Basissets

minimal basis (1 function per shell)

H-He: 1s (1)

Li-Ne: 1s, 2s, $2p_x$, $2p_y$, $2p_z$ (5)

Na-Ar: 1s, 2s, $2p_x$, $2p_y$, $2p_z$, 3s, $3p_x$, $3p_y$, $3p_z$ (9)

Slater-type orbitals

computationally demanding

$$f_{1s}(\zeta, \mathbf{r}) = \exp[-\zeta r]$$

Gaussian-type orbitals

computationally convenient

$$\begin{aligned} g_{1s}(\alpha, \mathbf{r}) &= (8\alpha^3/\pi^3)^{1/4} \exp[-\alpha r^2] \\ g_{2p_x}(\alpha, \mathbf{r}) &= (128\alpha^5/\pi^3)^{1/4} x \exp[-\alpha r^2] \\ g_{3d_{xy}}(\alpha, \mathbf{r}) &= (2048\alpha^7/\pi^3)^{1/4} xy \exp[-\alpha r^2] \end{aligned}$$

Basissets

Gaussian-type orbitals

computationally convenient, but not as accurate as Slater-type orbitals

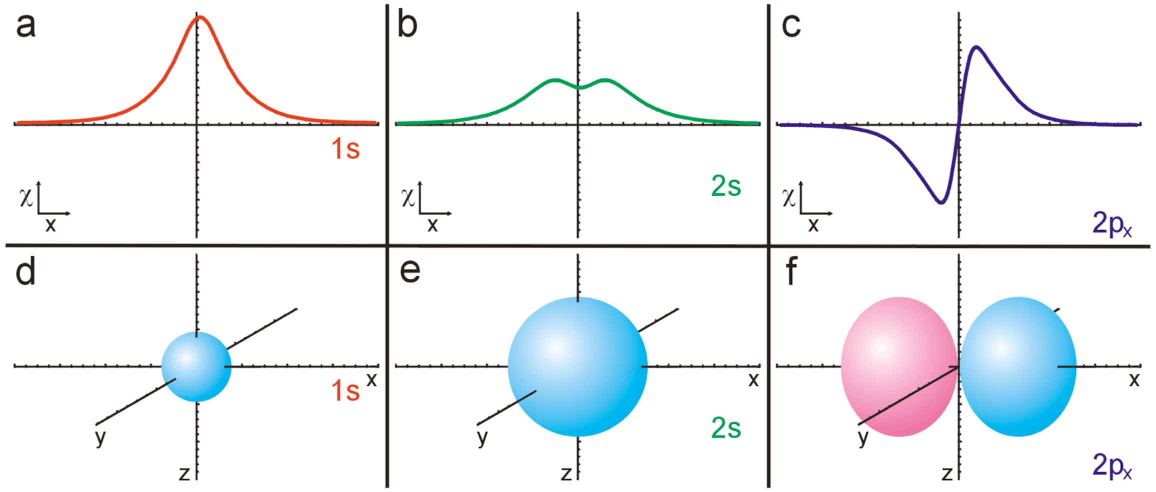
linear combination (contraction) of several gaussians (primitives)

STO-3G

$$\phi_{1s}^{\mathrm{CGF}} = \sum_i^3 d_{i,1s} g_{1s}(\alpha_{i,1s})$$

$$\phi_{2s}^{\mathrm{CGF}} = \sum_i^3 d_{i,2s} g_{1s}(\alpha_{i,2sp})$$

$$\phi_{2p}^{\mathrm{CGF}} = \sum_i^3 d_{i,2p} g_{2p}(\alpha_{i,2sp})$$



least-square fit to Slater orbitals

$$\min\left[\int\left(\phi_{1s}^{\mathrm{SF}}(\mathbf{r}) - \phi_{1s}^{\mathrm{CGF}}(\mathbf{r})\right)d\mathbf{r}\right]^2$$

$$\min\left[\int\left(\phi_{2s}^{\mathrm{SF}}(\mathbf{r}) - \phi_{2s}^{\mathrm{CGF}}(\mathbf{r})\right)d\mathbf{r} - \int\left(\phi_{2p}^{\mathrm{SF}}(\mathbf{r}) - \phi_{2p}^{\mathrm{CGF}}(\mathbf{r})\right)d\mathbf{r}\right]^2$$

notation (for 1st row elements)

$$(6s3p/3s)[2s1p/1s]$$

Basissets

Double-Zeta basis (split valence)

two basisfunctions (contractions) per valence orbital

3-21G

$$(6s3p/3s)[3s2p/2s]$$

H-He:

$$\begin{aligned}
\phi'_{1s} &= \textstyle\sum_i^2 d_{i,1s} g_{1s}(\alpha'_{i,1s}) && \text{compact} \\
\phi''_{1s} &= g_{1s}(\alpha''_{i,1s}) && \text{diffuse}
\end{aligned}$$

Li-Ne:

$$\begin{aligned}
\phi_{1s} &= \textstyle\sum_i^3 d_{i,1s} g_{1s}(\alpha_{i,1s}) && \\
\phi'_{2s} &= \textstyle\sum_i^2 d'_{i,2s} g_{1s}(\alpha'_{i,2sp}) && \text{compact} \\
\phi''_{2s} &= g_{1s}(\alpha''_{i,2sp}) && \text{diffuse} \\
\phi'_{2p} &= \textstyle\sum_i^2 d'_{i,2p} g_{2p}(\alpha'_{i,2sp}) && \text{compact} \\
\phi''_{2p} &= g_{2p}(\alpha''_{i,2sp}) && \text{diffuse}
\end{aligned}$$

Basissets

Double-Zeta basis (split valence)

two basisfunctions (contractions) per valence orbital

4-31G

$$(8s4p/4s)[3s2p/2s]$$

H-He:

$$\begin{aligned}
\phi'_{1s} &= \textstyle\sum_i^3 d_{i,1s} g_{1s}(\alpha'_{i,1s}) \\
\phi''_{1s} &= g_{1s}(\alpha''_{i,1s})
\end{aligned}$$

