



L3

Methods for excited state calculations

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How to solve the electronic equation

LIGHT AND
MOLECULES

$$(H_e - E_i)\psi_i = 0$$



Configuration Interaction (CI)

Slater determinant for N electrons

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix} \equiv |\chi_1 \chi_2 \cdots \chi_N\rangle$$

$$|\Psi_0\rangle = |\chi_1 \chi_2 \cdots \chi_a \chi_b \cdots \chi_N\rangle = |HF\rangle$$

$$|\Psi_a^r\rangle = |\chi_1 \chi_2 \cdots \chi_r \chi_b \cdots \chi_N\rangle = |S\rangle \quad \text{Single substitution}$$

$$|\Psi_{ab}^{rs}\rangle = |\chi_1 \chi_2 \cdots \chi_r \chi_s \cdots \chi_N\rangle = |D\rangle \quad \text{Double substitution}$$

\vdots

$$|\Phi\rangle = c_0|\Psi_0\rangle + \sum_S c_S|S\rangle + \sum_D c_D|D\rangle + \dots$$

Variational Principle

$$E[\Phi + \delta\Phi] = E[\Phi] \quad \langle\Phi|\Phi\rangle = 1$$



$$\mathbf{Hc} = E\mathbf{Sc}$$

$$H_{ij} = \langle\Psi_i|\hat{H}|\Psi_j\rangle$$

$$S_{ij} = \langle\Psi_i|\Psi_j\rangle$$

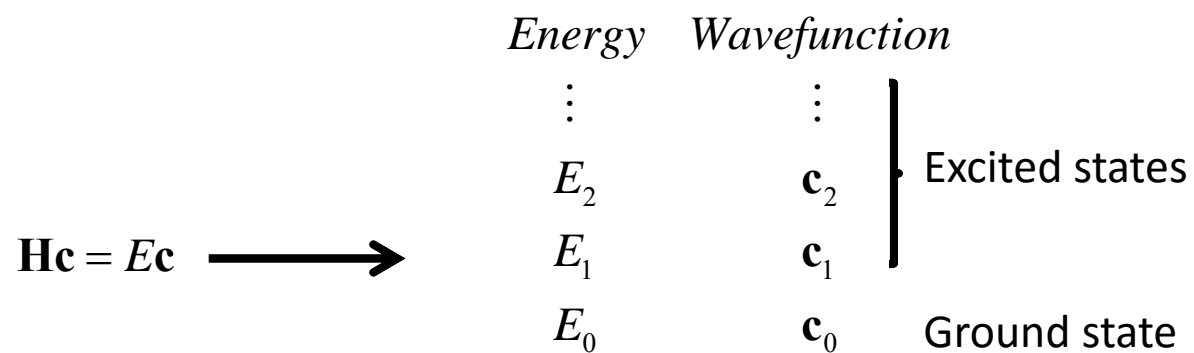
- Often, CI expansion is done in terms of CFS's (configuration state functions).
- CFS's are linear combinations of Slater Determinants that are orthogonal and eigenvectors of spin and angular momentum operators.
- Basis of CFS's are built with GUGA (graphical unitary group approach).

CI wavefunction

$$|\Phi\rangle = \sum_i c_i |\Psi_i^{CFS}\rangle \quad \langle \Psi_i^{CFS} | \Psi_j^{CFS} \rangle = \delta_{ij}$$

The CI problem is to solve

$$\mathbf{Hc} = E\mathbf{c}$$



- Clear hierarchy of levels:

CIS < CID < CISD < ... < Full CI

- CI is time consuming:

CIS < CID < CISD < CISD+Q



Davidson correction



Coupled Cluster (CC)

$$|CC\rangle = e^T |HF\rangle$$

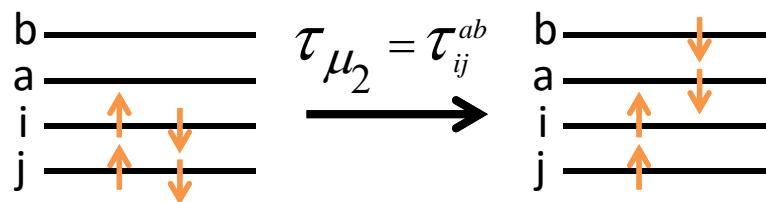
$$T = t_{\mu_1} \tau_{\mu_1} + t_{\mu_2} \tau_{\mu_2} + \dots + t_{\mu_n} \tau_{\mu_n}$$

- Sneskov and Christiansen, WIREs **2**, 566 (2011)

$$|CC\rangle = e^T |HF\rangle$$

$$T = t_{\mu_1} \tau_{\mu_1} + t_{\mu_2} \tau_{\mu_2} + \dots + t_{\mu_n} \tau_{\mu_n}$$

Excitation operator
 i^{th} -order
 $t_{\mu_i} \tau_{\mu_i}$
amplitudes



- Sneskov and Christiansen, WIREs **2**, 566 (2011)

$$|CC\rangle = e^T |HF\rangle$$

$$T = t_{\mu_1} \tau_{\mu_1} + t_{\mu_2} \tau_{\mu_2} + \dots + t_{\mu_n} \tau_{\mu_n}$$

