Electron Correlation - Methods beyond Hartree-Fock

how to approach chemical accuracy

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Hartree-Fock theory and accuracy

Hartree-Fock bond lengths [a.u.]

	sto-3g	4-31G	6-31G*	6-31G**	exp.
CH_4	2.047	2.043	2.048	2.048	2.050
NH_3	1.952	1.873	1.897	1.897	1.913
H_2O	1.871	1.797	1.791	1.782	1.809
HF	1.812	1.742	1.722	1.703	1.733

minimum structure of C_{20} - ring (R), bowl (B) or cage (C) ?
(energy difference in kcal/mol)

HF	R	20	B	78	C
correct	B	3	C	44	R

Hartree-Fock theory: a recommendation

- qualitative investigations of electronic structure
- interpretation of electron density at one electron level
- "good guess" for molecular properties
- relatively fast basis set convergence
- standard : HF-SCF/SV(P)
- note: DFT usually provides better results at comparable cost !!

Textbook recommendation :"A Chemist's guide to DFT" Holthausen, Koch, Wiley VCH

Hartree-Fock theory: interaction of electrons

Interaction of two electrons in HF theory :
coulomb and exchange

$$\int \phi_p^*(1)\phi_q^*(2)\frac{1}{r_{12}}\phi_p(1)\phi_q(2)d\tau_1\ d\tau_2$$

$$= \int \rho_p(1)\frac{1}{r_{12}}\rho_q(2)d\tau_1\ d\tau_2$$

BUT : particles only interact through their charge distribution mean field approximation - no explicit correlation of electron movement !

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in the HF Wavefunction two electrons will never "see" each other, only their charge clouds !
→ follows from one electron orbital approximation in HF

Electron correlation

Hartree Fock : Mean field approximation

no explicit correlation of electrons

definition (!) of correlation energy :

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

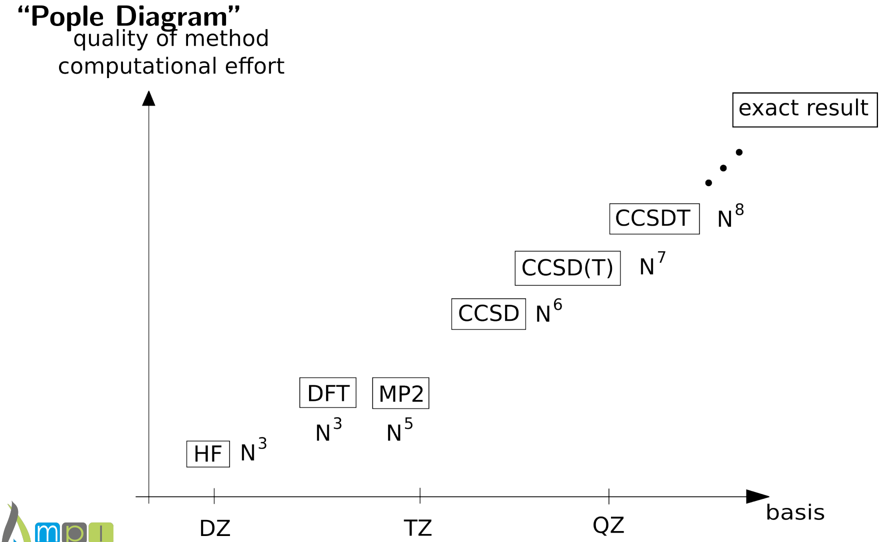
general Ansatz : improve HF method

$\rightarrow$ post Hartree-Fock methods

often needed even for qualitative agreement with experiment !

Hierarchy of quantum chemical methods

“Pople Diagram”



ab-initio methods : perturbation theory

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divide System into unperturbed part $\hat{H}_0$ and small perturbation $\hat{H}'$

$$\hat{H} = \hat{H}_0 + \lambda\ \hat{H}'$$

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expand energy and wavefunction in series

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + ... \qquad \Psi = \Psi^{(0)} + \lambda \Psi^{(1)} + \lambda^2 \Psi^{(2)} + ...$$