Li-Ne:

$$\begin{aligned}
\phi_{1s} &= \textstyle\sum_i^4 d_{i,1s} g_{1s}(\alpha_{i,1s}) \\
\phi'_{2s} &= \textstyle\sum_i^3 d'_{i,2s} g_{1s}(\alpha'_{i,2sp}) \\
\phi''_{2s} &= g_{1s}(\alpha''_{i,2sp}) \\
\phi'_{2p} &= \textstyle\sum_i^3 d'_{i,2p} g_{2p}(\alpha'_{i,2sp}) \\
\phi''_{2p} &= g_{2p}(\alpha''_{i,2sp})
\end{aligned}$$

Basissets

Double-Zeta basis

two basisfunctions (contractions) per valence orbital

6-31G

$$(10s4p/4s)[3s2p/2s]$$

H-He:

$$\begin{aligned}
\phi'_{1s} &= \sum_i^3 d_{i,1s} g_{1s}(\alpha'_{i,1s}) \\
\phi''_{1s} &= g_{1s}(\alpha''_{i,1s})
\end{aligned}$$

Li-Ne:

$$\begin{aligned}
\phi_{1s} &= \sum_i^6 d_{i,1s} g_{1s}(\alpha_{i,1s}) \\
\phi'_{2s} &= \sum_i^3 d'_{i,2s} g_{1s}(\alpha'_{i,2sp}) \\
\phi''_{2s} &= g_{1s}(\alpha''_{i,2sp}) \\
\phi'_{2p} &= \sum_i^3 d'_{i,2p} g_{2p}(\alpha'_{i,2sp}) \\
\phi''_{2p} &= g_{2p}(\alpha''_{i,2sp})
\end{aligned}$$

Basissets

Double-Zeta basis with polarization functions

two basisfunctions (contractions) per valence orbital

Li-Ne: 3d functions (*)

H-He: 2p functions (**)

3-21G*, 4-31G*, 6-31G*, 6-31G**

note 6 d-functions (i.e. 5 3d functions + 3s)

$$3d_{xx}, 3d_{yy}, 3d_{zz}, 3d_{xy}, 3d_{yz}, 3d_{zx}$$

linear combinbations of 5 pure 3d functions 1 3s:

$$3d_{xy}, 3d_{x^2-y^2}, 3d_{yz}, 3d_{zx}, 3d_{z^2}, 3s_{x^2+y^2+z^2}$$

contractions

6-31G*: $(11s4p1d/4s)[4s2p1d/2s]$

6-31G**: $(11s4p1d/4s1p)[4s2p1d/2s1p]$

Molecular Quantum Mechanics

molecular orbitals

linear combination of atomic orbitals (hydrogen)

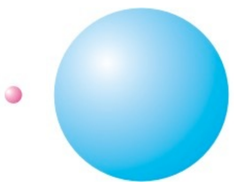
$$\phi_i(r) = \sum_j c_{ji} \chi_j(r)$$

example: hydrogen molecule, minimal basis

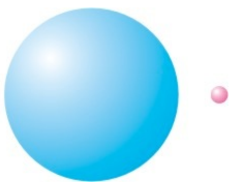
$$\phi_1(r) = \chi_1(r) + \chi_2(r)$$

$$\phi_2(r) = \chi_1(r) - \chi_2(r)$$

χ_1



χ_2



Molecular Quantum Mechanics

molecular orbitals

linear combination of atomic orbitals (hydrogen)

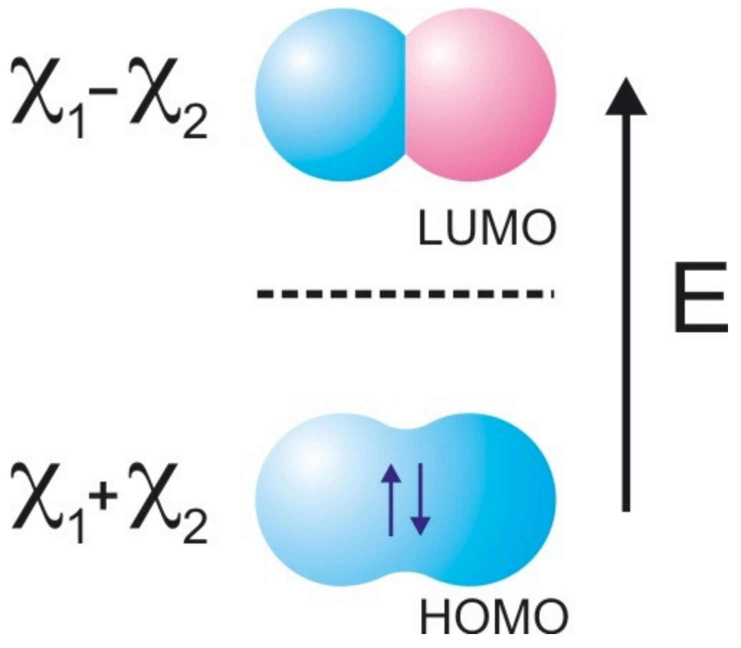
$$\phi_i(r) = \sum_j c_{ji} \chi_j(r)$$

example: hydrogen molecule, minimal basis

$$\phi_1(r) = \chi_1(r) + \chi_2(r)$$

$$\Psi(r_1, r_2) = |\phi_1(r_1)\overline{\phi_1}(r_2)|$$

$$\phi_2(r) = \chi_1(r) - \chi_2(r)$$



dissociation!!!

Molecular Quantum Mechanics

limitations of Hartree-Fock theory

- mean-field: no electron correlation

beyond Hartree-Fock

- configuration interaction (ci)

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

- multiconfiguration self-consistent field (mcscf)

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)

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

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

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

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

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

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

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

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)

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

molecular orbitals

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

Fock operator

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

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

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

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)

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

correlation energy

full configuration interaction

exact solution (within finite basisset)

