

Multireference methods and Nonadiabatic Effects

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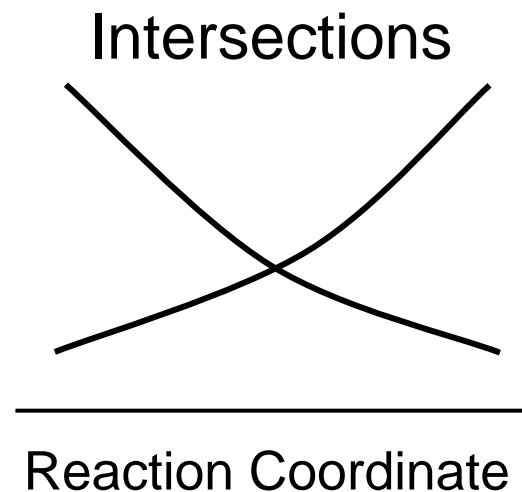
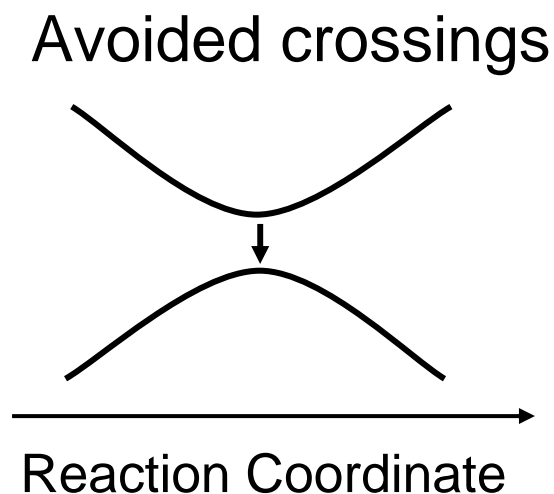


Contents

- Basic properties of conical intersections
 - Intersection seam
 - Minimum on the crossing seam (MXS)
- Born-Oppenheimer Approximation and nonadiabatic couplings
- Quantum Chemical Methods
 - What are multireference methods
 - Multiconfiguration self-consistent field and Multireference configuration interaction
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 - Definition of internal orbital spaces

Avoided Crossings vs. Conical Intersections

How does the electronically excited system return to the ground state?



Van der Lugt and Oosterhoff (1969): Photchemistry is dominated by avoided crossing

> 1990: **conical intersections are the rule not the exception**

Conditions for Intersections

v. Neumann und Wigner 1929^a:

- Real, symmetric matrix depending on a set of parameters (e.g. internal coordinates)
- What are the conditions that two eigenvalues coincide?
- **Two degrees of freedom** are necessary to achieve degeneracy

^aPhysik. Zeitschrift XXX, 467, 1929

Non-crossing Rule

Following v. Neumann und Wigner: Teller 1937^a, Herzberg and Longuet-Higgins 1963^b

All but two eigenstates are known

$$\begin{aligned} & \varphi_1, \varphi_2, \Psi_3, \dots, \Psi_n \\ & \Psi = c_1 \varphi_1 + c_2 \varphi_2 \\ & \begin{pmatrix} H_{11} - E & H_{12} \\ H_{12} & H_{22} - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \end{aligned}$$

Condition of degeneracy:

$$\begin{aligned} \Delta H &= H_{11} - H_{22} = 0 \\ H_{12} &= 0 \end{aligned}$$

Diatomic Molecules: only one parameter is available \Rightarrow
Non-crossing rule

^a J. Phys. Chem. **41**, 109 (1937)

^b Disc. Faraday Soc. **35**, 77 (1963)

Conical Intersections

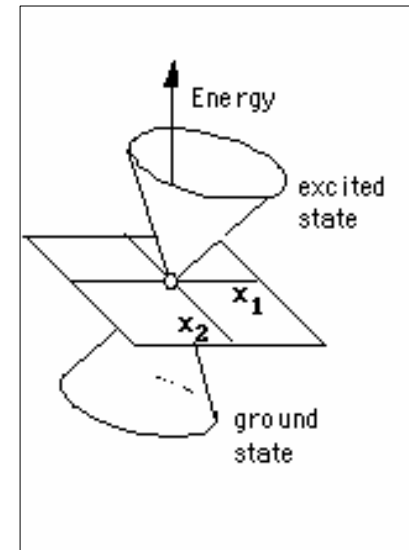
Linearized model:

$$\begin{pmatrix} W + (m+k)x_1 - E & lx_2 \\ lx_2 & W + (m-k)x_1 - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