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sort in powers of λ to obtain energy corrections :

$$\begin{aligned} E^{[0]} &= <\Psi^{(0)}|\hat{H}_0|\Psi^{(0)}> \\ E^{[1]} &= <\Psi^{(0)}|\hat{H}'|\Psi^{(0)}> \\ E^{[2]} &= <\Psi^{(0)}|\hat{H}'|\Psi^{(1)}> \end{aligned}$$

ab-initio methods : perturbation theory

define unperturbed and perturbed Hamiltonian for our problem :

$$\hat{H} = \hat{H}_0 + \hat{H}' \quad \hat{H}_0 = \sum_i \hat{F}(i)$$

$\hat{H}'$ as difference between exact electron electron interaction and mean field interaction :

$$\hat{H}' = \sum_{i<j} \frac{1}{r_{ij}} - \sum_i (\hat{J}_i - \hat{K}_i)$$

ab-initio methods : perturbation theory

Rayleigh-Schrödinger perturbation theory leads to :

$$E^{[0]} = \sum_i \epsilon_i$$

$$E^{[1]} = -\frac{1}{2}\sum_{ij} \langle ij| |ij\rangle$$

zeroth and first order give HF solution

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zeroth and first order give HF solution
first correction at 2nd order : Møller-Plesset PT - MP2

$$E^{[2]} = \frac{1}{4} \sum_{ij} \sum_{ab} \frac{|\langle ij||ab\rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

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bond lengths [a.u.]: HF and MP2

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	1.997	1.907	1.922	1.912	
H_2O	1.871	1.797	1.791	1.782	1.809
	1.916	1.842	1.831	1.816	
HF	1.812	1.742	1.722	1.703	1.733
	1.842	1.790	1.765	1.740	

ab-initio methods : perturbation theory

Problem : convergence of perturbation series

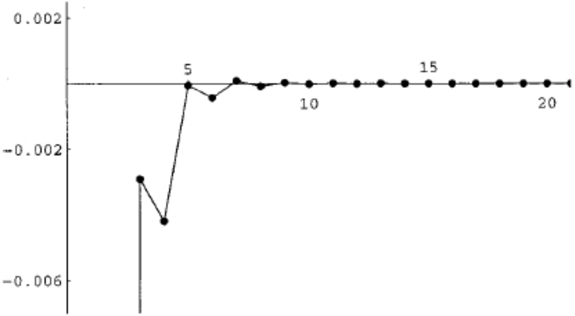

FIG. 7. The energy corrections for HF at equilibrium geometry in the cc-pVDZ basis.

ab-initio methods : perturbation theory

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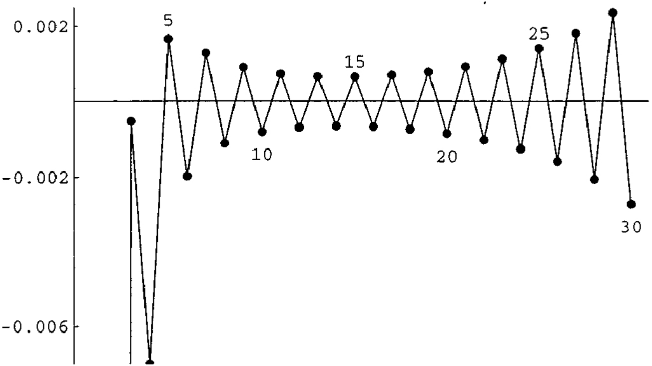

FIG. 9. The energy corrections for HF at equilibrium geometry in the aug′-cc-pVDZ basis.

ab-initio methods : perturbation theory

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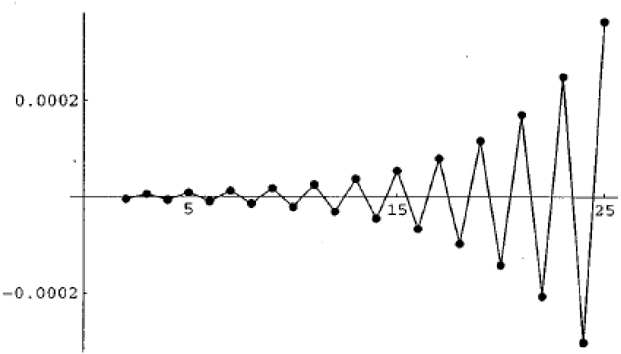

FIG. 4. The energy corrections for Ne in the two-state model using the parameters in Eqs. (32)–(34).

ab-initio methods : perturbation theory

$$E_{MP2} = \frac{1}{4} \sum_{ijab} \frac{|\langle ij||ab \rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

- MP2 often improves HF results significantly

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- recommendation : use other methods beyond MP2
- standard : RI-MP2 / TZ (note: RI approximation !)

ab-initio methods : configuration interaction

exact wavefunction is a many electron function !