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

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

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

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

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

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

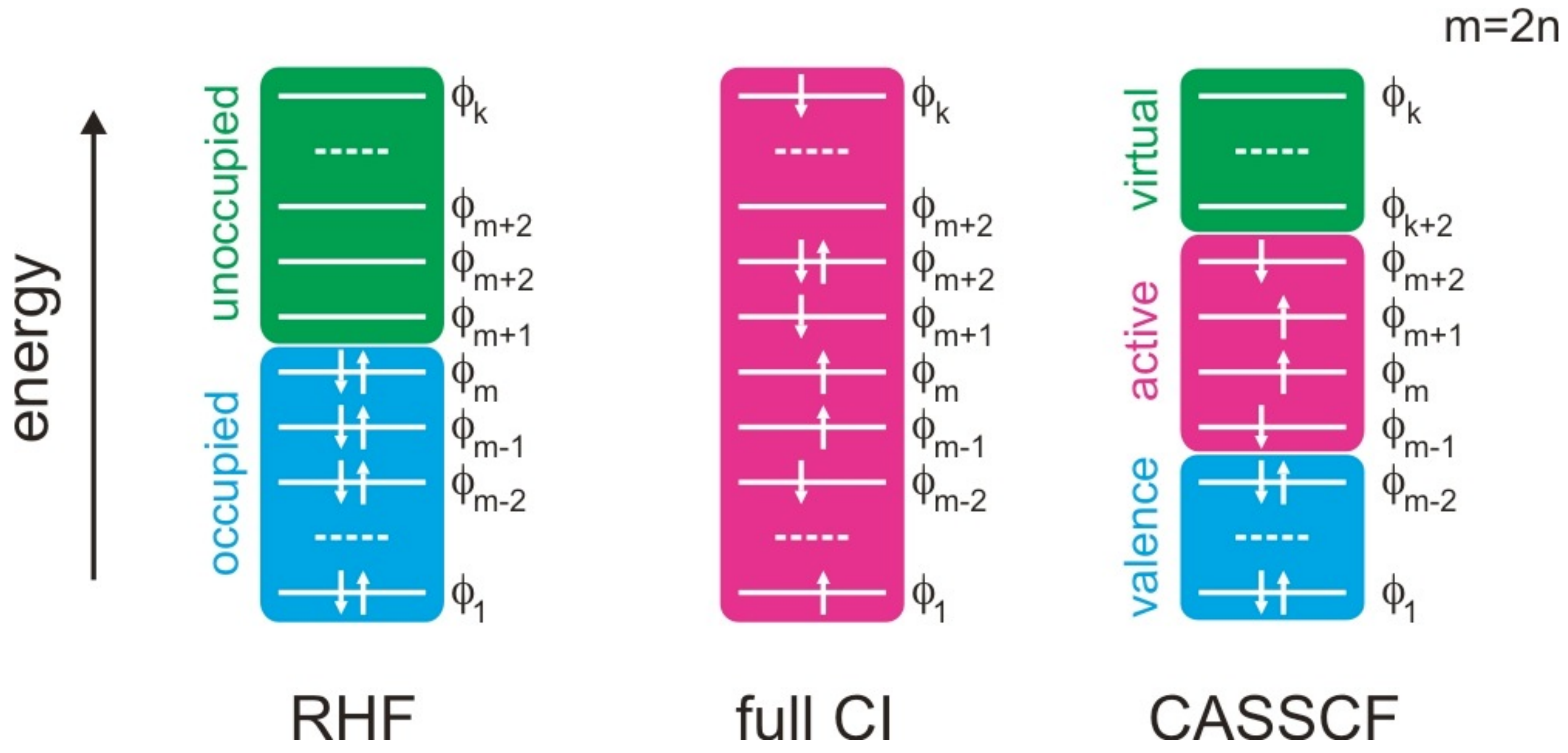
multi-configuration SCF

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

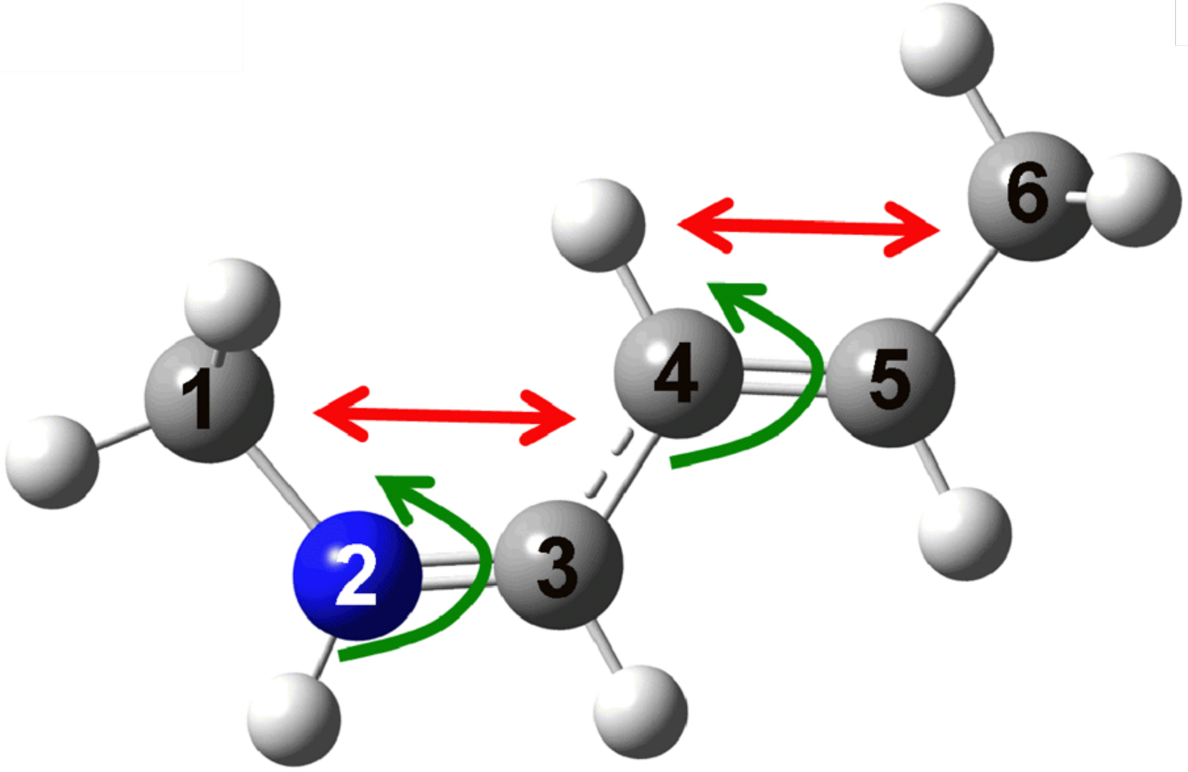
multi-configuration SCF

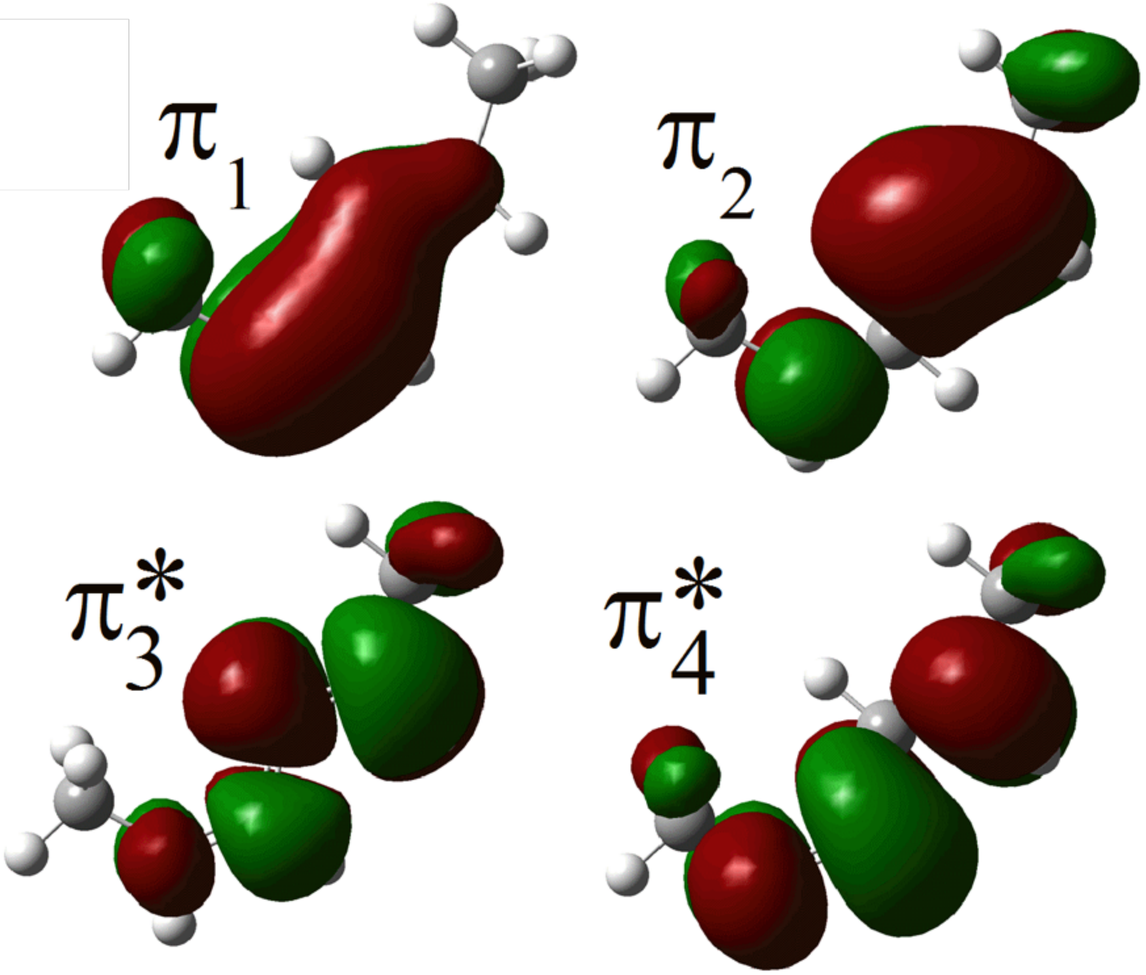
Complete Active Space SCF

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

example

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





beyond Hartree Fock

Configuration Interaction

linear combination of Slater determinants

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

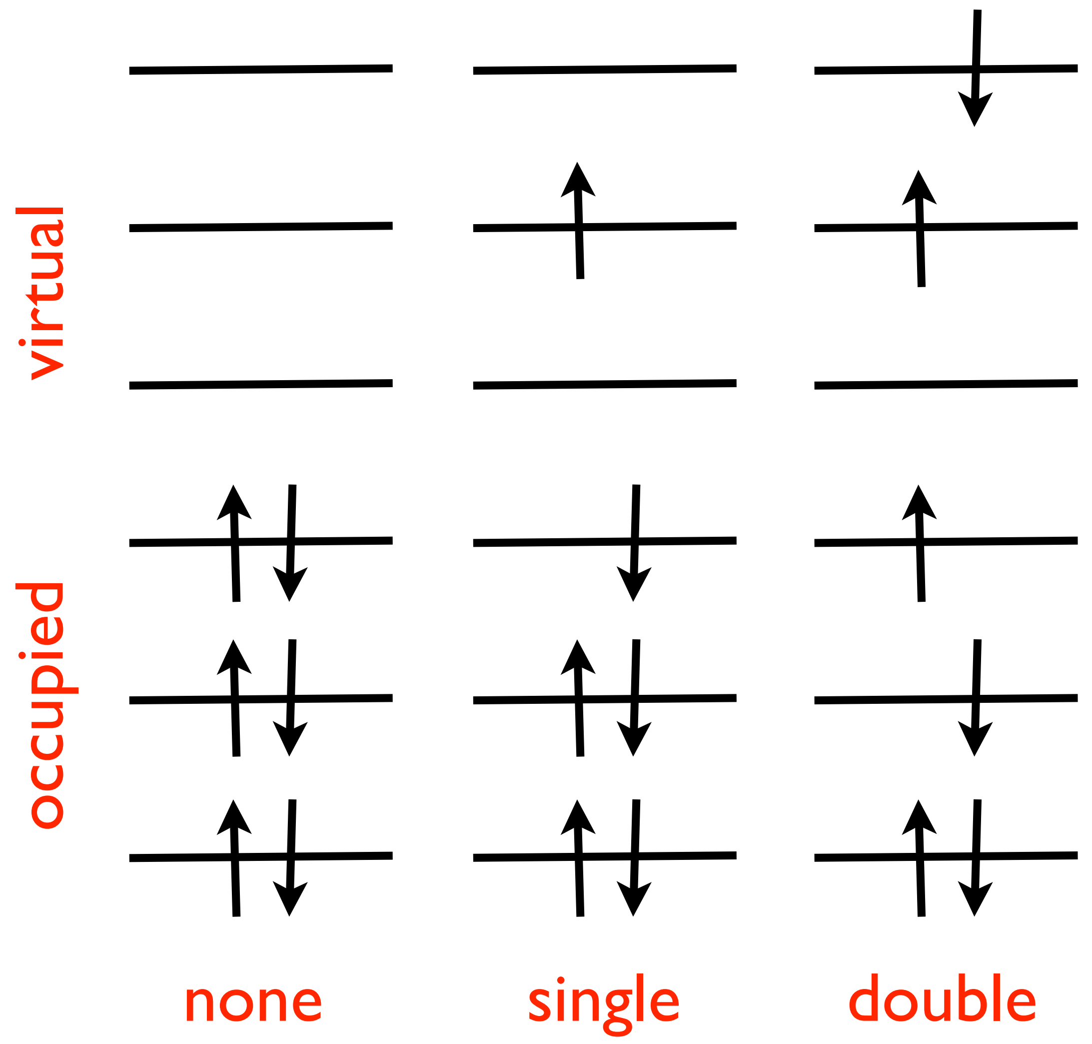
intermediate normalization

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

size consistent, if all determinants are included

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

$$\Psi \quad = \quad |\psi_0\rangle + \sum_a^r c_a^r \hat{X}_a^r |\psi_0\rangle + \sum_a^r \sum_{b>a}^{s>r} c_{ab}^{rs} \hat{X}_{ab}^{rs} |\psi_0\rangle$$

$$+ \sum_a^r \sum_{b>a}^{s>r} \sum_{c>b}^{t>s} c_{abc}^{rst} \hat{X}_{abc}^{rst} |\psi_0\rangle$$

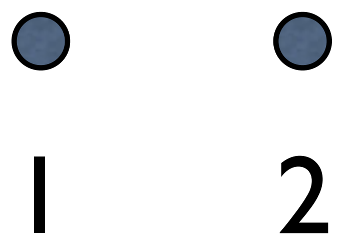
$$+ \sum_a^r \sum_{b>a}^{s>r} \sum_{c>b}^{t>s} \sum_{d>c}^{u>t} c_{abcd}^{rstu} \hat{X}_{abcd}^{rstu} |\psi_0\rangle + \ldots$$

