Multiconfigurational methods

…or when static correlation comes into play

Andrej Antalík

Introduction to electronic structure methods
4.12.2023

EPFL

Hartree-Fock equations

- An *n*-electron problem breaks down to a set of coupled one-electron equations

$$H|\Psi\rangle = E|\Psi\rangle$$

$$H = -\sum_a h_a + \sum_{ab} r_{ab}^{-1}$$

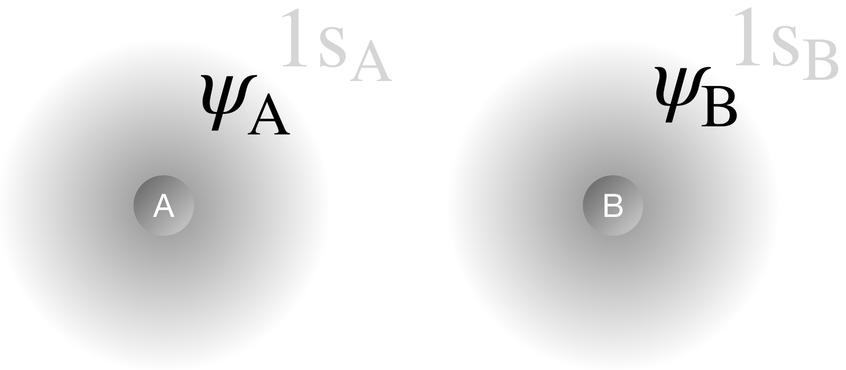
$$f|\varphi_a\rangle = \sum_{b=1}^{n} \varepsilon_{ab}|\varphi_b\rangle$$

$$f = h + \underbrace{\sum_{b=1}^{n} (J_b - K_b)}_{v_{\mathrm{HF}}}$$

- Wave function approximated by a single Slater determinant $|\varphi_1\varphi_2\ldots\varphi_n\rangle$
  - mean-field approximation $r_{ab}^{-1} \rightarrow v_{\mathrm{HF}}$
  - one Slater determinant = single configuration ground state only

Why multiconfigurational wave functions

- Let's have a look at H_2 dissociation
  - We assume RHF wave function with doubly occupied bonding orbital



$$\sigma = N\left(\psi_A + \psi_B\right)$$

$$|\Phi_0\rangle = |\Phi_{RHF}\rangle = |\sigma\bar{\sigma}\rangle = \begin{vmatrix} \sigma(1)\alpha(1) & \sigma(1)\beta(1) \\ \sigma(2)\alpha(2) & \sigma(2)\beta(2) \end{vmatrix} = \sigma(1)\sigma(2)\Theta_{2,0}$$

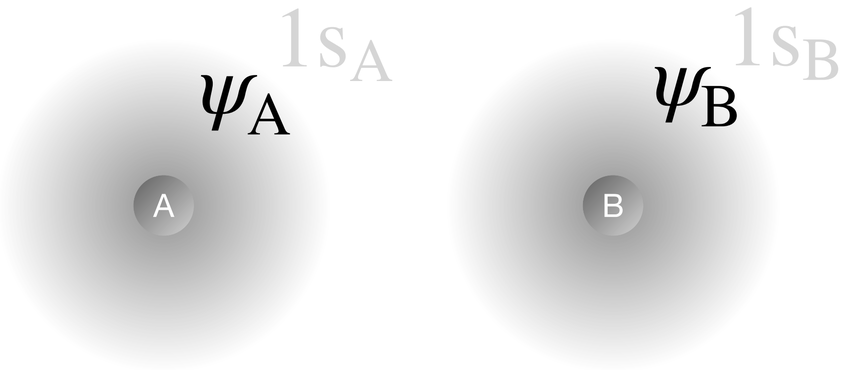
$$\Theta_{2,0} = \frac{1}{\sqrt{2}}\left(\alpha(1)\beta(2) - \beta(1)\alpha(2)\right)$$

$$= N^2\left(\psi_A(1)\psi_A(2) + \psi_A(1)\psi_B(2) + \psi_B(1)\psi_A(2) + \psi_B(1)\psi_B(2)\right)\Theta_{2,0}$$

Ionic terms present even when $|\mathbf{r}_A - \mathbf{r}_B| \rightarrow \infty$

H_2 dissociation MC wave function

- Now we add an excited configuration composed of a doubly occupied antibonding orbital



$$\sigma = N\left(\psi_A + \psi_B\right) \qquad \sigma^* = N\left(\psi_A - \psi_B\right)$$

$$|\Phi_0\rangle = N^2\left(\psi_A(1)\psi_A(2) + \psi_A(1)\psi_B(2) + \psi_B(1)\psi_A(2) + \psi_B(1)\psi_B(2)\right)\Theta_{2,0}$$

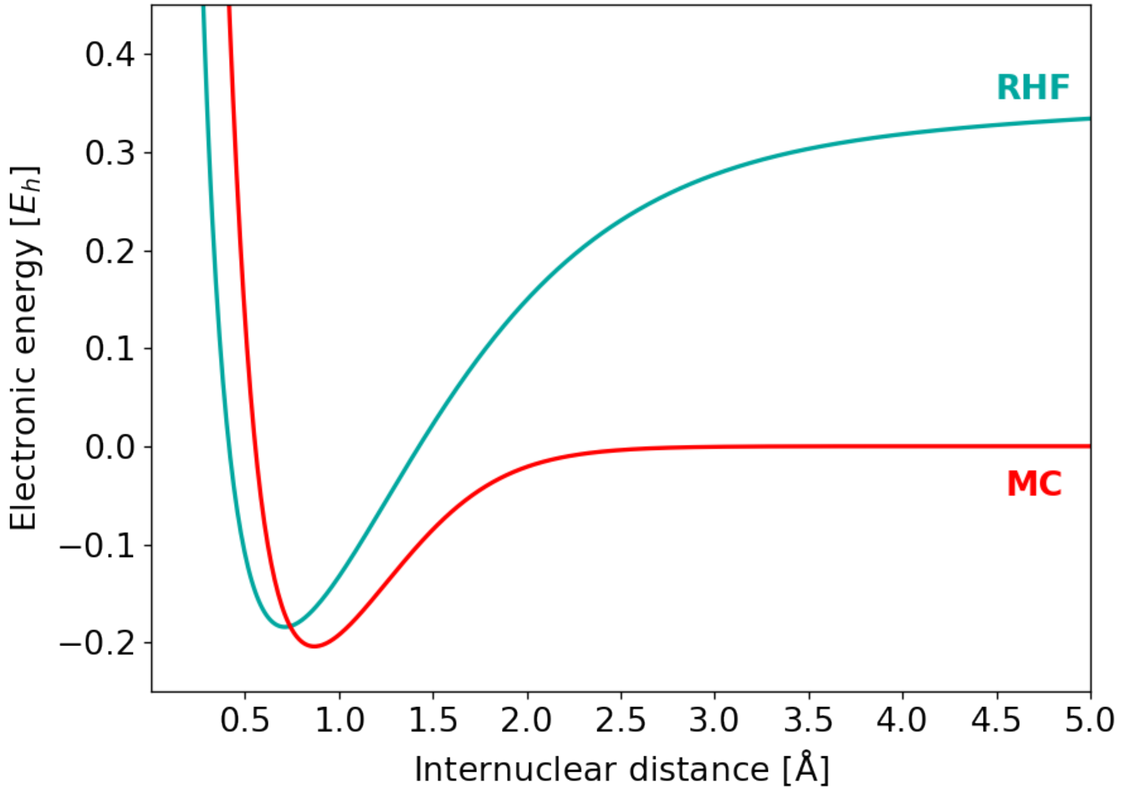
$$|\Phi_{1\bar{1}}^{2\bar{2}}\rangle = N^2\left(\psi_A(1)\psi_A(2) - \psi_A(1)\psi_B(2) - \psi_B(1)\psi_A(2) + \psi_B(1)\psi_B(2)\right)\Theta_{2,0}$$

