

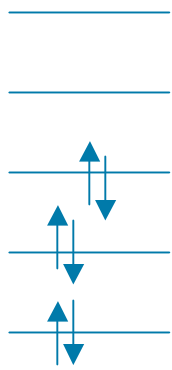
Electronic Structure for Excited States (multiconfigurational methods)

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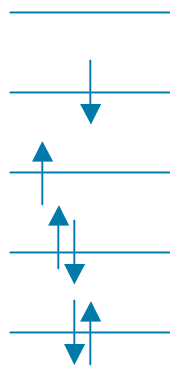
Excited Electronic States

- Theoretical treatment of excited states is needed for:
 - UV/Vis electronic spectroscopy
 - Photochemistry
 - Photophysics
- Electronic structure methods for excited states are more challenging and not at the same stage of advancement as ground state methods
 - Need balanced treatment of more than one states that may be very different in character
 - The problem becomes even more complicated when moving away from the ground state equilibrium geometry

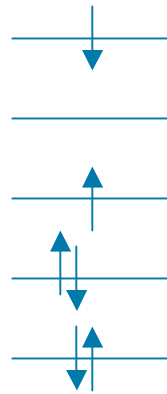
Excited states configurations



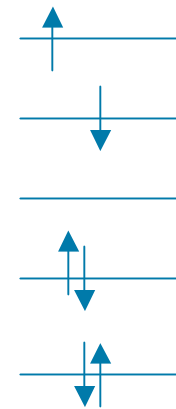
Ground state



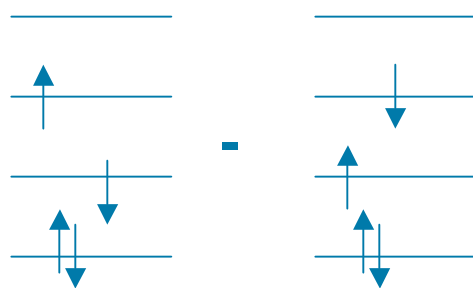
Singly excited conf.



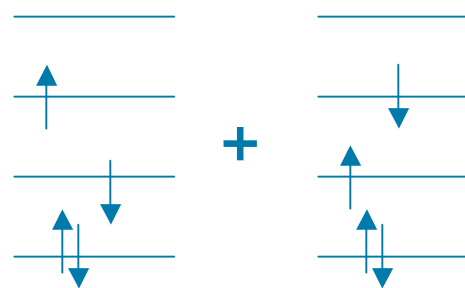
Doubly excited conf.



Configurations can be expressed as Slater determinants in terms of molecular orbitals. Since in the nonrelativistic case the eigenfunctions of the Hamiltonian are simultaneous eigenfunctions of the spin operator it is useful to use configuration state functions (CSFs)- spin adapted linear combinations of Slater determinants, which are eigenfunctions of S^2



Singlet CSF



Triplet CSF

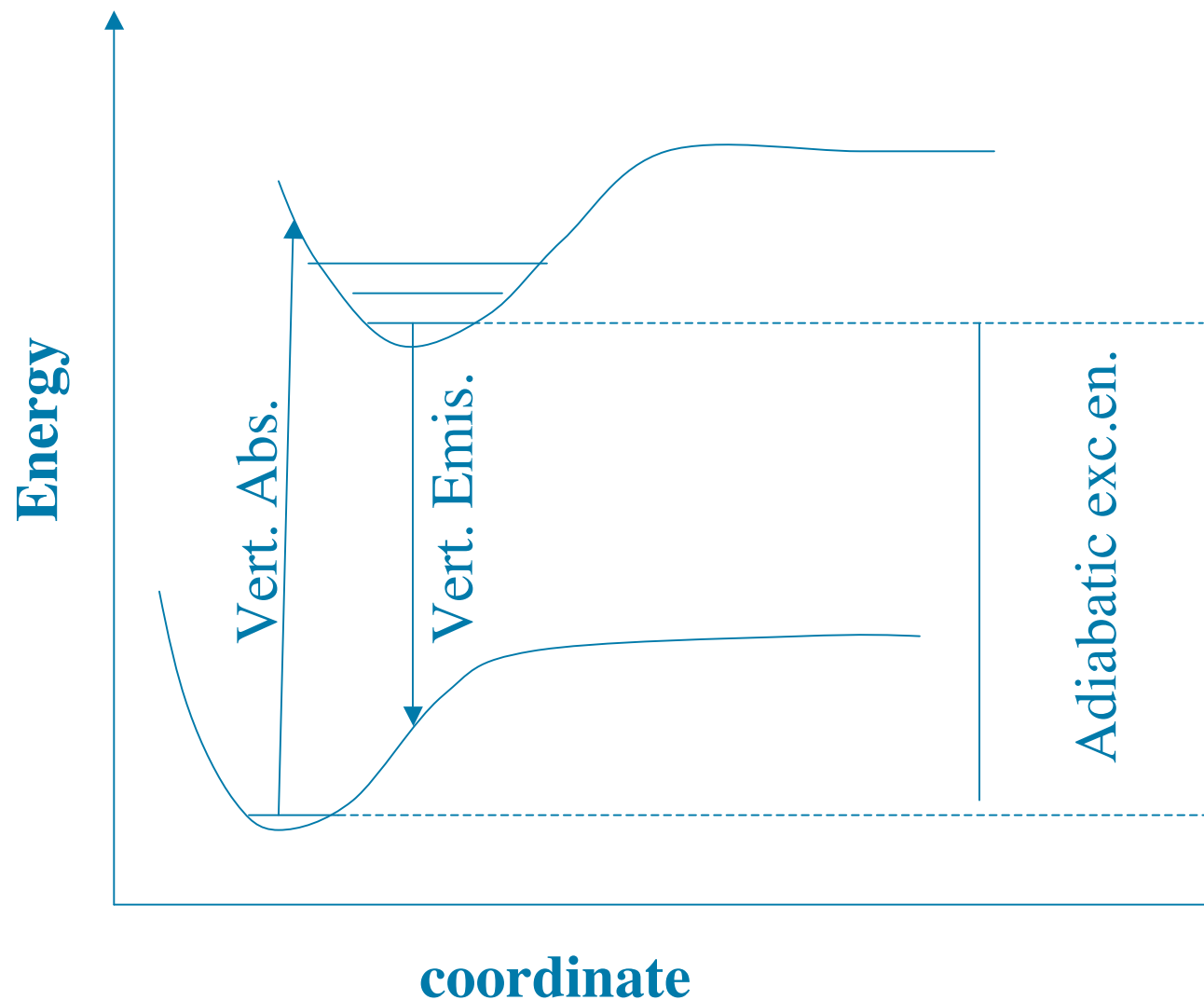
Excited states can have very different character and this makes their balanced description even more difficult. For example excited states can be:

- Valence states
- Rydberg states
- Charge transfer states

Rydberg states

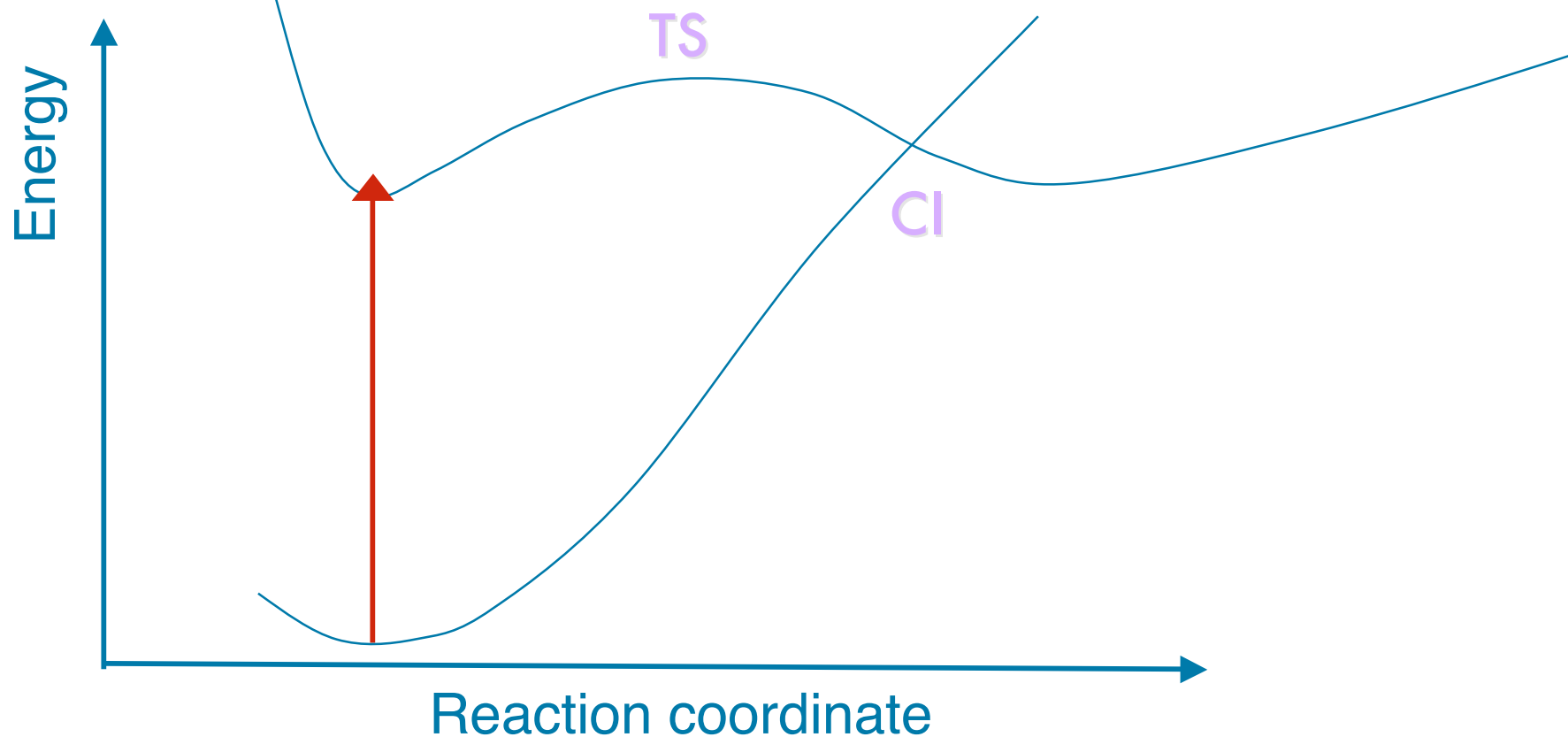
- Highly excited states where the electron is excited to a diffuse hydrogen-like orbital
- Low lying Rydberg states may be close to valence states
- Diffuse basis functions are needed for a proper treatment of Rydberg states, otherwise the states are shifted to much higher energies
- Diffuse orbitals need to be included in the active space or in a restricted active space (RAS)

