Electron correlation

definition

$$E^{\mathrm{corr.}} = E^{\mathrm{exact}} - E^{\mathrm{HF}}$$

Configuration Interaction

- sum over all possible Slater determinants/spin adapted-configuration state functions
- general expression for correlation energy (not so useful...)
- truncated CI
- MCSCF/CASSCF
- size consistency

Perturbation theory

- slater determinants, single, double, triple, ... excitations

Combinations of CI and PT

- MCSCF with xth order perturbation (x=2)

Concludes the ab initio, next is density functional theory

Configuration interaction

- restricted Hartree Fock in nutshell
  - one particle, mean field theory

Configuration interaction

restricted Hartree Fock in nutshell

one particle, mean field theory

Slater determinant (Pauli principle)

$$\psi_0(\mathbf{r}) = \det\left[\phi_1(\mathbf{r}_1)\bar{\phi}_1(\mathbf{r}_2)\phi_2(\mathbf{r}_3)\bar{\phi}_2(\mathbf{r}_4)....\phi_{n/2}(\mathbf{r}_{n-1})\bar{\phi}_{n/2}(\mathbf{r}_n)\right]$$

Configuration interaction

restricted Hartree Fock in nutshell

one particle, mean field theory

Slater determinant (Pauli principle)

$$\psi_0(\mathbf{r}) = \det\left[\phi_1(\mathbf{r}_1)\bar{\phi}_1(\mathbf{r}_2)\phi_2(\mathbf{r}_3)\bar{\phi}_2(\mathbf{r}_4)....\phi_{n/2}(\mathbf{r}_{n-1})\bar{\phi}_{n/2}(\mathbf{r}_n)\right]$$

molecular orbitals

$$\hat{f}\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

Configuration interaction

restricted Hartree Fock in nutshell

one particle, mean field theory

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molecular orbitals

$$\hat{f}\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

Fock operator

$$f_{ij} = \langle\phi_i(\mathbf{r}_1)|h(\mathbf{r}_1)|\phi_j(\mathbf{r}_1)\rangle + \sum_k \left\langle \phi_i(\mathbf{r}_1)\phi_k(\mathbf{r}_2)\left|\frac{2-\hat{p}_{12}}{|\mathbf{r}_1-\mathbf{r}_2|}\right|\phi_k(\mathbf{r}_1)\phi_j(\mathbf{r}_2)\right\rangle$$

Configuration interaction

restricted Hartree Fock in nutshell

one particle, mean field theory

Slater determinant (Pauli principle)

$$\psi_0(\mathbf{r}) = \det\left[\phi_1(\mathbf{r}_1)\bar{\phi}_1(\mathbf{r}_2)\phi_2(\mathbf{r}_3)\bar{\phi}_2(\mathbf{r}_4)....\phi_{n/2}(\mathbf{r}_{n-1})\bar{\phi}_{n/2}(\mathbf{r}_n)\right]$$

molecular orbitals

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Fock operator

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basisset

$$\phi_i(\mathbf{r}_1) = \sum_\alpha c_{i\alpha}\chi_\alpha(\mathbf{r}_1)$$

$$\hat{f} = h + \frac{1}{2}\sum_\lambda\sum_\sigma P_{\lambda\sigma}\left\langle \chi_\sigma \left| \frac{2-\hat{p}_{12}}{|\mathbf{r}_1-\mathbf{r}_2|} \right| \chi_\lambda \right\rangle$$

density matrix

$$P_{\mu\nu} = 2\sum_a^{\frac{1}{2}n_e} c_{\mu a}c^*_{\nu a}$$

Configuration interaction

restricted Hartree Fock in nutshell

one particle, mean field theory

Slater determinant (Pauli principle)

$$\psi_0(\mathbf{r}) = \det\left[\phi_1(\mathbf{r}_1)\bar{\phi}_1(\mathbf{r}_2)\phi_2(\mathbf{r}_3)\bar{\phi}_2(\mathbf{r}_4)....\phi_{n/2}(\mathbf{r}_{n-1})\bar{\phi}_{n/2}(\mathbf{r}_n)\right]$$

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density matrix

$$P_{\mu\nu} = 2\sum_a^{\frac{1}{2}n_e} c_{\mu a}c^*_{\nu a}$$

iterative self-consistent solution procedure

Configuration interaction

restricted Hartree Fock in nutshell

one particle, mean field theory, no e-e correlation

Slater determinant

$$\psi_0(\mathbf{r}) = \det\left[\phi_1(\mathbf{r}_1)\bar{\phi}_1(\mathbf{r}_2)\phi_2(\mathbf{r}_3)\bar{\phi}_2(\mathbf{r}_4)....\phi_{n/2}(\mathbf{r}_{n-1})\bar{\phi}_{n/2}(\mathbf{r}_n)\right]$$

Configuration interaction

restricted Hartree Fock in nutshell

- one particle, mean field theory
  - Slater determinant

$$\psi_0(\mathbf{r}) = \det\left[\phi_1(\mathbf{r}_1)\bar{\phi}_1(\mathbf{r}_2)\phi_2(\mathbf{r}_3)\bar{\phi}_2(\mathbf{r}_4)....\phi_{n/2}(\mathbf{r}_{n-1})\bar{\phi}_{n/2}(\mathbf{r}_n)\right]$$

electron-electron correlation

- static correlation
  - large separation of electrons in pair (*i.e.* H_2 dissociation)
  - near degeneracies: different spatial wavefunctions
  - multi-configuration SCF

