

Hartree-Fock Method & Beyond

Introduction to Molecular Modeling



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In Previous Episode

- Most of **molecular modeling** relies on non-relativistic QM.
- Due to the difference in mass of electrons & nuclei it is possible to approx. separate their motions.
- Born-Oppenheimer approx.** utilizes this fact to show, that electron E can be treated as potential energy for (vibrational) motions of nuclei (around eq. positions)

$$(\hat{T}_{nuc} + E_e(\mathbf{R}^N))\Psi_{nuc} = (T_{nuc} + E_e(\mathbf{R}^N))\Psi_{nuc}$$

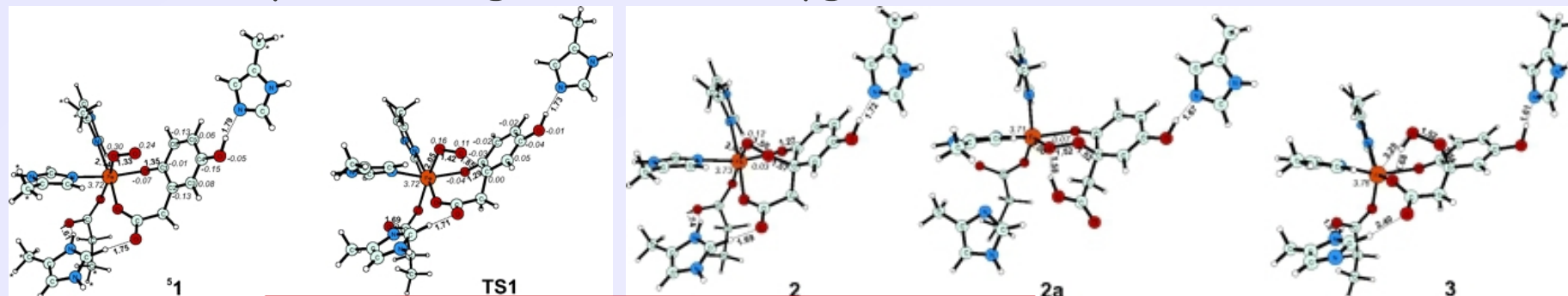
- Potential Energy (Hyper)Surface** - function of E_e vs. nuclear coords. Its (local) minima corresponds to (meta)stable conformations of molecules.
- BO approx. works as long as ΔE between el. states $\gg \Delta E$ between vibrational states, which is the case for many 'typical' molecules & semiconductors, at least in the vicinity of ground state E_e minimum.
- Molecular Mechanics** - approx. of E_e as the set of functions ('force fields') of interatomic distances, angles & torsions.

Comment to The Previous Talk

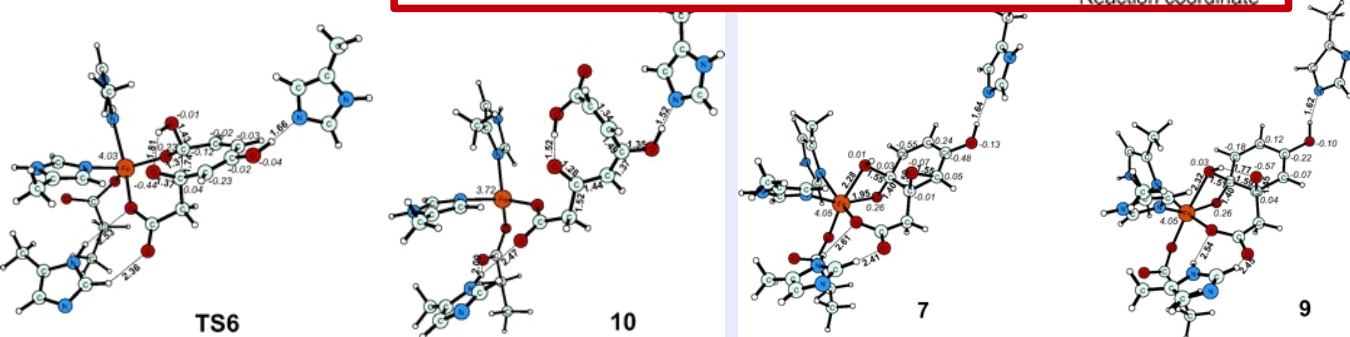
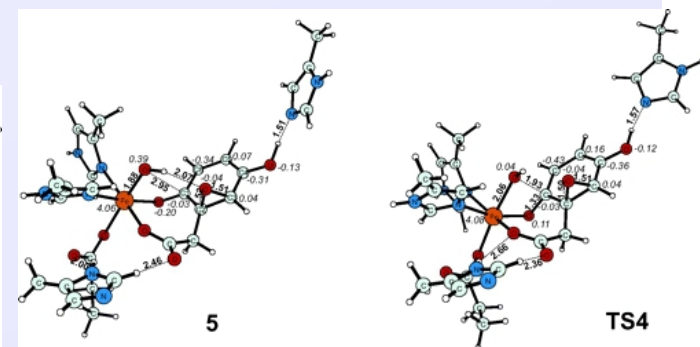
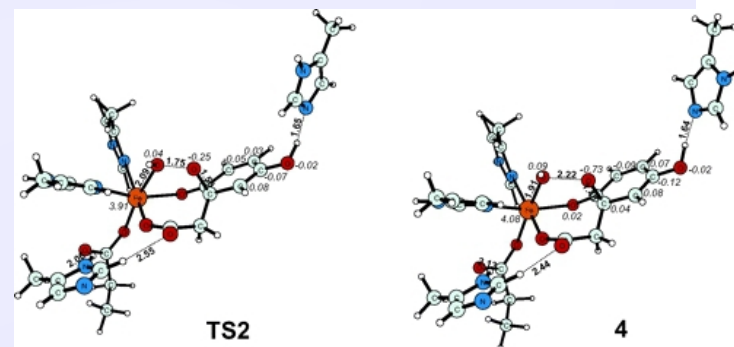
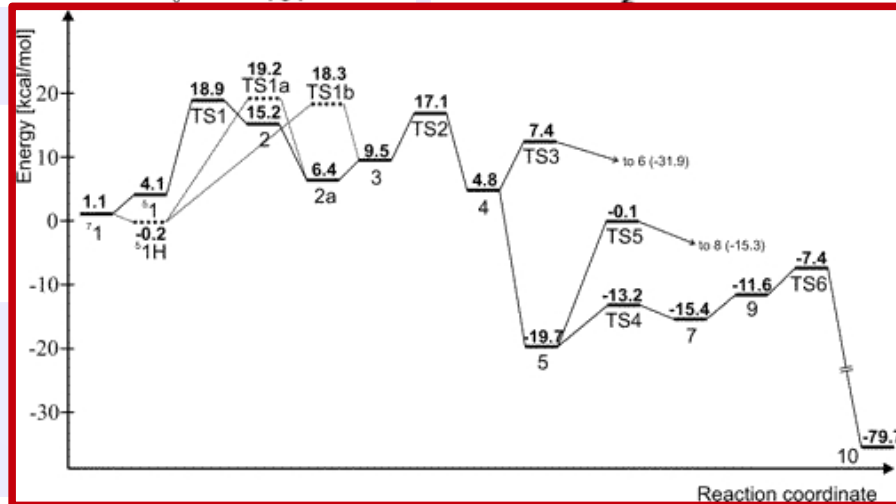
- ❑ Routine techniques of energy minimization typically find the nearest stationary point (minimum or transition state) to the input structure.
- ❑ It is possible to look for:
 - ▶ transition states or short-living intermediates, which are difficult to study experimentally.
 - ▶ validate the structure proposed on the basis of indirect exp. techniques in lack of 'hard' structural evidence.
 - ▶ local environments of defects & impurities in solids (take ideal crystal structure, remove/replace some atoms).
- ❑ It is possible to study time evolution of systems (chemical reactions, phase transitions etc.) by means of molecular dynamics, Monte Carlo & related methods.