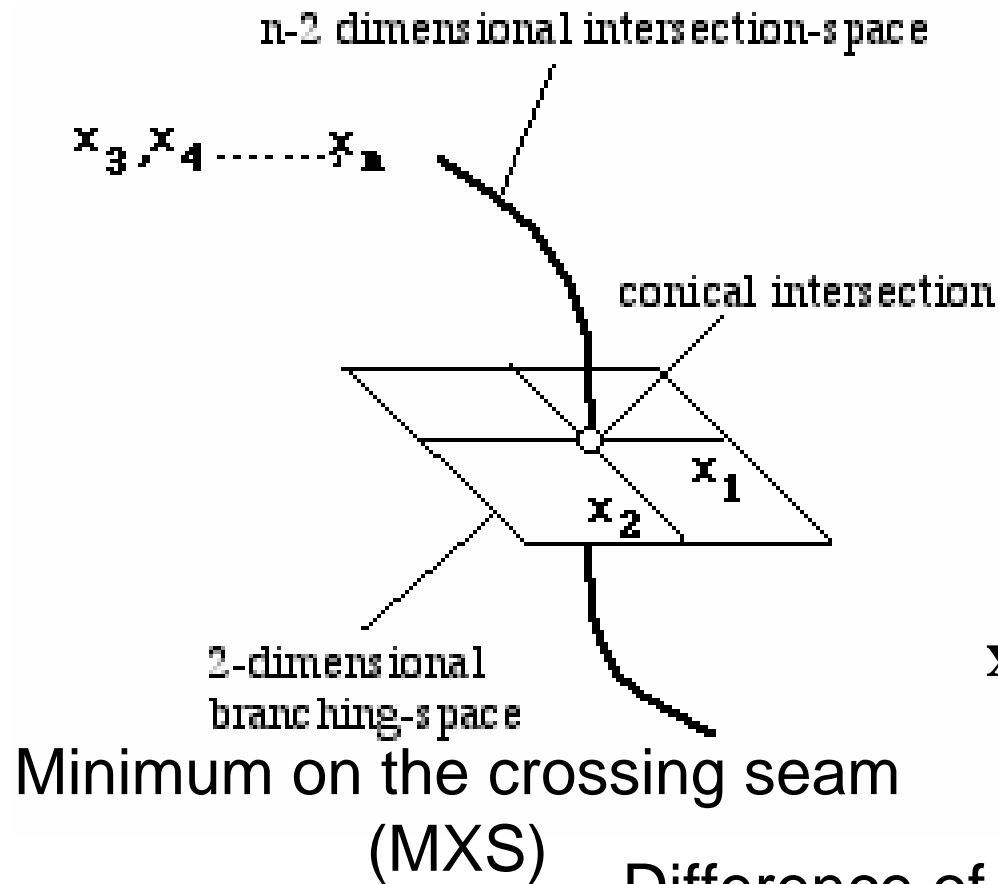
The solution of this eigenvalue equation leads to a double cone:

$$E = W + mx \pm \sqrt{k^2 x^2 + l^2 y^2}$$

Zimmermann 1966, Michl 1972: This cone can act as a **funnel** for a photochemical reaction:

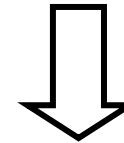


Intersection Seam



Linear approximation for the branching space:

$$\mathbf{x}_1 = \frac{\partial \Delta H(\mathbf{q})}{\partial \mathbf{q}}; \quad \mathbf{x}_2 = \frac{\partial H_{12}(\mathbf{q})}{\partial \mathbf{q}}$$

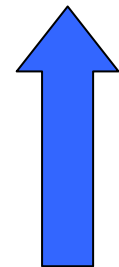


In MRCI language

$$\mathbf{x}_1 = \frac{\partial E_1 - \partial E_2}{\partial \mathbf{q}}; \quad \mathbf{x}_2 = \langle \Psi_1 | H^q | \Psi_2 \rangle$$