- Choose a truncation level
- Insert this Ansatz into TDSE
- Get a set of nonlinear equations for the amplitudes and ground-state energy

$$e_{\mu_i}(t) = \langle \mu_i | e^{-T} H e^T | HF \rangle$$

$$E_{CC} = \langle HF | e^{-T} H e^T | HF \rangle$$

- Sneskov and Christiansen, WIREs **2**, 566 (2011)

$$|CC\rangle = e^T |HF\rangle$$

$$T = t_{\mu_1} \tau_{\mu_1} + t_{\mu_2} \tau_{\mu_2} + \dots + t_{\mu_n} \tau_{\mu_n}$$

Truncation produces a well defined hierarchy of methods:

$$CCS < CCSD < CCSDT < \dots$$

$$\nearrow$$

CC3, CCSD(T)

With some exotic flavors

- Sneskov and Christiansen, WIREs **2**, 566 (2011)

For excited states, the important quantity is the CC Jacobian matrix **A**:

$$A_{\mu_i \nu_i} = \frac{\partial e_{\mu_i}}{\partial t_{\nu_i}}$$

$$e_{\mu_i}(t) = \langle \mu_i | e^{-T} H e^T | HF \rangle$$

Response Theory shows that:

- Excited-state energies Ω are eigenvalues of **A**
- Contribution **R** from each determinant is the eigenvector

The problem is to solve

$$\mathbf{AR} = \Omega \mathbf{R}$$

Jacobian is not a symmetric matrix!

$$A_{\mu_i\nu_i} = \frac{\partial e_{\mu_i}}{\partial t_{\nu_i}} \neq A_{\nu_i\mu_i} = \frac{\partial e_{\nu_i}}{\partial t_{\mu_i}}$$

$$\mathbf{AR} = \mathbf{\Omega R}$$

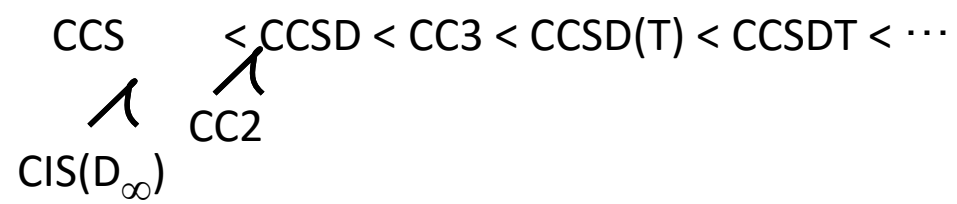
$$\mathbf{LA} = \mathbf{L\Omega}$$

$$\mathbf{LR} = 1$$

=====

Left and right eigenvalues converged to the same
Results within 0.42E-07 a.u.

CC is time-consuming...



CC doesn't work well for degenerated excited states

Non-symmetric Jacobian \rightarrow eigenvalues (energies) may be imaginary

$$\text{CCS} < \mathbf{CIS}(\mathbf{D}_\infty) < \text{CC2} < \text{CCSD} < \text{CC3} < \text{CCSD(T)} < \text{CCSDT} < \dots$$

$$\downarrow$$

$$\mathbf{A}(\text{CIS}(\mathbf{D}_\infty))$$

Build a symmetric Jacobian:

$$\mathbf{A}(\text{ADC}(2)) = \frac{1}{2} \left[\mathbf{A}(\text{CIS}(\mathbf{D}_\infty)) + \mathbf{A}(\text{CIS}(\mathbf{D}_\infty))^\dagger \right]$$

- Hättig, Köhn, J Chem Phys **117**, 6939 (2002)

CCS < CIS(D_∞) < CC2 < CCSD < CC3 < CCSD(T) < CCSDT < ...

↓
ADC(2)

ADC(2): Algebraic Diagrammatic Construction scheme up to second order

ADC(2) is not strictly a CC method

It is an excited-state propagator for ground-state MP2 (Schirmer1982)