Potential Energy Surfaces and Excited States



For absorption spectra one is interested in the Franck Condon (FC) region. In the simplest case a single point calculation is used to give vertical excitation energies

When one is interested in the photochemistry and photophysics of molecular systems the PES has to be explored not only in the FC region but also along distorted geometries. Minima, transition states, and conical intersections need to be found (gradients for excited states are needed)



Electronic structure methods for excited states

- Single reference methods
 - Δ SCF, Δ (DFT), Δ (CI),...
 - TDDFT
 - EOM-CCSD
- Multi-reference methods
 - MCSCF
 - CASPT2, MR-MP2
 - MRCI

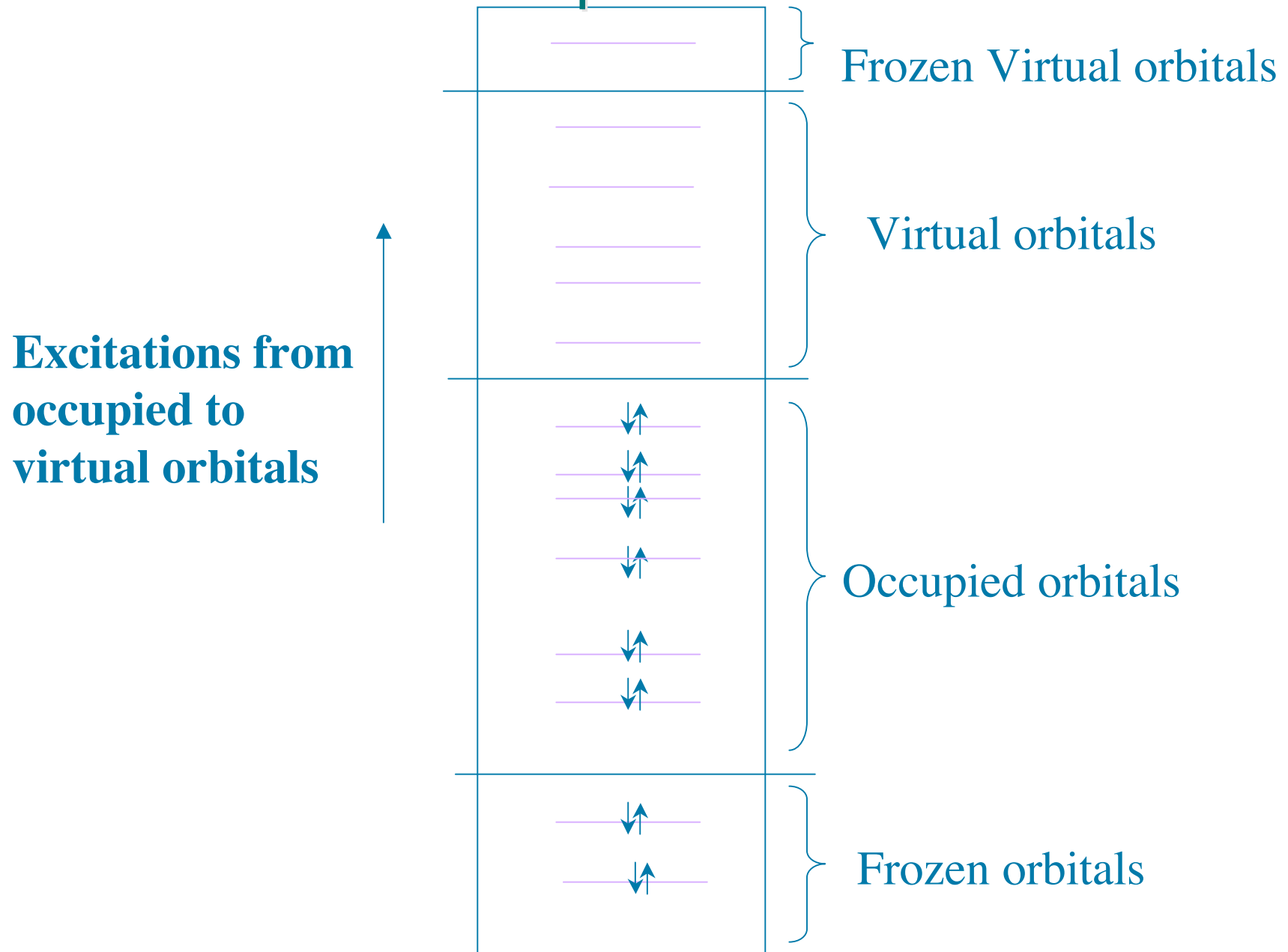
- In the simplest case one can calculate excited state energies as energy differences of single-reference calculations. $\Delta E = E(\text{e.s.}) - E(\text{g.s.})$. This can be done:
 - For states of different symmetry
 - For states of different multiplicity
 - Possibly for states that occupy orbitals of different symmetry