Configuration interaction

restricted Hartree Fock in nutshell

one particle, mean field theory

Slater determinant

$$\psi_0(\mathbf{r}) = \det\left[\phi_1(\mathbf{r}_1)\bar{\phi}_1(\mathbf{r}_2)\phi_2(\mathbf{r}_3)\bar{\phi}_2(\mathbf{r}_4)....\phi_{n/2}(\mathbf{r}_{n-1})\bar{\phi}_{n/2}(\mathbf{r}_n)\right]$$

electron-electron correlation

static correlation

- large separation of electrons in pair
- near degeneracies: different spatial wavefunctions
- multi-configuration SCF

dynamic correlation

- short distance: cusp
- not so dependent on orbitals/density
- perturbation theory

Configuration interaction

restricted Hartree Fock in nutshell

- one particle, mean field theory
  - Slater determinant

$$\psi_0(\mathbf{r}) = \det\left[\phi_1(\mathbf{r}_1)\bar{\phi}_1(\mathbf{r}_2)\phi_2(\mathbf{r}_3)\bar{\phi}_2(\mathbf{r}_4)....\phi_{n/2}(\mathbf{r}_{n-1})\bar{\phi}_{n/2}(\mathbf{r}_n)\right]$$

electron-electron correlation

- static correlation
  - large separation of electrons in pair
  - near degeneracies: different spatial wavefunctions
  - multi-configuration SCF
- dynamic correlation
  - short distance: cusp
  - not so dependent on orbitals/density
  - perturbation theory
- simple distinction not always possible

Beyond Hartree-Fock: Configuration Interaction

one-electron basisset

$$\Phi(\mathbf{x}_1) = \sum_i a_i \phi_i(\mathbf{x}_1)$$

two-electron basisset

$$\Phi(\mathbf{x}_1, \mathbf{x}_2) = \sum_i a_i(\mathbf{x}_2) \phi_i(\mathbf{x}_1)$$

$$\Phi(\mathbf{x}_1, \mathbf{x}_2) = \sum_i \sum_j b_{ij} \phi_i(\mathbf{x}_1) \phi_j(\mathbf{x}_2)$$

correlation energy

configuration interaction

functions of one electron

expansion in one-electron functions

$$\phi(x_1) = \sum_i a_i \chi_i(x_1)$$

functions of two electrons

correlation energy

configuration interaction

functions of one electron

expansion in one-electron functions

$$\phi(x_1) = \sum_i a_i \chi_i(x_1)$$

functions of two electrons

expansion in one-electron functions, keeping second electron fixed

$$\phi(x_1, x_2) = \sum_i a_i(x_2) \chi_i(x_1)$$

correlation energy

configuration interaction

functions of one electron

expansion in one-electron functions

$$\phi(x_1) = \sum_i a_i \chi_i(x_1)$$

functions of two electrons

expansion in one-electron functions, keeping second electron fixed

$$\phi(x_1, x_2) = \sum_i a_i(x_2) \chi_i(x_1)$$

expansion of coefficients in one-electron functions

$$a(x_2) = \sum_j b_{ij} \chi_j(x_2)$$

correlation energy

configuration interaction

functions of one electron

expansion in one-electron functions

$$\phi(x_1) = \sum_i a_i \chi_i(x_1)$$

functions of two electrons

expansion in one-electron functions, keeping second electron fixed

$$\phi(x_1, x_2) = \sum_i a_i(x_2) \chi_i(x_1)$$

expansion of coefficients in one-electron functions

$$a(x_2) = \sum_j b_{ij} \chi_j(x_2)$$

so that

$$\phi(x_1, x_2) = \sum_i \sum_j b_{ij} \chi_i(x_1) \chi_j(x_2)$$

correlation energy

configuration interaction

functions of two electrons

Pauli principle

$$\phi(x_1, x_2) = -\phi(x_2, x_1)$$

correlation energy

configuration interaction

functions of two electrons

Pauli principle

$$\phi(x_1, x_2) = -\phi(x_2, x_1)$$

antisymmetric superposition

$$\phi(x_1, x_2) = \sum_i \sum_{j>i} b_{ij} \left[\chi_i(x_1)\chi_j(x_2) - \chi_j(x_1)\chi_i(x_2)\right]$$

correlation energy

configuration interaction

functions of two electrons

Pauli principle

$$\phi(x_1, x_2) = -\phi(x_2, x_1)$$

antisymmetric superposition

$$\phi(x_1, x_2) = \sum_i \sum_{j>i} b_{ij} \left[\chi_i(x_1)\chi_j(x_2) - \chi_j(x_1)\chi_i(x_2)\right]$$

in determinants

$$\phi(x_1, x_2) = \sum_i \sum_j \frac{1}{\sqrt{2}} b_{ij} \det \left[\chi_i(x_1)\chi_j(x_2)\right]$$

correlation energy

configuration interaction

functions of two electrons

Pauli principle

$$\phi(x_1, x_2) = -\phi(x_2, x_1)$$

antisymmetric superposition

$$\phi(x_1, x_2) = \sum_i \sum_{j>i} b_{ij} \left[\chi_i(x_1)\chi_j(x_2) - \chi_j(x_1)\chi_i(x_2)\right]$$

in determinants

$$\phi(x_1, x_2) = \sum_i \sum_j \frac{1}{\sqrt{2}} b_{ij} \, \det\left[\chi_i(x_1)\chi_j(x_2)\right]$$

in general

n-electron wavefunction

$$\Psi_i = \sum_j C_{ij}\psi_j = C_{i0}\psi_0 + \sum_{ra} C_{ia}^{r}\psi_a^{r} + \sum_{\substack{a<b \\ r<s}} C_{iab}^{rs}\psi_{ab}^{rs} + \ldots$$

correlation energy

full configuration interaction

exact solution (within finite basisset)

$$\Psi_i = \sum_j C_{ij}\psi_j = C_{i0}\psi_0 + \sum_{ra} C_{ia}^{r}\psi_a^{r} + \sum_{\substack{a<b \\ r<s}} C_{iab}^{rs}\psi_{ab}^{rs} + \ldots$$