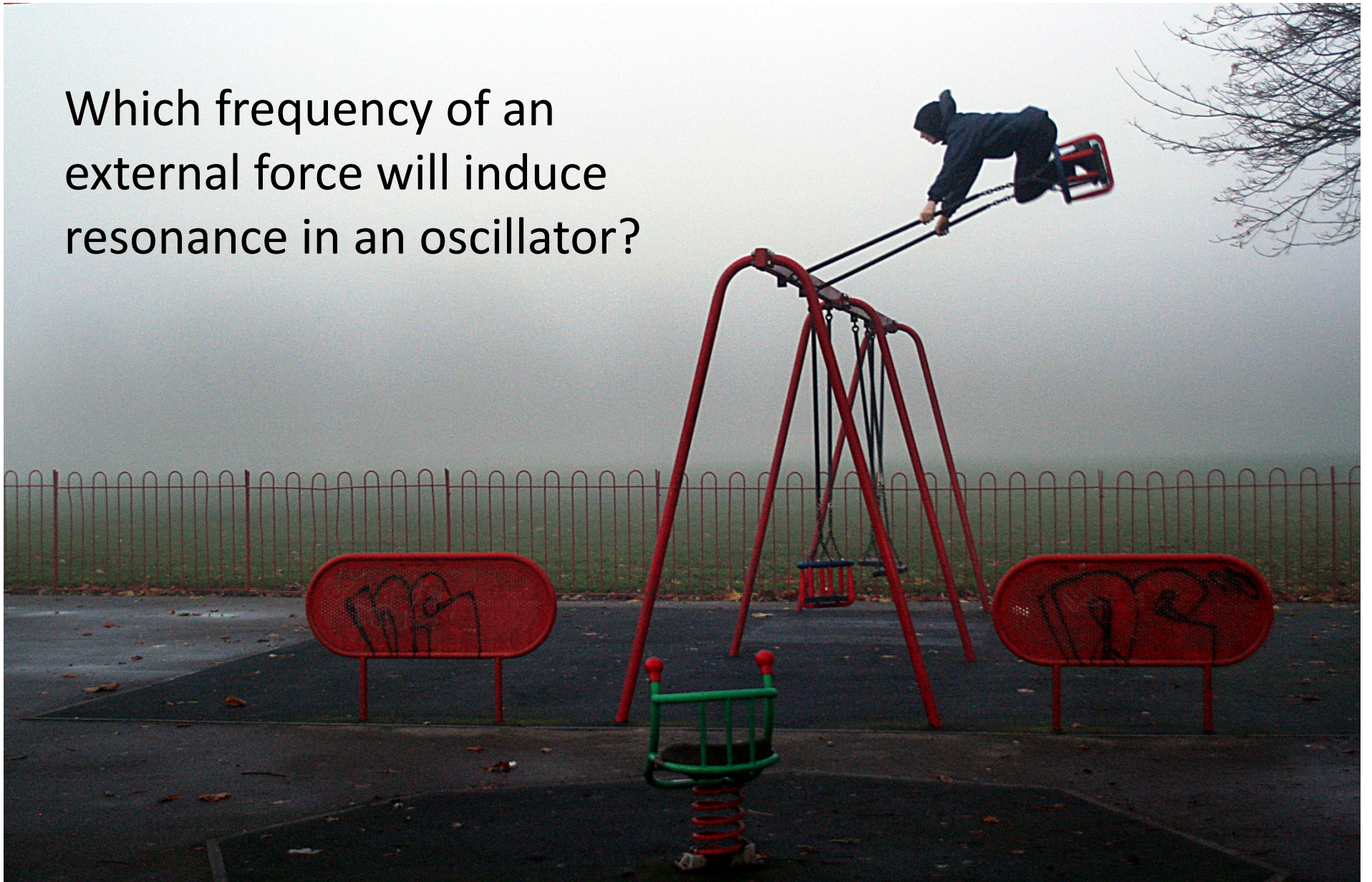
These excited states are equivalent to the symmetrized CIS(D_∞)

Trofimov, Krivdina, Weller, Schirmer, Chem Phys **329**, 1 (2006)



*Time-dependent Density Functional
Theory (TDDFT)*

Which frequency of an external force will induce resonance in an oscillator?



$$\langle \hat{O}(t) \rangle = \int_{-\infty}^{+\infty} \chi(t-t') \phi(t') dt'$$

↑ ↑ ↑
expected value susceptibility perturbation

$$x(t) = \int_{-\infty}^{+\infty} \chi(t-t') F(t') dt'$$

↑ ↑ ↑
position susceptibility force

$$\delta\rho(\mathbf{r}, t) = \int_{-\infty}^{+\infty} \int \chi(\mathbf{r}, \mathbf{r}', t-t') \delta v_{app}(\mathbf{r}', t') dt' d\mathbf{r}'$$

↑ ↑ ↑
density variation susceptibility perturbation

Linear response

$$\delta\rho(\mathbf{r},t) = \int \int_{-\infty}^{+\infty} \chi(\mathbf{r},\mathbf{r}',t-t') \delta v_{app}(\mathbf{r}',t') dt' d\mathbf{r}'$$

Fourier space

$$\delta\rho(\mathbf{r},\omega) = \int \chi(\mathbf{r},\mathbf{r}',\omega) \delta v_{app}(\mathbf{r}',\omega) d\mathbf{r}' = \chi * \delta v_{app}$$

Non-interacting Kohn-Sham

$$\delta\rho_s = \chi_s * \delta v_s$$

$$\begin{aligned} \delta v_s &= \delta \left[V_{eN} + \delta v_{app} + v_H[\rho] + v_{XC}[\rho] \right] \\ &= \frac{\delta v_H[\rho_0]}{\delta\rho} \delta\rho + \frac{\delta v_{XC}[\rho_0]}{\delta\rho} \delta\rho \\ &= K \delta\rho \end{aligned}$$

