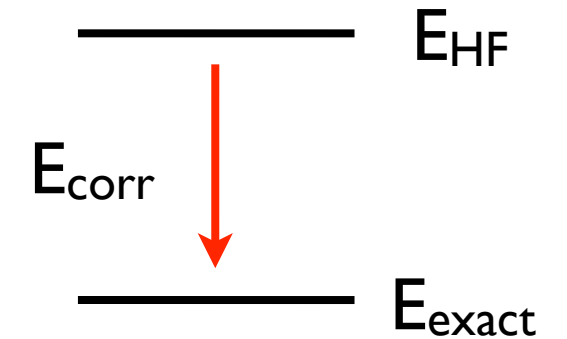# Configuration Interaction

Correlated wave function based methods

or sometimes "*Post Hartree Fock*"

- Three types of methods
  - ✓ Configuration Interaction
  - ✓ Perturbation theory
  - ✓ Coupled Cluster

$$E_{corr} = E_{exact} - E_{HF}$$

- Two different starting points
  - ✓ Hartree Fock: Single reference methods
  - ✓ Multireference methods (MR) like CASSCF

CISD	MRCI
MP2, MP4, …	CASPT2, NEVPT2, …
CCSD, CCSD(T), …	MR-CC (in development)

Configuration Interaction

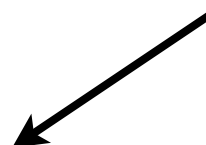⬤ Slater Determinant for a system with *k* electrons

$$\Phi_0 = |\phi_1 \phi_2 \dots \phi_i \phi_j \dots \phi_k\rangle$$

The molecular orbitals ϕ are constructed by making linear combinations of basis functions χ

$$\phi_p = a_1^p \chi_1 + a_2^p \chi_2 + \dots + a_m^p \chi_m = \sum_q^m a_q^p \chi_q$$

there are '*m*' of these molecular orbitals

Hartree-Fock considers the Slater Determinant in which the electrons occupy the MOs with the lowest energy but there are many other ways to distribute the electrons over the MOs
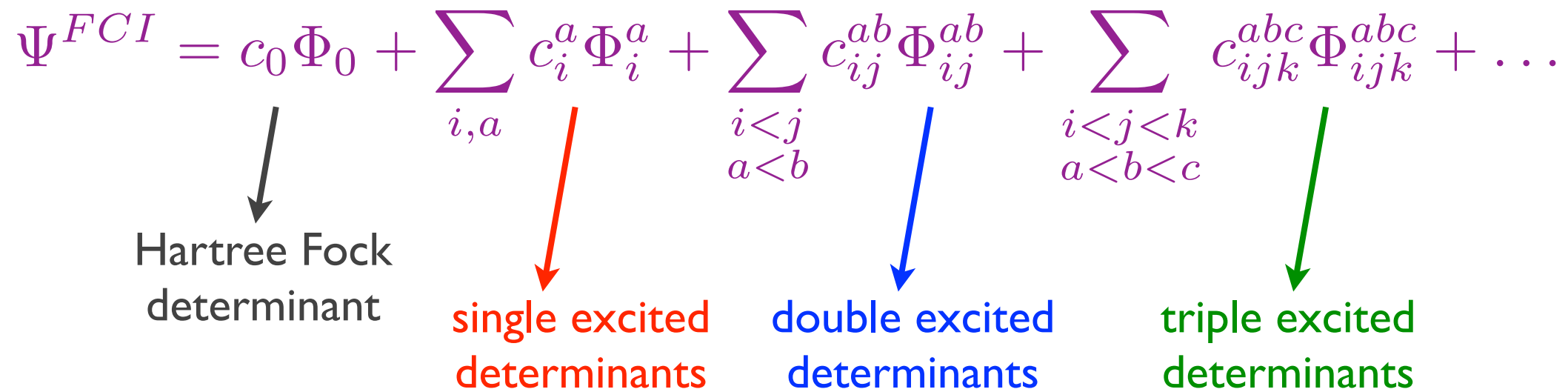
$$\frac{m!}{k!(m-k)!}$$

$$\Phi_i^a = |\phi_1 \phi_2 \dots \phi_j \dots \phi_k \phi_a\rangle$$

$$\Phi_{ij}^{ab} = |\phi_1 \phi_2 \dots \phi_k \phi_a \phi_b\rangle$$

$$\Phi_{ijk}^{abc} = |\phi_1 \phi_2 \dots \phi_a \phi_b \phi_c\rangle$$

Configuration Interaction

$$\Psi^{FCI} = c_0\Phi_0 + \sum_{\substack{i,a}} c_i^a \Phi_i^a + \sum_{\substack{i<j \\ a<b}} c_{ij}^{ab} \Phi_{ij}^{ab} + \sum_{\substack{i<j<k \\ a<b<c}} c_{ijk}^{abc} \Phi_{ijk}^{abc} + \dots$$

Hartree Fock determinant

single excited determinants

double excited determinants

triple excited determinants

In theory:

- Full CI gives the exact solution for m→∞

In practice:

- Full CI is the exact solution within a finite basis

- Normally, CI expansion is truncated at doubles or quadruples

Notation: - lower case (ϕ and χ) refer to one-electron functions

- upper case (Φ and Ψ) make reference to N-electron functions

- Φ is a determinant, not necessarily an N-electron state

- Ψ describes an N-electron state

CI matrix

$$|\Psi\rangle = c_0|\Phi_0\rangle + c_S|S\rangle + c_D|D\rangle + c_T|T\rangle + c_Q|Q\rangle + \ldots$$

Hamiltonian is hermitian

Hermitian matrix

$\hat{H}$	$|\Phi_0\rangle$	$|S\rangle$	$|D\rangle$	$|T\rangle$	$|Q\rangle$	...
$|\Phi_0\rangle$	$|E_0\rangle$	0	H_{0D}	0	0	...
$|S\rangle$	0	$|E_S\rangle$	H_{SD}	H_{ST}	0	...
$|D\rangle$	H_{D0}	H_{DS}	$|E_D\rangle$	H_{DT}	H_{DQ}	...
$|T\rangle$	0	H_{TS}	H_{TD}	$|E_T\rangle$	H_{TQ}	...
$|Q\rangle$	0	0	H_{QD}	H_{QT}	$|E_Q\rangle$	...
...	...	...	...	...	...	...

No direct interaction of $|S\rangle$ with Φ_0. Only through interaction with the doubles, the single excitations gain importance in the CISD wave function
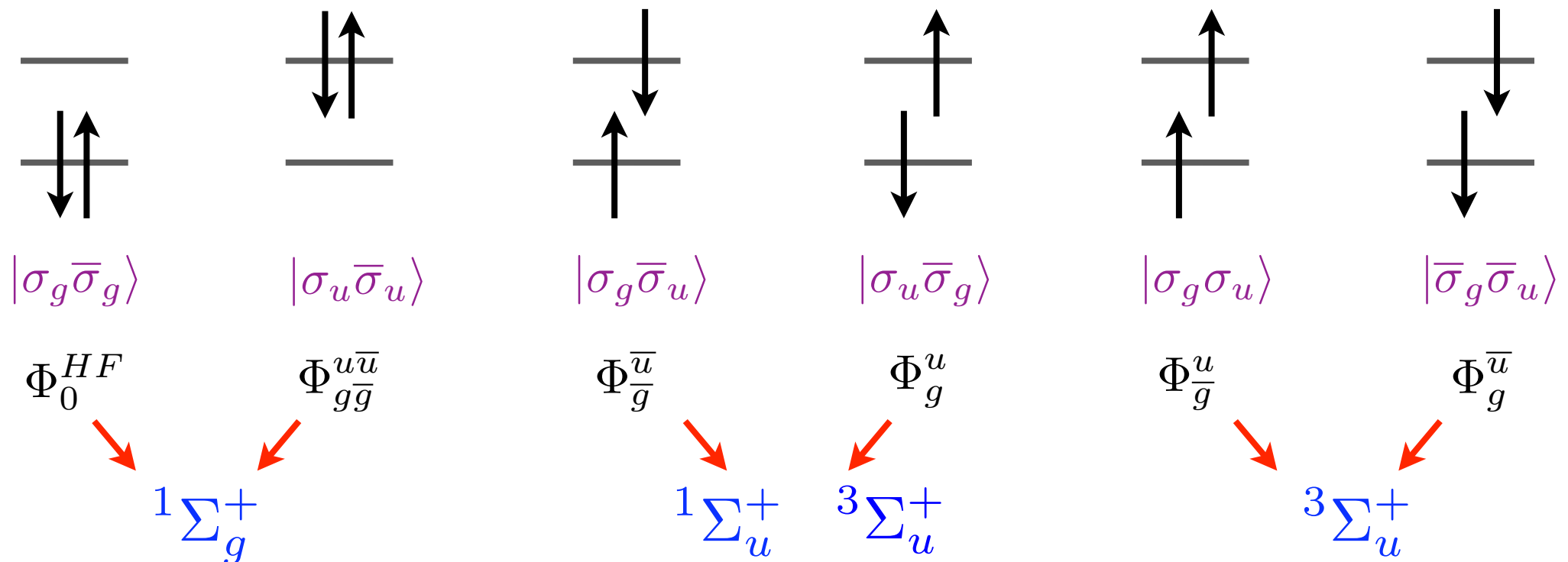
An example of Full CI