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$$\Psi_i = \sum_j C_{ij}\psi_j = C_{i0}\psi_0 + \sum_{ra} C_{ia}^{r}\psi_a^r + \sum_{\substack{a<b \\ r<s}} C_{iab}^{rs}\psi_{ab}^{rs} + \ldots$$

truncated configuration interaction

CISingles

- excited states (higher roots)
- no correlation in ground state

CISinglesDoubles

- stronger correlation in ground state

CISinglesDoublesTriples

- stronger correlation in excited states than in ground state

...

- too expensive: number of configurations blows up

correlation energy

truncated configuration interaction

- CISingles, Double, Triples ...
  - systematic
  - number of configurations blows up

correlation energy

truncated configuration interaction

- CISingles, Double, Triples ...
  - systematic
  - number of configurations blows up

multi-configuration SCF

- multiple configurations
  - free to choose, not black box!
  - optimize both CI and MO coefficients

$$\Psi_i = \sum_j^M C_{ij} \overset{\text{Slater}}{\psi_j}.$$

correlation energy

truncated configuration interaction

CISingles, Double, Triples ...

systematic

number of configurations blows up

multi-configuration SCF

multiple configurations

free to choose, not black box!

optimize both CI and MO coefficients

$$\Psi_i = \sum_j^M C_{ij}\psi_j .$$

Slater

basis for higher level methods

MultiReferenceCI

single excitations

double excitations

$$\Phi = \sum_I (K_I \Psi_I + \sum_{i,a} K_{Iia}\Psi_{Iia} + \sum_{i,a,j,b} K_{Iiajb}\Psi_{Iiajb} + ...)$$

a root in MCSCF

of Slaters in each configuration in root

correlation energy

truncated configuration interaction

CISingles, Double, Triples ...

systematic

number of configurations blows up

multi-configuration SCF

multiple configurations

free to choose, not black box!