In terms of KS orbitals ϕ , occupations f , orbital energies ε , and XC functional A_{XC} , the matrix elements of χ and K are:

$$\begin{aligned} [\chi^s]_{ij\sigma,kl\tau}^{-1} &= \delta_{\sigma,\tau} \delta_{i,k} \delta_{j,l} \frac{\omega - (\varepsilon_{k\sigma} - \varepsilon_{l\sigma})}{f_{l\sigma} - f_{k\sigma}} \\ K_{ij\sigma,kl\tau}(\omega) &= \int d\mathbf{r} d\mathbf{r}' \frac{\phi_{i\sigma}^*(\mathbf{r}) \phi_{j\sigma}(\mathbf{r}) \phi_{k\tau}(\mathbf{r}') \phi_{l\tau}^*(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ &+ \int d(t-t') e^{i\omega(t-t')} \int d\mathbf{r} d\mathbf{r}' \phi_{i\sigma}^*(\mathbf{r}) \phi_{j\sigma}(\mathbf{r}) \\ &\times \frac{\delta^2 A_{XC}[\rho]}{\delta\rho_\sigma(\mathbf{r}, t) \delta\rho_\tau(\mathbf{r}', t')} \phi_{k\tau}(\mathbf{r}') \phi_{l\tau}^*(\mathbf{r}'). \end{aligned}$$

Runge-Gross Theorem

$$\delta\rho_s = \chi_s * \delta v_s = \chi * \delta v = \delta\rho$$

$$\delta v_s = \mathbf{K} \delta\rho$$

$$\chi^{-1} = \chi_s^{-1} - \mathbf{K}$$

Reordering orbitals in terms of occupation:

$$\chi^{-1} = \omega \begin{bmatrix} \mathbf{I} & 0 \\ 0 & -\mathbf{I} \end{bmatrix} - \begin{bmatrix} \mathbf{A}(\omega) & \mathbf{B}(\omega) \\ \mathbf{B}^*(\omega) & -\mathbf{A}^*(\omega) \end{bmatrix}$$

Energies are poles of the susceptibility χ (*system resonance*).
 Therefore, they can be obtained by solving:

$$\begin{bmatrix} \mathbf{A}(\omega) & \mathbf{B}(\omega) \\ \mathbf{B}^*(\omega) & -\mathbf{A}^*(\omega) \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = \omega \begin{bmatrix} \mathbf{I} & 0 \\ 0 & -\mathbf{I} \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix}$$



*Multiconfigurational
self-consistent field (MCSCF)*

$$|\Phi\rangle = \sum_i c_i |\Psi_i\rangle \quad \text{CI combination of Slater determinants}$$

$$|\Psi_k\rangle = |\chi_1 \chi_2 \dots\rangle \quad \text{Slater determinants combination of spin-orbitals}$$

$$\chi_{2l} = \psi_l(\mathbf{r}) \alpha(\omega) \quad \text{Spin-orbital is product of molecular orbital and spin function}$$

$$\psi_n = \sum_m C_m \phi_m \quad \text{Molecular orbital combination of atomic orbitals (basis functions)}$$

To solve CI wavefunction, two sets of coefficients must be determined, \mathbf{C} and \mathbf{c} .

$$|\Phi\rangle = f(\mathbf{C}, \mathbf{c})$$

Two strategies:

CI (configuration interaction)

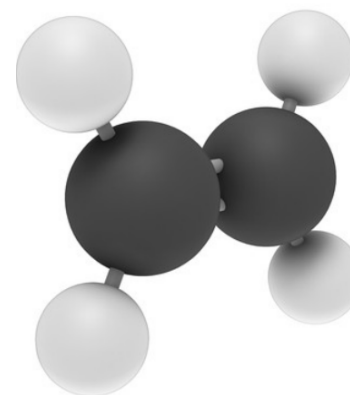
1. First, get molecular orbitals (find \mathbf{C})
2. Then, solve CI (find \mathbf{c})

MCSCF (multiconfigurational self-consistent field)

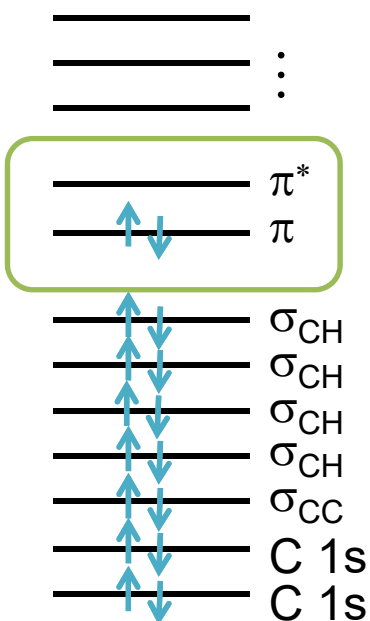
1. Get \mathbf{C} and \mathbf{c} simultaneously

MCSCF is expensive

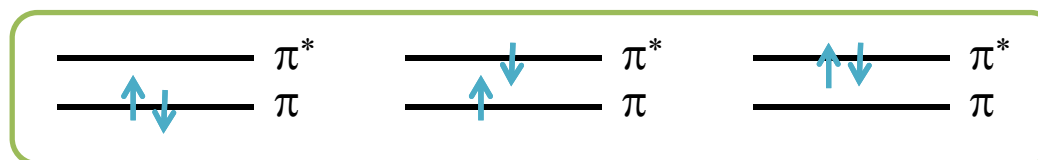
MCSCF in a small subspace of molecular orbitals