Configuration Interaction

- Initially in any electronic structure calculation one solves the HF equations and obtains MOs and a ground state solution that does not include correlation
- The simplest way to include dynamical correlation and improve the HF solution is to use configuration interaction. The wavefunction is constructed as a linear combination of many Slater determinants or configuration state functions (CSF). CI is a single reference method but forms the basis for the multireference methods

$$\Psi_{CI} = \sum_{m=1}^{N^{CSF}} c_m \Psi_m$$

Different orbital spaces in a CI calculation



CSFs are created by distributing the electrons in the molecular orbitals obtained from the HF solution.

$$\Psi_{CI} = c_0 |HF\rangle + \sum_i \sum_r^{occ. virt.} c_i^r \Psi_i^r + \sum_{i < j} \sum_{r < s}^{occ. virt.} c_{ij}^{rs} \Psi_{ij}^{rs} + \dots$$

The variational principle is used for solving the Schrodinger equation

$$\hat{H}\Psi = E\Psi$$

$$\hat{H} = \hat{T}^e + \hat{V}^{ee} + \hat{V}^{eN} + \hat{V}^{NN}$$

$$= \sum_i \frac{-1}{2m_e} \nabla_i^2 - \sum_{\alpha} \sum_i \frac{Z_{\alpha}}{r_{\alpha i}} + \sum_i \sum_{j>i} \frac{1}{r_{ij}} + \sum_{\alpha} \sum_{\beta>\alpha} \frac{Z_{\alpha} Z_{\beta}}{R_{\alpha\beta}}$$

$$= \sum_i \hat{h}_i + \sum_i \sum_{j>i} \frac{1}{r_{ij}} + \hat{V}_{NN}$$

$$E_{\text{var}} = \frac{\int \Psi^* \hat{H} \Psi d\tau}{\int \Psi^* \Psi d\tau} \geq 0$$

For a linear trial function the variational principle leads to solving the secular equation for the CI coefficients or diagonalizing the H matrix

Matrix formulation ($N^{\text{CSF}} \times N^{\text{CSF}}$)

$$\begin{vmatrix} H_{11} - E & H_{12} & \dots & H_{1N} \\ H_{21} & H_{22} - E & \dots & H_{2N} \\ \dots & \dots & \dots & \dots \\ H_{1N} & H_{2N} & \dots & H_{NN} - E \end{vmatrix} = 0$$
$$H_{mn} = \langle \Psi_m | H | \Psi_n \rangle$$

The Hamiltonian can be computed and then diagonalized. Since the matrices are very big usually a direct diagonalization is used that does not require storing the whole matrix.

Number of singlet CSFs for H2O with 6-31G(d) basis

| Excitation level | # CSFs | |
|------------------|----------|--|
| 1 | 71 | |
| 2 | 2556 | |
| 3 | 42596 | |
| 4 | 391126 | |
| 5 | 2114666 | |
| 6 | 7147876 | |
| 7 | 15836556 | |
| 8 | 24490201 | |
| 9 | 29044751 | |
| 10 | 30046752 | |

- (m,n): distribute m electrons in n orbitals

$$N = \frac{n!(n+1)!}{\left(\frac{m}{2}\right)!\left(\frac{m}{2}+1\right)!\left(n-\frac{m}{2}\right)!\left(n-\frac{m}{2}+1\right)!}$$

Today expansions with billion
of CSFs can be solved

| | Ψ_{HF} | singles | doubles | triples |
|-------------|-----------------------------------------------------------|-------------------------------------------------------------------|-----------------------------------------------------------|-------------------------------------------------------------------|
| Ψ_{HF} | E_{HF} | 0 | $\langle \Psi_{HF} H \Psi_{ij}^{rs} \rangle$ dense | 0 |
| CIS | 0 | $\langle \Psi_i^r H \Psi_j^s \rangle$ dense | $\langle \Psi_k^t H \Psi_{ij}^{rs} \rangle$ sparse | $\langle \Psi_{lm}^{qp} H \Psi_{ijk}^{rst} \rangle$ sparse |
| CISD | $\langle \Psi_{HF} H \Psi_{ij}^{rs} \rangle$ dense | $\langle \Psi_k^t H \Psi_{ij}^{rs} \rangle$ sparse | | |
| | 0 | $\langle \Psi_{lm}^{qp} H \Psi_{ijk}^{rst} \rangle$ sparse | | |