optimize both CI and MO coefficients

$$\Psi_i = \sum_j^M C_{ij}\psi_j .$$

basis for higher level methods

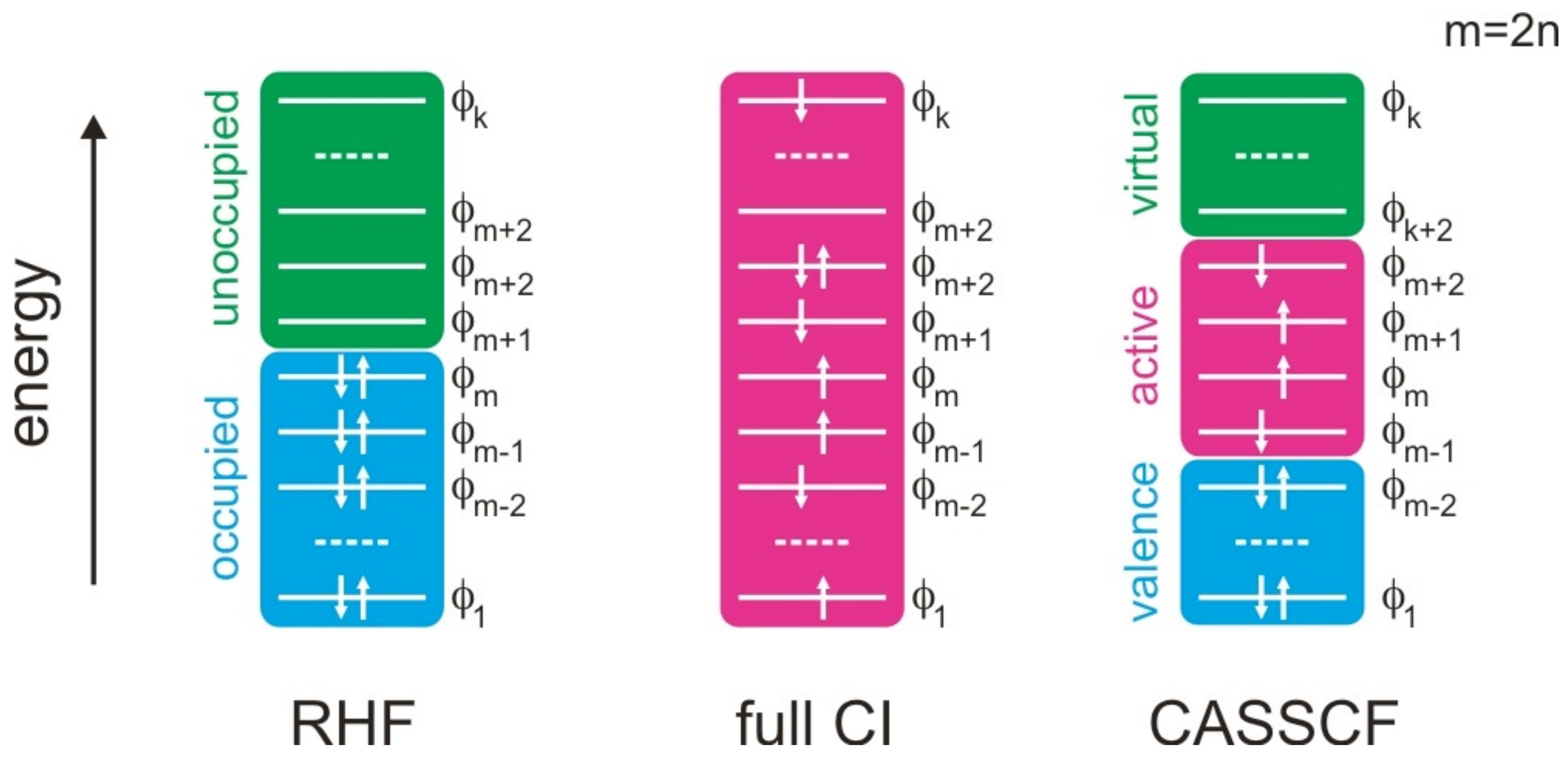
MultiReferenceCI

$$\Phi = \sum_I (K_I \Psi_I + \sum_{i,a} K_{Iia}\Psi_{Iia} + \sum_{i,a,j,b} K_{Iiajb}\Psi_{Iiajb} + \ldots)$$

perturbation theory: CASPT2

correlation energy

- multi-configuration SCF
  - multiple configurations
    - free to choose
    - not black box
  - Complete Active Space SCF
    - select orbitals for full CI



correlation energy

- multi-configuration SCF
  - Complete Active Space SCF
    - select electrons and orbitals for full CI (HF, NBO)
    - knowledge/intuition/luck

correlation energy

multi-configuration SCF

Complete Active Space SCF

select electrons and orbitals for full CI (HF, NBO)