For instance:

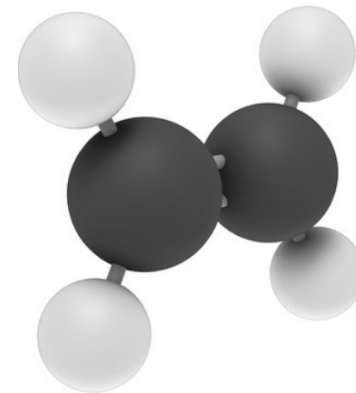


CAS(2,2)



But it can be much more complicated

$$\begin{aligned}
 \text{MCSCF} = & \{[\text{PP}_{\text{CC}}] \times 4[\text{PP}_{\text{CH}}] \times [\text{CAS}(2, 2)_{\pi} \rightarrow 4\text{AUX}_{\text{Ryd}}]\} \\
 & + \{[\text{PP}_{\text{CC}}] \times 3[\text{PP}_{\text{CH}}] \times [\text{CAS}(2, 2)_{\pi} \leftrightarrow \text{PP}_{\text{CH1}}]\} \\
 & + \{[\text{PP}_{\text{CC}}] \times 3[\text{PP}_{\text{CH}}] \times [\text{CAS}(2, 2)_{\pi} \leftrightarrow \text{PP}_{\text{CH2}}]\} \\
 & + \{[\text{PP}_{\text{CC}}] \times 3[\text{PP}_{\text{CH}}] \times [\text{CAS}(2, 2)_{\pi} \leftrightarrow \text{PP}_{\text{CH3}}]\} \\
 & + \{[\text{PP}_{\text{CC}}] \times 3[\text{PP}_{\text{CH}}] \times [\text{CAS}(2, 2)_{\pi} \leftrightarrow \text{PP}_{\text{CH4}}]\}.
 \end{aligned}$$



- Sellner, Barbatti, Müller, Domcke, Lischka, Mol Phys **111**, 2439 (2013)



Non-dynamical electron correlation?

- The non-relativistic Born-Oppenheimer WF is:

$$\underbrace{\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; s_1, s_2, \dots, s_N)}_{\text{Electronic wavefunction}} = \underbrace{\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)}_{\text{Spatial part}} \underbrace{\zeta(s_1, s_2, \dots, s_N)}_{\text{Spin-part}}$$

Pauli Principle: **A** = $\left\{ \begin{array}{ll} \mathbf{A} & \times \quad \mathbf{S} \\ \mathbf{S} & \times \quad \mathbf{A} \end{array} \right.$ or

The spatial part of the WF should belong to a representation of the permutation group S_N in the same ways that it belongs to a representation of the point group.

How should a 3- e^- (Doublet) WF look like?

- 3- e^- Slater Determinant $\Psi = |\psi_1 \bar{\psi}_2 \psi_3\rangle$

$$\Psi = \frac{1}{\sqrt{3!}} \{ \psi_1 \psi_2 \psi_3 \alpha \beta \alpha + \psi_2 \psi_3 \psi_1 \beta \alpha \alpha + \psi_3 \psi_1 \psi_2 \alpha \alpha \beta \\ - \psi_3 \psi_2 \psi_1 \alpha \beta \alpha - \psi_2 \psi_1 \psi_3 \beta \alpha \alpha - \psi_1 \psi_3 \psi_2 \alpha \alpha \beta \}$$

