of Energy Surfaces

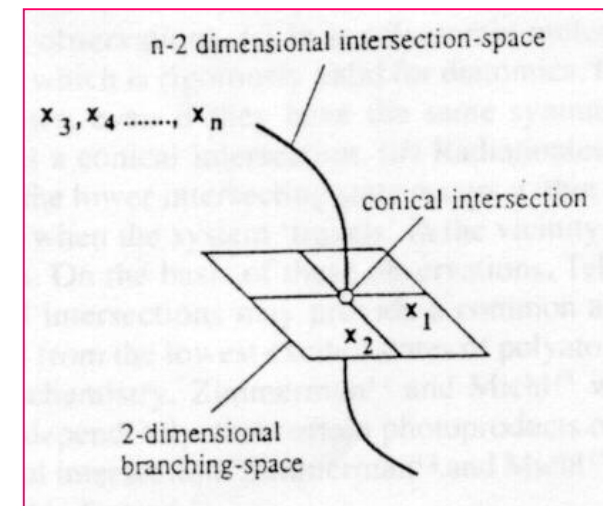


Example: Ethylene dimerization

Conical intersection Branching space



Intersection space



$$\mathbf{x}_1 = \frac{\partial(E_1 - E_2)}{\partial \mathbf{q}}, \quad \mathbf{x}_2 = \left\langle \mathbf{C}'_I \left(\frac{\partial H}{\partial \mathbf{q}} \right) \mathbf{C}_{II} \right\rangle$$

Search for minima on the crossing seam (MXS)

References

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