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

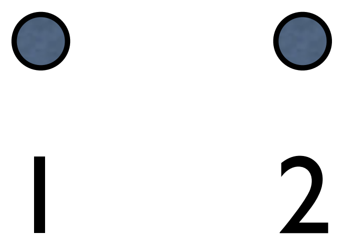
$$\underline{+c_{1_1\bar{1}_1 1_2\bar{1}_2}^{2_1\bar{2}_1 2_2\bar{2}_2}|2_1\bar{2}_1 2_2\bar{2}_2\rangle}$$

Truncated Configuration Interaction expansion

only include HF, single and doubly excited determinants

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

beyond Hartree Fock



Full Configuration Interaction expansion

all determinants included

2 H₂: $$\Psi^{12} = \quad |1_1\bar{1}_1 1_2\bar{1}_2\rangle + c_{1_1\bar{1}_1}^{2_1\bar{2}_1}|2_1\bar{2}_1 1_2\bar{1}_2\rangle + c_{1_2\bar{1}_2}^{2_2\bar{2}_2}|1_1\bar{1}_1 2_2\bar{2}_2\rangle$$

$$+c_{1_1\bar{1}_1 1_2\bar{1}_2}^{2_1\bar{2}_1 2_2\bar{2}_2}|2_1\bar{2}_1 2_2\bar{2}_2\rangle$$

Truncated Configuration Interaction expansion

only include HF, single and doubly excited determinants

2 H₂: $$\Psi^{12} = |1_1\bar{1}_1 1_2\bar{1}_2\rangle + c_{1_1\bar{1}_1}^{2_1\bar{2}_1}|2_1\bar{2}_1 1_2\bar{1}_2\rangle + c_{1_2\bar{1}_2}^{2_2\bar{2}_2}|1_1\bar{1}_1 2_2\bar{2}_2\rangle$$

not size consistent!

$$\lim_{N\to\infty} \frac{E_{\mathrm{CISD}}^{\mathrm{corr.}}}{N} = 0$$

beyond Hartree Fock

Full CI

all determinants included

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

at large separation: independent molecules!

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

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, ..

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

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