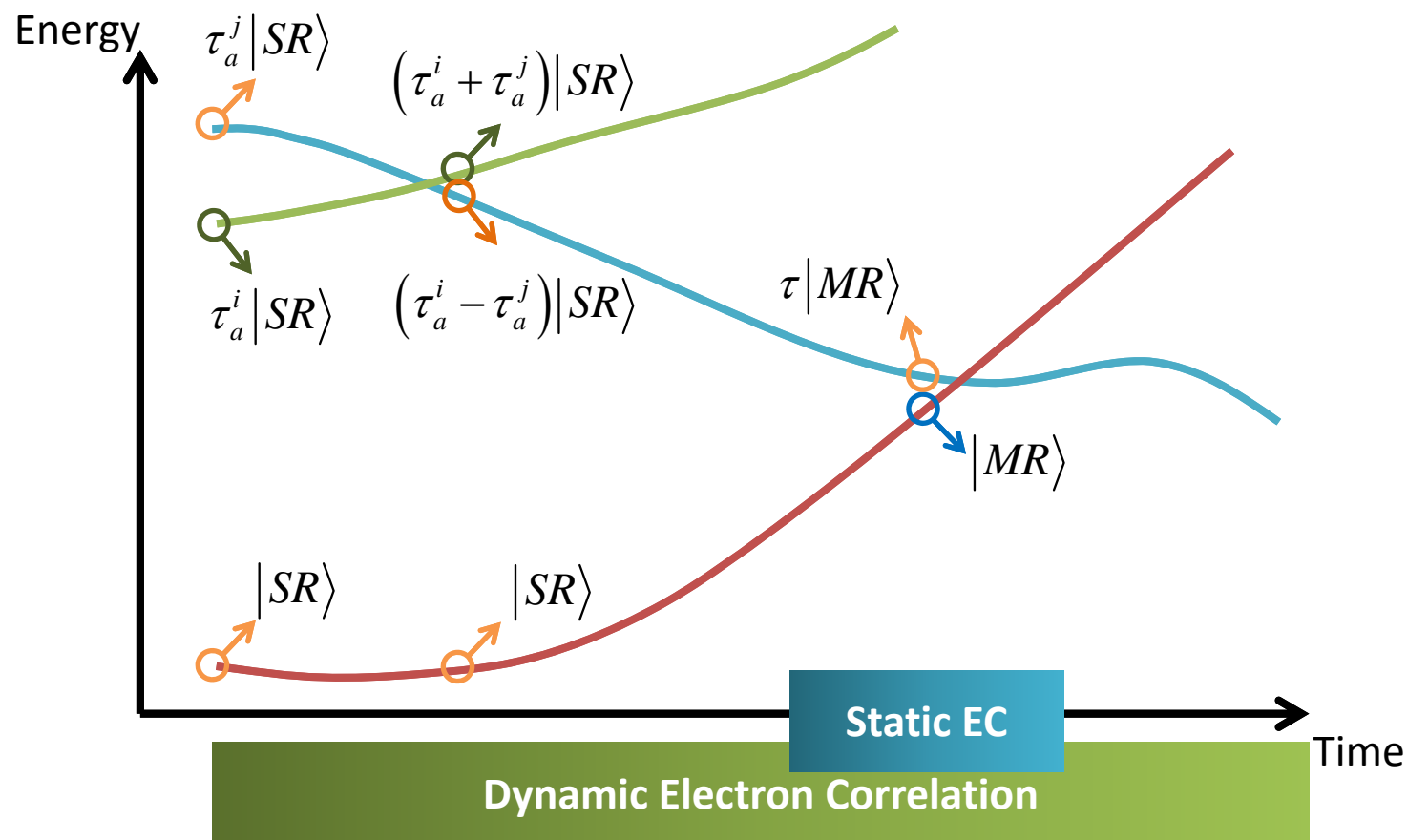
- 3- e^- WF with correct permutation symmetry (S_3 group):

$$\Psi = C \left\{ \left[\psi_1 \psi_2 \psi_3 + \psi_2 \psi_1 \psi_3 - \psi_3 \psi_2 \psi_1 - \psi_2 \psi_3 \psi_1 \right] \left[\alpha \beta \alpha - \beta \alpha \alpha \right] \right. \\ \left. + \left[\psi_1 \psi_2 \psi_3 - \psi_2 \psi_1 \psi_3 + \psi_3 \psi_2 \psi_1 - \psi_2 \psi_3 \psi_1 \right] \left[\alpha \alpha \beta - \beta \alpha \alpha \right] \right\}$$

- The wrong permutation symmetry of the Slater determinant is the origin of the non-dynamical correlation problem.



Multireference Methods (MR)



Certain states cannot be described by a single reference.
They need multireference methods

Usual way is to compute dynamics correlation on the top
of a multiconfigurational WF:

CASSCF + CI \rightarrow MRCI

CASSCF + CC \rightarrow MRCC

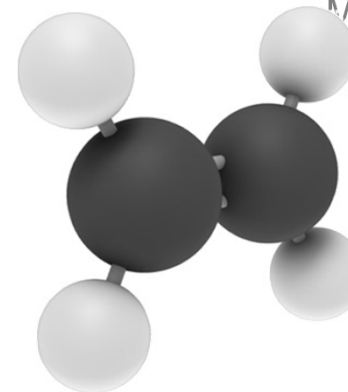
CASSCF + PT \rightarrow MRPT

Single-reference CI: expansion based on one single function $|\Psi_0\rangle$

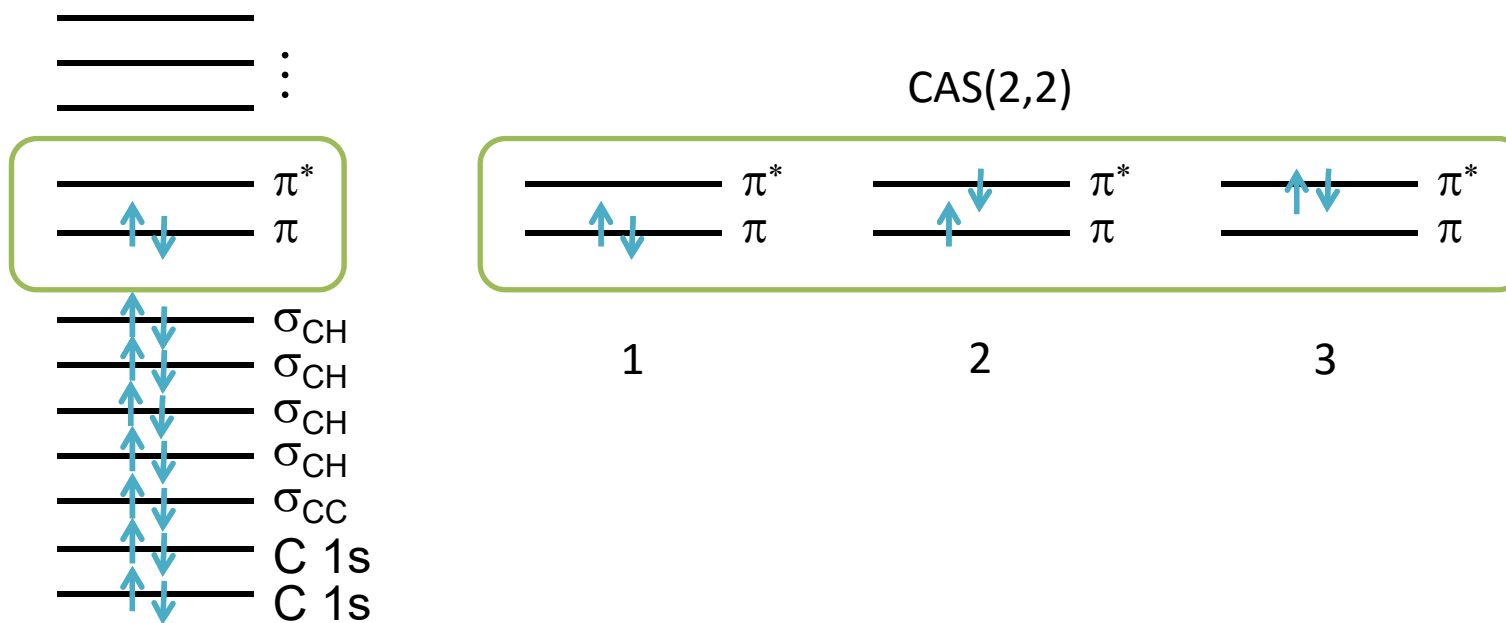
$$|\Phi_{SRCI}\rangle = c_0|\Psi_0\rangle + \sum_s c_s \hat{S}|\Psi_0\rangle + \sum_d c_d \hat{D}|\Psi_0\rangle + \dots$$

Multi-reference CI: expansion based on small set of functions $\{|\Psi_n\rangle\}$

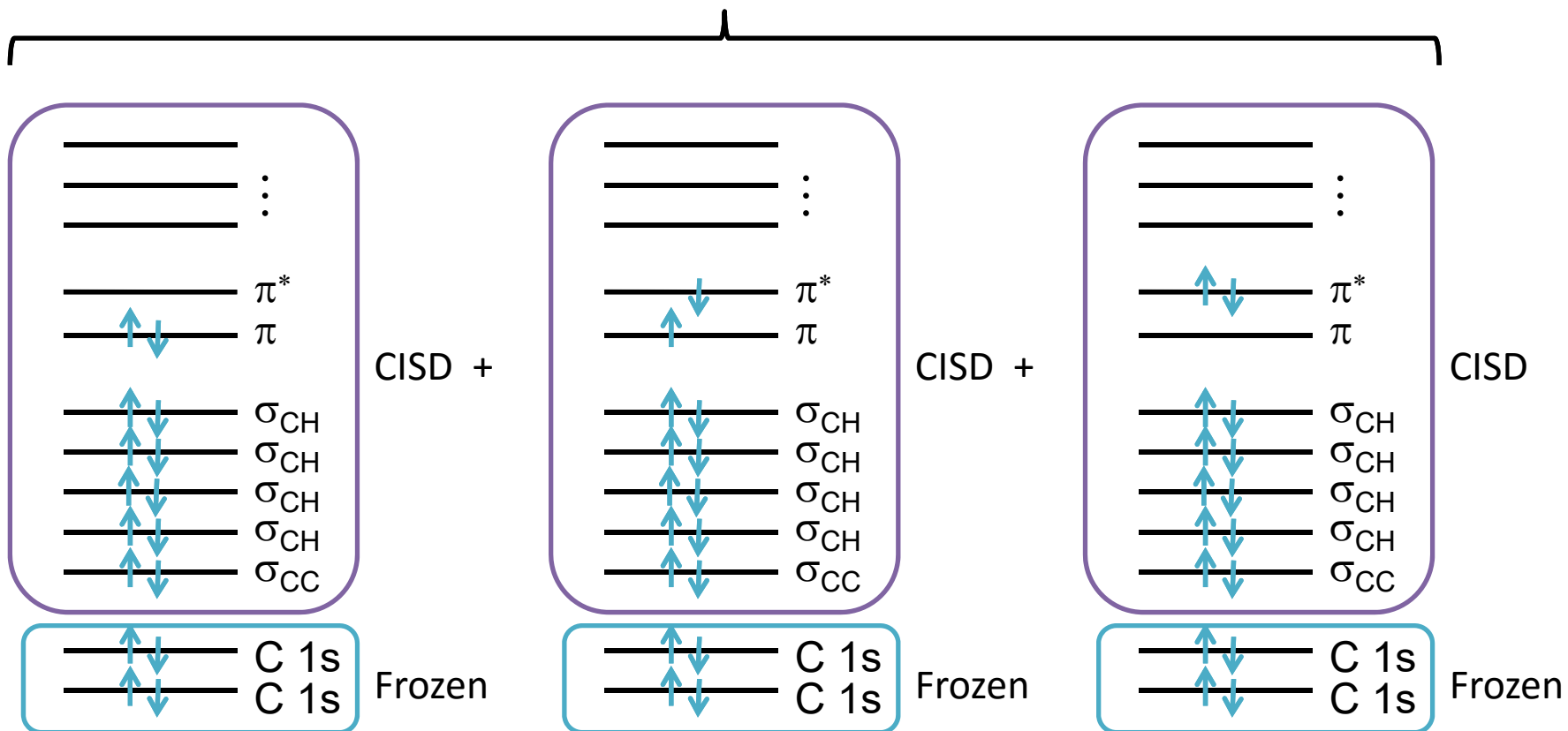
$$|\Phi_{MRCI}\rangle = \sum_n c_n |\Psi_n\rangle + \sum_s \sum_n c_{sn} \hat{S}|\Psi_n\rangle + \sum_d \sum_n c_{dn} \hat{D}|\Psi_0\rangle + \dots$$