Exemplary Energetic Profile of Chemical Reaction

🚩 DFT study on Homogentisate Dioxygenase.

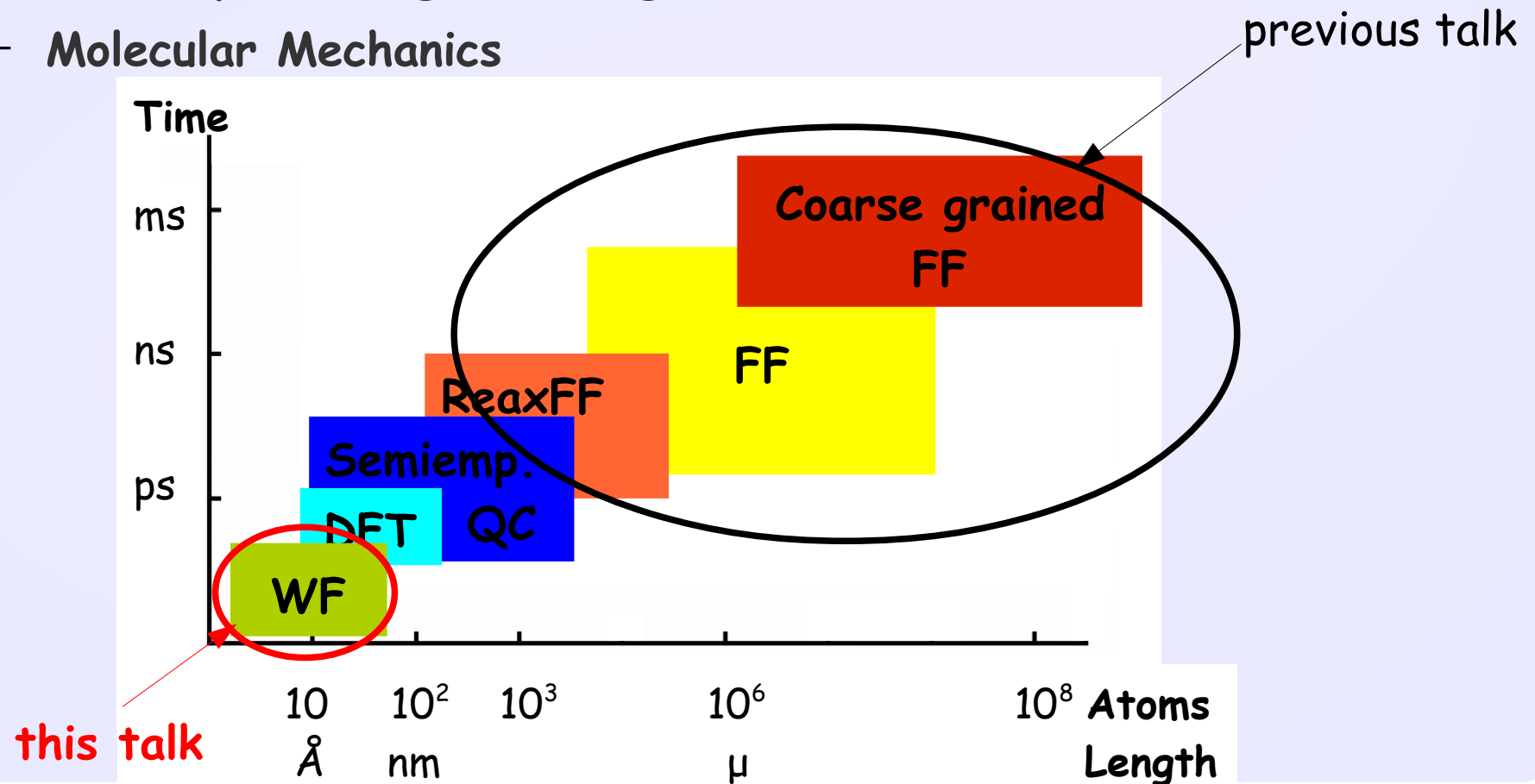


Borowski & co.
JACS 2005,
127, 17303.



But How to Calculate Electron Energy?

- Wavefunction (WF) based methods
- Density Functional Theory
- Semiempirical/Tight Binding methods
- Molecular Mechanics



1-Electron Approach For Many Electron Systems

- Due to Coulomb interactions we have many body problem, Schrödinger equation (SE) cannot be solved analytically, one must look for approx.

$$\hat{H}_e = \sum_i \left(-\frac{1}{2} \nabla_i^2 \right) + \sum_{i>j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{I,i} -\frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} \left(+ \sum_{I>J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} = \text{const.} \right)$$

- The exact WF for N fermions **noninteracting*** is Slater determinant made of N single particles WFs - **spinorbitals (SO)**

*with each other, can interact with external potential

$$\Psi_{SD} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(\mathbf{x}_1) & \varphi_1(\mathbf{x}_2) & \cdots & \varphi_1(\mathbf{x}_N) \\ \varphi_2(\mathbf{x}_1) & \varphi_2(\mathbf{x}_2) & \cdots & \varphi_2(\mathbf{x}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_N(\mathbf{x}_1) & \varphi_N(\mathbf{x}_2) & \cdots & \varphi_N(\mathbf{x}_N) \end{vmatrix} \equiv |\varphi_1 \varphi_2 \cdots \varphi_N|,$$

$$\varphi_i(\mathbf{x}_p) = \varphi(\mathbf{r}_p, \sigma_p), \quad \langle \varphi_i(\mathbf{x}_p) | \varphi_j(\mathbf{x}_p) \rangle = \delta_{ij}, \quad \langle \Psi_{SD} | \Psi_{SD} \rangle = 1$$

$$\hat{H}_{nonint} = \sum_{i=1}^N \hat{h}_i, \quad \hat{h}_i = -\frac{1}{2} \nabla_i^2 + \hat{V}_{ext}, \quad \hat{h}_i \varphi_i = \varepsilon_i \varphi_i, \quad E = \sum_{i=1}^N \varepsilon_i.$$

Energy of Slater Determinant WF

Energy is a **functional*** of WF: $E_i = \langle \Psi_i | \hat{H} | \Psi_i \rangle / \langle \Psi_i | \Psi_i \rangle$

*functional - function assigning number to function

Expected value of \hat{H}_e calc. with Slater determinant WF:

$$E[\Psi_{SD}] = \langle \Psi_{SD} | \hat{H}_e | \Psi_{SD} \rangle = \sum_a^N h_a + \frac{1}{2} \sum_{a \neq b}^N (J_{ab} - K_{ab}) (+V_{nn}) ,$$

▶ 1-el. energy
$$h_a = \left\langle \phi_a(1) \left| -\frac{1}{2} \nabla^2 + \sum_I \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_1|} \right| \phi_a(1) \right\rangle$$

▶ Coulomb integral
$$J_{ab} = \left\langle \phi_a(1) \phi_b(2) \left| \frac{1}{r_{12}} \right| \phi_a(1) \phi_b(2) \right\rangle \quad \text{('classical')}$$

▶ Exchange integral
$$K_{ab} = \left\langle \phi_a(1) \phi_b(2) \left| \frac{1}{r_{12}} \right| \phi_b(1) \phi_a(2) \right\rangle \quad \text{('quantum' / Pauli exclusion)}$$

J, K ≥ 0 & K ≠ 0 only for SO of equal spin, i. e. average Coulomb repulsion between el. of equal spin lower, because they are more spatially separated. $J_{aa} = K_{aa}$ (no self-interaction).