Difference of energy gradient vectors



Nonadiabatic coupling vector

Born-Oppenheimer Approximation and Nonadiabatic Coupling

Total Hamiltonian $H = T_{el} + T_N + V(r, R)$

Electronic Hamiltonian $H^{el} = T_{el} + V(r, R)$

Electronic Schrödinger Equation $(H^{el} - E_n^{el}(R))\phi_n(r, R) = 0$

Total Schrödinger Equation $(H - E)\Psi(r, R) = 0$

Total wavefunction $\Psi(r, R) = \sum_n \psi_n(R)\phi_n(r, R)$

Nonadiabatic Coupling

Coupled Equations

$$\left(T_N + E_m^{el}(R) - E\right)\psi_m(R) = \sum_n C_{mn}(R, P)\psi_n(R)$$

Single state

Coupling of States

Derivative coupling

$$C_{mn} = \sum_k \frac{1}{M_k} (A_{mn}^k P_k + B_{mn}^k)$$

$$A_{mn}^k(R) = \langle \phi_m(r, R) | P_k | \phi_n(r, R) \rangle$$

$$B_{mn}^k(R) = \frac{1}{2} \langle \phi_m(r, R) | P_k^2 | \phi_n(r, R) \rangle$$

Final Result

$$\phi_n(r, R) \text{ can be chosen to be real } \Rightarrow A_{mn}^k(R) = -\frac{i}{2} \frac{\partial}{\partial R_k} \int \phi_n^2(r, R) dr = 0$$

Schrödinger equation:

$$(T_N + U_m(R) - E) \psi_m(R) + \sum_{n \neq m} C_{mn}(R, P) \psi_n(R) = 0$$

with

$$U_m(R) = E_m^{el}(R) + \sum_k \frac{1}{M_k} B_{mm}^k$$

Coupling

Neglect of the coupling elements C_{mn} leads to the adiabatic approximation

$$(T_N + U_m(R) - E) \psi_m(R) = 0 \quad \text{Nuclear Schrödinger equation for one electronic state}$$

Neglect of B_{mm}^k to the Born-Oppenheimer approximation

Minimum on the Crossing Seam (MXS)

- N-2 fold dimensionality of the seam
- Minimum on the crossing seam (MXS)
 - Minimization under constraints^a
(Lagrange function)

$$L_{IJ}(\mathbf{R}, \xi) = E_I(\mathbf{R}) + \xi_1 \Delta E_{IJ}(\mathbf{R}) + \xi_2 H_{IJ}(\mathbf{R}) / 2$$

- Projection into N-2 dimensional subspace^b

^a M.R. Manaa und D.R. Yarkony, J. Chem. Phys. **99**, 5251 (1993)

^b M.J. Bearpark, M.A. Robb und B.H. Schlegel, Chem. Phys. Lett. **223**, 269 (1994)

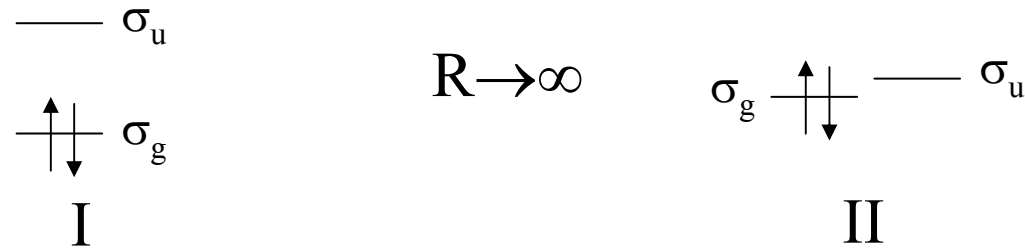
Quantum Chemical Methods for Excited States

	Analytic Gradient	Nonadiabatic Coupling
MCSCF	Yes	Yes
MR-CISD	Yes	Yes
ACPF/AQCC	Yes	No
CASPT2	Yes	No
EOM-CCSD/ RI-CC2	Yes	(Yes)
TDDFT	Yes	(Yes)

Why multireference methods: H₂ dissociation

Minimal basis: two orbitals - σ_g and σ_u , state Σ_g^+

MO scheme:



- $R \approx R_{\min}$: configuration I will be a qualitatively good representation
- $R \rightarrow \infty$: σ_u will become degenerate or quasi-degenerate, configuration I will not describe the system well, a second configuration, σ_u^2 , has to be taken into account.