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

general case

non-linear expansion in coefficients and excitations

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

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

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

we can use 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

Beyond Hartree-Fock: Perturbation Theory

Møller-Plesset

zeroth order Hamiltonian

$$\hat{H}^0 = \sum_i^{n_e} \hat{f}(\mathbf{r}_i) = \sum_i^{n_e} \left(\hat{h}^0(\mathbf{r}_i) + \hat{v}^{\mathrm{mf}}(\mathbf{r}_i) \right)$$

zeroth order wave function

$$\Psi(\mathbf{x}_1, \mathbf{x}_1, ...\mathbf{x}_n) = \det[\varphi_1(\mathbf{x}_1)\varphi_2(\mathbf{x}_2)...\varphi_n(\mathbf{x}_n)]$$

zeroth order energy (!!)

$$E^0 = \sum_i^{n_e} \epsilon_i$$

true Hamiltonian

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

perturbation

$$\hat{H} = \sum_i^{n_e} \hat{h}^0(\mathbf{r}_i) + \frac{1}{2} \sum_i^{n_e} \sum_j^{n_e} \frac{1}{r_{ij}}$$

Beyond Hartree-Fock: Perturbation Theory

Møller-Plesset

zeroth order Hamiltonian

$$\hat{H}^0 = \sum_i^{n_e} \hat{f}(\mathbf{r}_i) = \sum_i^{n_e} \left(\hat{h}^0(\mathbf{r}_i) + \hat{v}^{\mathrm{mf}}(\mathbf{r}_i) \right)$$

true Hamiltonian

$$\hat{H} = \sum_i^{n_e} \hat{h}^0(\mathbf{r}_i) + \frac{1}{2} \sum_i^{n_e} \sum_j^{n_e} \frac{1}{r_{ij}}$$

perturbation

$$\hat{V} = \hat{H} - \hat{H}^0$$

$$\hat{V} = \frac{1}{2} \sum_i^{n_e} \sum_j^{n_e} \frac{1}{r_{ij}} - \sum_i^{n_e} v^{\mathrm{mf}}$$