Hartree-Fock Method

HF method is (variational) search for the best Ψ_{SD} approx. to true (& unknown) N electron WF. $\langle \Psi_{HF} | \hat{H}_e | \Psi_{HF} \rangle = \min \langle \Psi_{SD} | \hat{H}_e | \Psi_{SD} \rangle$

One minimizes $E[\Psi_{SD}]$ with constraint on SO orthonormalization:

$$L = E[\Psi_{SD}] - \sum_{a,b}^N (\lambda_{ab} \langle \phi_a(1) | \phi_b(1) \rangle - \delta_{ab}) \rightarrow \delta L = 0$$

after some maths & introducing one electron Fock operators

$$\delta L = \sum_{a=1}^N \langle \delta \phi_a(1) | \hat{f}(1) | \phi_a(1) \rangle - \sum_{a,b}^N \lambda_{ab} \langle \delta \phi_a(1) | \phi_b(1) \rangle \quad (+ \text{complex conjugates})$$

Because δL must be 0 for arbitrary variation $\delta \phi$, we get N 1-el. equations

$$\hat{f}(1) \phi_a(1) = \sum_b^N \lambda_{ab} \phi_b(1) \xrightarrow[\text{transformation}]{\text{unitary}} \hat{f}(1) \chi_a(1) = \varepsilon_a \chi_a(1)$$

SO diagonalizing Fock eq. are called **canonical spinorbitals**, they are more convenient.

$\lambda_{ab} / \varepsilon_a$ are just indefinite Lagrange multipliers in minimization procedure.

Fock operators

$$\hat{f}(1) \chi_a(1) = \left\{ \hat{h}(1) + \sum_{b \neq a}^N (\hat{J}_b(1) - \hat{K}_b(1)) \right\} \chi_a(1)$$

- ☐ Fock equations - **pseudoeigenvalue** problem, operator depends on the function it acts on:

$$\hat{h}(1) = -\frac{1}{2} \nabla^2(1) + \sum_I \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_1|}$$

$$\hat{J}_b(1) = \left\langle \chi_b(2) \left| \frac{1}{r_{12}} \right| \chi_b(2) \right\rangle \equiv \int \frac{|\chi_b(2)|^2 d\mathbf{r}_2}{r_{12}} \rightarrow \hat{J}_b(1) \chi_a(1) = f(1) \cdot \chi_a(1)$$

$$\hat{K}_b(2) \chi_a(1) = \left\langle \chi_b(2) \left| \frac{1}{r_{12}} \right| \chi_a(2) \right\rangle \chi_b(1)$$

- ☐ **Local potential** (like Coulomb) - its action on $f(x_1)$ depends only on the value of $f(x)$ in this point.
- ☐ **Nonlocal potential** (like exchange) - its action on $f(x_1)$ depends on the value of $f(x)$ in certain neighborhood of x_1 (can be all space).

Fock eigenfunctions/eigenvalues

- Assume we solved set of N Fock eqs. $\hat{f}(1)\chi_a(1)=\varepsilon_a\chi_a(1)$, $a=1,\dots,N$
We got N spinorbitals & their eigenvalues - '**orbital energies**'.

- \hat{f} depends on occ. orbitals, but once they are established \hat{f} became 'good' Hermitian operator with infinite no. of eigenfunctions

$$\hat{f}_{occ}(1)\chi_i(1)=\varepsilon_i\chi_i(1), \quad i=1,\dots,\infty$$

we should have 1,...,N occupied & N+1,..., ∞ unocc. '**virtual**' SO.

- In HF total E depends only on N occupied SO & only occ. SO are optimized, virtual SO are kind of byproduct.

- Orbital energies for occ. & virt orbitals are:

$$\bullet \quad \varepsilon_a = h_a + \sum_{a \neq b}^{occ} (J_{ab} - K_{ab}) \quad \text{interaction with (N-1) e (OK)}$$

$$\bullet \quad \varepsilon_p = h_p + \sum_b^{occ} (J_{pb} - K_{pb}) \quad \text{interaction with N electrons.}$$

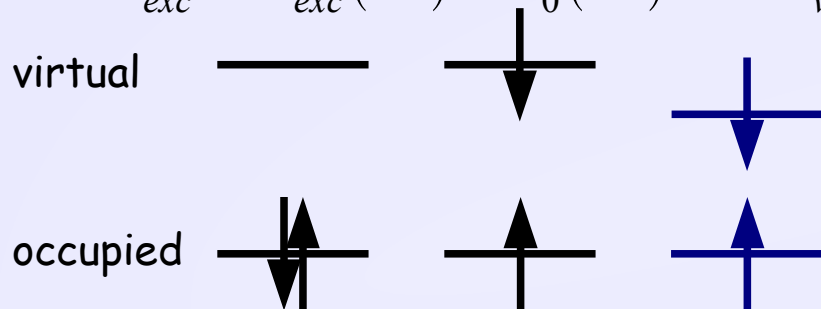
What Are (Not) Orbital Energies?

- Physical meaning? - **none** (strictly speaking).
- Total E is not a sum of orbital energies! (it would 2x count interactions)

$$E_{HF} = \sum_a^{occ.} h_a + \frac{1}{2} \sum_{a \neq b}^N (J_{ab} - K_{ab}) \neq \sum_a^{occ.} \varepsilon_a = \sum_a^{occ.} h_a + \sum_{a \neq b}^N (J_{ab} - K_{ab})$$

- Differences of ε_i are not excitation energies!

$$\Delta E_{exc} = E_{exc}(N) - E_0(N) \neq \varepsilon_{virt} - \varepsilon_{occ}$$



$\varepsilon_{virtual}$ for HF ground states too high, because they feel potential of N el.

One needs to solve HF eqs. for excited state.

- Koopman's theorem** (valid for canonical SO only!)
 - occ. $-\varepsilon_a \approx a$ -th ionization energy $I = E(N-1) - E(N)$
 - virt. $-\varepsilon_p \approx p$ -th electron affinity $A = E(N) - E(N+1)$
 - For exact HF I & A one needs HF optimized $N \pm 1 \Psi_{SD}$.