MCSCF Approach

Single-configuration wave function: $\Psi_{\text{SR}} = |\Phi_1 \bar{\Phi}_1 \dots \Phi_i \bar{\Phi}_i \dots \Phi_n \bar{\Phi}_n|$

Multi-configuration wave function: $\Psi_{\text{MR}} = \sum c_I \Psi_I \{\Phi_i\}$

$\Phi_i = \sum_{j=1}^{N_{\text{BAS}}} d_{ji} \chi_j$, and $\{\chi_j\}$ is the atomic basis

In an MCSCF calculation **two types** of optimizations have to be performed:

- (i) w.r.t. the expansion coefficients of the Ψ_I and
- (ii) w.r.t. the MO coefficients d_{ji}

Result: MCSCF energies, MOs Φ_i

Single reference case (closed shell)

Reference wave function Ψ_0 :

$$\Psi_{\text{HF}} = |\Phi_1 \bar{\Phi}_1 \dots \Phi_n \bar{\Phi}_n|$$

excitation (substitution) of occupied orbitals by virtual ones

$$|\Phi_1 \bar{\Phi}_1 \dots \Phi_i \bar{\Phi}_i \dots \Phi_n \bar{\Phi}_n|$$

$$\downarrow \Phi_i \rightarrow \Phi_a$$

$$|\Phi_1 \bar{\Phi}_1 \dots \Phi_a \bar{\Phi}_i \dots \Phi_n \bar{\Phi}_n|$$

⋮
=

virtual orbitals

⋮
↑↓
↑↓
↑↓

doubly occupied orbitals

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

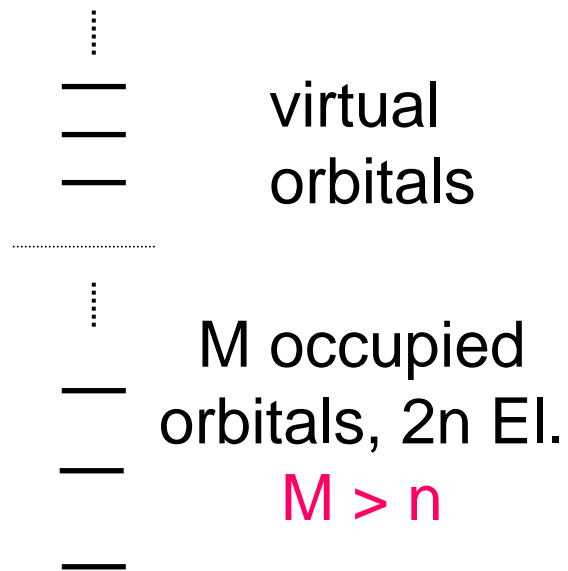
$$\Psi_i^a, \Psi_{ij}^{ab}, \Psi_{ijk}^{abc} \dots$$

Method of configuration interaction (CI):

$$\Psi_{\text{SR-CI}} = c_0 \Psi_0 + \sum_{i,a} c_i^a \Psi_i^a + \sum_{i,j,a,b} c_{ij}^{ab} \Psi_{ij}^{ab} + \dots$$

Variation principle (Ritz)

Multi-reference case



reference wave function Ψ_0 :

$$\Psi_1 \dots \Psi_{N_{ref}}$$

For each $\Psi_i, i = 1 \dots N_{ref}$
 S,D,T...excitations $\Phi_i \rightarrow \Phi_a$
 $\rightarrow \{\Psi_I\}$

MR-CI

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

Truncation to SD

MR-CISD

MR-CISD+Q (Davidson correction for Q)

Ritz Variational Principle

Expectation value $E[\Psi] = \langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle$

Linear ansatz for the trial function Ψ (Ritz variation principle)

$$\Psi = \sum_{s=1}^n c_s \Psi_s$$

leads to the following matrix eigenvalue problem

$$\mathbf{H}\mathbf{c}_i = E_i \mathbf{c}_i, \quad i = 1 \dots n$$

$$H_{st} = \langle \Psi_s | H | \Psi_t \rangle$$

and assuming orthonormality of the Ψ 's, i.e. $\langle \Psi_s | \Psi_t \rangle = \delta_{st}$

Dimension of \mathbf{H} : million, hundreds of millions, billion, hundreds of billions, 10^{24} ...