Beyond Hartree-Fock: Perturbation Theory

Møller-Plesset

perturbation

$$\hat{V} = \frac{1}{2}\sum_{i}^{n_e}\sum_{j}^{n_e}\frac{1}{r_{ij}} - \sum_{i}^{n_e}\hat{v}^{\mathrm{mf}}$$

first order correction to energy

$$E_0^{(1)} = -\frac{1}{2}\sum_{j}^{n_e}\sum_{j}^{n_e}\int\int \varphi_i^*(\mathbf{x}_1)\varphi_j^*(\mathbf{x}_2)\frac{1-\hat{P}_{12}}{r_{12}}\varphi_i(\mathbf{x}_1)\varphi_j(\mathbf{x}_2)d\mathbf{x}_1 d\mathbf{x}_2$$

second order correction to energy

$$E_0^{(2)} = \sum_{j\neq 0}\frac{|\langle\Psi_0|\hat{V}|\Psi_j\rangle|^2}{E_0^{(0)} - E_j^{(0)}}$$

$$E_0^{(2)} = \frac{1}{4}\sum_{a}^{n_{\mathrm{occ}}}\sum_{b}^{n_{\mathrm{occ}}}\sum_{r}^{n_{\mathrm{virt}}}\sum_{s}^{n_{\mathrm{virt}}}\frac{|\langle\Psi_0|\hat{V}|\Psi_{ab}^{rs}\rangle|^2}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}$$

$$E_0^{(2)} = \frac{1}{4}\sum_{a}^{n_{\mathrm{occ}}}\sum_{b}^{n_{\mathrm{occ}}}\sum_{r}^{n_{\mathrm{virt}}}\sum_{s}^{n_{\mathrm{virt}}}\frac{|\int\int \varphi_a^*(\mathbf{x}_1)\varphi_b^*(\mathbf{x}_2)\frac{1-\hat{P}_{12}}{r_{12}}\varphi_r(\mathbf{x}_1)\varphi_s(\mathbf{x}_2)d\mathbf{x}_1 d\mathbf{x}_2|^2}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}$$

Semi-empirical quantum chemistry

Fock Matrix elements

basisfunctions (N^5 operations)

$$\begin{aligned} F_{\mu\nu} &= h^0_{\mu\nu} \\ &+2\sum_a\sum_\kappa\sum_\lambda c^*_{\kappa a}c^*_{\lambda a}\int\int\gamma^*_\mu(\mathbf{r}_1)\gamma^*_\kappa(\mathbf{r}_2)\frac{1}{r_{12}}\gamma_\lambda(\mathbf{r}_2)\gamma_\nu(\mathbf{r}_1)d\mathbf{r}_1 d\mathbf{r}_2 \\ &-\sum_a\sum_\kappa\sum_\lambda c^*_{\kappa a}c^*_{\lambda a}\int\int\gamma^*_\mu(\mathbf{r}_1)\gamma^*_\kappa(\mathbf{r}_2)\frac{1}{r_{12}}\gamma_\nu(\mathbf{r}_2)\gamma_a(\mathbf{r}_1)d\mathbf{r}_1 d\mathbf{r}_2 \end{aligned}$$

speeding up the calculation of Fock matrix

only valence electrons (2s,2p)

minimal basis, one function per electron

zero differential overlap

$$S_{\mu\nu} = \langle\gamma_\mu|\gamma_\nu\rangle = \delta_{\mu\nu}$$

replace remaining integral by parameters fitted to experimental data (NIST)

NDDO, MNDO, MNDO/d, AM1, PM3

Density functional theory

Hohenberg-Kohn theorems

exact mapping between non-interacting and interacting electronic systems

$$\Psi^{\text{real}} \longleftarrow V^{\text{eff}}[\rho(\mathbf{r})] \longrightarrow \Psi^{\text{non-int.}}$$

effective potential exists, so that densities are the same (ground-state only!!)

$$H^{\text{non-int.}} = \sum_i^N (-\frac{1}{2}\nabla^2 + V^{\text{eff}})$$

one-electron wavefunctions: Kohn-Sham orbitals

$$(-\frac{1}{2}\nabla^2 + V^{\text{eff}})\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

density of both systems

$$\rho(\mathbf{r}) = \sum_i^n |\phi(\mathbf{r})|^2$$

with exact effective potential

$$\rho(\mathbf{r}) = \rho^{\text{real}}(\mathbf{r})$$

Density functional theory

Hohenberg-Kohn theorems

exact mapping between non-interacting and interacting electronic systems

$$\Psi^{\text{real}} \longleftarrow V^{\text{eff}}[\rho(\mathbf{r})] \longrightarrow \Psi^{\text{non-int.}}$$

ground-state only

energy functional

$$E[\rho] = T[\rho] + E_{ee}[\rho] + E_{ne}[\rho] + E_{XC}[\rho]$$

variational principle

$$E[\rho(\mathbf{r})] = \min_{\Psi\rightarrow\rho} \langle\Psi|\hat{H}|\Psi\rangle \geq E_0$$

Density functional theory

energy functional

$$E[\rho] = T[\rho] + E_{ee}[\rho] + E_{ne}[\rho] + E_{XC}[\rho]$$

electron-electron repulsion

$$E_{ee}[\rho] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}|} d\mathbf{r} d\mathbf{r}'$$

electron-nuclei attraction

$$E_{en}[\rho] = \int \sum_{A}^{N} \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} \rho(\mathbf{r}) d\mathbf{r} = \int V_{en}(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r}$$

exchange-correlation energy (uniform electron gas)

$$E_{XC}^{\mathrm{LDA}}[\rho] = \int \epsilon_{XC}(\rho(\mathbf{r}))\rho(\mathbf{r}) d\mathbf{r}$$

kinetic energy of non-interacting systems

$$T[\rho(\mathbf{r})] = \min_{\Psi \to \rho} \langle \Psi | \hat{T}^{\text{non-int.}} | \Psi \rangle$$