$$\langle \Psi_{HF} | H | \Psi_i^r \rangle = 0$$

Brillouin's thm

CIS will give excited states but will leave the HF ground state unchanged

Condon-Slater rules are used to evaluate matrix elements

$$\mathbf{H}\mathbf{t}_i = E_i \mathbf{t}_i$$

$$H_{ij} = \int \psi_i H \psi_j d\tau$$

$$\int \psi_0 H \psi_0 d\tau = E_{HF}$$

$$\int \psi_0 H \psi_i^a d\tau = 0 \quad (\text{Brillouin's theorem})$$

$$\int \psi_i^a H \psi_i^a d\tau = E_{HF} + \varepsilon_a - \varepsilon_i + (ia || ia)$$

$$\int \psi_i^a H \psi_j^b d\tau = (ja || ib) \quad (i \neq j, a \neq b)$$

$$\text{where } (pq || st) = \int \phi_p(1)\phi_q(2) \frac{1}{r_{12}} [\phi_s(1)\phi_t(2) - \phi_s(2)\phi_t(1)] d\tau$$

CIS

- For singly excited states
- HF quality of excited states
- Overestimates the excitation energies
- Can be combined with semiempirical methods

Table 14.2 Energies (eV) for singlet excited states of benzene relative to the $^1A_{1g}$ ground state as predicted by various methods^a

| Excited state | CIS | RPA | TD-BPW91 | TD-B3LYP | Expt. |
|------------------|------|------|----------|----------|-------|
| $^1B_{2u}$ | 6.15 | 5.96 | 5.19 | 5.40 | 4.9 |
| $^1B_{1u}$ | 6.31 | 6.01 | 5.93 | 6.06 | 6.2 |
| $^1E_{1g}$ | 7.13 | 7.12 | 6.34 | 6.34 | 6.33 |
| $^1A_{2u}$ | 7.45 | 7.43 | 6.87 | 6.84 | 6.93 |
| $^1E_{2u}$ | 7.75 | 7.74 | 6.85 | 6.88 | 6.95 |
| $^1E_{1u}$ | 7.94 | 7.52 | 6.84 | 6.96 | 7.0 |
| Mean abs. error: | 0.7 | 0.6 | 0.1 | 0.1 | |

^aFrom Stratmann, Scuseria, and Frisch (1998). All calculations employed the 6-31+G(d) basis set.

Size extensivity/consistency

Size-Extensivity: For N independent systems the energy scales linearly

$$E(N) = N \cdot E(1):$$

Size-Consistency: dissociation $E(A+B) \neq E(A) + E(B)$

Example: consider H_2 and then two non-interacting H_2 molecules

$$\Psi_{CID}(H_2) = (1-c)^2 \Psi_{HF} + c^2 \Psi_{1\bar{1}}^{2\bar{2}}$$

$$\Psi_{CID}(2H_2) = ((1-c)^2 \Psi_{HF} + c^2 \Psi_{1\bar{1}}^{2\bar{2}})((1-c)^2 \Psi_{HF} + c^2 \Psi_{1\bar{1}}^{2\bar{2}})$$

$$= (1-c)^4 \Psi_{HF} \Psi_{HF} + c^4 \Psi_{1\bar{1}}^{2\bar{2}} \Psi_{1\bar{1}}^{2\bar{2}} + 2(1-c)^2 c^2 \Psi_{HF} \Psi_{1\bar{1}}^{2\bar{2}}$$

Corrections:

$$\text{Davidson correction: } E_{\text{cor}} = (E - E_0)(1 - c_0^2)$$

Single reference vs. multireference

- RHF for H₂ : The Hartree-Fock wavefunction for H₂ is

$$\begin{aligned}\Psi &= \frac{1}{\sqrt{2}} \begin{vmatrix} \sigma(1)\alpha(1) & \sigma(1)\beta(1) \\ \sigma(2)\alpha(2) & \sigma(2)\beta(2) \end{vmatrix} = \\ &= \frac{1}{\sqrt{2}} (\sigma(1)\alpha(1)\sigma(2)\beta(2) - \sigma(1)\beta(1)\sigma(2)\alpha(2)) = \\ &= \frac{1}{\sqrt{2}} (\sigma(1)\sigma(2))(\alpha(1)\beta(2) - \beta(1)\alpha(2))\end{aligned}$$



- The MO is a linear combinations of AOs: $\sigma = 1s_A + 1s_B$ (spin is ignored)

$$\begin{aligned}\Psi &= \frac{1}{\sqrt{2}} (1s_A(1) + 1s_B(1))(1s_A(2) + 1s_B(2)) = \\ &= \frac{1}{\sqrt{2}} (1s_A(1)1s_B(2) + 1s_B(1)1s_A(2) + \underbrace{1s_A(1)1s_A(2)}_{\text{Covalent H}\cdot\text{H}\cdot} + \underbrace{1s_B(1)1s_B(2)}_{\text{ionic H}^+\text{H}^-})\end{aligned}$$

Covalent H·H·

ionic H⁺H⁻

- This wavefunction is correct at the minimum but dissociates into 50% H⁺H⁻ and 50% H·H·