Davidson Subspace Method

Orthonormal subspace v_1, v_2, \dots, v_n

Expansion of the wave function in the subspace:

$$\Psi = \sum_{i=1}^n c_i v_i$$

n is increased in steps until convergence

Main computational step is: $\mathbf{w}_i = \mathbf{H}\mathbf{v}_i$

Matrix-vector product

Matrix-vector product

Matrix elements

$$\langle \Psi_s | H | \Psi_t \rangle = \sum_{ij} a_{ij}^{st} h_{ij} + \sum_{ijkl} b_{ijkl}^{st} g_{ijkl}$$

Orbital integrals h_{ij} and g_{ijkl} are defined by

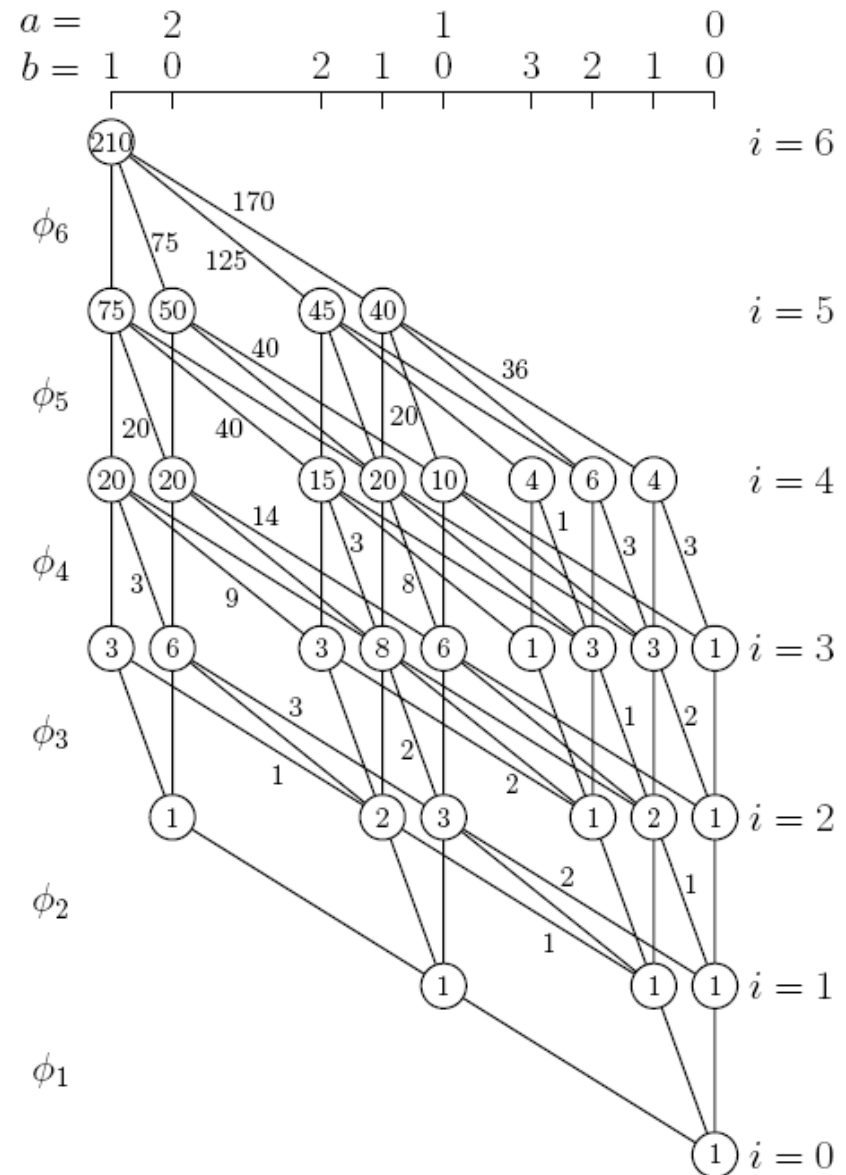
$$h_{ij} = (\varphi_i | h_1 | \varphi_j) \text{ and } g_{ijkl} = (\varphi_i \varphi_j | g_{12} | \varphi_k \varphi_l)$$