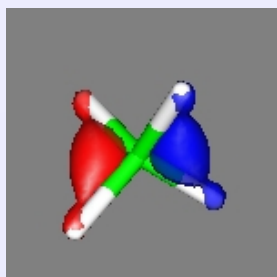
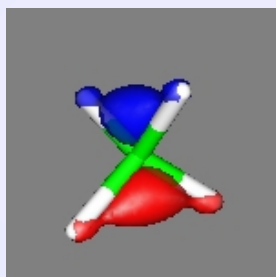
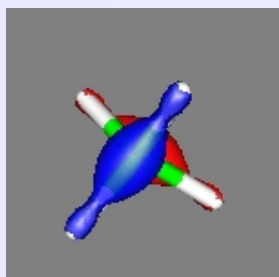
Orbitals vs Orbitals

CH₄ molecule, HF results

Canonical Orbitals



$2a_1, \epsilon = -25.724 \text{ eV}$

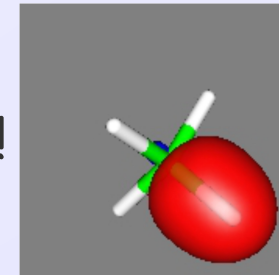
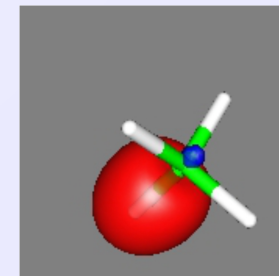
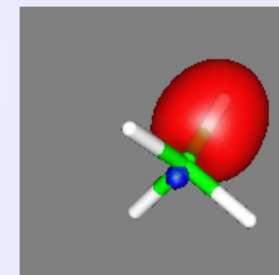
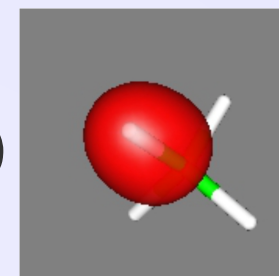
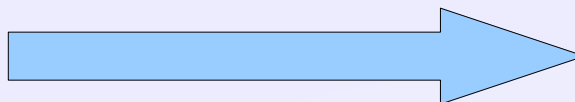


$1t_2, \epsilon = -14.877 \text{ eV}$

Localized Orbitals

known from school sp orbitals:)

unitary transformation



$\epsilon' = -17.821 \text{ eV}$

- ☑ Only ϵ or canonical orbitals (roughly) fulfill Koopman's theorem!
- ☑ Total E is the same, both sets of orbital are 'equally good'!

Let's Solve Fock Equations

- It's hard, because \mathbf{f} itself depends on yet unknown SO.

$$\hat{\mathbf{f}}[\{\chi_a(2)\}]\chi_i(1) = \varepsilon_i \chi_i(1) \quad \begin{matrix} a=1,\dots,N \\ i=1,\dots,\infty \end{matrix} .$$

- Iterative procedure necessary:

for some (reasonable) guess of $N \{\chi_i\}^0$ calc. $\mathbf{f}^0[\{\chi_i\}^0]$,

then find eigenfunctions of $\{\chi_i\}^1$, calc. $\mathbf{f}^1[\{\chi_i\}^1]$ from them ...

repeat until convergence achieved - e. g. when the difference between $E_{\text{tot}}[\{\chi_a\}]$ in $(i+1)$ and i -th iteration ≈ 0 .

- In practice **Roothan-Hall method**, algebraization of HF, is applied.

SO are expanded in (finite) **basis set** (BS) of known functions:

$$\chi_i(1) = \sum_v^K C_{vi} \phi_v(1), \quad i=1,\dots,K$$

Solving HF eqs. reduced to finding optimal expansion coefficients, for which E_{tot} is minimal.

Comments on 'Standard' Basis Sets

☑ Physicists choice - **plane wave** (PW) BS.

$$\exp(-\mathbf{k}_i \cdot \mathbf{r})$$

(+) Convergence of PW BS smoothly controlled by single parameter (increasing wavevector).

(-) One needs enormous no. of PW to represent nodal structure of WF near nuclei - typically this part removed in pseudopotential approach & only monotonic tail of WF in valence region expanded in PW.

(-) Computational costs increases with size of unit cell.

☑ Chemists choice - **Gaussian** basis sets, centered on atoms.

(+) Rather simple handling 2-el. integrals. $x_i^p y_i^q z_i^r \exp(-\alpha (\mathbf{r}_i - \mathbf{R}_I)^2)$

(+) Core electrons can be treated explicitly. $p + q + r = l$ **number**

(-) Nonmonotonic decrease of E with increasing size of Gaussian BS.

(-) Computational artifacts due to incompleteness of BS.

(-) Somewhat tricky procedure of differentiation E with respect to \mathbf{R} , due to dependence of basis functions on \mathbf{R} .

See e. g. www.ccl.net/cca/documents/basis-sets/basis.html

HF-Roothan Machinery

- Dimension of basis set $K \geq N$ of electrons (if = 'minimal BS')

$$\hat{f} \sum_{v=1}^K C_{vi} \phi_v(1) = \varepsilon_i \sum_{v=1}^K C_{vi} \phi_v(1), \quad i=1, \dots, K$$

multiply by $\phi_\mu^*(1)$ & integrate

$$\sum_{v=1}^K F_{\mu v} C_{vi} = \varepsilon_i \sum_{v=1}^K S_{\mu v} C_{vi}, \quad i=1, \dots, K \rightarrow \mathbf{FC} = \mathbf{SC} \boldsymbol{\varepsilon} \quad (K \times K)$$

$$F_{\mu v} = \langle \mu(1) | \hat{f}(1) | v(1) \rangle, \quad S_{\mu v} = \langle \mu(1) | v(1) \rangle \text{ overlap integrals} \quad \varepsilon_{i\alpha} = \varepsilon_i \delta_{i\alpha}$$

- Remember that \mathbf{f} depends on SO , thus now depends on basis functions!

$$F_{\mu v} = F_{\mu v} \left(C_{\alpha i}, \langle \mu(1) | \hat{h} | v(1) \rangle, \langle \mu(1) v(2) | \mathbf{r}_{12}^{-1} | \lambda(1) \sigma(2) \rangle \right)$$

There are $\sim K^4$ 2-el. integrals! - main bottleneck of SCF calculation.

Don't panic, there are tricks to diminish the no. of needed integrals.

- Again (after orthogonalization of BS) we get pseudoeigenvalue problem:

$$\mathbf{F}(\mathbf{C})\mathbf{C} = \mathbf{SC} \boldsymbol{\varepsilon} \rightarrow \mathbf{F}(\mathbf{C}')\mathbf{C}' = \mathbf{C}' \boldsymbol{\varepsilon}$$

Self Consistent Field at Work

SCF Procedure

- 1 Specify molecule $\{R_I, Z_I, \text{no. of electrons \& spin}\}$ & BS $\{\varphi_v\}$.
- 2 Guess initial SO = guess initial coeffs. $\{C_{i\alpha}^0\}$
- 3 Calculate needed integrals (overlap, 1 & 2 el.) $S_{\mu\nu}, h_{\mu\nu}, \langle \mu\nu | r_{12}^{-1} | \lambda\sigma \rangle$.
- 4 Calculate $F_{\mu\nu} \left(C_{a\alpha}^0, h_{\mu\nu}, \langle \mu\nu | r_{12}^{-1} | \lambda\sigma \rangle \right)_{\mu\nu\lambda\sigma=1,\dots,K}^{a=1,\dots,N}$
- 5 Diagonalize **F** (form **F'** using **S**^{-1/2}) to get ϵ & **C**¹.
- 6 Go back (again with **S**^{-1/2}) from **C**¹ to **C**.
- 7 Compare **C**¹ with **C**⁰ (or $E_{\text{tot}}(\mathbf{C}^1)$ with $E_{\text{tot}}(\mathbf{C}^0)$)*
 - the same? celebrate!**
 - different? go to step 4 with **C**¹.