CI for H₂

- When two configurations are mixed:

$$\Psi_{CI} = c_1 \begin{vmatrix} \sigma(1)\alpha(1) & \sigma(1)\beta(1) \\ \sigma(2)\alpha(2) & \sigma(2)\beta(2) \end{vmatrix} + c_2 \begin{vmatrix} \sigma^*(1)\alpha(1) & \sigma^*(1)\beta(1) \\ \sigma^*(2)\alpha(2) & \sigma^*(2)\beta(2) \end{vmatrix} =$$

- Ignore spin

$$c_1(\sigma(1)\sigma(2) + c_2\sigma^*(1)\sigma^*(2))$$

$$\begin{aligned} \Psi &= c_1(1s_A(1) + 1s_B(1))(1s_A(2) + 1s_B(2)) + \\ &c_2(1s_A(1) - 1s_B(1))(1s_A(2) - 1s_B(2)) = \\ &= c_1(1s_A(1)1s_A(2) + 1s_B(1)1s_B(2) + 1s_A(1)1s_B(2) + 1s_B(1)1s_A(2)) \\ &+ c_2(1s_A(1)1s_A(2) + 1s_B(1)1s_B(2) - 1s_A(1)1s_B(2) - 1s_B(1)1s_A(2)) \end{aligned}$$



Ψ_1

Ψ_2

- The coefficients c_1 and c_2 determine how the conf. Are mixed in order to get the right character as the molecule dissociates. At the dissociation limit the orbitals σ , σ^* are degenerate and $c_1=c_2$.

Multireference methods

- Multireference methods are needed for:
 - Near-degeneracy
 - Bond breaking
 - Excited states
 - radicals
- Nondynamical correlation
 - MCSCF
- Dynamical correlation
 - Variational: MRCI
 - Based on perturbation theory: CASPT2 , MS-CASPT2, MRMP2
 - Not widely spread yet: MRCC, MRCI/DFT

Multiconfiguration Self-Consistent Field Theory (MCSCF)

- CSF: spin adapted linear combination of Slater determinants

$$\Psi_{MCSCF} = \sum_{n=1}^{CSFs} c_n |CSF\rangle$$

- Two optimizations have to be performed
 - Optimize the MO coefficients
 - optimize the expansion coefficients of the CSFs

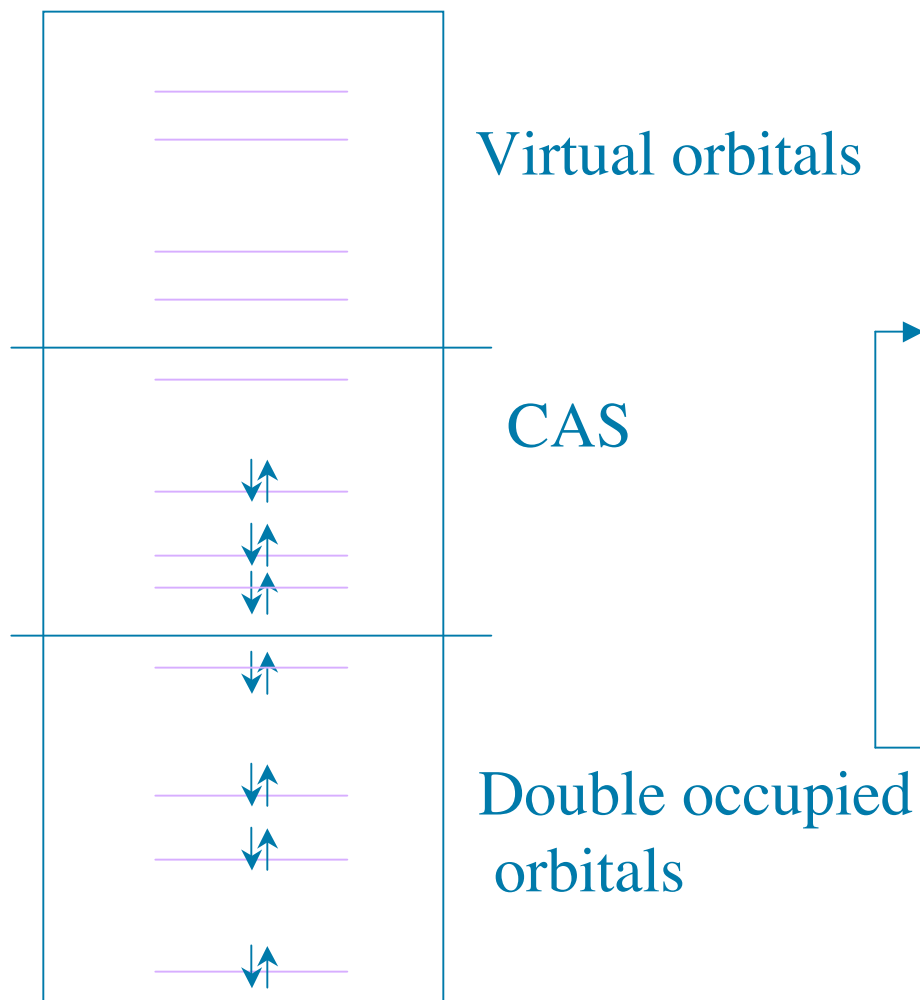
- Choose the active orbitals
 - Depends on the problem and the questions being asked
 - For a π system all π orbitals should be included if possible
 - If bond breaking include bonding, antibonding
 - Check occupation numbers of orbitals (between 0.02 - 0.98)
 - Trial and error
- Choose the configurations obtained using these orbitals
 - Complete active space (CASSCF or CAS): allow all possible configurations (Full CI within the active space)
 - (m,n): distribute m electrons in n orbitals