CAS(2,2) as reference space for MRCI



MR-CISD(2,2)



Perturbation approach

$$H = H_0 + V$$

$$H_0 |\Psi_I^{CAS}\rangle = E_I^0 |\Psi_I^{CAS}\rangle$$

Energy to the second order

$$E^{CASPT2} = \langle \Phi_i^{CAS} | H_0 | \Phi_i^{CAS} \rangle + \sum_I \frac{\langle \Phi_i^{CAS} | V(H_0) | \Psi_I^{CSF} \rangle \langle \Psi_I^{CSF} | V(H_0) | \Phi_i^{CAS} \rangle}{E_i^0 - \epsilon_I^0}$$



*Overview of methods
for excited states*

- Single-reference
- NAC not available

Available for EOM-CC: Tajti and Szalay, J Chem Phys **131**, 124104 (2009)

- Relatively fast (CC2)
- Good vertical energies

Schreiber et al., J Chem Phys **128**, 134110 (2008)

- Problems with charge-transfer and Rydberg states
Dreuw and Head-Gordon, Chem Rev 105, 4009 (2005)
- Problems with Kohn-Sham convergence at multireference regions
Perdew et al., JCTC 5, 902 (2009)
- Conical intersections have wrong dimensionality

- Very fast
- Gradients
- Good vertical energies
Silva-Junior et al., J Chem Phys **129**, 104103 (2008)
Jacquemin et al., JCTC **5**, 2420 (2009)

- Tip: crossing between excited states are well described
 - Barbatti et al., Chem Phys **375**, 26 (2010)

TDDFTB

- Same advantages and disadvantages than TDDFT, but with poorer results
- Very fast (semi-empirical)
 - Elstner, Theor Chem Acc **116**, 316 (2006)

DFT/MRCI

- Fast and good results (KS convergence still a problem at MR regions)
- No gradients available
 - Grimme and Waletzke, J Chem Phys **111**, 5645 (1999)

Single-determinant Kohn-Sham

- Large (condensed-phase) systems can be treated
- Quality of simulations is unclear
 - Craig et al., Phys Rev Lett **95**, 163001 (2005)

- Bad description of ionic states
Angeli, J Comput Chem **30**, 1319 (2009)
- Too expensive
- Too sensitive to active-space choice
Szymczak et al., Int J Quantum Chem **111**, 3307 (2011)

- Clear and intuitive
- Multireference / multiconfigurational
- Gradients, nonadiabatic couplings (NAC) available

- Tip: Combination of CAS + GVB-PP stabilizes the dynamics
 - Sellner et al., J Chem Phys **131**, 024312 (2009)

- Sensitive to active-space choice
- Too expensive for dynamics
- Analytic gradients and NACs not available

- Much faster than MRCI
- Multiconfigurational
- Good vertical excitations
Schreiber et al., J Chem Phys **128**, 134110 (2008)
- The best option for potential-surface calculation

- Tip: Beware of good results for wrong reason! It tends to overestimate ionic states ↑
Conventional zero-order Hamiltonian tends to underestimate energies ↓
- Ghigo et al., Chem Phys Lett **396**, 142 (2004)

- Excited-state surfaces are not fully reliable
- Parameters are neither complete nor fully transferable

- Very, very fast
- Good vertical energies at OMx levels
Silva-Junior and Thiel, JCTC **6**, 1546 (2010)

- Tip: MRCI available in combination with AM1, PM3, and OM2
- Granucci et al., J Chem Phys **114**, 10608 (2001)
 - Koslowski et al. J Comput Chem **24**, 714 (2003)

- There are many different methods available to compute excited states.
- They differ in terms of accuracy and computational costs.
- To be able to determine which one is the most adequate for each case is essential.