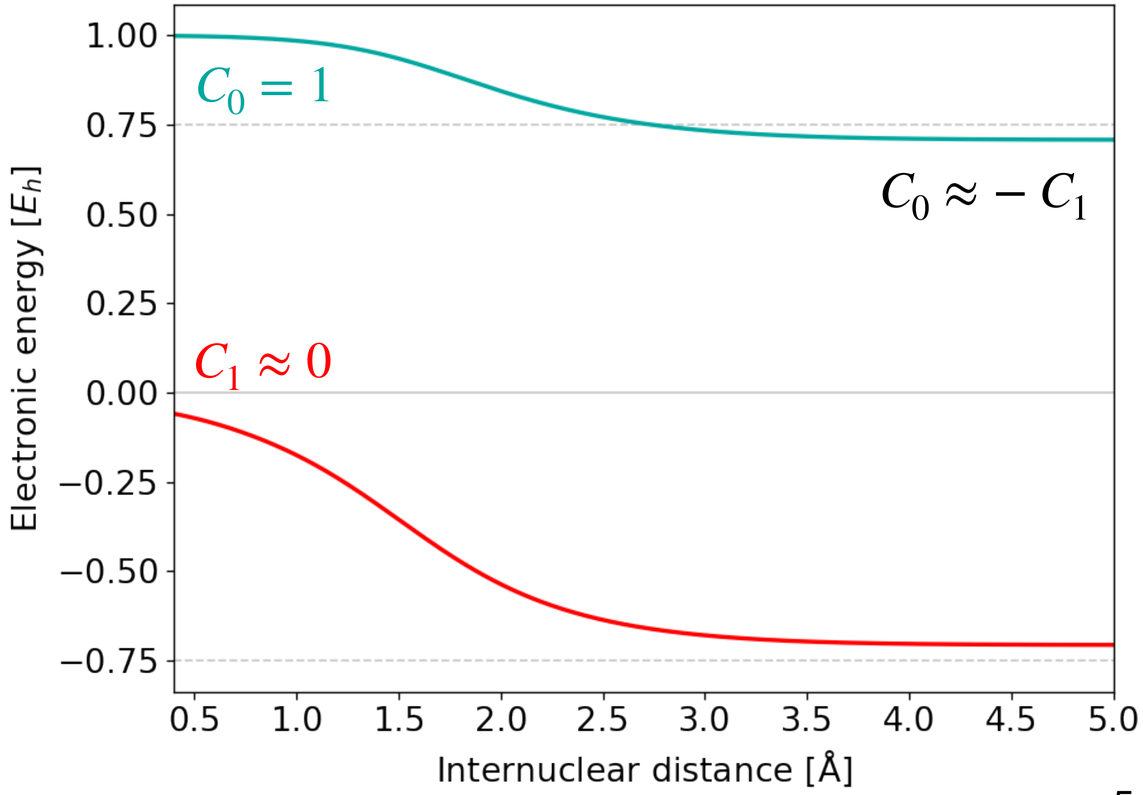
$$|\Psi_{MC}\rangle = C_0|\Phi_0\rangle + C_1|\Phi_{1\bar{1}}^{2\bar{2}}\rangle$$

H_2 dissociation **MC wave function**

- Additional wave function flexibility allows for correct dissociation process

$$|\Psi_{\mathrm{MC}}\rangle = C_0\,|\Phi_0\rangle + C_1\,|\Phi_{1\bar{1}}^{2\bar{2}}\rangle$$

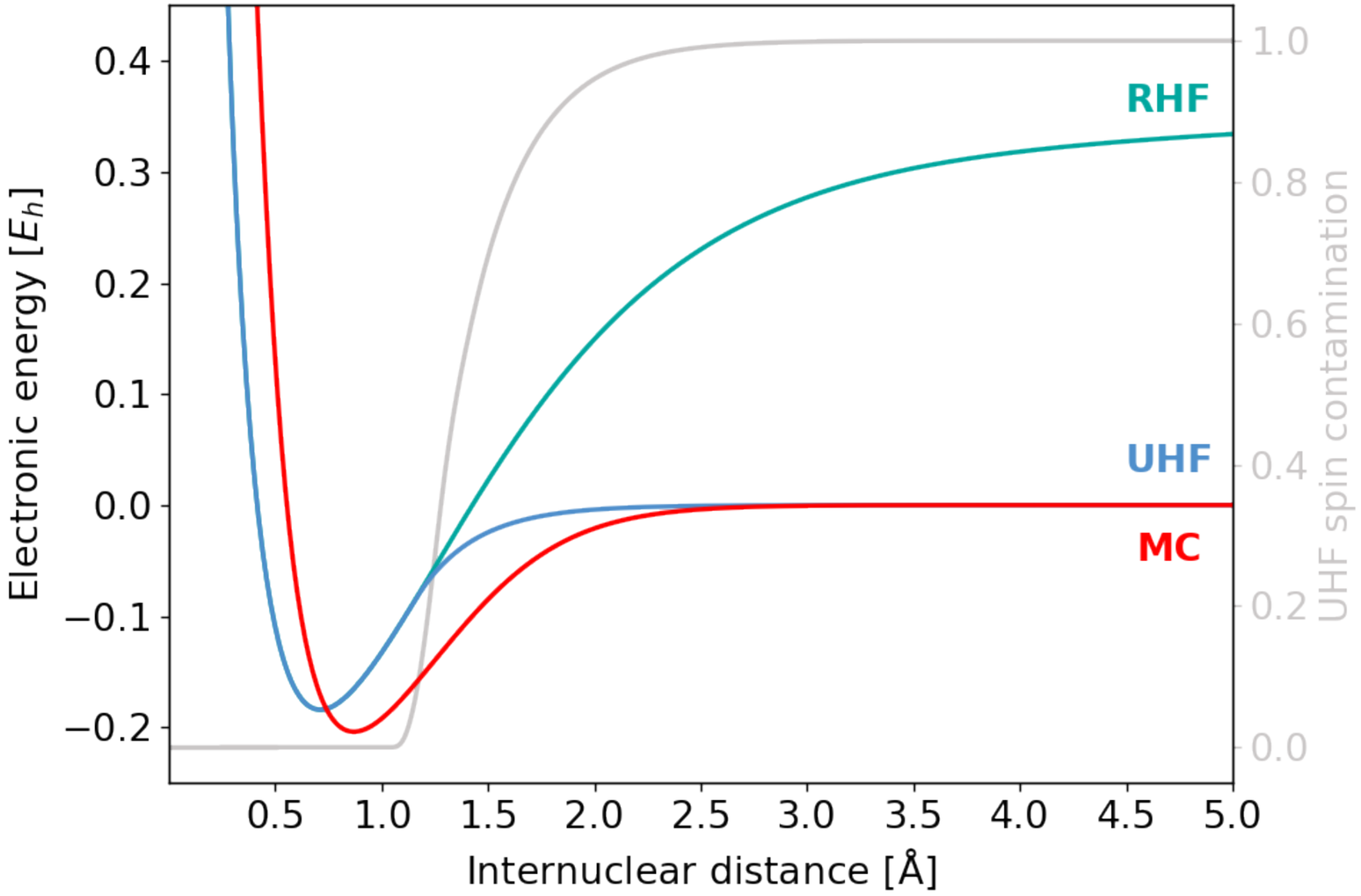




H_2 dissociation What about UHF

- Additional flexibility of a UHF wave function allows for correct dissociation process
- …yet, it suffers from spin-contamination

$$\langle S^2 \rangle - S^2_{\text{exact}} \neq 0$$



Electron correlation

- In electronic structure theory, correlation energy defined as

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

- HF energy correct within 1% of the exact energy

Not good enough for relative energies!