$$N = \frac{n!(n+1)!}{\left(\frac{m}{2}\right)!\left(\frac{m}{2}+1\right)!\left(n-\frac{m}{2}\right)!\left(n-\frac{m}{2}+1\right)!}$$

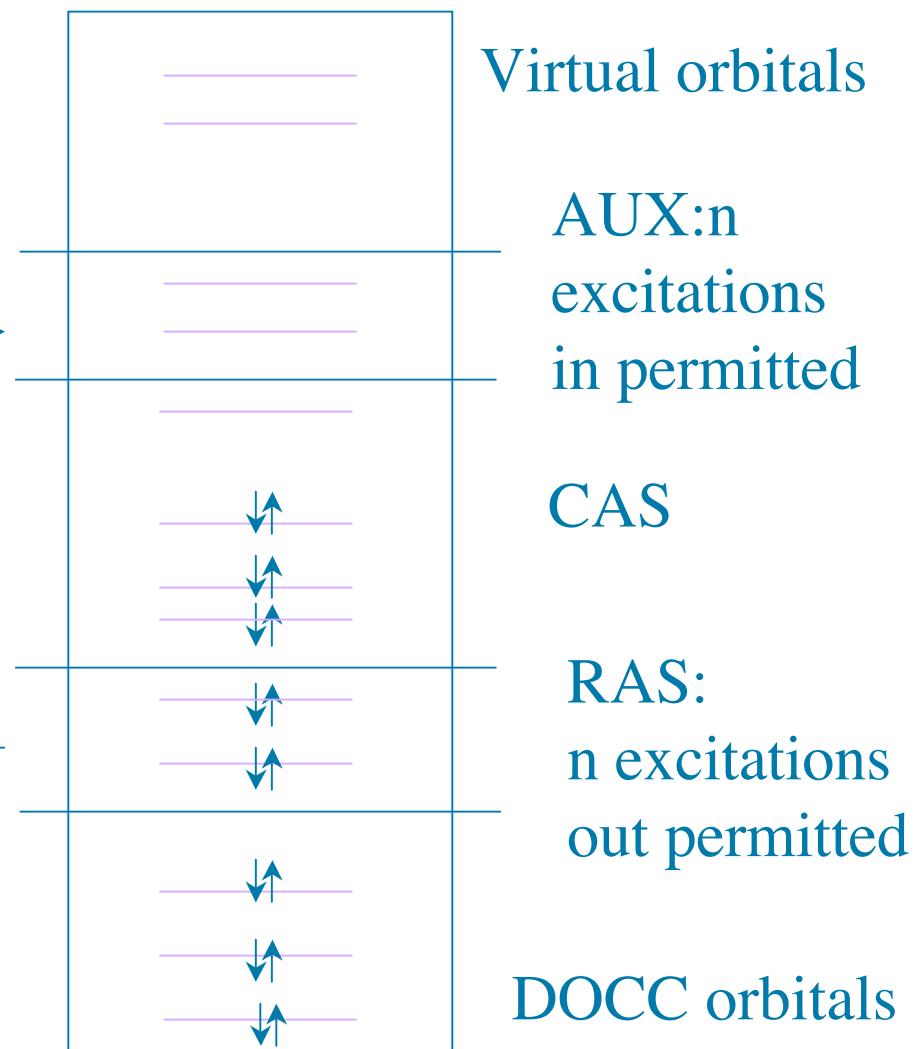
- i.e. (14,12) generates 169,883 CSFs
- Restricted active space (RASSCF): allow n-tuple excitations from a subset of orbitals (RAS) and only n-tuple excitations into an auxiliary originally empty set (AUX)
- Generalized valence bond (GVB)

Orbital spaces in an MCSCF calculations

CASSCF



RASSCF



The most important question in multireference methods: Choosing the active space

- The choice of the active space determines the accuracy of the method. It requires some knowledge of the system and careful testing.
- For small systems all valence orbitals can be included in the active space
- For conjugated systems all π orbitals if possible should be included in the active space. For heteroatomic rings the lone pairs should be included also. What cas should be chosen for the following systems?
 - N_2
 - Ozone
 - Allyl radical
 - Benzene
 - Uracil