knowledge/intuition/luck/

correlation energy

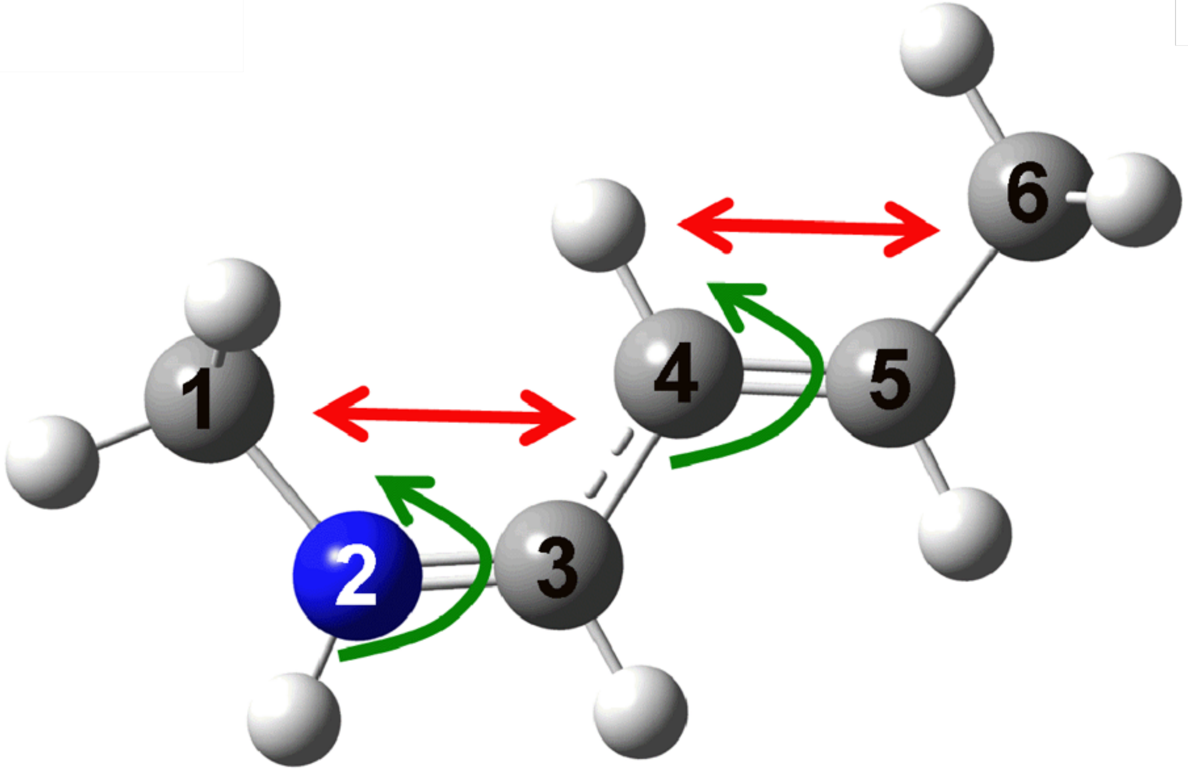
multi-configuration SCF

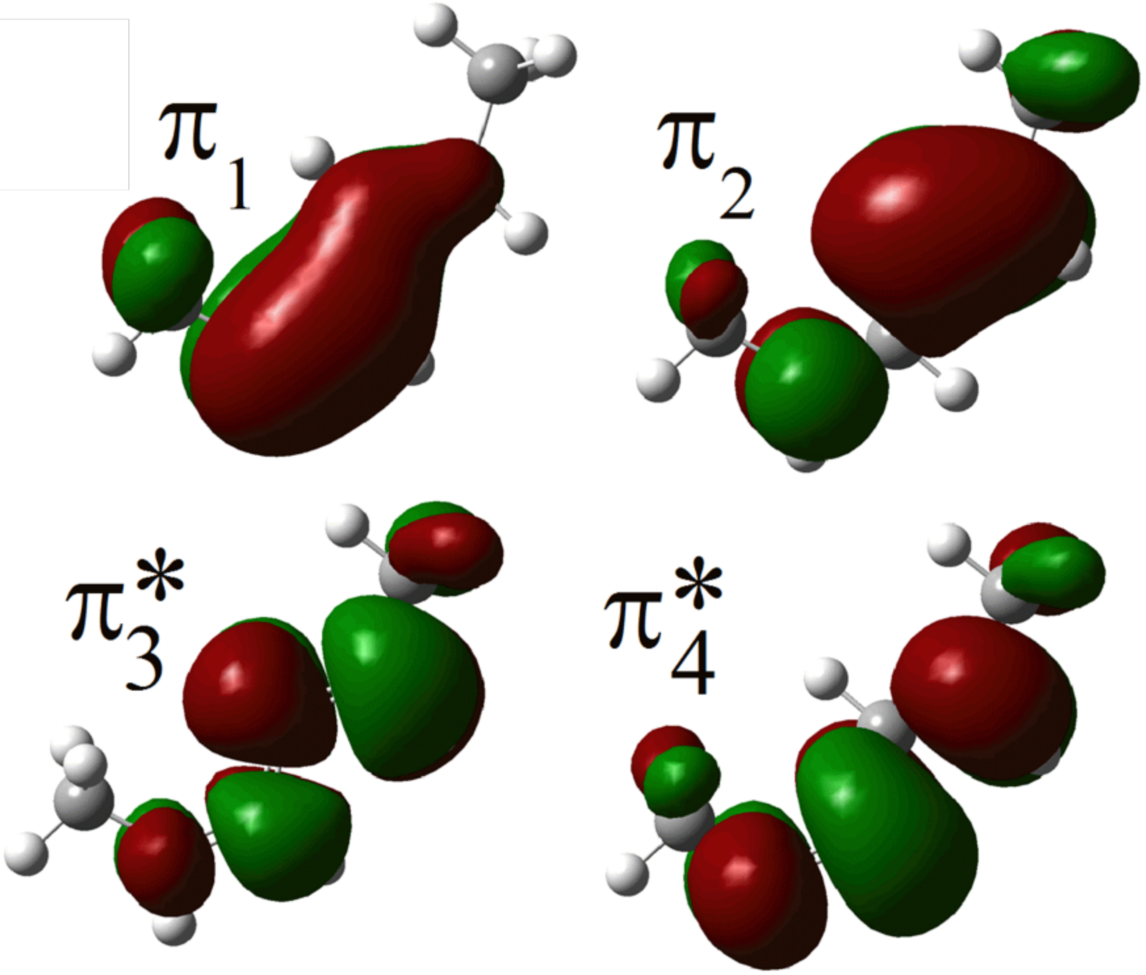
Complete Active Space SCF

- select electrons and orbitals for full CI (HF, NBO)
- knowledge/intuition/luck

example

- protonated schiff base
- CAS(4,4) with all π orbitals





correlation energy

- CASSCF
  - recovers static correlation
    - near degeneracy

correlation energy

CASSCF

- recovers static correlation
    - near degeneracy
- excited states
    - optimize second root in CI

correlation energy

CASSCF

- recovers static correlation
  - near degeneracy
- excited states
  - optimize second root in CI
  - problem: need expectation values involving both states

$$\langle \psi_{S_0} | \nabla_{\mathbf{R}} H | \psi_{S_1} \rangle$$

correlation energy

CASSCF

- recovers static correlation
  - near degeneracy
- excited states
  - optimize second root in CI
  - problem: need expectation values involving both states

$$\langle \psi_{S_0} | \nabla_{\mathbf{R}} H | \psi_{S_1} \rangle$$

  - problem: root flipping

correlation energy

CASSCF

- recovers static correlation
  - near degeneracy
- excited states
  - optimize second root in CI
  - problem: need expectation values involving both states

$$\langle\psi_{S_0}|\nabla_{\mathbf{R}}H|\psi_{S_1}\rangle$$

  - problem: root flipping
- state average CASSCF
  - same molecular orbitals for all states
  - optimize the weighted average energy

$$E^{\mathrm{SA}} = \sum_i \omega_i E_i$$

  - average density matrix

correlation energy

SA-CASSCF

same molecular orbitals for all states

sometimes orbitals change drastically upon excitation

wavefunction is not variational minimum

$$\begin{aligned}
\nabla_{\mathbf{R}} E &= \nabla_{\mathbf{R}} \langle \psi | H | \psi \rangle \\
&= \langle \nabla_{\mathbf{R}} \psi | H | \psi \rangle + \langle \psi | \nabla_{\mathbf{R}} H | \psi \rangle + \langle \psi | H | \nabla_{\mathbf{R}} \psi \rangle
\end{aligned}$$

correlation energy

SA-CASSCF

same molecular orbitals for all states

sometimes orbitals change drastically upon excitation

wavefunction is not variational minimum

$$\begin{aligned}\nabla_{\mathbf{R}} E &= \nabla_{\mathbf{R}} \langle \psi | H | \psi \rangle \\ &= \langle \nabla_{\mathbf{R}} \psi | H | \psi \rangle + \langle \psi | \nabla_{\mathbf{R}} H | \psi \rangle + \langle \psi | H | \nabla_{\mathbf{R}} \psi \rangle\end{aligned}$$