Density functional theory

minimize functional with respect to density

$$\partial E = \int \left(\frac{\partial}{\partial \rho} T + V_{ee} + E_{ne} + V_{XC} \right) \partial \rho d\mathbf{r} = 0$$

electron-electron repulsion

$$V_{ee}([\rho], r) = \frac{1}{2} \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}|} d\mathbf{r}'$$

electron-nuclei attraction

$$V_{en}([\rho], \mathbf{r}) = \sum_{A} \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|}$$

exchange-correlation energy (uniform electron gas)

$$V_{XC}^{\mathrm{LDA}}([\rho], \mathbf{r}) = \frac{\partial}{\partial \rho} E_{XC}^{\mathrm{LDA}} = \rho(\mathbf{r}) \frac{\partial \epsilon_{XC}(\rho(\mathbf{r}))}{\partial \rho} \Big|_{\rho = \rho(r)} + \epsilon_{XC}(\rho(\mathbf{r}))$$

Density functional theory

energy functional of non-interacting system

$$E^{\text{non-int.}}[\rho] = T[\rho] + \int V^{\text{eff}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$$

minimize functional of non-interacting system

$$\partial E^{\text{non-int.}}[\rho] = \int \left(\frac{\partial}{\partial \rho} T[\rho] + \quad V^{\text{eff}}(\mathbf{r}) \right) \partial \rho(\mathbf{r}) d\mathbf{r} = 0$$

kinetic energy functional

$$\frac{\partial}{\partial \rho} T[\rho] = -V^{\text{eff}}(\mathbf{r})$$

effective potential function of true potentials

$$V^{\text{eff}}(\mathbf{r}) = V_{en}(\mathbf{r}) + V_{ee}([\rho], \mathbf{r}) + V_{XC}([\rho], \mathbf{r})$$

Density functional theory

Practical DFT scheme

Step 1: guess density $\rho(\mathbf{r})$

Step 2: construct effective potential

$$V^{\text{eff}}(\mathbf{r}) = V_{en}(\mathbf{r}) + V_{ee}([\rho], \mathbf{r}) + V_{XC}([\rho], \mathbf{r})$$

Step 3a: solve the Schrödinger equation for non-interacting electrons

$$(-\frac{1}{2}\nabla^2 + V^{\text{eff}})\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

Step 3b: compute new density & kinetic energy

$$\rho(\mathbf{r}) = \sum_i^n |\phi(\mathbf{r})|^2$$

$$T[\rho] = \sum_i^n \langle \phi_i | -\frac{1}{2}\nabla^2 | \phi_i \rangle = \sum_i^n \epsilon_i - \int V^{\text{eff}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$$

Step 4: goto step 2, until convergence is reached

final energy:

$$E[\rho_0] = \sum_i^n \epsilon_i - \int V^{\text{eff}}(\mathbf{r})\rho_0(\mathbf{r})d\mathbf{r} + E_{en}[\rho_0] + E_{ee}[\rho_0] + E_{XC}[\rho_0]$$

Quantum Monte Carlo

Variational Monte Carlo

expectation value of energy

$$\frac{\int \Psi_T^*(\mathbf{r},\{\alpha\})\hat{H}\Psi_T(\mathbf{r},\{\alpha\})d\mathbf{r}}{\int \Psi_T^*(\mathbf{r},\{\alpha\})\Psi_T(\mathbf{r},\{\alpha\})d\mathbf{r}} = E(\{\alpha\}) \geq E_0$$

importance sampling (Monte Carlo)

$$p(\mathbf{r}) = \frac{|\Psi(\mathbf{r})|}{\int |\Psi(\mathbf{r}')|d\mathbf{r}'}$$

local energy

$$E_L(\mathbf{r}) = \frac{\hat{H}\Psi_T(\mathbf{r})}{\Psi_T(\mathbf{r})}$$

Sampling of energy, optimize coefficients in wavefunction

$$\langle \hat{H} \rangle = \int p(\mathbf{r})E_L(\mathbf{r})d\mathbf{r}$$

$$\langle \hat{H} \rangle = \frac{1}{M}\sum_{i=1}^{M} E_L(\mathbf{r}_i) = \frac{1}{M}\sum_{i=1}^{M} \frac{\hat{H}\Psi_T(\mathbf{r})}{\Psi_T(\mathbf{r})}$$

Quantum Monte Carlo

Variational Monte Carlo

wavefunction

$$\Psi_T(\mathbf{x}) = \exp[J(\mathbf{x})] \sum_i c_i D_i(\mathbf{x})$$

determinant (antisymmetric)

$$D_i(\mathbf{x}) = \begin{vmatrix} \varphi_1(\mathbf{x}_1) & \varphi_1(\mathbf{x}_2) & \dots & \varphi_1(\mathbf{x}_n) \\ \varphi_2(\mathbf{x}_1) & \varphi_2(\mathbf{x}_2) & \dots & \varphi_2(\mathbf{x}_n) \\ \dots & \dots & & \dots \\ \varphi_n(\mathbf{x}_1) & \varphi_n(\mathbf{x}_2) & \dots & \varphi_n(\mathbf{x}_n) \end{vmatrix}$$

Jastrow factor

$$J(\mathbf{r}) = \sum_{i>j}^{N} u(r_{ij}) + \sum_{i=1}^{N} \sum_{I=1}^{N_I} \chi_I(r_{iI}) + \sum_{i>j}^{N} \sum_{I=1}^{N_I} f_I(r_{ij}, r_{iI}, r_{jI})$$

Quantum Monte Carlo

Diffusion Monte Carlo

propagate Schrödinger equation in imaginary time

$$i\frac{\partial\Psi(\mathbf{r},t)}{\partial t} = -\frac{1}{2}\nabla^2\Psi(\mathbf{r},t) + V(\mathbf{r},t)\Psi(\mathbf{r},t)$$

$$\tau = it$$

diffusion equation of electronic possitions

$$-\frac{\partial\Psi^{\mathrm{DMC}}(\mathbf{R},t)}{\partial\tau} = -\frac{1}{2}\nabla^2\Psi(\mathbf{r},\tau) + (V(\mathbf{r}) - E_T)\Psi(\mathbf{r},t)$$

project out ground state

Quantum Monte Carlo

Diffusion Monte Carlo

propagate Schrödinger equation in imaginary time

$$-\frac{\partial\Psi^{\mathrm{DMC}}(\mathbf{R},t)}{\partial\tau} = -\frac{1}{2}\nabla^2\Psi(\mathbf{r},\tau) + (V(\mathbf{r}) - E_T)\Psi(\mathbf{r},t)$$

expansion in (unknown) eigenstates

$$\Psi(\mathbf{r},t) = \sum_{n=0}^{\infty} c_n\psi_n(\mathbf{r})e^{-i(E_n-E_t)t}$$

$$\Psi(\mathbf{r},\tau) = \sum_{n=0}^{\infty} c_n\psi_n(\mathbf{r})e^{-(E_n-E_t)\tau}$$

with $E_T = E_0$ we can single out ground state in diffusion process

$$\Psi(\mathbf{r},\tau) = c_0\psi_0(\mathbf{r}) + \sum_{n=1}^{\infty} c_n\psi_n(\mathbf{r})e^{-(E_n-E_0)\tau}$$