State averaged MCSCF

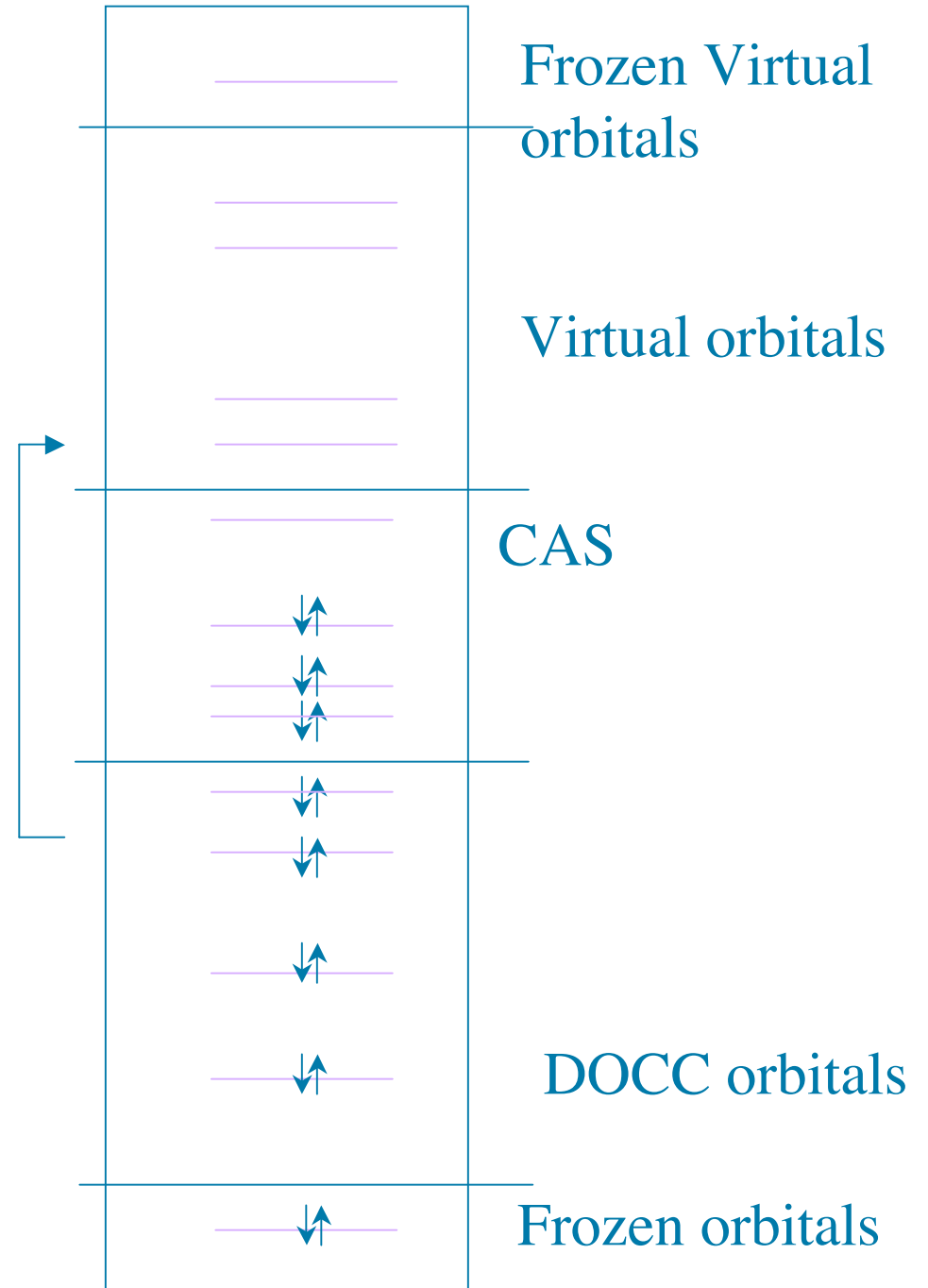
- All states of interest must be included in the average
- When the potential energy surface is calculated, all states of interest across the coordinate space must be included in the average
- State-averaged MOs describe a particular state poorer than state-specific MOs optimized for that state
- State-average is needed in order to calculate all states with similar accuracy using a common set of orbitals. This is the only choice for near degenerate states, avoided crossings, conical intersections.
- Provides common set of orbitals for transition dipoles and oscillator strengths

Multireference configuration interaction

- Includes dynamical correlation beyond the MCSCF
- Orbitals from an MCSCF (state-averaged) are used for the subsequent MRCI
- The states must be described qualitatively correct at the MCSCF level. For example, if 4 states are of interest but the 4th state at the MRCI level is the 5th state at the MCSCF level a 5-state average MCSCF is needed

MRCI

- A reference space is needed similar to the active space at MCSCF
- References are created within that space
- Single and double excitations using each one of these references as a starting point
- $\Psi^{\text{MRCI}} = \sum c_i \Psi^i$



CASPT2

- Second order perturbation theory is used to include dynamic correlation
- Has been used widely for medium size conjugated organic systems
- Errors for excitation energies ~ 0.3 eV
- There are no analytic gradients available so it is difficult to be used for geometry optimizations and dynamics

COLUMBUS

- Ab initio package
- MCSCF
- MRCI
- Analytic gradients for MRCI
- Graphical Unitary Group Approach (GUGA)

Colinp (input script)

- Integral
- SCF
- MCSCF
- CI
- Control input