$$F'(\mathbf{C}'^s) \mathbf{C}'^{(s+1)} = \epsilon \mathbf{C}'^{(s+1)}$$

* In basis set $E_{\text{HF}} = \sum_a^{\text{occ.}} \sum_{\mu\nu}^K C_{\mu a} C_{\nu a} h_{\mu\nu} + \frac{1}{2} \sum_{a,b}^{\text{occ.}} \sum_{\nu\mu\lambda\sigma}^K C_{\mu a} C_{\nu a} C_{\lambda b} C_{\sigma b} \langle \mu\nu | r_{12}^{-1} | \lambda\sigma \rangle - \langle \mu\nu | r_{12}^{-1} | \sigma\lambda \rangle$

** Or not. We just calc. E_{HF} for initial configuration of nuclei, if we want to optimize geometry, we likely have to do SCF for many probed configurations.

Comments on SCF Convergence

- As in every iteration procedure the convergence & the results strongly depends on initial guess.
- The simplest (but not the best!) way of getting initial SO (=set of expansion coeffs.) is to diagonalize \mathbf{F} consisting only of 1-el. operators
$$F_{\mu\nu}^0 = h_{\mu\nu} \rightarrow \mathbf{F}^0 \mathbf{C}^0 = \boldsymbol{\varepsilon} \mathbf{C}^0$$
- Usually better guess is to take $\{C_{a\alpha}^0\}$ from fast semiempirical QM calc., like extended Hückel method.
- Even for 'good' guess SCF may have slow/oscillatory convergence. Various techniques have been proposed to improve SCF convergence (level shifting, mixing etc.).
- Sometimes problem with SCF convergence indicates some fundamental problem - very bad 'unphysical' geometry, wrong spin state or even that HF is not suitable for our system (see further).

Exemplary Semiempirical Method: Extended Hückel

- ❑ Hückel was method developed for the description of π electrons in conjugated hydrocarbon.
- ❑ EHM is kind of simplified HF in minimal basis set. Fock matrix el. are approximated as:

$$F_{\mu\mu} = -I_{\mu} \text{ \& } F_{\mu\nu} = -const * (I_{\mu} + I_{\nu}) S_{\mu\nu} ,$$

where I_{α} is α -ith. exp. atom ionization potential & is $S_{\mu\nu}$ overlap integral.

- ❑ EHM, unlike 'true' HF, is not iterative, because F does not depend on C . Thus HF eqs. $FC=ESC$ can be solved very fast (E & C) for large systems.
- ❑ EHM is frequently used to generate initial orbitals for SCF procedure (e. g. in Turbomole).
- ❑ It is possible to optimize geom. in EHM, because overlaps S depends on interatomic distances. However, the results are rather poor.
- ❑ Another drawback of EHM is lack of spin, for example singlet & triplet state of molecule would have the same energy in EHM.

Let's Talk About Spin

Nonrelativistic \hat{H} does not depend on spin, thus $[\hat{S}^2, \hat{H}] = [\hat{S}_z, \hat{H}] = 0$, thus eigenfunctions should be eigenfunctions of \hat{S}^2 & \hat{S}_z .

2 main flavors of HF

Unrestricted HF - each SO is either pure α & β state

$$N^\alpha \left\{ \chi_a(\mathbf{x}_1) = \psi_a^\alpha(\mathbf{r}_1) \omega(\alpha_1) \right\} \quad \& \quad N^\beta \chi_b(\mathbf{x}_1) = \psi_b^\beta(\mathbf{r}_1) \omega(\beta_1), \quad N^\alpha + N^\beta = N$$

Derivations in this presentations done for UHF case!

UHF Ψ_{SD} is an eigenfunction of \hat{S}_z , but (in general) not of \hat{S}^2 .

Restricted HF - for closed shell singlet we have $N/2$ spatial molecular orbitals, each doubly occupied.

$$\frac{N}{2} \left\{ \chi_a(\mathbf{x}_1) = \psi_a(\mathbf{r}_1) \omega(\alpha_1) \right\} \quad \& \quad \frac{N}{2} \chi_a(\mathbf{x}_1) = \psi_a(\mathbf{r}_1) \omega(\beta_1),$$

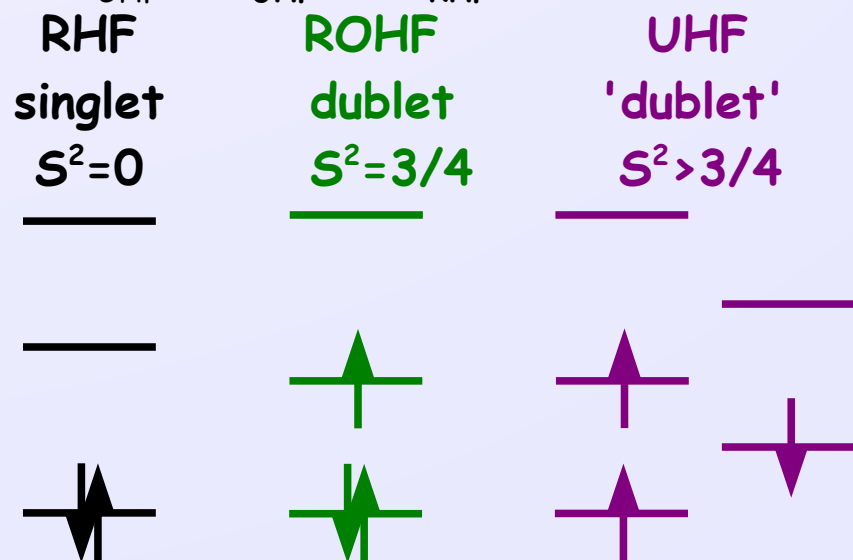
General HF - each SO is mixture of α & β states: rarely used, because GHF Ψ_{SD} is not even an eigenfunction of \hat{S}_z . Note that UHF is actually more restricted case of GHF.

Restricted vs. Unrestricted

- For open-shell system UHF needed, for closed shell RHF can be used
→ only N/2 Fock equations.
- Spin contamination:** UHF Ψ_{SD} generally* are not eigenfunctions of \hat{S}^2 , actually it can be expanded as a sum of several of different Ψ_{UHF} being eigenfunctions of different \hat{S}^2 .
$$\langle \hat{S}^2 \rangle_{UHF} > \langle \hat{S}^2 \rangle_{exact}$$
- It is possible formulate **Restricted Open-Shell HF**, but this approach is troublesome (e. g. ROHF eqs. cannot be diagonalized).
- Due to larger variational freedom $(E_{GHF} \leq) E_{UHF} \leq E_{RHF}^{**}$

* Only for closed shell singlet
& fully spin polarized state.

**** For closed shell singlet**
E of all flavors of HF are
equal.



How Good is HF?