- Consequence of having the wave function approximated by a single Slater determinant

$r_{ab}^{-1} \rightarrow v_{\text{HF}}$	dynamic correlation	always present due to the lack of instantaneous Coulomb repulsion
$\lvert \varphi_1 \varphi_2 \ldots \varphi_n \rangle$	static correlation	when there are near-degeneracies present in the ground state

n-electron expansions

- Wave function expansion into a basis of excited Slater determinants

$$|\Psi_{\mathrm{FCI}}\rangle = C_0|\Phi_0\rangle + \sum_{ar} C_a^r|\Phi_a^r\rangle + \frac{1}{2}\sum_{abrs} C_{ab}^{rs}|\Phi_{ab}^{rs}\rangle + \frac{1}{6}\sum_{abcrst} C_{abc}^{rst}|\Phi_{abc}^{rst}\rangle + \cdots$$

$$|\Psi_{\mathrm{CI}}\rangle = (1 + \hat{C}_1 + \cdots + \hat{C}_n)|\Phi_0\rangle$$

$$|\Psi_{\mathrm{CC}}\rangle = e^{\hat{T}_1+\hat{T}_2+\cdots+\hat{T}_n}|\Phi_0\rangle$$

All $n \to \infty$ roads lead to the exact energy

$$\hat{C}_1|\Phi_0\rangle = \sum_{ar} C_a^r|\Phi_a^r\rangle$$

FCI wave function and correlation

- Weights of a FCI wave function reflect the dominant type of electron correlation for a particular system

purely dynamic

- dominant HF determinant
- many low-weight determinants

$$|\Psi_{\mathrm{FCI}}\rangle = C_0|\Phi_0\rangle + C_{ab}^{rs}|\Phi_{ab}^{rs}\rangle + C_{ab}^{rt}|\Phi_{ab}^{rt}\rangle + C_a^r|\Phi_a^r\rangle + C_a^s|\Phi_a^s\rangle + C_a^t|\Phi_a^t\rangle + \cdots$$

static

- a few high-weight determinants

Cutting the FCI costs

- We can limit the maximum excitation rank… → e.g. CISD

$$|\Psi_{\text{CISD}}\rangle = C_0|\Phi_0\rangle + \sum_{ar} C_a^r|\Phi_a^r\rangle + \frac{1}{2}\sum_{abrs} C_{ab}^{rs}|\Phi_{ab}^{rs}\rangle \Big| + \frac{1}{6}\sum_{abcrst} C_{abc}^{rst}|\Phi_{abc}^{rst}\rangle + \cdots$$

- …or the orbital space in which we perform excitations → CAS-CI

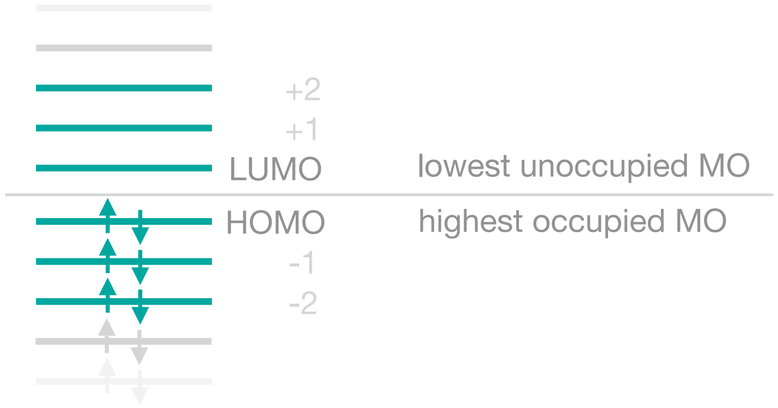
$$|\Psi_{\text{CAS-CI}}\rangle = C_0|\Phi_0\rangle + \sum_{ar} C_a^r|\Phi_a^r\rangle + \frac{1}{2}\sum_{abrs} C_{ab}^{rs}|\Phi_{ab}^{rs}\rangle + \frac{1}{6}\sum_{abcrst} C_{abc}^{rst}|\Phi_{abc}^{rst}\rangle + \cdots$$

HOMO

$$a, b, c\ldots \in \{1, 2\ldots, \Big| H-2, H-1, H\}$$

$$r, s, t\ldots \in \{L, L+1, L+2, \Big| \ldots N-1, N\}$$

LUMO

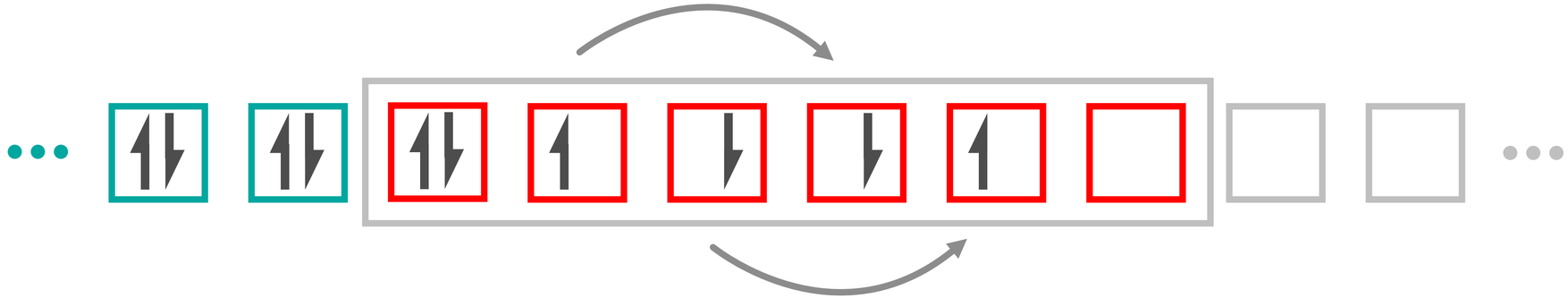


Complete active space

- Complete active space CAS(*n*, *k*)
  - all possible configurations using *n* electrons in *k* orbitals

still FCI scaling!

$$\binom{2k}{n}$$



occupied	active	virtual
2	**FCI**	**0**
fixed occupation	performed	fixed occupation

CAS-CI = FCI restricted to a CAS!

Multiconfigurational SCF

- MCSCF wave function for the state *I*

$$|\Psi_{\mathrm{MC}}\rangle = \sum_I C_I |\Phi_I(\mathbf{c})\rangle \qquad \text{where} \quad |\Phi_I(\mathbf{c})\rangle = |\varphi_1(\mathbf{c_1})\,\varphi_2(\mathbf{c_2})\ldots\rangle$$ Slater determinants

- This wave function is then optimized variationally
  - …but w.r.t. to two sets of variational parameters:

$\mathbf{C}$ CI coefficients
$\mathbf{c}$ orbitals coefficients

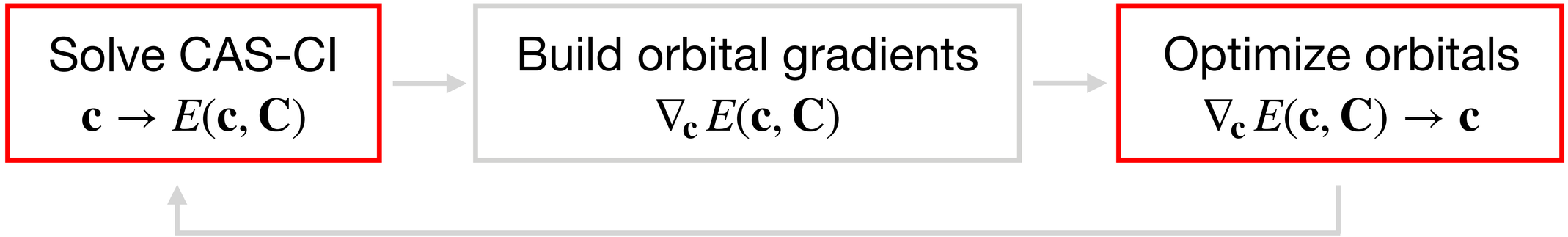
$$E_{\mathrm{MCSCF}} = \min_{\mathbf{c},\mathbf{C}} E(\mathbf{c},\mathbf{C}) = \min_{\mathbf{c},\mathbf{C}} \frac{\langle\Psi(\mathbf{c},\mathbf{C})|H|\Psi(\mathbf{c},\mathbf{C})\rangle}{\langle\Psi(\mathbf{c},\mathbf{C})|\Psi(\mathbf{c},\mathbf{C})\rangle} \qquad \text{with the constraint} \quad \sum_I |C_I|^2 = 1$$

MCSCF Solution

- Varying parameters $\mathbf{c}$ and $\mathbf{C}$ so that $E(\mathbf{c}, \mathbf{C})$ becomes stationary…

OR

- …might be decoupled into a two-step procedure



- Compared to SCF, where only the occupied orbitals are optimized, now we optimize all orbitals contained within the active space

Multireference methods

- MRCI — Multireference configuration interaction
  - Linear excitation operator applied to a MC(SCF) wave function
  - Each reference determinant has its own set of CI coefficients

$$|\Psi_{\mathrm{MRCI}}\rangle = (1 + \hat{C}_1 + \hat{C}_2 + \cdots)|\Psi_{\mathrm{MC}}\rangle \longleftarrow \sum_I C_I |\Phi_I\rangle \qquad C(I) \equiv C_I$$