$\bullet$ H$_2$ ground state in minimal basis

$$\sigma_g = N_g(1s_A + 1s_B)$$
$$\sigma_u = N_u(1s_A - 1s_B)$$

Hartree Fock: $\Phi_0^{HF} = |\sigma_g \overline{\sigma}_g\rangle$ $E_0^{HF} = 2\langle \sigma_g|\hat{h}|\sigma_g\rangle + J_{gg}$

Generation of all determinants

|$\sigma_g\overline{\sigma}_g\rangle$ |$\sigma_u\overline{\sigma}_u\rangle$ |$\sigma_g\overline{\sigma}_u\rangle$ |$\sigma_u\overline{\sigma}_g\rangle$ |$\sigma_g\sigma_u\rangle$ |$\overline{\sigma}_g\overline{\sigma}_u\rangle$

Φ_0^{HF} $\Phi_{g\overline{g}}^{u\overline{u}}$ $\Phi_{\overline{g}}^{\overline{u}}$ Φ_g^u $\Phi_{\overline{g}}^u$ $\Phi_g^{\overline{u}}$

$^1\Sigma_g^+$ $^1\Sigma_u^+$ $^3\Sigma_u^+$ $^3\Sigma_u^+$

Only determinants with same spatial and spin symmetry interact

An example of Full CI

$$\Psi_0^{FCI} = \Phi_0^{HF} + c\Phi_{g\bar{g}}^{u\bar{u}} = \Phi_0 + c_D\Phi_D$$

Hamiltonian matrix:

$$\begin{bmatrix} \langle\Phi_0|\hat{H}|\Phi_0\rangle & \langle\Phi_0|\hat{H}|\Phi_D\rangle \\ \langle\Phi_0|\hat{H}|\Phi_D\rangle & \langle\Phi_D|\hat{H}|\Phi_D\rangle \end{bmatrix}$$

Matrix elements with Slater Condon rules

$$\langle\Phi_0|\hat{H}|\Phi_0\rangle = E_0^{HF} = 2\langle\sigma_g|\hat{h}|\sigma_g\rangle + J_{gg}$$

$$\langle\Phi_D|\hat{H}|\Phi_D\rangle = E_D = 2\langle\sigma_u|\hat{h}|\sigma_u\rangle + J_{uu}$$

$$\langle\Phi_0|\hat{H}|\Phi_D\rangle = \langle\sigma_g\bar{\sigma}_g||\sigma_u\bar{\sigma}_u\rangle = \langle\sigma_g\bar{\sigma}_g|\sigma_u\bar{\sigma}_u\rangle - \overset{0}{\langle\sigma_g\bar{\sigma}_g|\bar{\sigma}_u\sigma_u\rangle} = J_{gu}$$

Secular CI equation:

$$\begin{pmatrix} E_0 & J_{gu} \\ J_{gu} & E_D \end{pmatrix} \begin{pmatrix} 1 \\ c_D \end{pmatrix} = E \begin{pmatrix} 1 \\ c_D \end{pmatrix} \quad \xrightarrow{-E_0}$$

Secular determinant:

$$\begin{vmatrix} 0 - E & J_{gu} \\ J_{gu} & 2\Delta - E \end{vmatrix} = 0$$

$$2\Delta = E_D - E_0 = 2\langle\sigma_u|\hat{h}|\sigma_u\rangle - 2\langle\sigma_g|\hat{h}|\sigma_g\rangle + J_{uu} - J_{gg}$$

$$\Longrightarrow \quad E = \Delta - \sqrt{\Delta^2 + J_{gu}^2}$$

Size consistency

$$E_A + E_B = E_{AB}(r \to \infty) \qquad\qquad E(A_n) = n \times E(A)$$

	2 x H_2O	$(H_2O)_2$	Binding energy	$(H_2O)_2$ $(r \to \infty)$
MP2	-152.49204 au	-152.49975 au	4.8 kcal/mol	-152.49204 au
CISD	-152.49144 au	-152.47869 au	-8.0 kcal/mol	-152.47186 au

⬤ Importance of core-valence correlation: Ar(8 el.) versus Ar(18 el.)

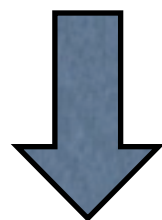⬤ Comparing reaction energies: R–AB → R–A + B for different R-groups

Separability of Full CI

Two non-interacting H_2 molecules

$$\Psi = \Phi_0 + c_{D_1}\Phi_{g_1\overline{g}_1}^{u_1\overline{u}_1} + c_{D_2}\Phi_{g_2\overline{g}_2}^{u_2\overline{u}_2} + c_Q\Phi_{g_1\overline{g}_1 g_2\overline{g}_2}^{u_1\overline{u}_1 u_2\overline{u}_2}$$

Hamiltonian matrix:

$$\begin{bmatrix} E_0 & J_{gu} & J_{gu} & 0 \\ J_{gu} & E_0+2\Delta & 0 & J_{gu} \\ J_{gu} & 0 & E_0+2\Delta & J_{gu} \\ 0 & J_{gu} & J_{gu} & E_0+4\Delta \end{bmatrix}$$

In[12]:=

$$A = \begin{pmatrix} 0 & J & J & 0 \\ J & 2\,D & 0 & J \\ J & 0 & 2\,D & J \\ 0 & J & J & 4\,D \end{pmatrix}$$

Out[12]= {{0, J, J, 0}, {J, 2 D, 0, J}, {J, 0, 2 D, J}, {0, J, J, 4 D}}

In[13]:= **Eigenvalues[A]**

Out[13]= $\left\{ 2\,D,\ 2\,D,\ 2\left(D - \sqrt{D^2 + J^2}\right),\ 2\left(D + \sqrt{D^2 + J^2}\right)\right\}$

$$E_{corr} = 2\left(\Delta - \sqrt{\Delta^2 + J_{gu}^2}\right)$$

$$E = E_0 + 2\left(\Delta - \sqrt{\Delta^2 + J_{gu}^2}\right) = 2E_1$$
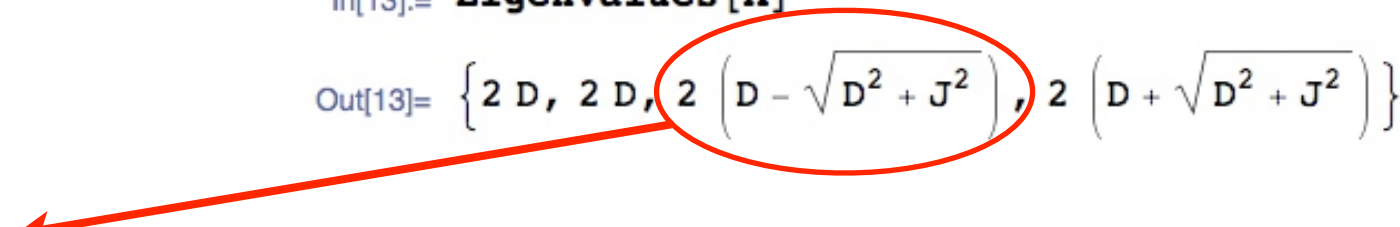
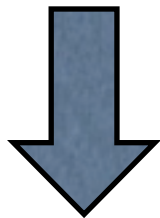$$c_{D_1} = c_{D_2} \qquad c_Q = c_{D_1}^2$$

Separability of SDCI

Two non-interacting H_2 molecules

$$\Psi = \Phi_0 + c_{D_1} \Phi_{g_1 \bar{g}_1}^{u_1 \bar{u}_1} + c_{D_2} \Phi_{g_2 \bar{g}_2}^{u_2 \bar{u}_2} + c_Q \Phi_{g_1 \bar{g}_1 g_2 \bar{g}_2}^{u_1 \bar{u}_1 u_2 \bar{u}_2}$$

Hamiltonian matrix:

$$\begin{bmatrix} E_0 & J_{gu} & J_{gu} \\ J_{gu} & E_0 + 2\Delta & 0 \\ J_{gu} & 0 & E_0 + 2\Delta \end{bmatrix}$$

In[7]:= $A = \begin{pmatrix} 0 & J & J \\ J & 2D & 0 \\ J & 0 & 2D \end{pmatrix}$

Out[7]= {{0, J, J}, {J, 2 D, 0}, {J, 0, 2 D}}

In[9]:= **Eigenvalues[A]**

Out[9]= $\left\{ 2\,D,\ D - \sqrt{D^2 + 2\,J^2},\ D + \sqrt{D^2 + 2\,J^2} \right\}$

$$E_{corr} = \Delta - \sqrt{\Delta^2 + 2J_{gu}^2}$$

$$E = E_0 + \Delta - \sqrt{\Delta^2 + 2J_{gu}^2} \neq 2E_1$$

Truncated CI - size consistency corrections

$$E_{AB}^{CISD} \neq E_A^{CISD} + E_B^{CISD}$$

Solutions to the size consistency error

- Complete Active Space (CAS) = Full CI in a limited number of MO's and e⁻

- Davidson correction

$$E_{corr} = E_{corr}^{SDCI} + \Delta E_{Dav} \quad \Delta E_{Dav} = (1 - c_0^2)E_{corr}^{SDCI} \quad \Psi = c_0\Psi_0 + \sum_{I=S,D} c_I\Psi_I$$

- Selected CI, including the most 'significant' contributions, estimated by PT

- Other methods as Perturbation theory and Coupled Cluster

Perturbation theory

Configuration Interaction or Perturbation Theory?