Some practical guidelines

Basissets

- STO-3G too small
- 6-31G* & 6-31G** reasonable results
  - DFT often less sensitive to basisset
  - often better than cc-pVDZ
- higher accuracy with cc-pVTZ, better than 6-311G**, etc.
- diffuse functions (aug- or +)
  - anions
  - excited states
  - dispersion bound complexes

Some practical guidelines

Methods

- prefer DFT over HF
- HF < DFT ~ MP2 < CCSD < CCSD(T)
- MPn may not converge with n
  - beyond MP2, use CC
- CASSCF/CASPT2
  - bond breaking, diradicals, excited states, transition metals
  - DFT can be dangerous
- HF, semi-empirical and DFT fail for VDW complexes
  - MP2, CC, dispersion corrected DFT

Some practical guidelines

Always do!

- check if SCF converged!
  - check for multiconfigurational character (MPn/CC:T2)
- check if geometry converged
  - NMA analysis
  - minimum: all postive frequencies
  - transition state: one negative frequency.
  - non-covalent complexes: flat surface, difficult, go by hand
- think of symmetry
  - optimization cannot break symmetry
- know what to expect: think first
  - never thrust the computer
- CASSCF/CASPT2
  - check final natural orbital density matrix
  - check for large orbital rotations

Gradients

Analytical derivatives

$$\frac{\partial E}{\partial X_A} = \frac{\partial \tilde{E}}{\partial X_A} + \sum_{\mu a} \frac{\partial E}{\partial C_{\mu a}} \frac{\partial C_{\mu a}}{\partial X_A}$$

Hartree Fock solution

$$\frac{\partial E}{\partial X_A} = \frac{\partial \tilde{E}}{\partial X_A}$$

Hartree-Fock energy

$$E = \sum_{\mu\nu} P_{\mu\nu} H^{\text{core}}_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} \langle \mu\nu | \frac{1 - \frac{1}{2}\hat{p}_{12}}{r_{12}} | \lambda\sigma \rangle + V_{NN}$$

$$P_{\mu\nu} = 2 \sum_{a}^{n/2} C^*_{\mu a} C_{\nu a}$$

Gradients

Analytical derivatives

Hartree Fock energy

$$E = \sum_{\mu\nu} P_{\mu\nu} H^{\text{core}}_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} \langle \mu\nu | \frac{1 - \frac{1}{2}\hat{p}_{12}}{r_{12}} | \lambda\sigma \rangle + V_{NN}$$

gradient

$$\begin{aligned} \frac{\partial E}{\partial X_A} \quad = \quad & \textstyle\sum_{\mu\nu} P_{\mu\nu} \frac{\partial H^{\text{core}}_{\mu\nu}}{\partial X_A} \\ & + \tfrac{1}{2} \textstyle\sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} \frac{\partial}{\partial X_A} \langle \mu\nu | \frac{1 - \frac{1}{2}\hat{p}_{12}}{r_{12}} | \lambda\sigma \rangle + \frac{V_{NN}}{\partial X_A} \\ & + \textstyle\sum_{\mu\nu} \frac{\partial P_{\mu\nu}}{\partial X_A} H^{\text{core}}_{\mu\nu} + \textstyle\sum_{\mu\nu\lambda\sigma} \frac{\partial P_{\mu\nu}}{\partial X_A} P_{\lambda\sigma} \langle \mu\nu | \frac{1 - \frac{1}{2}\hat{p}_{12}}{r_{12}} | \lambda\sigma \rangle \end{aligned}$$

Gradients

Analytical derivatives

orthogonality of RHF molecular orbitals

$$\sum_{\mu\nu} C_{\mu a} S_{\mu\nu} C_{\nu b} = \delta_{ab}$$

$$2\sum_{\mu\nu} \frac{\partial C_{\mu a}}{\partial X_A} S_{\mu\nu} \quad = -\sum_{\mu\nu} C_{\mu a} C_{\nu a} \frac{\partial S_{\mu\nu}}{\partial X_A}$$

gradient

$$\frac{\partial E}{\partial X_A} \quad = \quad \sum_{\mu\nu} P_{\mu\nu} \frac{\partial H^{\mathrm{core}}_{\mu\nu}}{\partial X_A}$$

$$+\frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} \frac{\partial}{\partial X_A} \langle \mu\nu | \frac{1-\frac{1}{2}\hat{p}_{12}}{r_{12}} | \lambda\sigma \rangle + \frac{V_{NN}}{\partial X_A}$$

$$-\sum_{\mu\nu} Q_{\mu\nu} \frac{\partial S_{\mu\nu}}{\partial X_A}$$

with

$$Q_{\mu\nu} = 2\sum_{a}^{n/2} \epsilon_a C_{\mu a} C_{\nu a}$$

Gradients

Analytical derivatives

Configuration interaction

$$|\Psi\rangle = \sum_I c_I |\psi_I\rangle$$

general gradient

$$\frac{\partial E}{\partial X_A} = \frac{\partial \tilde{E}}{\partial X_A} + \sum_{\mu a} \frac{\partial E}{\partial C_{\mu i}} \frac{\partial C_{\mu i}}{\partial X_A} + \sum \frac{\partial E}{\partial c_I} \frac{\partial c_I}{\partial X_A}$$

MCSCF gradient

$$\frac{\partial E}{\partial X_A} = \frac{\partial \tilde{E}}{\partial X_A}$$

CI gradient

$$\frac{\partial E}{\partial X_A} = \frac{\partial \tilde{E}}{\partial X_A} + \sum_{\mu a} \frac{\partial E}{\partial C_{\mu i}} \frac{\partial C_{\mu i}}{\partial X_A}$$