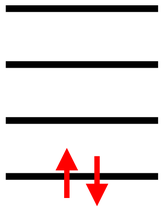
$$= \sum_I \left(C(I)|\Phi_I\rangle + \sum_{ar} C_a^r(I)|(\Phi_I)_a^r\rangle + \frac{1}{2}\sum_{abrs} C_{ab}^{rs}(I)|(\Phi_I)_{ab}^{rs}\rangle + \cdots \right)$$

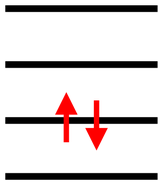
- CASPT2 — CAS perturbation theory through second order
  - Rayleigh-Schrödinger PT applied to a CASSCF wave function

Quiz

- What active space composition would you choose for the study of N_2 dissociation? How many electrons in how many orbitals? Which ones?
- Consider a degenerate ground state described by a wave function $|\Psi_0\rangle$ comprising two Slater determinants $|\Phi_0\rangle$ and $|\Phi_1\rangle$. If we only take $|\Phi_0\rangle$ as a reference for a CID calculation instead of $|\Psi_0\rangle$, how many configurations would be missing in the CID expansion?

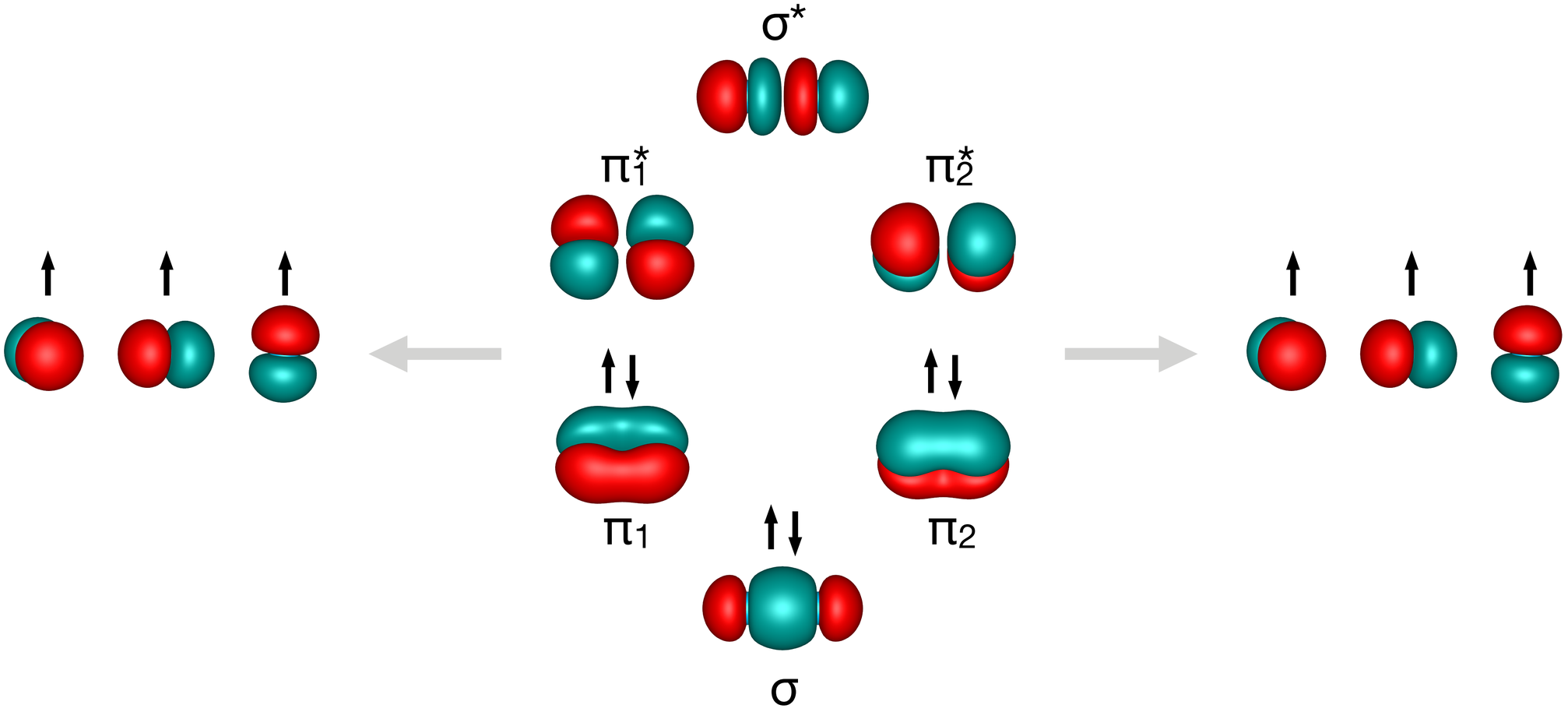
$$|\Psi_0\rangle = |\Phi_0\rangle + |\Phi_1\rangle$$

$|\Phi_0\rangle =$ 

$|\Phi_1\rangle =$ 

Why SR methods fail? N_2 dissociation

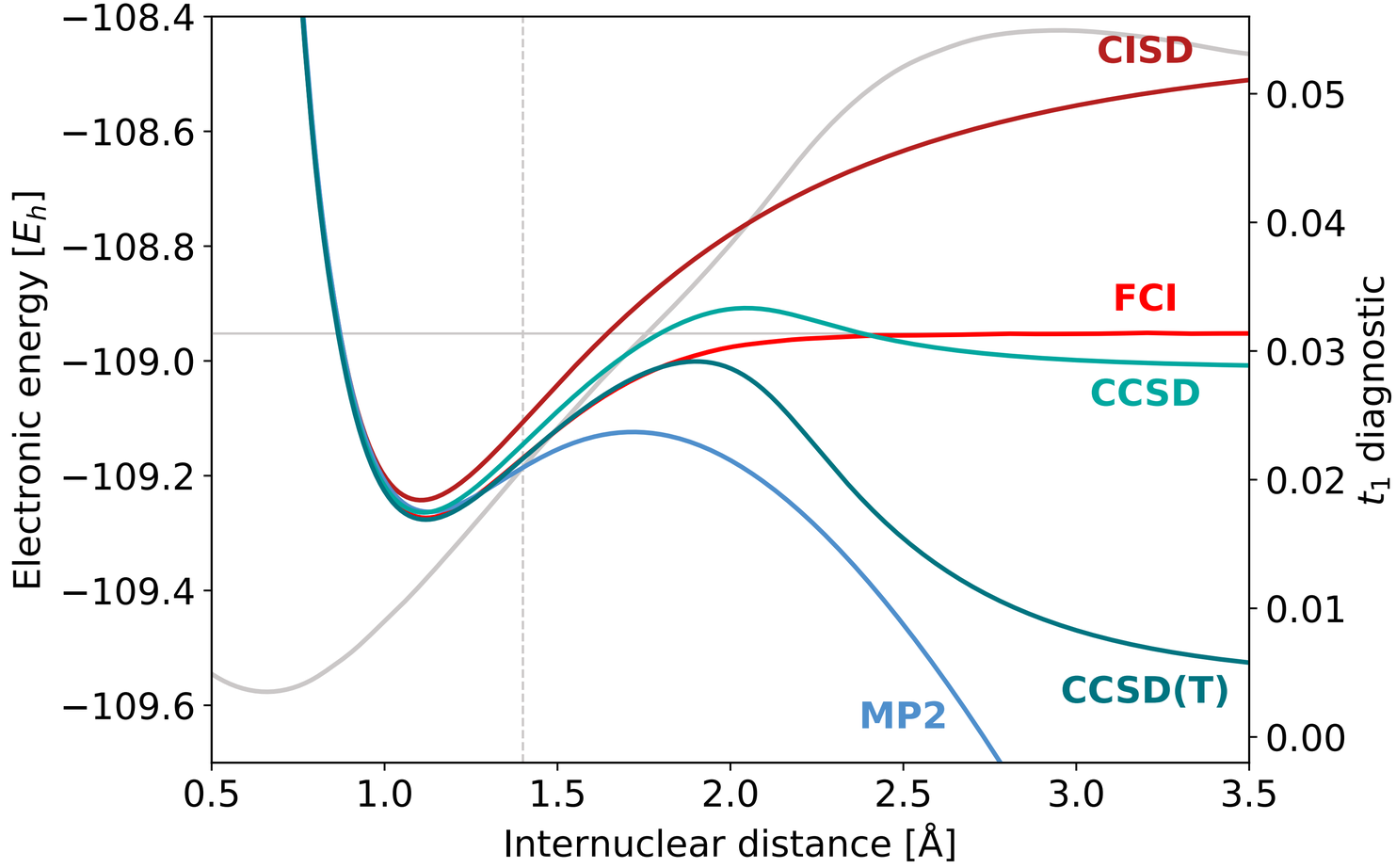
- Singlet N_2 dissociates into two quartet nitrogen atoms