Configuration Interaction:

Advantages   - Variational procedure, upper bound to the exact energy

- Invariance under rotations of the MOs

- Higher order interactions are included

Disadvantages   - Size-consistency in truncated CI

- Computation requirements, CPU time, disk storage, memory

Perturbation theory:

Advantages   - Size-consistent

- Relatively cheap computationally

Disadvantages   - Non-variational, unknown sign error

- Convergence problems

- Intruder states may appear

- No interaction between excited configurations at 2nd order

Rayleigh-Schrödinger Perturbation Theory

Electronic Hamiltonian:
$$\hat{H} = \sum_i \hat{h}_i + \sum_i \sum_{j>i} \frac{1}{r_{ij}}$$

Schrödinger equation:
$$\hat{H}\Psi_i = E_i\Psi_i$$
where E_i and Ψ_i are the exact energy and wave function of state i

The perturbative treatment is based on the partition of the Hamiltonian

$$\hat{H} = \hat{H}^{(0)} + \hat{V}$$

Hamiltonian of a model system with known solutions

Perturbation operator

$$\hat{H}^{(0)}\Psi_k^{(0)} = E_k^{(0)}\Psi_k^{(0)}$$

The zero[th]-order solution

Rayleigh-Schrödinger Perturbation Theory

$$\hat{H}\Psi_i = E_i\Psi_i$$

Complicated system without analytical solution

$$\hat{H} = \hat{H}^{(0)} + \lambda\hat{V}$$

$$\hat{H}^{(0)}\Psi_i^{(0)} = E_i^{(0)}\Psi_i^{(0)}$$

Simple, well-known system

$$\langle\Psi_i^{(0)}|\Psi_j^{(0)}\rangle = \delta_{ij}$$

$$E_0 = E_0^{(0)} + \lambda E_0^{(1)} + \lambda^2 E_0^{(2)} + \ldots$$

$$\Psi_0 = \Psi_0^{(0)} + \lambda\Psi_0^{(1)} + \lambda^2\Psi_0^{(2)} + \ldots$$

subscript '0' refers to the ground state

$$\hat{H}^{(0)}\Psi_0^{(0)} = E_0^{(0)}\Psi_0^{(0)}$$

$$\hat{H}^{(0)}\Psi_0^{(1)} + \hat{V}\Psi_0^{(0)} = E_0^{(0)}\Psi_0^{(1)} + E_0^{(1)}\Psi_0^{(0)}$$

$$\hat{H}^{(0)}\Psi_0^{(2)} + \hat{V}\Psi_0^{(1)} = E_0^{(0)}\Psi_0^{(2)} + E_0^{(1)}\Psi_0^{(1)} + E_0^{(2)}\Psi_0^{(0)}$$

Rayleigh-Schrödinger Perturbation Theory

First-order correction to the energy

$$\hat{H}^{(0)}\Psi_0^{(1)} + \hat{V}\Psi_0^{(0)} = E_0^{(0)}\Psi_0^{(1)} + E_0^{(1)}\Psi_0^{(0)}$$

$\downarrow$ *Multiply by $\Psi_0^{*(0)}$ and integrate*

$$E_0^{(1)} = \langle\Psi_0^{(0)}|\hat{H}^{(0)}|\Psi_0^{(1)}\rangle + \langle\Psi_0^{(0)}|\hat{V}|\Psi_0^{(0)}\rangle - E_0^{(0)}\langle\Psi_0^{(0)}|\Psi_0^{(1)}\rangle$$

$\downarrow$ *Expand $\Psi_0^{(1)}$ in functions of the unperturbed system and substitute*

$$\Psi_0^{(1)} = \sum_{i\neq 0} a_i \Psi_i^{(0)}$$

orthogonal to $\Psi_0^{(0)}$

$$E_0^{(1)} = \sum_{i\neq 0}\langle\Psi_0^{(0)}|\hat{H}^{(0)}|\Psi_i^{(0)}\rangle + \langle\Psi_0^{(0)}|\hat{V}|\Psi_0^{(0)}\rangle - \sum_{i\neq 0} E_0^{(0)}\langle\Psi_0^{(0)}|\Psi_i^{(0)}\rangle$$

$$\boxed{E_0^{(1)} = \langle\Psi_0^{(0)}|\hat{V}|\Psi_0^{(0)}\rangle}$$

Rayleigh-Schrödinger Perturbation Theory

First-order correction to the wave function

$$\hat{H}^{(0)}\Psi_0^{(1)} + \hat{V}\Psi_0^{(0)} = E_0^{(0)}\Psi_0^{(1)} + E_0^{(1)}\Psi_0^{(0)}$$

$$\Psi_0^{(1)} = \sum_{i \neq 0} a_i \Psi_i^{(0)}$$

Substitute $\Psi_0^{(1)}$, multiply by $\Psi_k^{*(0)}$ and integrate

$$\sum_{i \neq 0} a_i \langle \Psi_k^{(0)} | \hat{H}^{(0)} | \Psi_i^{(0)} \rangle + \langle \Psi_k^{(0)} | \hat{V}^{(1)} | \Psi_0^{(0)} \rangle =$$

$$\sum_{i \neq 0} a_i \langle \Psi_k^{(0)} | \Psi_i^{(0)} \rangle E_0^{(0)} + \langle \Psi_k^{(0)} | \Psi_0^{(0)} \rangle E_0^{(1)}$$

$$a_k E_k^{(0)} + \langle \Psi_k^{(0)} | \hat{V}^{(1)} | \Psi_0^{(0)} \rangle = a_k E_0^{(0)} + 0$$

$$a_k = \frac{\langle \Psi_k^{(0)} | \hat{V}^{(1)} | \Psi_0^{(0)} \rangle}{E_k^{(0)} - E_0^{(0)}}$$

$$\Psi^{(1)} = \sum_{i \neq 0} \frac{\langle \Psi_i^{(0)} | \hat{V}^{(1)} | \Psi_0^{(0)} \rangle}{E_i^{(0)} - E_0^{(0)}} \Psi_i^{(0)}$$

Rayleigh-Schrödinger Perturbation Theory

Second-order correction to the energy

$$
E^{(2)} = \sum_{i \neq 0} \frac{\langle \Psi_i^{(0)} | \hat{V}^{(1)} | \Psi_0^{(0)} \rangle \langle \Psi_0^{(0)} | \hat{V}^{(1)} | \Psi_i^{(0)} \rangle}{E_i^{(0)} - E_0^{(0)}}
$$

Expressions for $\Psi^{(2)}$, $E^{(3)}$, etc. get more complicated very rapidly

Many Body Perturbation theory: Møller Plesset

If the Hartree-Fock solution is known, the zeroth-order Hamiltonian

can be defined as the sum of the Fock operators:

$$\hat{H}^{(0)} = \sum_i^N \hat{f}(i)$$

The perturbation operator is:

$$\hat{V} = \hat{H} - \hat{H}^{(0)} = \sum_i \hat{h}_i + \sum_i \sum_{j>i} \frac{1}{r_{ij}} - \sum_i \hat{f}(i)$$

since, $\hat{f}(i) = \hat{h}(i) + \sum_k \left(\hat{J}_k(i) - \hat{K}_k(i) \right) = \hat{h}(i) + \hat{g}(i)$

$$\hat{V} = \sum_i \sum_{j>i} \frac{1}{r_{ij}} - \sum_i \hat{g}(i)$$

electron-electron interaction

Mean-field Coulomb and exchange interactions

Møller Plesset Perturbation theory

The zeroth-order (known) solutions:

$$\hat{H}^{(0)}\Psi_k^{(0)} = E_k^{(0)}\Psi_k^{(0)}$$

$$\Psi_0^{(0)} = \Phi_{HF} = |\phi_1\phi_2\ldots\phi_i\phi_j\ldots\phi_N\rangle$$

$$E_0^{(0)} = \sum_m^N \epsilon_m$$

$$\Psi_j^{(0)} = |\phi_1\phi_2\ldots\phi_j\ldots\phi_N\ldots\phi_a\rangle = \Phi_i^a$$

$$E_j^{(0)} = E_0^{(0)} - \epsilon_i + \epsilon_a$$

$$\Psi_k^{(0)} = |\phi_1\phi_2\ldots\phi_N\ldots\phi_a\phi_b\rangle = \Phi_{ij}^{ab}$$

$$E_k^{(0)} = E_0^{(0)} - \epsilon_i - \epsilon_j + \epsilon_a + \epsilon_b$$

The first-order correction to the energy:

$$E_0^{(1)} = \langle\Psi_0^{(0)}|\hat{V}|\Psi_0^{(0)}\rangle = \langle\Psi_0^{(0)}|\sum_i\sum_{j>i}\frac{1}{r_{ij}}|\Psi_0^{(0)}\rangle - \langle\Psi_0^{(0)}| - \sum_i\hat{g}(i)|\Psi_0^{(0)}\rangle$$

$$= \frac{1}{2}\sum_i\langle i|\sum_j\left(\hat{J}_j - \hat{K}_j\right)|i\rangle - \sum_i\langle i|\sum_j\left(\hat{J}_j - \hat{K}_j\right)|i\rangle$$

$$= -\frac{1}{2}\sum_i\langle i|\sum_j\left(\hat{J}_j - \hat{K}_j\right)|i\rangle$$