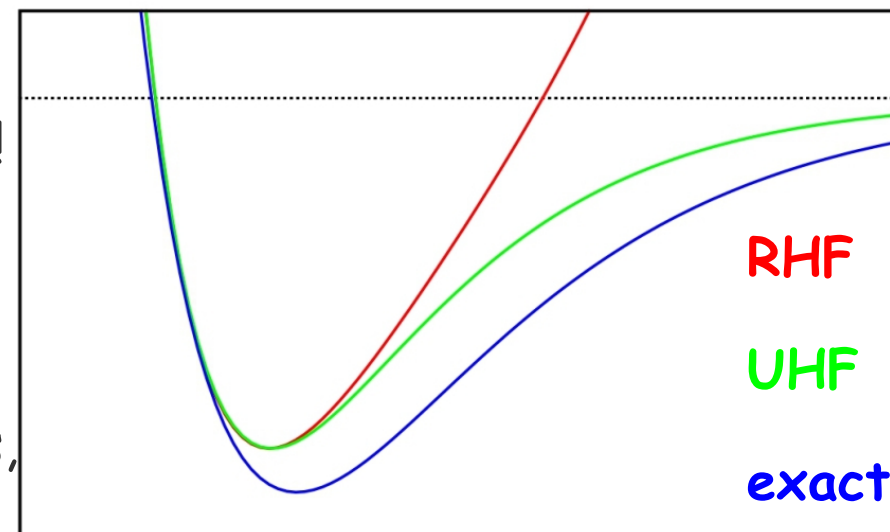
- For closed shell systems reasonably good equilibrium geometries (a bit too short bonds) & vibrational freqs. (somewhat too high), ΔE between isomers/conformers roughly fine.
- HF reproduce 99% of total E - but we are interested in ΔE . HF error in ΔE (for example between ground & exc. state) can be huge!
- Spectacular HF failures:** (1) H_2 dissociation. RHF can't split H_2 into 2 open shell H; UHF, has correct asymptotic behavior, but too high E in the intermediate region, due to the triplet admixture.

$$\Psi_{H_2} = c_{ion} \Psi_{ion}(H^+ - H^-) + c_{cov} \Psi_{cov}(H - H)$$

near $R_{AB,0}$ $c_{ion} = c_{cov} = 1/2$ always in RHF!

but $R_{AB} \rightarrow \infty$ $c_{ion} = 0$ & $c_{cov} = 1$

- (2) F_2 molecule unstable in HF - too strong repulsion between el. pairs,
- (3) no van der Waals interaction.



Hartree-Fock Summary

- ❑ **Hartree-Fock method** is variational search for the best single determinant approx. for the unknown true N-electron wavefunction.
- ❑ HF method is **mean field approx.**, namely each electron interacts with the average electric field created by (N-1) remaining el.
- ❑ Although HF methods delivers set of 1-el. spinorbitals, they & their eigenvalues should be interpreted with cautions. Particularly, the total E is not a sum of orbital energies & unoccupied SO are not optimized.
- ❑ In order to make HF equations solvable in practice, one has to expand SO in some finite, thus incomplete, known basis set. The quality of HF & post-HF results depends on the type & size of the basis.
- ❑ HF methods correctly describes, due to antisymmetric form of determinant, **exchange correlation**, i. e. between el. of the same spin. **Coulomb correlation** is missing, due to the mean field treatment of e-e interactions.

Small Details Matter

▣ **Correlation Energy** $E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}} \sim 1\% \text{ of } E < 0$.

*nonrelativistic, E converged with respect to BS.

▣ In HF electrons don't see each other, everyone interacts with average electric field generated by $(N-1)$ electrons. Real electrons interact with each other & it cannot be captured by Ψ_{SD} approach.

▣ **Coulomb correlation** can be approx. divided in two groups.

- ▶ **dynamical** - electrons move in a way to avoid each other (like in F_2).
- ▶ **static** - when N -el. WF can't be approx. by one SD (H_2 dissociation).

▣ E_{corr} is the largest within electron pairs, i. e. for el. occupying the same orbitals. Although small fractions of total E , E_{corr} becomes large component of ΔE in processes where no. of el. pairs 'is not conserved', like chemical reactions or electronic excitation.

▣ With increasing no. of el. also interpair correlation becomes important!

Is There Life After Hartree-Fock?

- ❑ **Configuration Interaction** - the exact N-electron WF can be expanded in a complete basis set of N-el. Slater determinants. Such BS can be made of all possible N-el. SD built of occ. & virt. SO from HF.

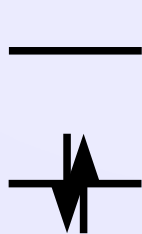
$$\Psi_{CI} = c_0 \Psi_0 + \sum_{a,r} c_a^r \Psi_a^r + \sum_{a<b, r<s} c_{ab}^{rs} \Psi_{ab}^{rs} + \sum_{a<b<c, r<s<t} c_{abc}^{rst} \Psi_{abc}^{rst} + \dots$$

where Ψ_0 is HF SD WF and $\Psi_{ab\dots m}^{rs\dots x}$ is SD n -time **excited determinant**, obtained by replacing n occ. (in initial HF WF) SO by n virtual ones.

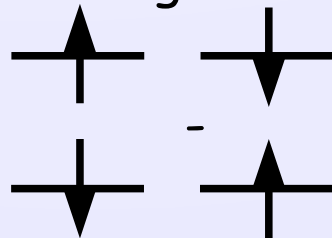
The coefficients c_i are variationally optimized.

- ❑ **Configuration** - combination of SD, being an eigenfunction of \hat{S}^2 .

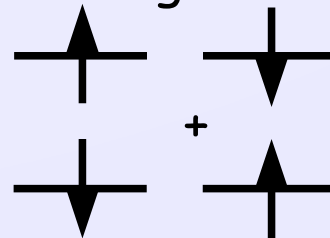
singlet
ground state



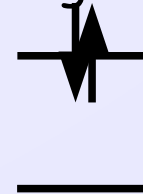
singlet, 1 exc.
configuration



triplet, 1 exc.
configuration



singlet, 2 exc.
configuration



Mind The Language!

❑ Correlation $P(\mathbf{x}_1, \mathbf{x}_2) \neq P(\mathbf{x}_1)P(\mathbf{x}_2)$

In 'quantum chemistry' jargon by **correlation** we mean **Coulomb correlation**, which is missing in HF picture, due to the averaged treatment of Coulomb repulsion.

Note that, owing to antisymmetric form of SD, HF takes into account **Fermi/exchange correlation** (simply '**exchange**' in jargon), because P finding of 2 electrons are not independent in HF.

❑ Excitation/Excited Determinant

This is just HF SD, where 1 or more occupied SO where replaced by virtual orbitals. By no means it is SD describing exc. electronic state!

To have the latter one HF calc. for excited state electronic configuration are needed (& it would be poor approx. for true excited state WF, as HF is even worse for excited states than for ground one).