N_2 dissociation A single-reference catastrophe

- CCSD → t_1 diagnostic
  - calculation reliable if

$$t_1 = \frac{|\mathbf{t}_1|}{\sqrt{n}} < 0.02$$

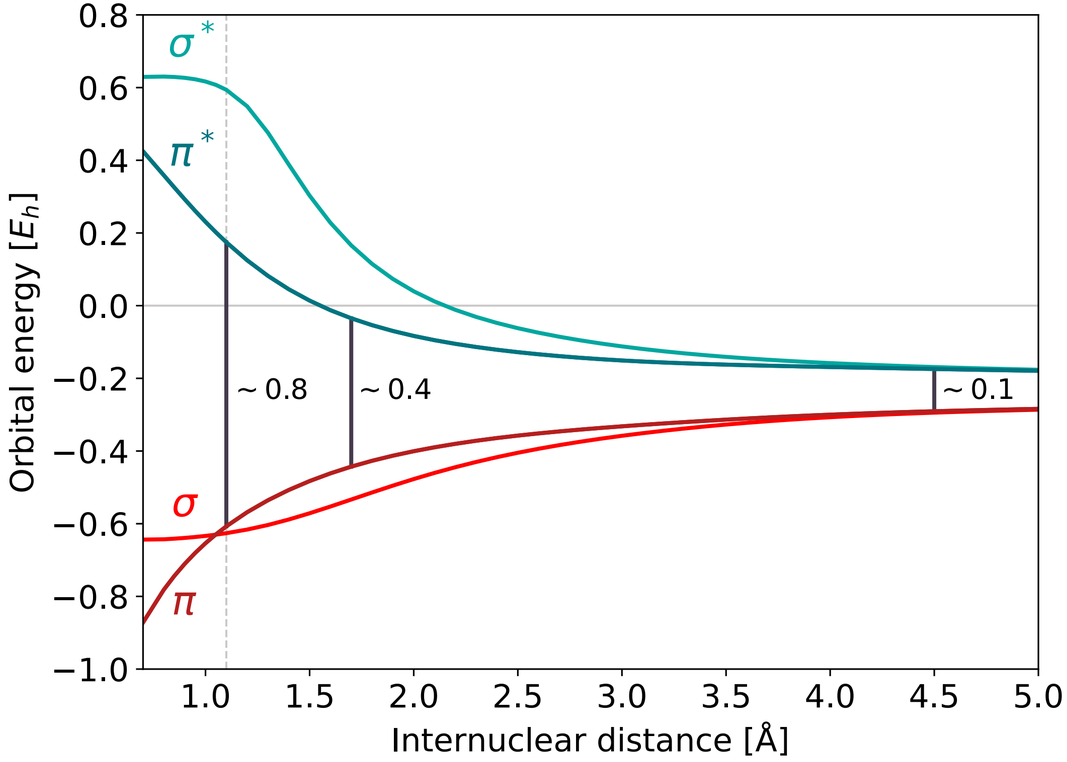


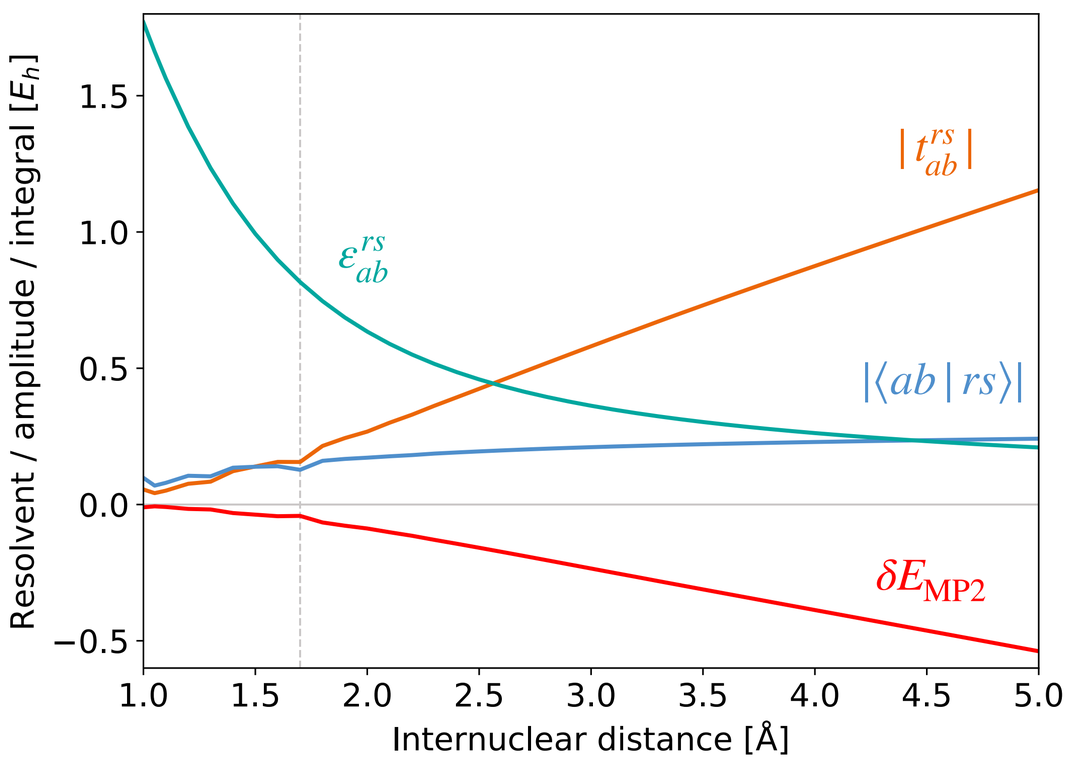
N_2 dissociation **MBPT and CC**

- Let's have a look at the energy corresponding to the $t^{\pi_1^* \pi_2^*}_{\pi_1 \pi_2}$ amplitude

$$\delta E_{\mathrm{MP2}} = t^{rs}_{ab} \left(2\langle ab \,|\, rs \rangle - \langle ab \,|\, sr \rangle \right)$$

$$t^{rs}_{ab} = \frac{\langle ab \,|\, rs \rangle}{\underbrace{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}_{\varepsilon^{rs}_{ab}}}$$