Møller Plesset Perturbation theory

Energy at first-order:

$$E_0 = E_0^{(0)} + E_0^{(1)} = \sum_i \epsilon_i - \frac{1}{2} \sum_i \langle i | \sum_j \left(\hat{J}_j - \hat{K}_j \right) | i \rangle = E_{HF}$$

First-order wave function correction:

$$\Psi_0^{(1)} = \sum_{i \neq 0} \frac{\langle \Psi_i^{(0)} | \hat{V}^{(1)} | \Psi_0^{(0)} \rangle}{E_i^{(0)} - E_0^{(0)}} \Psi_i^{(0)}$$

$$= \langle \Psi_i^{(0)} | \hat{H} | \Psi_0^{(0)} \rangle - \langle \Psi_i^{(0)} | \hat{H}^{(0)} | \Psi_0^{(0)} \rangle = \langle \Psi_i^{(0)} | \hat{H} | \Psi_0^{(0)} \rangle - E_0^{(0)} \overset{0}{\cancel{\langle \Psi_i^{(0)} | \Psi_0^{(0)} \rangle}} = \langle \Psi_i^{(0)} | \hat{H} | \Psi_0^{(0)} \rangle$$
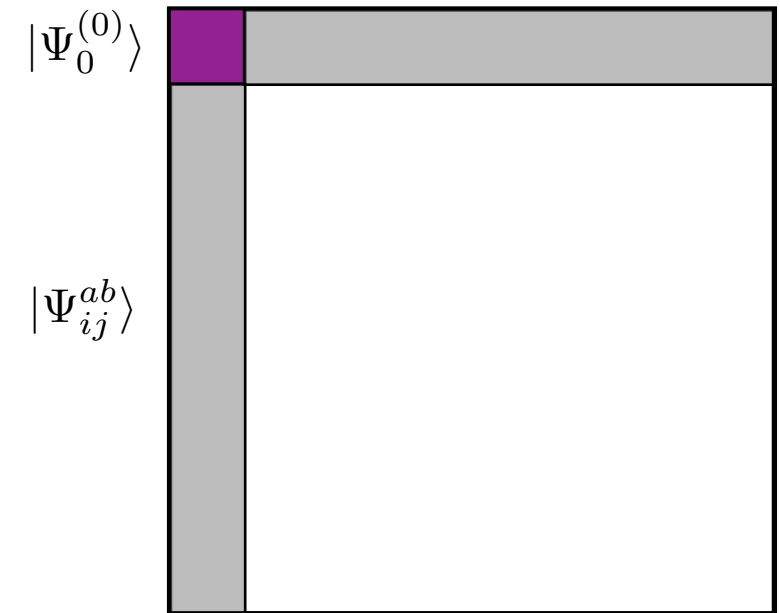
- *zero for single excitations (Brillouin theorem)*
- *zero for more than two electron replacements*
- *only double excitations need to be considered*

Møller Plesset Perturbation theory

Second-order correction to the energy:

$$E^{(2)} = \sum_{i \neq 0} \frac{\langle \Psi_i^{(0)} | \hat{V}^{(1)} | \Psi_0^{(0)} \rangle \langle \Psi_0^{(0)} | \hat{V}^{(1)} | \Psi_i^{(0)} \rangle}{E_i^{(0)} - E_0^{(0)}}$$

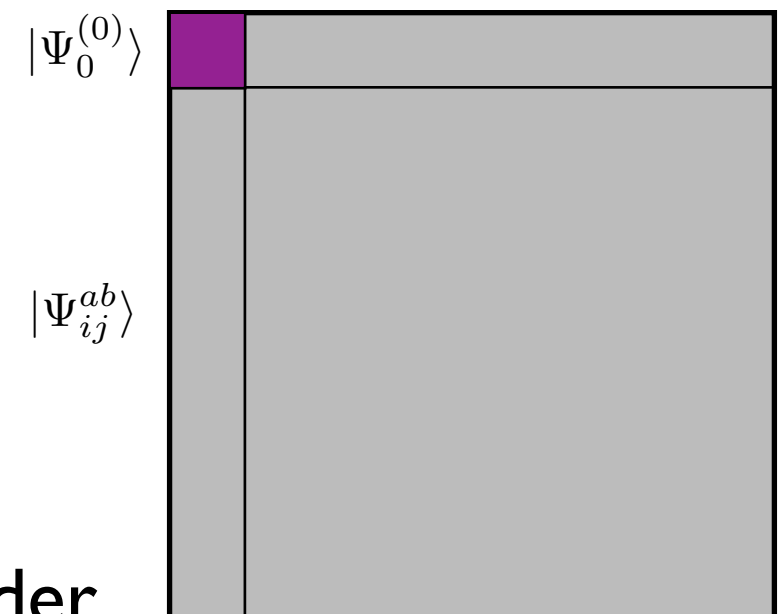At second-order only doubles,

no interaction between doubles

$|\Psi_0^{(0)}\rangle$

$|\Psi_{ij}^{ab}\rangle$

CISD matrix

Third-order correction to the energy:

$$E_0^{(3)} = \sum_{\substack{a<b \ c<d \\ i<j \ k<l}} \frac{\langle \Psi_0^{(0)} | \hat{H} | \Psi_{ij}^{ab} \rangle \langle \Psi_{ij}^{ab} | \hat{V} | \Psi_{kl}^{cd} \rangle \langle \Psi_{kl}^{cd} | \hat{H} | \Psi_0^{(0)} \rangle}{(\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j)(\epsilon_c + \epsilon_d - \epsilon_k - \epsilon_l)}$$

$$- E_0^{(1)} \sum_{\substack{a<b \\ i<j}} \frac{|\langle \Psi_0 | \hat{V} | \Psi_{ij}^{ab} \rangle|^2}{(\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j)^2}$$

$|\Psi_0^{(0)}\rangle$

$|\Psi_{ij}^{ab}\rangle$

Interaction between doubles at third-order

CISD matrix

Møller Plesset Perturbation theory

$$E_i^{(0)} - E_0^{(0)} = \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j$$

☞ Intruder states

In case of quasi-degenerate occupied and virtual orbitals
(e.g. dissociation), very small denominators can appear,
leading to a breakdown of the perturbation theory

$$\sigma_g = \tfrac{1}{\sqrt{2}}(1s_a + 1s_b)$$

$$\sigma_u = \tfrac{1}{\sqrt{2}}(1s_a - 1s_b)$$

Example: H$_2$ in minimal basis

zero$^{\text{th}}$-order $\Psi_0^{(0)} = |\sigma_g \overline{\sigma}_g\rangle$ $E_0^{(0)} = 2\epsilon_g$

first-order $\Psi_0^{(1)} = |\Psi_{ij}^{ab}\rangle = |\sigma_u \overline{\sigma}_u\rangle$ $E_0^{(1)} = -J_{gg}$

$$E_0 = E_0^{(1)} + E_0^{(1)} = 2\epsilon_g - J_{gg} = E_{HF}$$

second-order $E_0^{(2)} = \dfrac{|\langle\Psi_0^{(0)}|\hat{V}|\Psi_0^{(1)}\rangle|^2}{E_i^{(0)} - E_0^{(0)}} = \dfrac{|\langle\sigma_g\overline{\sigma}_g|\hat{H}|\sigma_u\overline{\sigma}_u\rangle|^2}{2(\epsilon_u - \epsilon_g)}$

tends to zero for large distances

Møller Plesset Perturbation theory

☞ Separability $\qquad\qquad E_{AB}(r \to \infty) = E_A + E_B$

The separability is preserved at all perturbation orders.