$$\begin{aligned}\langle \nabla_{\mathbf{R}} \psi | H | \psi \rangle = &\langle \nabla_{\mathbf{c}_{\mathrm{MO}}} \psi | H | \psi \rangle \nabla_{\mathbf{R}} \mathbf{c}_{\mathrm{MO}} + \\ &\langle \nabla_{\mathbf{c}_{\mathrm{CI}}} \psi | H | \psi \rangle \nabla_{\mathbf{R}} \mathbf{c}_{\mathrm{CI}} +\end{aligned}$$

beyond Hartree Fock

Configuration Interaction

linear combination of Slater determinants

$$\Psi = |\psi_0\rangle + \sum_a^r c_a^r|\psi_a^r\rangle + \sum_a^r \sum_{b>a}^{s>r} c_{ab}^{rs}|\psi_{ab}^{rs}\rangle$$

$$+ \sum_a^r \sum_{b>a}^{s>r} \sum_{c>b}^{t>s} c_{abc}^{rst}|\psi_{abc}^{rst}\rangle$$

$$+ \sum_a^r \sum_{b>a}^{s>r} \sum_{c>b}^{t>s} \sum_{d>c}^{u>t} c_{abcd}^{rstu}|\psi_{abcd}^{rstu}\rangle + \dots$$

intermediate normalization

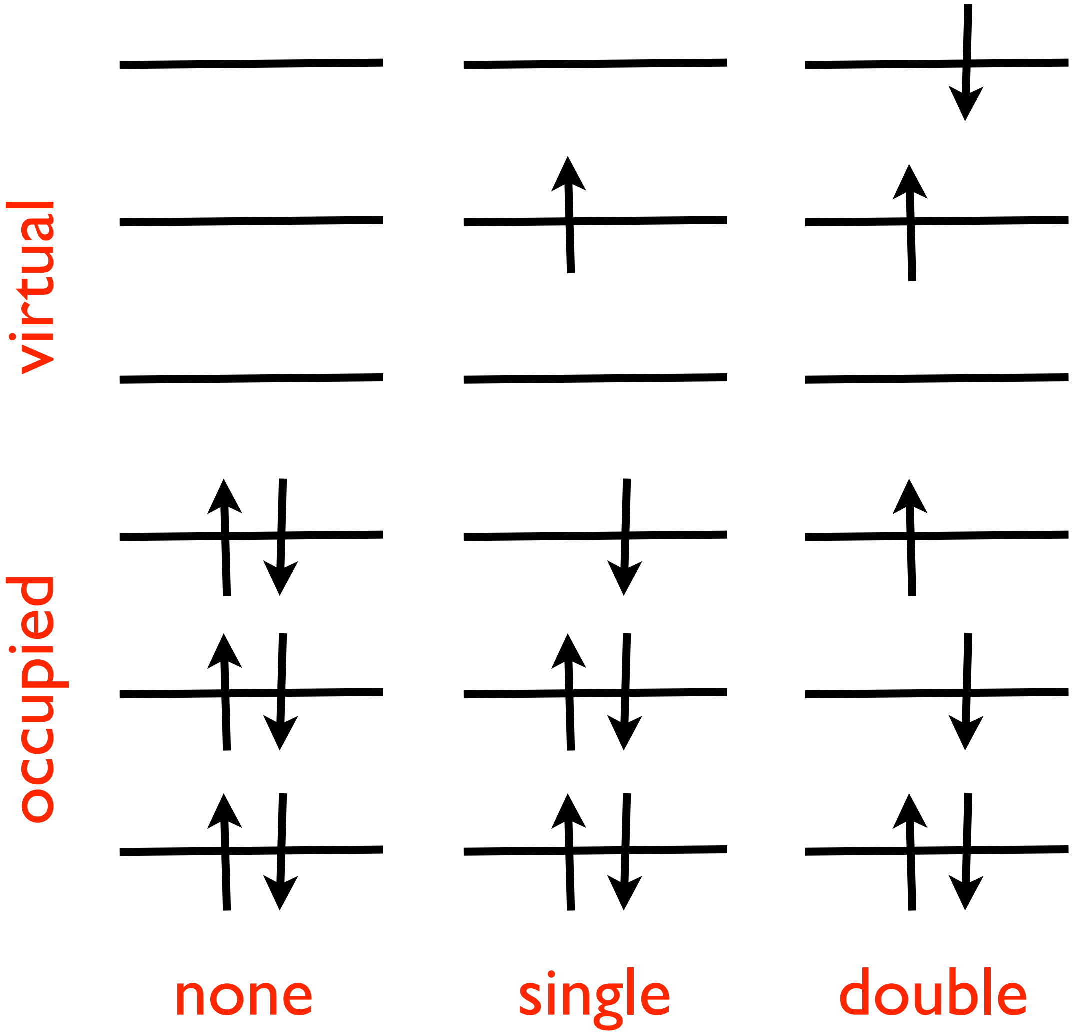
$$\langle\Psi|\psi_0\rangle = 1$$

size consistent, only if *all* determinants are included

impossible in practice!