N_2 dissociation **CASSCF**

- difference in bond energy

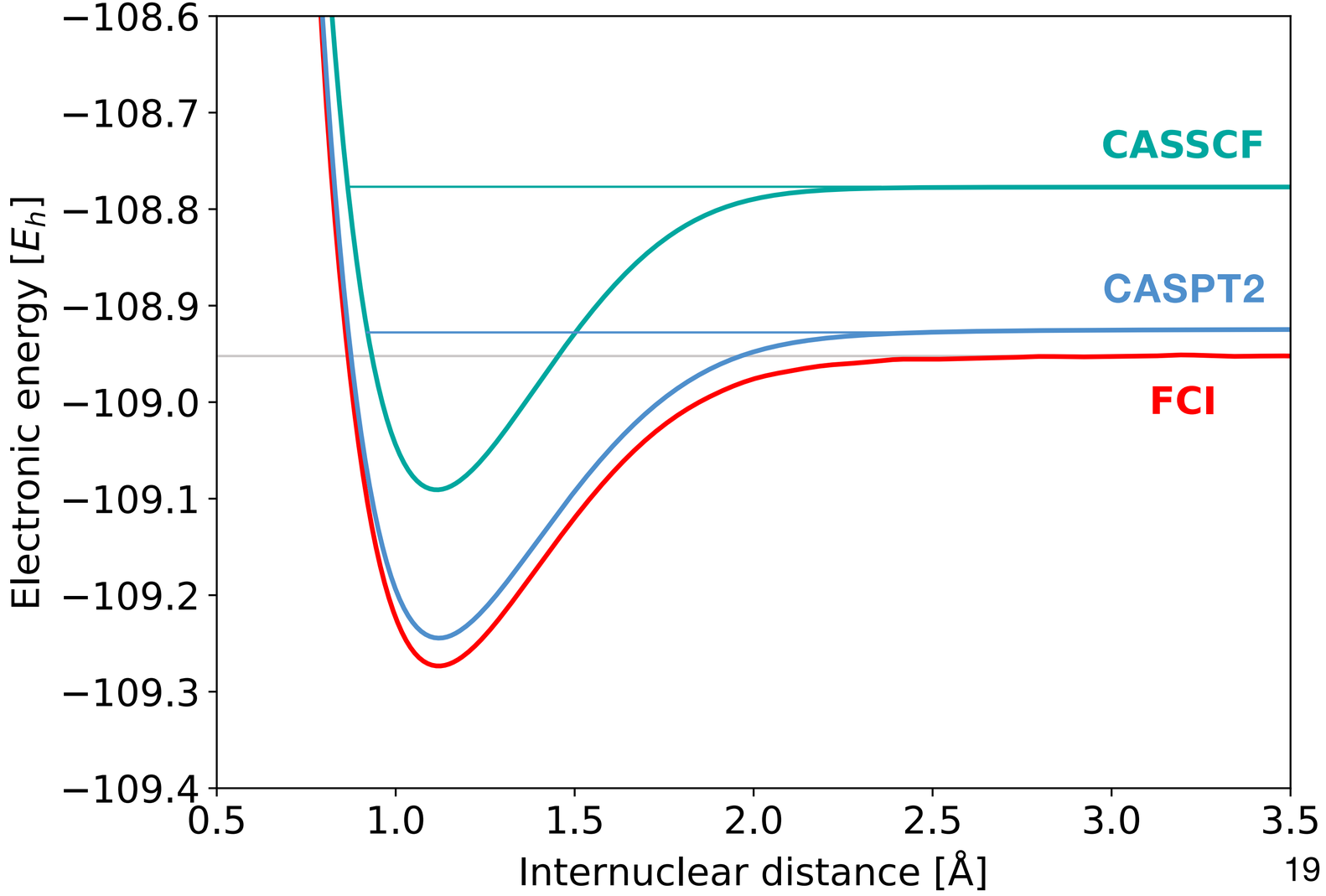
CASPT2 − CASSCF

$\Delta D_e \approx 4\,\mathrm{kcal/mol}$

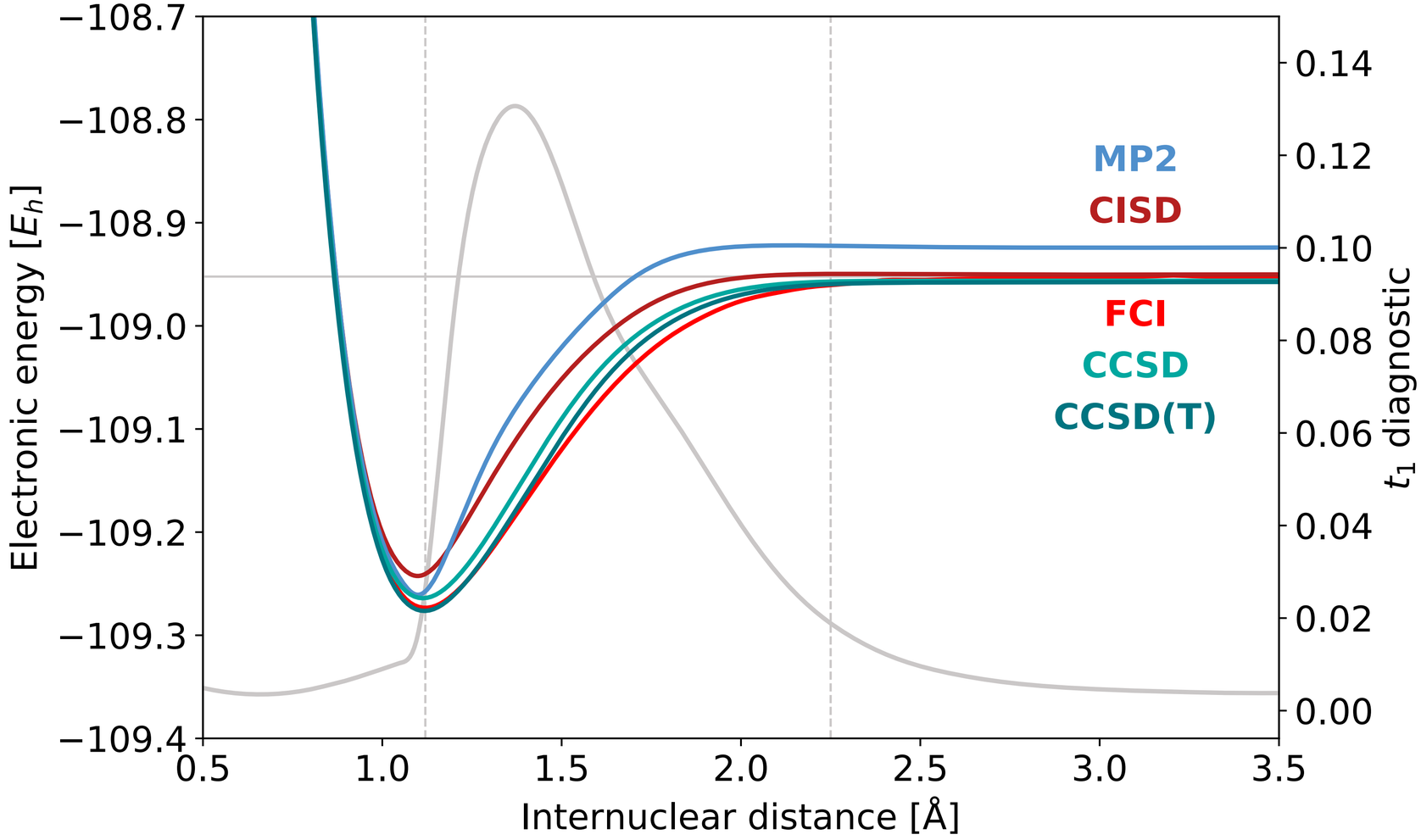
but only

FCI − CASPT2

$\Delta D_e \approx 0.75\,\mathrm{kcal/mol}$



N_2 dissociation **UHF reference**



Active space selection

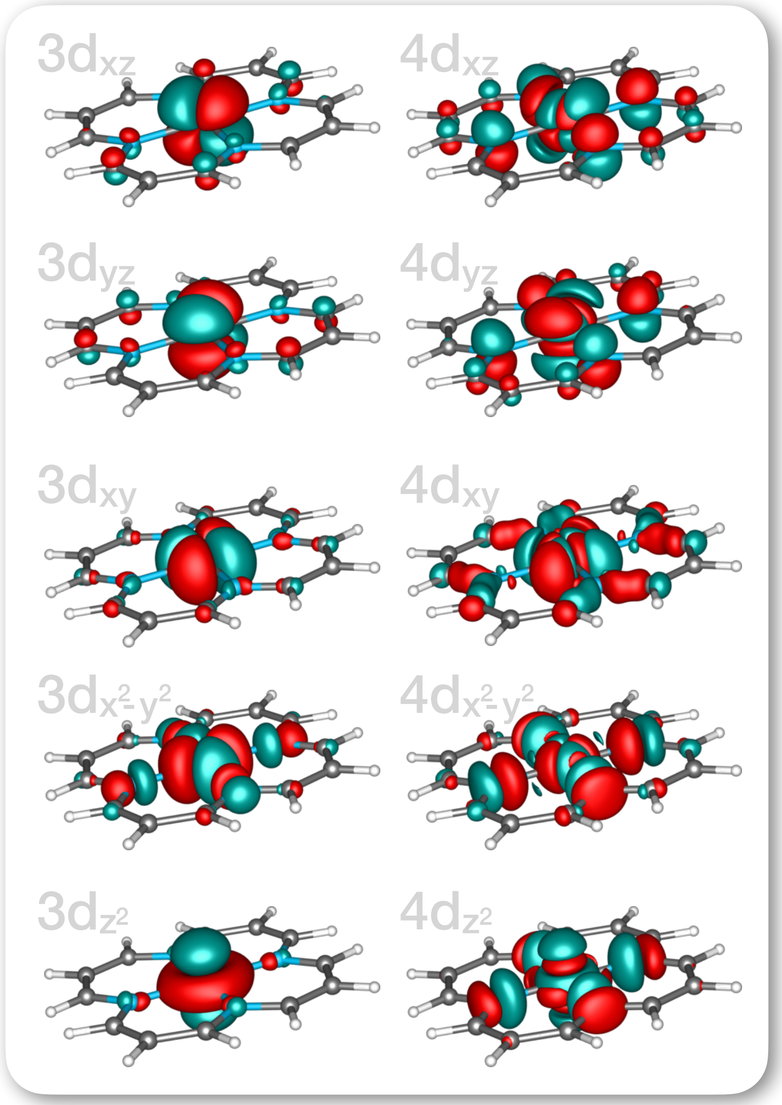
- Ideal: all valence orbitals — usually not an option
- Bond formation/dissociation:
  - Correlating pairs σ-σ* and π-π*
- Electron spectroscopy:
  - All potential excitation sites
  - All planar unsaturated π, π*
- Double-shell effect — important for first-row transition metals starting from Cr
  - Ideal: inclusion of all 3d + all 4d orbitals