Easy to demonstrate up to second-order

Consider and AB system of non-interaction A and B subsystems

$$\hat{H}_{AB} = \hat{H}_A + \hat{H}_B \qquad \hat{H}_{AB}^{(0)} = \hat{H}_A^{(0)} + \hat{H}_B^{(0)} \qquad \hat{V}_{AB} = \hat{V}_A + \hat{V}_B$$

zeroth-order $\qquad \Psi_{AB}^{(0)} = \Psi_{Ai}^{(0)} \Psi_{Bi}^{(0)} \qquad\qquad E_{AB}^{(0)} = E_A^{(0)} + E_B^{(0)}$

first-order $\qquad \Psi_{AB}^{(1)} = \{ \Psi_{Ai}^{(0)} \Psi_{Bj}^{(0)}, \Psi_{Aj}^{(0)} \Psi_{Bi}^{(0)}, \Psi_{Aj}^{(0)} \Psi_{Bk}^{(0)} \}$

$$E_{AB}^{(1)} = \langle \Psi_{Ai}^{(0)} \Psi_{Bi}^{(0)} | \hat{V}_A + \hat{V}_B | \Psi_{Ai}^{(0)} \Psi_{Bi}^{(0)} \rangle = \langle \Psi_{Ai}^{(0)} | \hat{V}_A | \Psi_{Ai}^{(0)} \rangle \langle \Psi_{Bi}^{(0)} | \Psi_{Bi}^{(0)} \rangle$$

$$+ \langle \Psi_{Bi}^{(0)} | \hat{V}_B | \Psi_{Bi}^{(0)} \rangle \langle \Psi_{Ai}^{(0)} | \Psi_{Ai}^{(0)} \rangle = E_A^{(1)} + E_B^{(1)}$$

Labels: i ground state; j,k excited state

Møller Plesset Perturbation theory

second-order

$$E_{AB}^{(2)} = \sum_{j \neq i} \frac{\langle \Psi_{Ai}^{(0)} \Psi_{Bi}^{(0)} | \hat{V}_A + \hat{V}_B | \Psi_{Ai}^{(0)} \Psi_{Bj}^{(0)} \rangle \langle \Psi_{Ai}^{(0)} \Psi_{Bj}^{(0)} | \hat{V}_A + \hat{V}_B | \Psi_{Ai}^{(0)} \Psi_{Bi}^{(0)} \rangle}{E_{Ai}^{(0)} + E_{Bi}^{(0)} - (E_{Ai}^{(0)} + E_{Bj}^{(0)})}$$

$$+ \sum_{j \neq i} \frac{\langle \Psi_{Ai}^{(0)} \Psi_{Bi}^{(0)} | \hat{V}_A + \hat{V}_B | \Psi_{Aj}^{(0)} \Psi_{Bi}^{(0)} \rangle \langle \Psi_{Aj}^{(0)} \Psi_{Bi}^{(0)} | \hat{V}_A + \hat{V}_B | \Psi_{Ai}^{(0)} \Psi_{Bi}^{(0)} \rangle}{E_{Ai}^{(0)} + E_{Bi}^{(0)} - (E_{Aj}^{(0)} + E_{Bi}^{(0)})}$$

$$+ \sum_{j \neq i} \frac{\langle \Psi_{Ai}^{(0)} \Psi_{Bi}^{(0)} | \hat{V}_A + \hat{V}_B | \Psi_{Aj}^{(0)} \Psi_{Bj}^{(0)} \rangle \langle \Psi_{Aj}^{(0)} \Psi_{Bj}^{(0)} | \hat{V}_A + \hat{V}_B | \Psi_{Ai}^{(0)} \Psi_{Bi}^{(0)} \rangle}{E_{Ai}^{(0)} + E_{Bi}^{(0)} - (E_{Aj}^{(0)} + E_{Bj}^{(0)})}$$

zero due to the orthogonality of the zero[th]-order solutions of each fragment

$$\langle \Psi_{Ai}^{(0)} | \Psi_{Aj}^{(0)} \rangle = 0$$

$$\langle \Psi_{Bi}^{(0)} | \Psi_{Bj}^{(0)} \rangle = 0$$

Labels: i ground state; j,k excited state

Møller Plesset Perturbation theory

$$\langle \Psi_{Ai}^{(0)} \Psi_{Bi}^{(0)} | \hat{V}_A + \hat{V}_B | \Psi_{Ai}^{(0)} \Psi_{Bj}^{(0)} \rangle =$$

$$\langle \Psi_{Ai}^{(0)} | \hat{V}_A | \Psi_{Ai}^{(0)} \rangle \langle \Psi_{Bi}^{(0)} | \Psi_{Bj}^{(0)} \rangle + \langle \Psi_{Bi}^{(0)} | \hat{V}_B | \Psi_{Bj}^{(0)} \rangle \langle \Psi_{Ai}^{(0)} | \Psi_{Ai}^{(0)} \rangle = \langle \Psi_{Bi}^{(0)} | \hat{V}_B | \Psi_{Bj}^{(0)} \rangle$$

zero

$$\langle \Psi_{Ai}^{(0)} \Psi_{Bi}^{(0)} | \hat{V}_A + \hat{V}_B | \Psi_{Aj}^{(0)} \Psi_{Bi}^{(0)} \rangle =$$

$$\langle \Psi_{Ai}^{(0)} | \hat{V}_A | \Psi_{Aj}^{(0)} \rangle \langle \Psi_{Bi}^{(0)} | \Psi_{Bi}^{(0)} \rangle + \langle \Psi_{Bi}^{(0)} | \hat{V}_B | \Psi_{Bi}^{(0)} \rangle \langle \Psi_{Ai}^{(0)} | \Psi_{Aj}^{(0)} \rangle = \langle \Psi_{Ai}^{(0)} | \hat{V}_A | \Psi_{Aj}^{(0)} \rangle$$

zero

$$E_0^{(2)} = \sum_{j \neq i} \frac{|\langle \Psi_{Ai}^{(0)} | \hat{V}_A | \Psi_{Aj}^{(0)} \rangle|^2}{E_{Ai}^{(0)} - E_{Aj}^{(0)}} + \sum_{j \neq i} \frac{|\langle \Psi_{Bi}^{(0)} | \hat{V}_B | \Psi_{Bj}^{(0)} \rangle|^2}{E_{Bi}^{(0)} - E_{Bj}^{(0)}} = E_A^{(2)} + E_B^{(2)}$$

Labels: i ground state; j,k excited state

Coupled Cluster

Coupled Cluster

- Introduced by Sinanoğlu and Čžižek in the 1960's

- Main feature: The wave function is generated through an exponential development (exponential Ansatz)

- Advantage: correct separability and size-extensivity

- Disadvantage: non-linear equations, non-variational, CPU time-consuming

- In general, only for single configurational reference wave functions

The exponential Ansatz

$$\Psi = \hat{\Omega}\Phi_0$$

Configuration Interaction

Coupled Cluster

$$\hat{\Omega}^{CI} = 1 + \hat{C}_1 + \hat{C}_2 + \hat{C}_3 + \dots$$

$$\hat{\Omega}^{CC} = e^{\hat{T}}$$

$$\hat{C}_1 = \sum_{i,a} c_i^a \hat{a}_a^\dagger \hat{a}_i$$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots$$

$$\hat{T}_1 = \sum_{i,a} t_i^a \hat{a}_a^\dagger \hat{a}_i$$

$$\hat{C}_2 = \sum_{\substack{a<b \\ i<j}} c_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_i \hat{a}_j$$

$$\hat{T}_2 = \sum_{\substack{a<b \\ i<j}} t_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_i \hat{a}_j$$

$$\hat{C}_3 = \sum_{\substack{a<b<c \\ i<j<k}} c_{ijk}^{abc} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_c^\dagger \hat{a}_i \hat{a}_j \hat{a}_k$$

CI coefficients

$$\hat{T}_3 = \sum_{\substack{a<b<c \\ i<j<k}} t_{ijk}^{abc} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_c^\dagger \hat{a}_i \hat{a}_j \hat{a}_k$$

Cluster amplitudes

The exponential Ansatz

Taylor expansion: $\quad \hat{\Omega}^{CC} = e^{\hat{T}} = 1 + \hat{T} + \dfrac{1}{2!}\hat{T}^2 + \dfrac{1}{3!}\hat{T}^3 + \dfrac{1}{4!}\hat{T}^4 + \ldots$

$$\hat{\Omega}^{CC} = 1 + (\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \ldots) + \dfrac{1}{2!}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \ldots)^2$$

$$+\dfrac{1}{3!}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \ldots)^3 + \dfrac{1}{4!}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \ldots)^4 + \ldots$$

$$= 1 + (\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \ldots) + \dfrac{1}{2}(\hat{T}_1^2 + \hat{T}_2^2 + \hat{T}_3^2 + 2\hat{T}_1\hat{T}_2 + 2\hat{T}_1\hat{T}_3 + \ldots)$$

$$+\dfrac{1}{6}(\hat{T}_1^3 + \hat{T}_2^3 + \hat{T}_3^3 + 3\hat{T}_1^2\hat{T}_2 + 3\hat{T}_1^2\hat{T}_3 + \ldots) + \ldots$$

$e^2 = 7.3890561 \approx 1 + 2 + {}^1/_2\, 2^2 + {}^1/_6\, 2^3 + {}^1/_{24}\, 2^4 + {}^1/_{120}\, 2^5 + \ldots \approx 1 + 2 + 2 + 1.333 + 0.667 + 0.2667 + 0.0889 \approx 7.3556$