Correlated Energy At Last

CI Energy

$$E_{CI} = \langle \Psi_{CI} | \hat{H} | \Psi_{CI} \rangle \rightarrow Hc = Ec$$

$$S_{ij} = \langle \Psi_i | \Psi_j \rangle = \delta_{ij}, \quad H_{ij} = \langle \Psi_i | \hat{H} | \Psi_j \rangle, \quad E_{ij} = E_i \delta_{ij}$$

Eigenvalues of H_{CI} are E_{tot} (correlation included!), 1st root is ground state energy, 2nd is the 1st excited state E etc.

In principle E are obtained from diagonalization of H_{CI} , in practice from certain iterative algorithms giving few lowest eigenvalues of interest (direct CI).

- Set of SD forms BS for N el. WF, but SD itself are made of HF SO, which are expanded in 1-electron basis set. **The quality of CI results depends on both levels of BS!**

(e. g. there is little sense in doing full CI in minimal 1-el. BS).

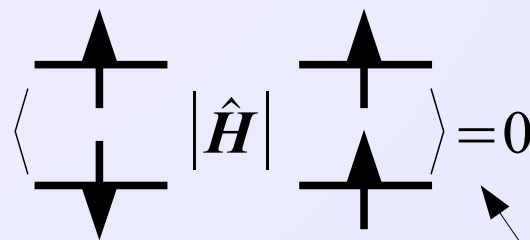
- For N el. & K 1-el. basis functions one has $\binom{N}{n} \binom{K-N}{n}$ n -tuply excited SD. There is **FACTORIAL** ($\sim K!$) no. of SD & handling matrix of this size is impossible for anything with more than 10 electrons.

How to Tame CI Matrix

Formally, one has to deal with $\sim K!$ exc. SD -it's too much. Luckily, full CI (all possible SD in finite 1-el. BS) matrix can be strongly depopulated.

Brillouin's theorem $\langle \Psi_0 | \hat{H}_e | \Psi_a^r \rangle = 0$

Due to the presence only 2-body interactions in our \hat{H}_e , if $|n-m| > 2$, then $\langle \Psi^{n \times \text{exc.}} | \hat{H} | \Psi^{m \times \text{exc.}} \rangle = 0$, e. g. Ψ_0 doesn't mix with triply exc. SD & higher.

$$H_{CI} = \begin{vmatrix} H_{00} & 0 & H_{02} & 0 & 0 & 0 & 0 & \dots \\ 0 & H_{11} & H_{12} & H_{13} & 0 & 0 & 0 & \dots \\ H_{20} & H_{21} & H_{22} & H_{23} & H_{24} & 0 & 0 & \dots \\ 0 & H_{31} & H_{32} & H_{33} & H_{34} & H_{35} & 0 & \dots \end{vmatrix}$$


$$\langle \text{Diagram 1} | \hat{H} | \text{Diagram 2} \rangle = 0$$

(each H_{ij} block consists of (no. of i -th exc.) \times (no. of j -th exc.) H_{CI} elements).

Only SD of equal N^α/N^β interacts.

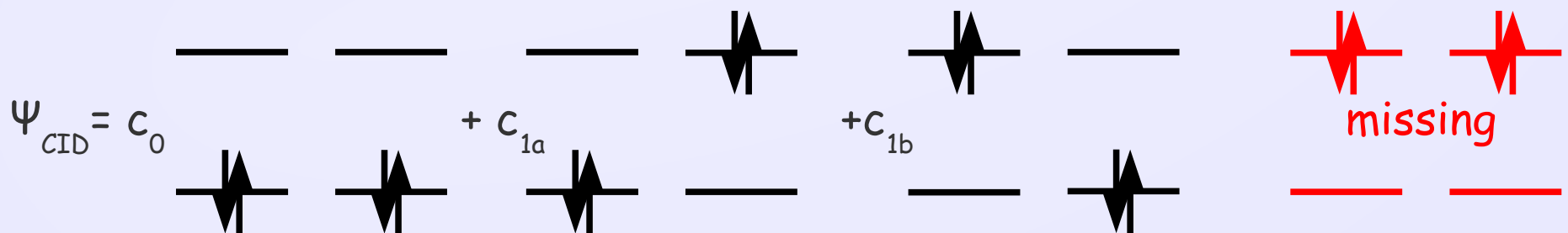
Some matrix elements are 0 due to the symmetry of studied molecule.

Still, it's just improvement from hopeless to a bit less hopeless task. There is a need for approximations to full CI method.

Truncated CI & Size Consistency

- Brute force solution - **truncate full CI** @ given order of exc. SD, for example use only CI with doubles (CID):

$$\Psi_{CID} = c_0 \Psi_0 + \sum_{a < b, r < s} c_{ab}^{rs} \Psi_{ab}^{rs}$$
- Size Consistency** - the energy of supersystem is sum of its noninteracting components, i. e. for $R_{AB} \rightarrow \infty$ $E(A+B) = E(A) + E(B)$.
- Truncated CI (in general) is not size consistent!
- Consider $2H_2$ molecules in minimal BS, double exc. due to single exc. in each molecule give 0 contribution due to symmetry, thus we have:



CID cannot describe simultaneous double exc. in both molecules, because it demands quadruply exc. SD $\rightarrow E(2H_2) < 2E(H_2)$. Yes, we could fix it with

Ψ_{abcd}^{rstu} but it won't be sc for $3H_2$ molecules (lack of sextuple exc.) etc.

Many Body Perturbation Theory

☑ **Møller-Plesset method** - treat electron correlation as perturbation to fictional system with \hat{H} being sum of 1-electron Fock operators.

▶ **MPO**: $\hat{H}_0 = \sum f_i$, $E_0 = \sum \epsilon_i$ (>true E due to 2x counting interactions).

▶ **MP1**: mean field type e-e interactions → **MP1=HF**

▶ **MP2 & higher**: correlation turned on.

$$E_{corr}^{MP2} = \sum_{a < b}^{occ} \sum_{r < s}^{virt} \frac{\left| \left\langle \Psi_{ab}^{rs} \left| r_{12}^{-1} \right| \Psi_0 \right\rangle \right|^2}{\epsilon_r + \epsilon_s - \epsilon_a - \epsilon_b} \quad (\leftarrow \text{only 2-el. integrals in nominator})$$

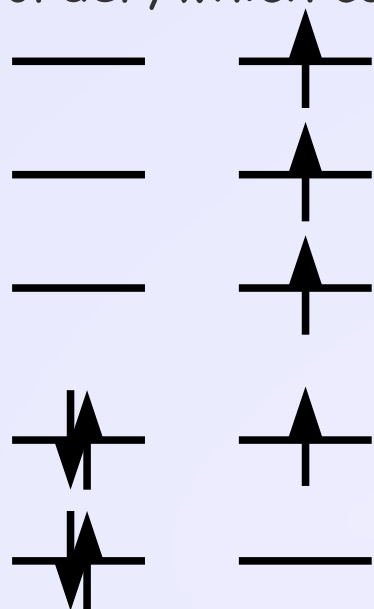
☑ MP2 works well for system with reasonably large gap, otherwise perturbation diverge & system would be 'overcorrelated'.

☑ MP2 covers up to 90% of E_{corr} , it describes **dynamical correlation** only, e. g. dispersion interaction between closed shell molecules.

☑ MP2 is the least expensive corr. method $\sim K^5$ (K^4 2-e integrals \times \times K operations on coeffs.). With some tricks MP2 can be made linearly scaling & it was usef for periodic calc. for solids with large band gaps.