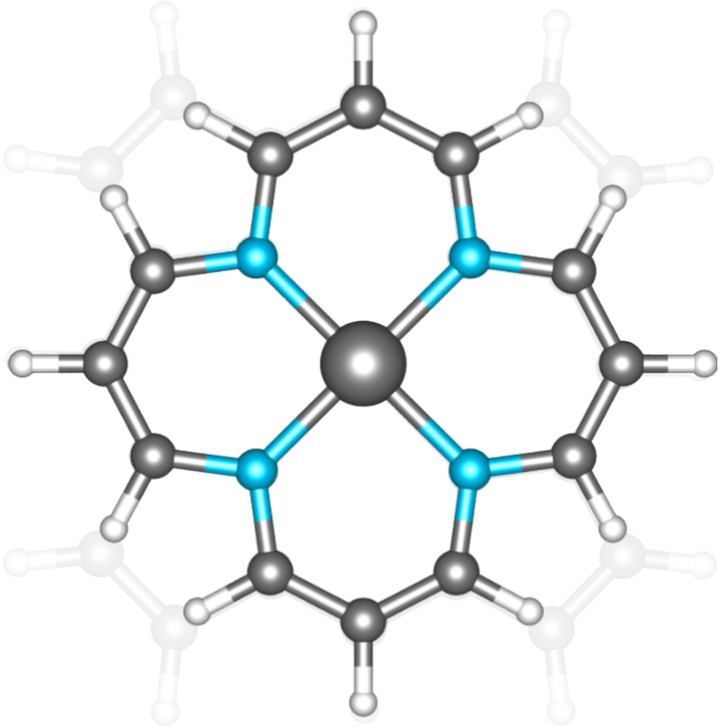
If you want to compare CASSCF energies,

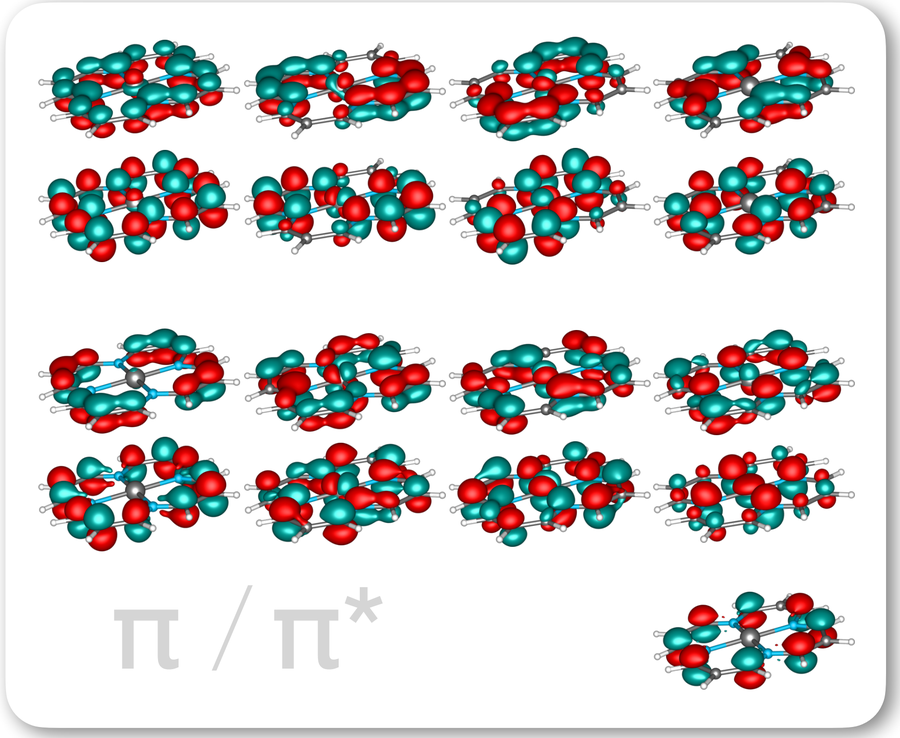
CAS has to be consistent along the entire studied process!

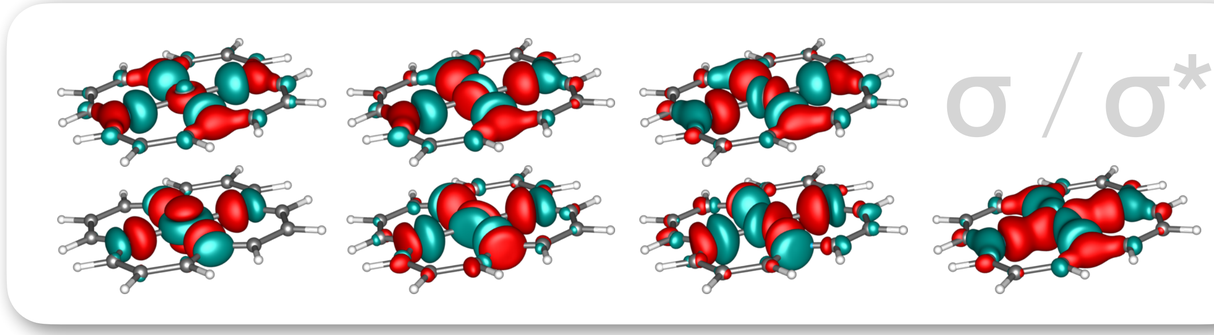
Veryazov, Malmquist, Roos; Int. J. Quantum Chem. 111, 3329 (2011)

CAS selection **Fe(II)-porphyrin model** CAS(32,34)









Going large scale with approximate FCI

- Contemporary FCI: maximum CAS(24,24), practical possibly CAS(19,19)

Selected CI

- Systematically include determinants based on their coupling to the reference determinant(s)

FCI Quantum Monte Carlo

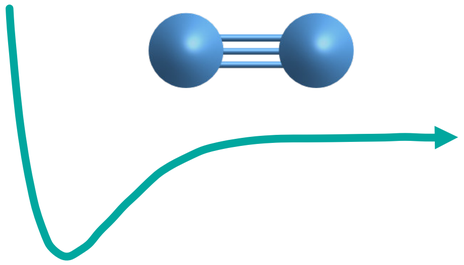
- Stochastic approach, walkers sample the determinant space

Density Matrix Renormalization Group

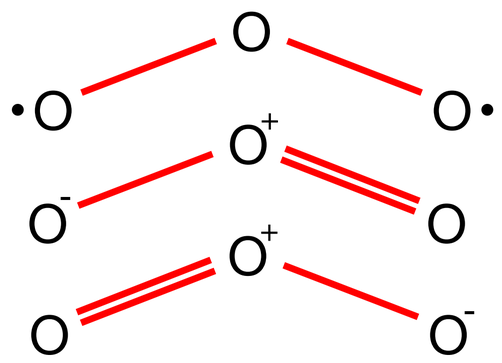
- Numerical variational approximation to FCI — keeps maximum number of parameters capped while minimizes the loss of information