The exponential Ansatz

Ordering by excitation level

$$\hat{\Omega}^{CC} = 1$$

$$+\hat{T}_1 \qquad\qquad\longrightarrow \text{Singles}$$

$$+\hat{T}_2 + \frac{1}{2}\hat{T}_1^2 \qquad\qquad\longrightarrow \text{Doubles}$$

$$+\hat{T}_3 + \hat{T}_1\hat{T}_2 + \frac{1}{6}\hat{T}_1^3 \qquad\qquad\longrightarrow \text{Triples}$$

$$+\hat{T}_4 + \hat{T}_1\hat{T}_3 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{2}\hat{T}_1^2\hat{T}_2 + \frac{1}{24}\hat{T}_1^4 \longrightarrow \text{Quadruples}$$

$$+\ldots \qquad\qquad\longrightarrow \text{Higher excitations}$$

- ● Quadruple excitations are generated by five different mechanisms

Simultaneous interaction of four electrons – Connected terms

Interaction of two independent electron pairs – Disconnected terms

The exponential Ansatz

The CCSD wave function operator

$$\hat{\Omega}^{CCSD} = e^{\hat{T}_1 + \hat{T}_2}$$

$$= 1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{6}\hat{T}_1^3 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{2}\hat{T}_1^2\hat{T}_2 + \frac{1}{24}\hat{T}_1^4 + \ldots$$
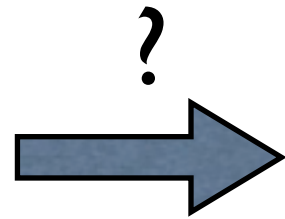
single excitations

double excitations

triple excitations

quadruple excitations

higher excitations
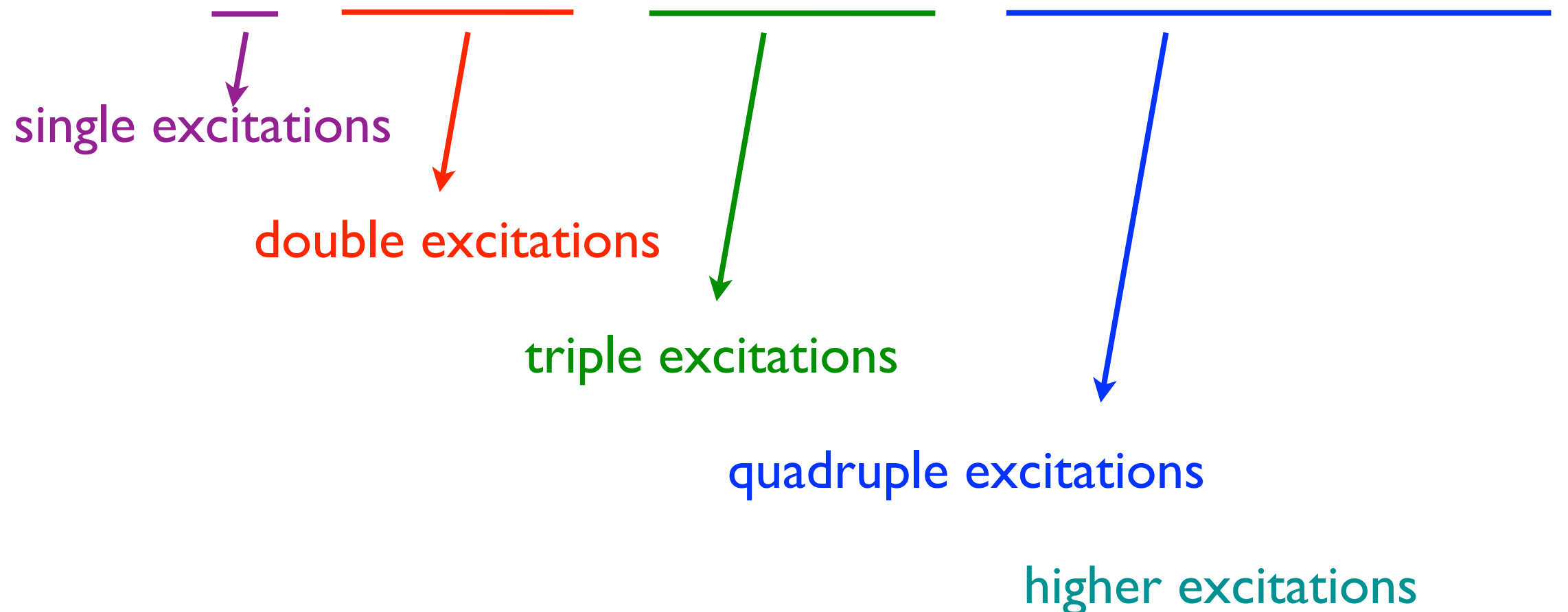
The separability of the CC wave function

Two non-interacting fragments *A* and *B*:
$$\hat{T}_{AB} = \hat{T}_A + \hat{T}_B$$

$$\Psi_A^{CC} = e^{\hat{T}_A} \Psi_{0,A}$$

?

$$\Psi_{AB}^{CC} = \Psi_A^{CC} \Psi_B^{CC}$$

$$\Psi_B^{CC} = e^{\hat{T}_B} \Psi_{0,B}$$

$$e^{\hat{T}_{AB}} = e^{(\hat{T}_A + \hat{T}_B)} = e^{\hat{T}_A} \cdot e^{\hat{T}_B}$$

$$\Psi_{AB}^{CC} = e^{\hat{T}_{AB}} \Psi_{0,AB}$$

$$\Psi_{0,AB} = \Psi_{0,A} \Psi_{0,B}$$

$$e^{\hat{T}_{AB}} \Psi_{0,AB} = e^{\hat{T}_A} \cdot e^{\hat{T}_B} \Psi_{0,A} \Psi_{0,B} = \Psi_A^{CC} \Psi_B^{CC}$$

$$E_{AB}^{CC} = \langle \Psi_{AB}^{CC} | \hat{H}_A + \hat{H}_B | \Psi_{AB}^{CC} \rangle = \langle \Psi_A^{CC} \Psi_B^{CC} | \hat{H}_A + \hat{H}_B | \Psi_A^{CC} \Psi_B^{CC} \rangle$$

$$= \langle \Psi_A^{CC} | \hat{H}_A | \Psi_A^{CC} \rangle + \langle \Psi_B^{CC} | \hat{H}_B | \Psi_B^{CC} \rangle = E_A^{CC} + E_B^{CC}$$

The CCSD energy and amplitudes

Energy and amplitudes are obtained by projecting onto $\{\Psi_0, \Psi_i^j, \Psi_{ij}^{ab}, \ldots\}$

$$\hat{H}|e^{(\hat{T}_1 + \hat{T}_2)}\Psi_0\rangle = E^{CCSD}|e^{(\hat{T}_1 + \hat{T}_2)}\Psi_0\rangle$$

⬤ Projection on $\langle\Psi_0|$ gives the CCSD energy

$$\langle\Psi_0|\hat{H}|(1 + \hat{T}_1 + \hat{T}_2 + \tfrac{1}{2}\hat{T}_1^2 + \ldots)\Psi_0\rangle = E\langle\Psi_0|(1 + \hat{T}_1 + \hat{T}_2 + \tfrac{1}{2}\hat{T}_1^2 + \ldots)\Psi_0\rangle$$

Because of the bielectronic character of the Hamiltonian, all higher excitations disappear

$$\boxed{\langle\Psi_0|\hat{H}|(1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2)\Psi_0\rangle = E}$$

Only singles and doubles cluster amplitude contribute directly to the CC energy (at any level of truncation)

The CCSD energy and amplitudes

○ Projection on $\langle\Psi_i^a|$ gives the cluster amplitudes of the single excitations

$$\langle\Psi_i^a|\hat{H}|(1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{6}\hat{T}_1^3)\Psi_0\rangle = t_i^a E$$

○ Projection on $\langle\Psi_{ij}^{ab}|$ gives the cluster amplitudes of the double excitations

$$\langle\Psi_i^a|\hat{H}|\left[1 + \hat{T}_1 + \hat{T}_2 + \tfrac{1}{2}(\hat{T}_1^2 + \hat{T}_2^2 + 2\hat{T}_1\hat{T}_2) + \tfrac{1}{6}(\hat{T}_1^3 + 3\hat{T}_1^2\hat{T}_2) + \tfrac{1}{24}\hat{T}_1^4\right]\Psi_0\rangle = t_{ij}^{ab} E$$

Set of non-linear equations ⟶ Iterative solutions

All amplitudes are coupled ⟶ Indirect influence of higher cluster amplitudes on E^{CCSD}

Beyond CCSD

CCSD (and CISD) O^2V^4 *(N⁶ scaling)*

CCSDT O^3V^5 *(N⁸ scaling)*   *computationally expensive*

Perturbative estimates of the connected triples $\hat{T}_3$

- CCSD+T(MP4)

permutation operator   *two-electron integrals*

$$T(MP4) = \sum_{\substack{i<j<k \\ a<b<c}} \frac{|\frac{1}{4}\hat{\mathcal{P}}_{ijk}^{abc}\{\sum_d \langle bc||dk\rangle t_{ij}^{ad} - \sum_l \langle lc||jk\rangle t_{il}^{ab}\}|^2}{\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c}$$

first-order estimate of the doubles amplitudes

- CCSD+T(CCSD): replace $t_{ij}^{ab}(1)$ by the CCSD amplitudes

- CCSD(T):   add a perturbative correction of a fifth-order term involving singles amplitudes

Multiconfigurational methods

Approximations to full CI

⬤ HF, CC, MP2, SDCI, etc ⟹ all approximations to full CI

A. How to select the most important configurations in the wave function?

B. How to choose the molecular orbitals?

For one dominant electronic configuration:
- Optimize molecular orbitals by HF
- Add effect of other electronic configurations by CC, MP2, etc.