variational in c

Beyond Hartree-Fock: Configuration Interaction



one-electron basisset

$$\Phi(\mathbf{x}_1) = \sum_i a_i \phi_i(\mathbf{x}_1)$$

two-electron basisset

$$\Phi(\mathbf{x}_1, \mathbf{x}_2) = \sum_i a_i(\mathbf{x}_2) \phi_i(\mathbf{x}_1)$$

$$\Phi(\mathbf{x}_1, \mathbf{x}_2) = \sum_i \sum_j b_{ij} \phi_i(\mathbf{x}_1) \phi_j(\mathbf{x}_2)$$

n-electron basisset

slater determinants, single, double, triple, ... excitations

$$\Phi = |\Psi_0\rangle + \sum_a^{n_{\text{occ}}} \sum_r^{n_{\text{virt}}} c_a^r |\Psi_a^r\rangle + \sum_a^{n_{\text{occ}}} \sum_b^{n_{\text{occ}}} \sum_r^{n_{\text{virt}}} \sum_s^{n_{\text{virt}}} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \ldots$$

Brillouin's theorem

$$\langle \Psi_0 | \hat{H} | \Psi_a^r \rangle = 0$$

truncate: CIS, CISD, CISDT, CISDTQ, ... (size inconsistent!!)

beyond Hartree Fock

Configuration Interaction

linear combination of Slater determinants

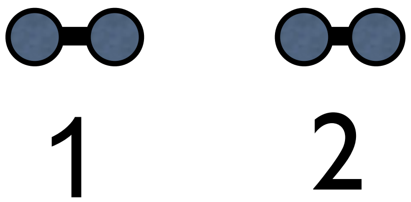
$$\begin{aligned}\Psi &= |\psi_0\rangle + \sum_a^r c_a^r \hat{X}_a^r |\psi_0\rangle + \sum_a^r \sum_{b>a}^{s>r} c_{ab}^{rs} \hat{X}_{ab}^{rs} |\psi_0\rangle \\ &+ \sum_a^r \sum_{b>a}^{s>r} \sum_{c>b}^{t>s} c_{abc}^{rst} \hat{X}_{abc}^{rst} |\psi_0\rangle \\ &+ \sum_a^r \sum_{b>a}^{s>r} \sum_{c>b}^{t>s} \sum_{d>c}^{u>t} c_{abcd}^{rstu} \hat{X}_{abcd}^{rstu} |\psi_0\rangle + \ldots\end{aligned}$$

truncation of full CI to limit computational effort

CISD, CISDT, CISDTQ, ...

not size consistent because not all determinants are included

beyond Hartree Fock



Full Configuration Interaction expansion

all determinants included

example H_2 and 2 H_2

1 H_2:
$$\Psi^1 = |\phi_1^1\alpha\phi_1^1\beta\rangle + c_{1_1\bar{1}_1}^{2_1\bar{2}_1}|\phi_2^1\alpha\phi_2^1\beta\rangle$$
$$= |1_1\bar{1}_1\rangle + c_{1_1\bar{1}_1}^{2_1\bar{2}_1}|2_1\bar{2}_1\rangle$$

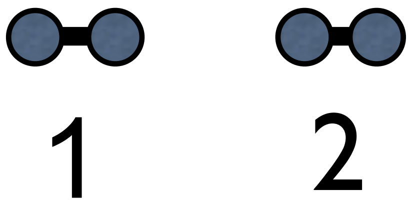
2 H_2:
$$\Psi^{12} = |1_1\bar{1}_11_2\bar{1}_2\rangle + c_{1_1\bar{1}_1}^{2_1\bar{2}_1}|2_1\bar{2}_11_2\bar{1}_2\rangle + c_{1_2\bar{1}_2}^{2_2\bar{2}_2}|1_1\bar{1}_12_2\bar{2}_2\rangle$$
$$\underline{+c_{1_1\bar{1}_11_2\bar{1}_2}^{2_1\bar{2}_12_2\bar{2}_2}|2_1\bar{2}_12_2\bar{2}_2\rangle}$$

Truncated Configuration Interaction expansion

only include HF, single and doubly excited determinants

2 H_2: $\Psi^{12} = |1_1\bar{1}_11_2\bar{1}_2\rangle + c_{1_1\bar{1}_1}^{2_1\bar{2}_1}|2_1\bar{2}_11_2\bar{1}_2\rangle + c_{1_2\bar{1}_2}^{2_2\bar{2}_2}|1_1\bar{1}_12_2\bar{2}_2\rangle$

beyond Hartree Fock



Full CI

all determinants included

$$
\begin{aligned}
\Psi^{12} \; = \;& |1_1\bar{1}_1 1_2\bar{1}_2\rangle + c^{2_1\bar{2}_1}_{1_1\bar{1}_1}|2_1\bar{2}_1 1_2\bar{1}_2\rangle + c^{2_2\bar{2}_2}_{1_2\bar{1}_2}|1_1\bar{1}_1 2_2\bar{2}_2\rangle \\
& \boxed{+c^{2_1\bar{2}_1 2_2\bar{2}_2}_{1_1\bar{1}_1 1_2\bar{1}_2}|2_1\bar{2}_1 2_2\bar{2}_2\rangle}
\end{aligned}
$$

at large separation: independent molecules!