When to be cautious

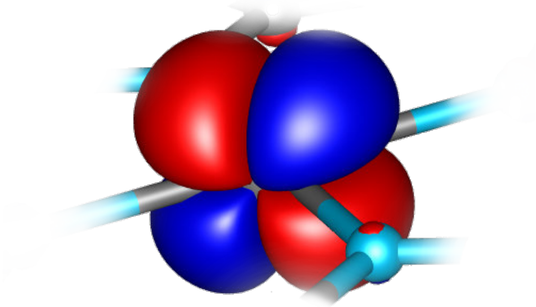
Bond breaking/formation



Competing valence structures

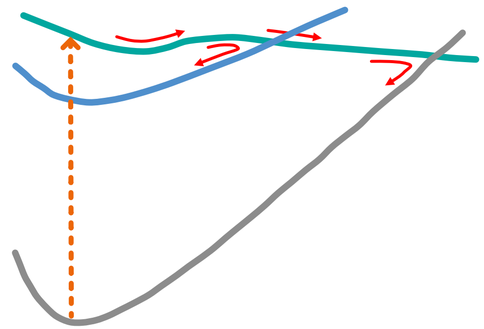


Transition metals



$d^n s^2$ $d^{n+1} s^1$ d^{n+2}
spin multiplets

Excited states



The following slides are just FYI

…and if you are more interested in MC

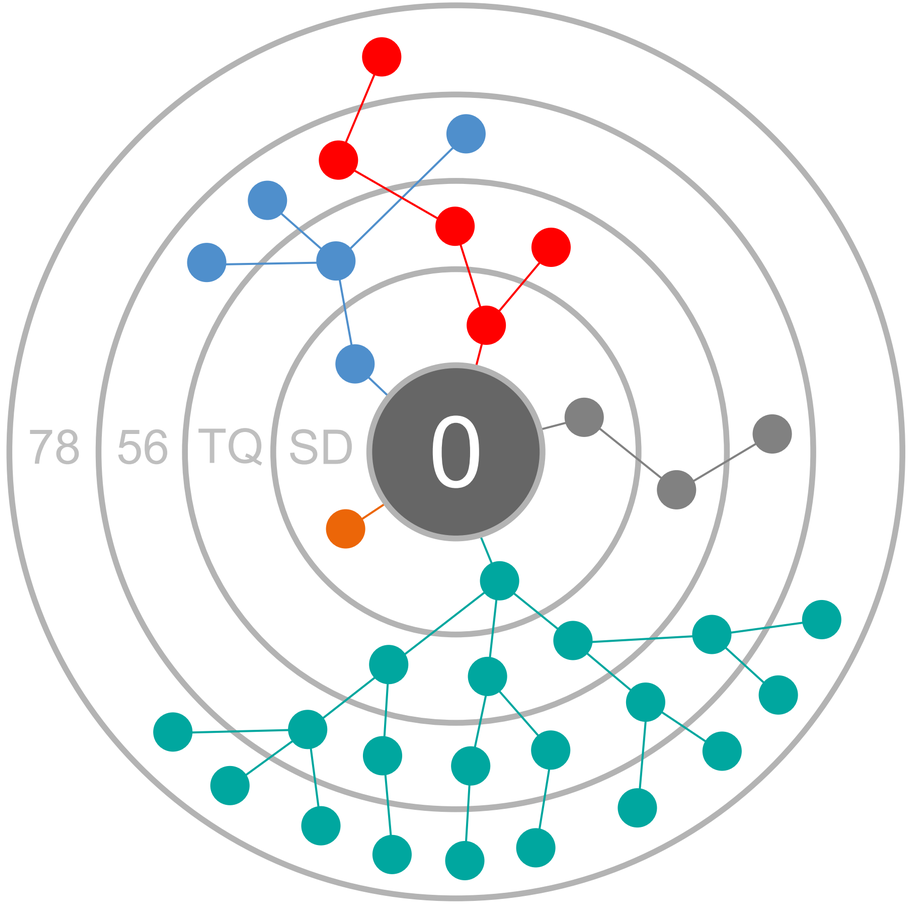
Roos et al.: Multiconfigurational Quantum Chemistry (2016)

Approximate FCI: **Selected CI**

- Determinants selected iteratively
- Example: CIPSI Algorithm

1. Reference WF $|\Psi_0\rangle = \sum_i c_i |\Phi_i\rangle \quad \rightarrow \quad E_0$
2. Generate SD $|\Psi_0\rangle \rightarrow |\alpha\rangle \in \{|\Psi_i^a\rangle, |\Psi_{ij}^{ab}\rangle\}$
3. Evaluate PT2 contributions $\Delta E_\alpha = \dfrac{\langle\Psi_0|H|\alpha\rangle\langle\alpha|H|\Psi_0\rangle}{E_0 - \langle\alpha|H|\alpha\rangle}$
4. Add dets. $\text{if } \Delta E_\alpha > \text{Thr} \quad \rightarrow \quad |\Psi_0\rangle \mathrel{+}= |\alpha\rangle$
5. Solve $\mathbf{HC} = E\mathbf{C} \quad \rightarrow \quad |\Psi_{\text{new}}\rangle, E_{\text{new}}$

If NOT CONVERGED



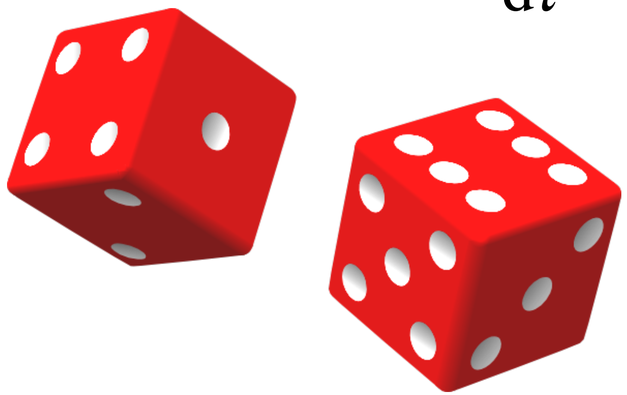
Huron, Malrieu, Rancurel; J. Chem. Phys. 58, 5745 (1973)

Approximate FCI: FCIQMC

- Stochastic approach to FCI — determinant space sampled by walkers
- Rules:
  - Signed walkers spawn, die, and annihilate
  - Population dynamics governed by

$$\frac{\mathrm{d}N_i}{\mathrm{d}\tau} = \left(H_{ii} - S\right)N_i + \sum_{j \neq i} H_{ij}N_j$$

N_i number of walkers on $|\Phi_i\rangle$
τ imaginary time
S population control parameter



In the long time limit $E_0 = \lim_{\tau \to \infty} E(\tau)$ and $c_i \propto N_i$

Booth, Thom, Alavi; J. Chem. Phys. 131, 054106 (2009)

Approximate FCI: DMRG

- FCI wave function in occupation number representation

parameters 4^k

$$|\Psi_{\mathrm{FCI}}\rangle = \sum_{\{\alpha\}} C^{\alpha_1\alpha_2\cdots\alpha_k} |\alpha_1\alpha_2\cdots\alpha_k\rangle \qquad \text{where} \qquad |\alpha_i\rangle \in \{|-\rangle, |\downarrow\rangle, |\uparrow\rangle, |\downarrow\uparrow\rangle\}$$

- Repeated application of SVD — matrix product state

parameters $\mathcal{O}(kM^2)$

$$|\Psi_{\mathrm{MPS}}\rangle = \sum_{\{\alpha\}} \mathbf{A}^{\alpha_1}\mathbf{A}^{\alpha_2}\cdots\mathbf{A}^{\alpha_{k-1}}\mathbf{A}^{\alpha_k} |\alpha_1\alpha_2\cdots\alpha_{k-1}\alpha_k\rangle$$

M ← bond dimension

- Iteratively optimized, with dimension of matrices $\mathbf{A}^{\alpha_i}$ kept at M by truncation using SVD

Chan, Sharma; Annu. Rev. Phys. Chem. 62, 465 (2011)
Wouters, Van Neck; Eur. Phys. J. D 68, 272 (2014)