Typical case: Ground state of molecules near equilibrium geometry

Approximations to full CI

What to do when more electronic configurations are essential?

Example 1: Bond breaking H_2

$$\Psi = c_1 |\sigma_g \overline{\sigma}_g\rangle + c_2 |\sigma_u \overline{\sigma}_u\rangle$$

$$\sigma_g = \frac{1}{\sqrt{2}} [H_1(1s) + H_2(1s)]$$

$$\sigma_u = \frac{1}{\sqrt{2}} [H_1(1s) - H_2(1s)]$$

R(H–H)	$|\sigma_g \overline{\sigma}_g\rangle$	$|\sigma_u \overline{\sigma}_u\rangle$
0.7 Å	0.995	-0.102
1.0 Å	0.987	-0.167
1.4 Å	0.962	-0.274
2.0 Å	0.881	-0.473
5.0 Å	0.710	-0.705
10 Å	0.707	-0.707

Examples of multiconfigurational situations

Example 2: Transition state of $2\ C_2H_4 \rightarrow C_4H_4$

$$\Psi = -0.58\ \Phi_1 + 0.63\ \Phi_2 - 0.40\ \Phi_3 + \dots$$

$$\Psi = -0.12\ \Phi_1 + 0.95\ \Phi_2 + \dots$$

$$\Psi = -0.99\ \Phi_1 + \dots$$
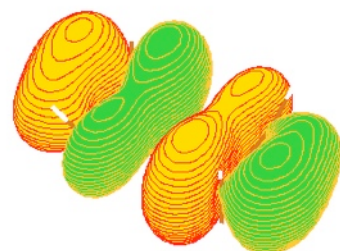
Energy [au] vs Distance between the C_2H_4 units
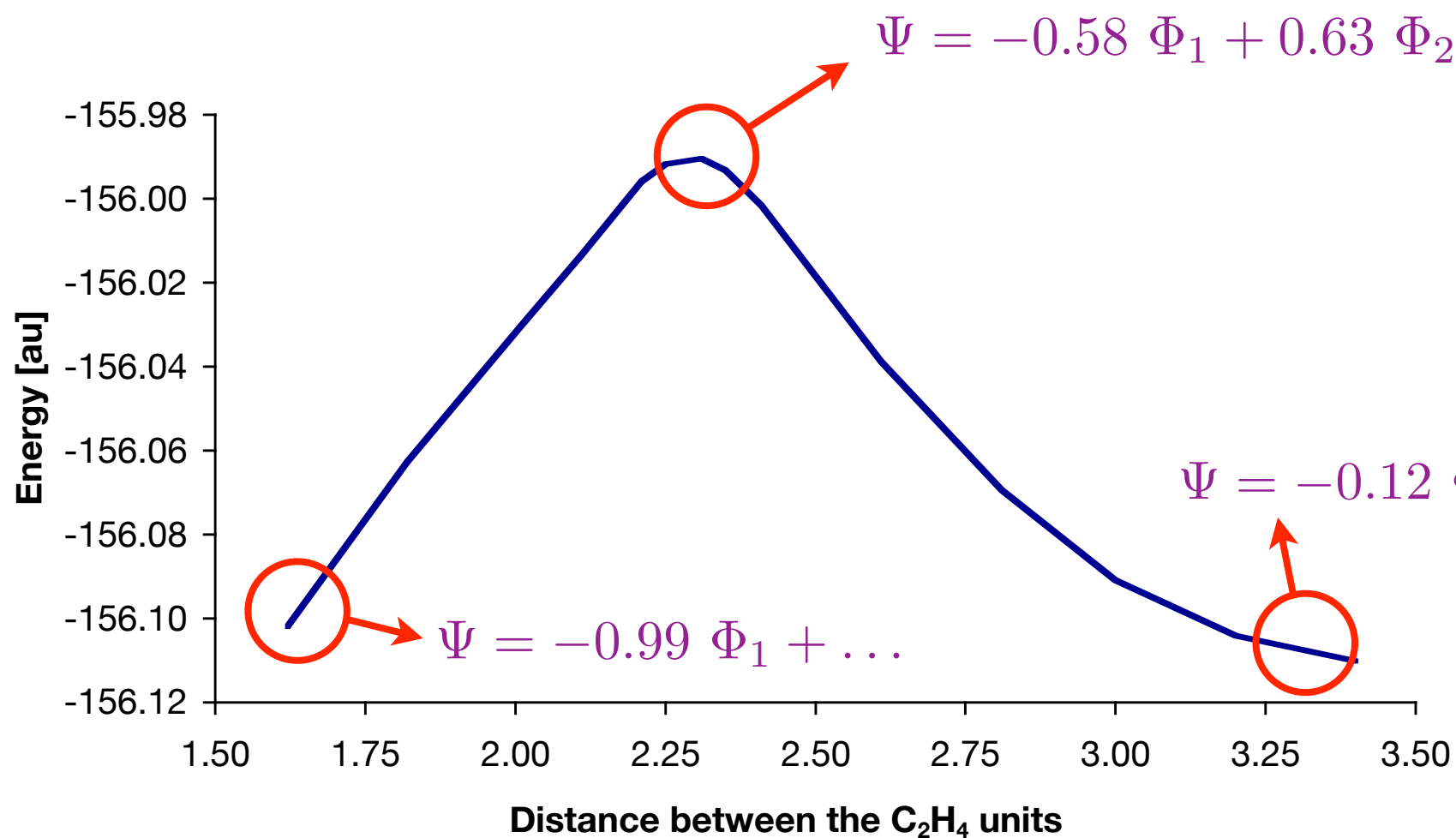
$$\Phi_1 = |\phi_1^2 \phi_2^2|$$
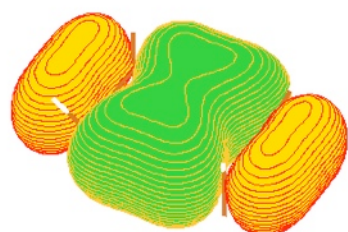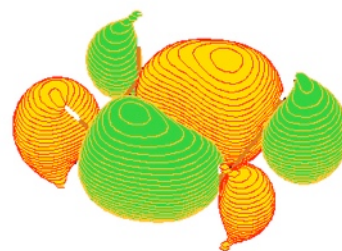
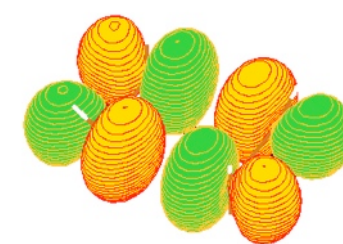$$\Phi_2 = |\phi_1^2 \phi_3^2|$$

$$\Phi_3 = |\phi_1^2 \phi_2^1 \phi_3^1|$$
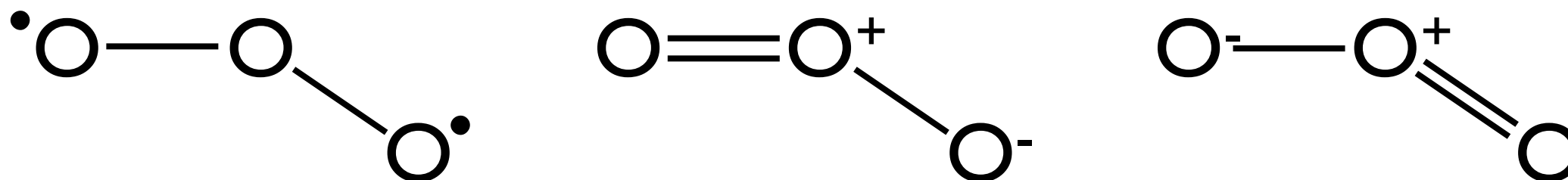
$\phi_1 = \pi + \pi$ $\phi_2 = \pi - \pi$ $\phi_3 = \pi^* + \pi^*$ $\phi_4 = \pi^* - \pi^*$

Examples of multiconfigurational situations

Example 3: Unsaturated valencies O_3

Molecular orbitals

$$\pi_1 = c_{11}\pi_A + c_{12}(\pi_b + \pi_c)$$

$$\pi_2 = c_{21}(\pi_b - \pi_c)$$

$$\pi_3 = c_{31}\pi_a - c_{32}(\pi_b + \pi_c)$$

Electronic configurations

$$\Phi_{HF} = |\pi_1^2\pi_2^2|$$

$$\Phi_2 = |\pi_1^2\pi_3^2|$$

$$\Phi_3 = |\pi_2^2\pi_3^2|$$

$$\Phi_4 = |\pi_1^2\pi_2^1\pi_3^1|$$

Multiconfigurational wave function: $\Psi = -0.89\ \Phi_{HF} + 0.45\ \Phi_2 + \dots$

Examples of multiconfigurational situations

Other examples

- Transition metal systems: $3d^n4s^2$, $3d^{n+1}4s^1$, $3d^{n+2}$ configurations can give rise to different multiplets with similar energy

- Excited states (important in photochemistry)

- Weak bonds (famous example: Cr_2)

Multiconfigurational Self-Consistent Field methods

* Starting point: choice of configurations $\Psi = \sum_i C_i |\Phi_i\rangle$

depends on the physics of the system.