Coupled Cluster

- Way of truncating full CI in size consistent manner (full CC = full CI).
- In truncated CC with up to n -th order exc. one considers exc. SD of any order, which can be presented as products of lower order exc.



$$\sum_{\substack{a < b < c \\ r < s < u}} C_{abc}^{rst} = \sum_{\substack{a < b < c \\ r < s < u}} t_{abc}^{rsu} + \sum_a \sum_{\substack{b < c \\ r \quad s < u}} t_a^r t_{bc}^{su} + \sum_a \sum_b \sum_c t_a^r t_b^s t_c^u$$

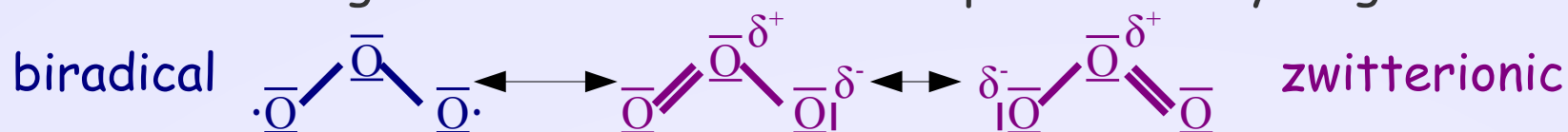
(1) **simultaneous triple exc.**, (2) **single exc. followed by double exc.**, (3) **three consecutive single exc.**

CI with single & doubles (CISD) misses 3ple exc., CCSD has (2) & (3) contributions.

- CC amplitudes $\{t\}$ are taken from set of nonlinear & **novariational** eqs.
- CCSD(T) - "gold standard of quantum chemistry". Parenthesis denotes that triple amplitudes are approx. perturbationally. CCSD(T) deals well with dynamical corr. & also with the cases of not too strong static corr.

Multi-Reference Systems - Real Troublemakers

- Sometimes even ground state cannot be represented by single HF SD:



Any SD (radical or zwitterionic) from HF will be very poor starting point for CI calc. & one would need huge no. of exc. SD to reproduce static correlation. Better to take $\Psi = c_1 \Psi_{\text{biradical}} + c_2 \Psi_{\text{zwitterionic}}$, optimize both coefficients c_i & SO in both SD.

- Multi-Configurational SCF (MC SCF)** - truncated CI exp., where both coeff. & SO are optimized (for single SD MC SCF=HF). For good description of static corr. one needs smaller no. of SD in MC SCF than in truncated CI.
- Typically only excitations within a certain range of SO close to the gap are considered ('active space').
- It is possible to formulate multi-reference CI/CC/MP n using MC SCF as Ψ_0 (yes, it's accurate & computationally expensive).

Not So Bad, But Could Be Better...

	scaling	variational	size consistent
MP2	K^5	N	Y
CISD	K^6	Y	N
CCSD	K^6	N	Y
MP4	K^7	N	Y
CCSD(T)	K^7	N	Y
CCSDT	K^8	N	Y
CISDT	K^8	Y	N

- ❑ In practice scaling is somewhat lower, e. g. if overlap between 2 basis function is small, 2-el. integrals with these functions can be neglected. Still, scaling can't be done linear (with exception of MP2).
- ❑ Geometry optimization are rarely performed using advanced corr. methods. Usually one uses HF/DFT/MP2 level geometry for calc. of E & electronic response quantities (UV-Vis, EPR, NMR etc.). Problem is with multireference systems, where even HF geometry may be poor.

Shopping Quantum Chemistry Software

http://en.wikipedia.org/wiki/List_of_quantum_chemistry_and_solid-state_physics_software

Commercial

Gaussian MP2-5, MCSCF . John Pople - Nobel prize in chemistry, 1998

Molcas MP2, CISD & QCISD, MCSCF, MRCC, CASSCF, CASPT2.

PQS MP2-4, CCSD(T), CISD, QCISD(T).

Turbomole MP2-4, CC2, CIS(D), CC2, CCSD(T).

Free for academia

ORCA MP2-4, CCSD(T), QCISD(T), MRMP2-4, MRCC.

Dalton MP2, MCSCF, CCSD(T).

NwChem MP2-4, MCSCF, CIS-CISDTQ, QCISD, CCSD(T), CCSDTQ.

*All these codes do HF, most of them also DFT & semiempirical methods.

Post HF - Summary

- ❑ Coulomb correlation is a tiny fraction of total E , but is large component of measurable ΔE , like ΔE of chemical reaction or electronic excitations.
- ❑ Coulomb corr. can be approx. divided into **dynamic**, due to the correlated motions of electrons (always present), & **static**, if WF can't be reasonably approx. by SD (e. g. open-shell singlet biradicals).
- ❑ Formally exact & thus correlated N -el. wavefunction can be expanded in the complete basis set of N -el. single determinant wavefunctions. Such basis set can be formed by all N -el. SD which can be constructed from all HF SO, both occupied & unoccupied in HF optimal function. This is **Configuration Interactions** approach.
- ❑ In practice full CI can be done for systems with less than 10 el. Many approximations to full CI have been proposed, most of them suffering from certain drawbacks & , even if less handful than full CI, still computationally challenging...
- ❑ Any hope for low cost correlated method?

Further Reading

- ❑ Literature given in previous lecture (Pielka, Jensen, Crammer, Lewars).
- ❑ J. Kohanoff "Electronic Structure Calculations for Solids & Molecules: Theory & Computational Methods" Cambridge 2006.
- ❑ A. Szabo & N. S. Ostlund "Modern Quantum Chemistry" Dover 1996.
- ❑ T. Veszprémi & M. Fehér "Quantum Chemistry: Fundamentals to Applications" Springer 1999.*
- ❑ I. Mayer "Simple Theorems, Proofs, and Derivations in Quantum Chemistry" Springer 2003.*
- ❑ ... & many others.

THANK YOU FOR YOUR ATTENTION!

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Appendix: More on Correlated Wavefunctions

- It is possible to correlated explicitly many electron WF.

Due to singularity of Coulomb potential for $r_{12}=0$ $\left(\frac{\partial \Psi}{\partial r_{12}}\right)_0 = \frac{1}{2} \Psi(r_{12}=0)$
the exact Ψ must obey 'cusp condition':

- Hyleraas function for singlet He (1929), C_{klm} variational parameters

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = e^{-\alpha_1 r_1} e^{-\alpha_2 r_2} \sum_{klm} C_{klm} (\mathbf{r}_1 + \mathbf{r}_2)^k (\mathbf{r}_1 + \mathbf{r}_2)^l |\mathbf{r}_1 - \mathbf{r}_2|^m$$

- James-Coolidge & Kłos-Wolniewicz functions for H_2 $\Psi(\mathbf{r}_1, \mathbf{r}_2) \propto \left(\frac{r_{12}}{R_{12}}\right)^k$
- Accuracy equal experiments, but in practice limited to few atoms molecules. Also simple orbital picture, convenient for saying 'where electrons are', is missing.
- But keep an eye on the field, it's still active: Ten-No *Theor. Chem. Acc.* **2012**, 131, 1070; J. Rychlewski (ed.) "Explicitly Correlated Wavefunctions in Chemistry & Physics" Springer **2003**.