and

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

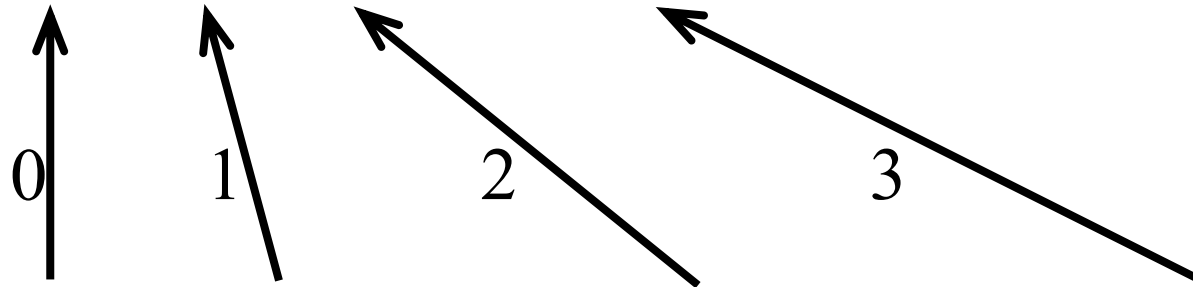
Graphical Unitary Group Approach (GUGA)

- Configuration State Functions (CSFs): spin adapted functions (not single determinants!)
- Distinct Row Table (DRT) and Shavitt Graph
- CSFs are presented as directed walks on this graph



What possibilities do we have to connect one node with another one above or below?
There are only 4 possibilities!

Different step numbers d_i are represented by arcs of different slope:



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

1 0 3 1 0 2

so uo do so uo so

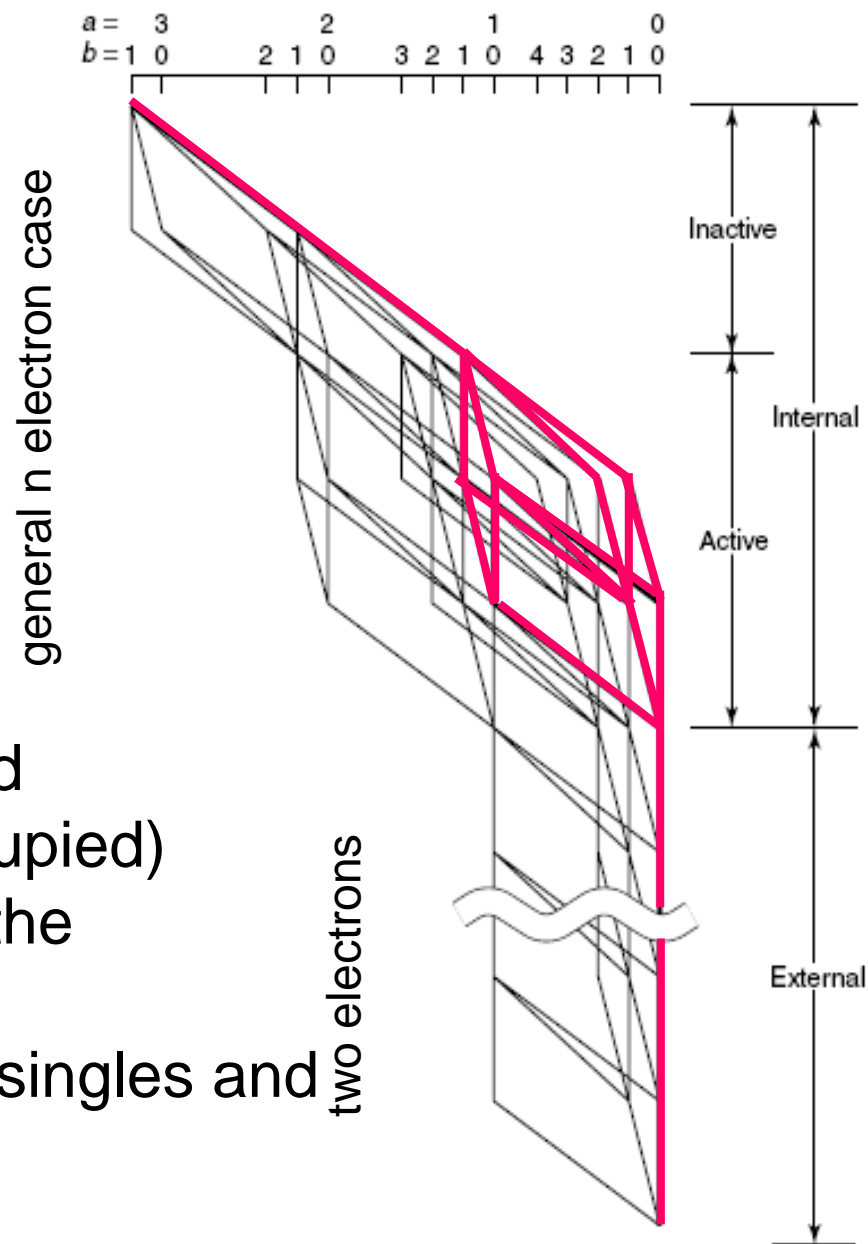


COLUMBUS Program System



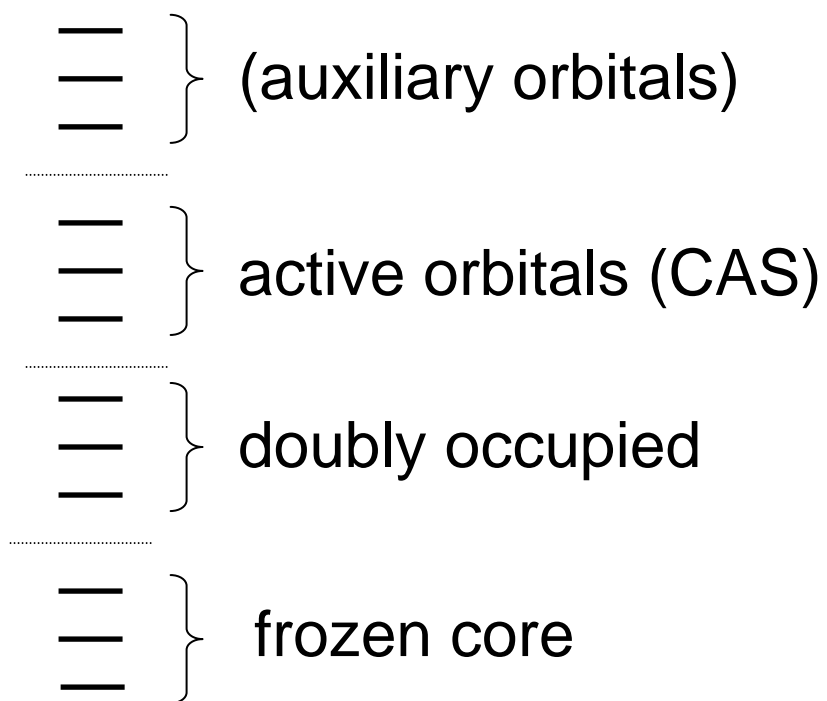
- Focus: multireference calculations on ground and excited states
- Methods: MCSCF, MR-CISD, MR-ACPF/AQCC, Spin-orbit CI
- **Analytic MR-CI gradients, nonadiabatic couplings, parallel CI**
- Authors: R. Shepard, I. Shavitt, R. M. Pitzer, H. Lischka
 - Vienna: M. Barbatti, M. Ruckebauer, J. Szymczak, B. Sellner
 - Budapest: P. G. Szalay
 - Jülich: Th. Müller
 - Columbus/Ohio S. Brozell, ...
- Web page: <http://www.univie.ac.at/columbus>

Multireference CI singles and doubles



Reference configurations in red
 Inactive (reference doubly occupied)
 Active (variable occupation in the reference)
 External (virtual) orbitals: only singles and doubles

Construction of reference wave functions



CAS: complete active space

COLUMBUS Input

- [Columbus Input Form](#)

COLUMBUS Input and Execution

Preparation of inputs

```
$COLUMBUS/colinp
```

Integral program input (basis set)

SCF input

MCSCF input

CI input

Set up job control

Program execution

```
$COLUMBUS/runc >&runls &
```

Input data

- Cartesian geometry
- number of electrons
- *orbital scheme including symmetry classification*

Results

LISTINGS

scfls

mcscfsm

ciudgsm

MOLDEN

molden molden.all