* Energy mean-value: $\langle E \rangle = E(c_\mu, C_i)$

depends on the shape of the MO's (c_μ) and the

configuration expansion (C_i)

*Variational method: minimization with respect to both sets of parameters

$$\frac{\partial}{\partial c_\mu} \langle E \rangle = 0, \quad \frac{\partial}{\partial C_i} \langle E \rangle = 0$$

- Orbitals adapted to the double optimization process
- Minimal energy with respect to all parameters
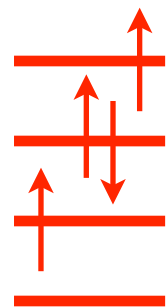- Orbital occupations are no longer integers

CASSCF

☞ In general not evident how to choose the configuration space
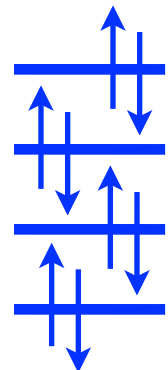
⟹ **C**omplete **A**ctive **S**pace SCF

Full CI in a limited set of MO's

Virtual orbitals
empty in all configurations

Active orbitals
variable occupation

Inactive orbitals
doubly occupied in all configurations

The MC space includes the configurations –*allowed by spin and spatial symmetry*– generated by all the possible occupations of a set of orbitals by a given number of electrons.

typically, the valence orbitals

typically, the valence electrons

Notation: CAS(n_{el},n_{orb})

CASSCF

How to choose the active space: No universal recipe!

Need for *chemical knowledge* of the system

Examples:

from our chemical knowledge on H_2

- Single bond dissociation → σ_g and σ_u → CAS(2,2)

- Ethylene cycloaddition
  - minimal active space: CAS(2,2) ($\phi_2 = \pi - \pi$
    $\phi_3 = \pi^* + \pi^*$)
  - better, full π space: CAS(4,4)
  - best, adding 2 σ and 2 σ^* orbitals: CAS(8,8)

- Transition metal atoms: 3d and 4s orbitals *(eventually adding 4p and 4d)*

Advice:

- Read the literature to see what active spaces have been applied in related systems
- Check (if possible) with larger active spaces

Beyond CASSCF

Starting point, Reference wave function

HF	CASSCF
CISD	MRCI
MP2, MP4, . . .	CASPT2, NEVPT2, . . .
CCSD, CCSD(T), . . .	MR-CC (in development)

MRCI: configuration interaction for MC systems

CASPT2: multiconfigurational equivalent of MP2

- CASPT2 is generally applicable, precision of ~0.15 eV in the relative energies of electronically excited states.
- Suffers the intruder state problem

- MR-CISD computationally very demanding, only applicable for small molecules.
- Variants: DDCI and SORCI

difference dedicated CI   spectroscopy oriented CI

CASPT2

Basic notions

- Definition of the zeroth-order Hamiltonian

$$\hat{H}^{(0)} = \hat{P}_0 \hat{F} \hat{P}_0 + \hat{P}_K \hat{F} \hat{P}_K + \hat{P}_{SD} \hat{F} \hat{P}_{SD} + \hat{P}_X \hat{F} \hat{P}_X$$

$$\hat{P}_0 = |0\rangle\langle 0| \qquad \hat{F} = \sum_{pq\sigma} f_{pq\sigma} \hat{E}_{pq} \qquad f_{pq\sigma} = -\langle 0|[[\hat{H}, \hat{a}_{q\sigma}^\dagger], \hat{a}_{p\sigma}]_+|0\rangle$$

- Construction of the first-order wave function

Uncontracted: $\Psi^{(1)} = \sum_i C_i |\Psi_i^{SD}\rangle \longrightarrow$ simple, but huge amount of parameters

Contracted: $\Psi^{(1)} = \sum_{pqrs} c_{pqrs} \hat{E}_{pq} \hat{E}_{rs} |0\rangle \rightarrow$ complicated, but less parameters, once programmed, very fast!

Important:

Due to the contracted nature of the first-order wave function, the ratio of the different configuration in the CAS cannot change under the influence of dynamical electron correlation.

CASPT2

Intruder state problem

$$\Psi = \Psi^{(0)} + \Psi^{(1)}$$

Reference weight: $\omega = 1 - \sum_{i=1}^{M} |C_i|^2$

Order of magnitude: $\omega \sim (1 + \alpha)^{-\frac{N}{2}}$ $\alpha \approx 0.015$

N = number of electrons

N = 10 → ω ~ 0.93

N = 100 → ω ~ 0.47

N = 200 → ω ~ 0.23

• Compare the reference weight of the different states!!!

☞ For low reference weight: $c_j = \dfrac{\langle \Phi_j | \hat{V} | \Psi^{(0)} \rangle}{E^{(0)} - E_j}$ is huge

1. External configuration has a large matrix element → add Φ_j to the CAS

2. $\langle \Phi_j | \hat{V} | \Psi^{(0)} \rangle$ is small; $E_j \approx E^{(0)}$ → Intruder state
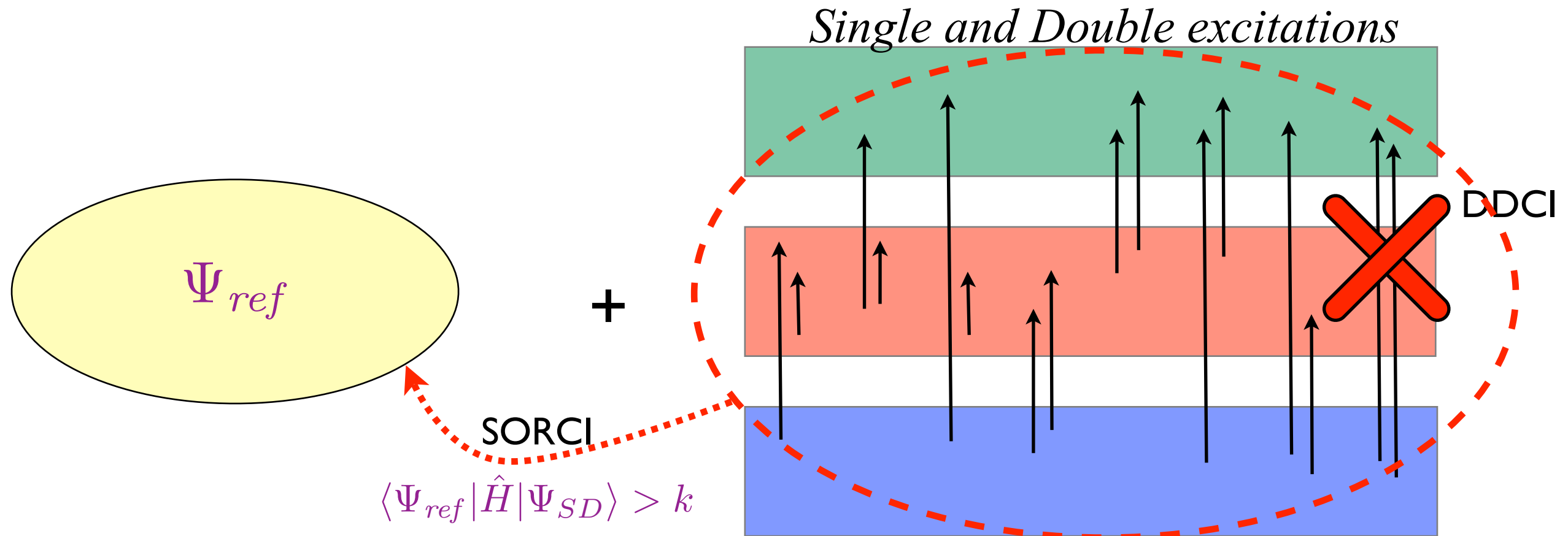
Apply level-shifted CASPT2

CASPT2

Intruder state problem: Add an arbitrary shift to the expectation values of $\hat{H}^{(0)}$ of the external configurations to avoid the near-degeneracy

$$\tilde{c}_j = \frac{\langle \Phi_j | \hat{V} | \Psi^{(0)} \rangle}{E^{(0)} - E_j + \mu}$$

$$\tilde{E}^{(2)} = \sum_j \frac{\langle \Psi^{(0)} | \hat{V} | \Phi_j \rangle \langle \Phi_j | \hat{V} | \Psi^{(0)} \rangle}{E^{(0)} - E_j + \mu}$$

$$E^{(2)} = \tilde{E}^{(2)} + \mu \left(1 - \frac{1}{\omega} \right)$$

DDCI and SORCI

DDCI

- Eliminating the double excitations from inactive to virtual orbitals
- Based on perturbation theory arguments that show that these configurations do not affect the energy difference between states
- Good for vertical excitations, no geometries

SORCI

- Excited configurations are ordered by importance based on the interaction with the reference wave function
- CI is performed between Ψ_{ref} and the most important excited configurations