$$
\begin{aligned}
\Psi^{12} \; &= \; \Psi^1\Psi^2 \\
&= \left(|1_1\bar{1}_1\rangle + c^{2_1\bar{2}_1}_{1_1\bar{1}_1}|2_1\bar{2}_1\rangle\right)\left(|1_2\bar{1}_2\rangle + c^{2_2\bar{2}_2}_{1_2\bar{1}_2}|2_2\bar{2}_2\rangle\right) \\
&= |1_1\bar{1}_1\rangle|1_2\bar{1}_2\rangle + c^{2_1\bar{2}_1}_{1_1\bar{1}_1}|2_1\bar{2}_1\rangle|1_2\bar{1}_2\rangle + c^{2_2\bar{2}_2}_{1_2\bar{1}_2}|1_1\bar{1}_1\rangle|2_2\bar{2}_2\rangle \\
& \quad \boxed{+c^{2_1\bar{2}_1}_{1_1\bar{1}_1}c^{2_2\bar{2}_2}_{1_2\bar{1}_2}|2_1\bar{2}_1\rangle|2_2\bar{2}_2\rangle}
\end{aligned}
$$

Coupled Clusters

idea

approximate the quadruples coefficients by doubles...

$$c_{abcd}^{rstu} \approx c_{ab}^{rs} * c_{cd}^{tu}$$

due to anti-symmetry there are 18 such terms:

$$c_{abcd}^{rstu} \approx c_{ab}^{rs} c_{cd}^{tu} - c_{ac}^{rs} c_{bd}^{tu} + c_{ad}^{rs} c_{bc}^{tu} + \ldots$$

coupled-clusters doubles wavefunction

$$\Psi^{CCD} = \Pi_{ab,rs} \left(1 + c_{ab}^{rs} X_{ab}^{rs}\right) |\psi_0\rangle$$

non-linear expansion in coefficients

all (2n)-tuply excited determinants included: size consistent!

only uses doubles coefficients

non-variational

Coupled Clusters

idea

approximate the n-tuply coefficients by singles, doubles, ..

$$c^{rstu}_{abcd} \approx c^{rs}_{ab} * c^{tu}_{cd}$$

$$c^{rstuv}_{abcde} \approx c^{rs}_{ab} * c^{tu}_{cd} * c^{v}_{e}$$

$$c^{rstuvw}_{abcdef} \approx c^{rs}_{ab} * c^{tu}_{cd} * c^{vw}_{ef}$$

general case

non-linear expansion in coefficients and excitations

$$\Psi^{CC} = \left[\Pi_{a,r}(1 + c^r_a X^r_a)\right] \left[\Pi_{ab,rs}(1 + c^{rs}_{ab} X^{rs}_{ab})\right] \ldots |\psi_0\rangle$$

identical to full CI if all possible excitation levels are considered

Coupled Clusters

general case

non-linear expansion in coefficients and excitations

$$\Psi^{CC} = \left[\Pi_{a,r}(1 + c_a^r X_a^r)\right]\left[\Pi_{ab,rs}(1 + c_{ab}^{rs} X_{ab}^{rs})\right] \ldots |\psi_0\rangle$$

identical to full CI if all possible excitation levels are considered

close to full CI otherwise, because all excitations are approximately included

restrict excitation level to doubles: CCSD

$$\Psi^{CCSD} = \left[\Pi_{a,r}(1 + c_a^r X_a^r)\right]\left[\Pi_{ab,rs}(1 + c_{ab}^{rs} X_{ab}^{rs})\right] |\psi_0\rangle$$

all n-tuply excited determinants included: size consistent!

only singles and doubles coefficients needed

optimization of coefficients

Coupled Clusters

general case

non-linear expansion in coefficients and excitations

$$\Psi^{CC} = [\Pi_{a,r}(1 + c_a^r X_a^r)]\,[\Pi_{ab,rs}(1 + c_{ab}^{rs} X_{ab}^{rs})]\,...|\psi_0\rangle$$

exponential ansatz

since

$$\hat{X}_{ab}^{rs}\hat{X}_{ab}^{rs} = 0$$

$$\exp(x) = 1 + x + \frac{1}{2}x^2 + \frac{1}{6}x^3 + ..$$

we can invert the Taylor series

$$1 + c_{ab}^{rs}\hat{X}_{ab}^{rs} = 1 + c_{ab}^{rs}\hat{X}_{ab}^{rs} + \frac{1}{2}(c_{ab}^{rs})^2\hat{X}_{ab}^{rs}\hat{X}_{ab}^{rs} + ... = \exp(c_{ab}^{rs}\hat{X}_{ab}^{rs})$$

to recast the coupled clusters expansion

$$\Psi^{CC} = \Pi_{a,r}\exp(c_a^r\hat{X}_a^r)\Pi_{ab,rs}\exp(c_{ab}^{rs}\hat{X}_{ab}^{rs})...|\psi_0\rangle$$

$$\Psi^{CC} = \exp\left(\sum_{a,r} c_a^r\hat{X}_a^r + \sum_{ab,rs} c_{ab}^{rs}\hat{X}_{ab}^{rs} + ...\right)|\psi_0\rangle$$

Coupled Clusters

exponential ansatz of CC

$$\Psi^{CC} = \exp\left(\sum_{a,r} c_a^r \hat{x}_a^r + \sum_{ab,rs} c_{ab}^{rs} \hat{X}_{ab}^{rs} + \ldots.\right)|\psi_0\rangle$$

restrict excitation level up to doubles: CCSD

$$\Psi^{CCSD} = \exp\left(\sum_{a,r} c_a^r \hat{x}_a^r + \sum_{ab,rs} c_{ab}^{rs} \hat{X}_{ab}^{rs}\right)|\psi_0\rangle$$

includes all excited determinants: size consistent!

only uses singles and doubles coefficients

single reference methods

works only if HF is reasonable approximation

fails if ground state has multi-configurational character: dissociation!

UHF reference