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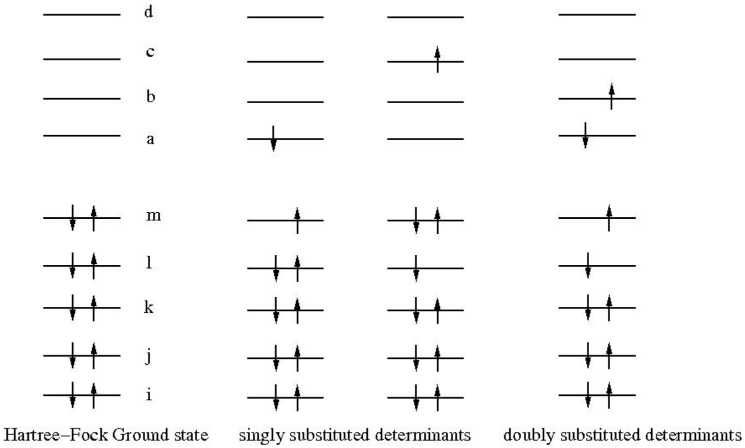
idea :
expand exact wavefunction in complete basis
of many electron functions

ab-initio methods : configuration interaction



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expand exact wavefunction in complete basis
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many electron function : HF-SCF slater determinant

complete basis of many electron functions :

all possible determinants from occupied and virtuals

→ Configuration Interaction (CI) :

linear expansion, one parameter per determinant,
optimized variationally

ab-initio methods : configuration interaction

wavefunction expression as linear CI expansion :

$$|\Psi_{CI}\rangle = |\Psi_0\rangle + \sum_{ia} c_i^a |\Psi_i^a\rangle + \frac{1}{4}\sum_{ijab} c_{ij}^{ab} \left|\Psi_{ij}^{ab}\right\rangle + ...$$

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$$|\Psi_{CI}\rangle = |\Psi_0\rangle + \hat{C}_1 |\Psi_0\rangle + \hat{C}_2 |\Psi_0\rangle + ...$$

diagonalization of Hamiltonian matrix yields energies for ground and excited states

$$\langle\Psi_{CI}| \hat{H} |\Psi_{CI}\rangle$$

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use all determinants that can be constructed
→ expansion in complete basis
(number of determinants grows exponentially !!)

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→ exact solution of electronic problem in given AO basis
(Full Configuration Interaction FCI)

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in practice only truncated expansion feasible :
CIS : only singly substituted determinants
CISD : singly and double substituted determinants
CISDT : single, double and triple substitutions
...

ab-initio methods : configuration interaction

correlation energy contributions from different levels of excitations in BeH_2

ab-initio methods : configuration interaction

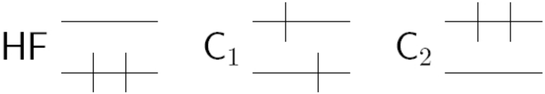
correlation energy contributions from different levels of excitations in BeH_2

excitation level	E_{CI} (DZ basis) [a.u.]
1+2	-0.074033
3	-0.000428
4	-0.001439
5	-0.000011
6	-0.000006
total	-0.075917
exact	-0.14

0.1 a.u.= 262.6 kJ/mol = 2.7 eV = 21947 cm^{-1}

configuration interaction and size consistency

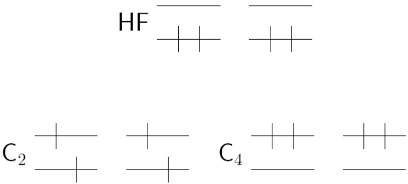
example : H_2 molecule in minimal basis - 2 electrons, 2 orbitals :



CISD $\hat{=}$ FCI !

configuration interaction and size consistency

example : two noninteracting hydrogen molecules $(H_2)_2$



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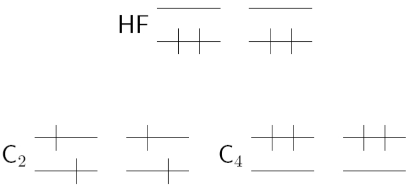

CISDTQ $\hat{=}$ FCI !

configuration interaction and size consistency

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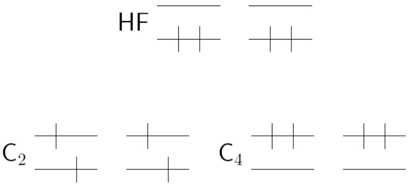

CISDTQ $\hat{=}$ FCI !

CISD does not allow for simultaneous double excitations

configuration interaction and size consistency

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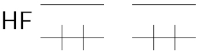

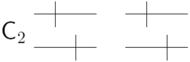

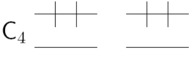

CISDTQ $\widehat{=}$ FCI !

CISD does not allow for simultaneous double excitations

at the CISD level of theory a single hydrogen molecule is treated more accurately than an isolated hydrogen molecule in a system of non interacting molecules !

configuration interaction and size constancy

unphysical description leads to wrong asymptotic
of energy for extended systems

extensivity of energy not given !!
(CI is not size-extensive)

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the larger the system, the smaller the fraction of correlation energy from a truncated CI

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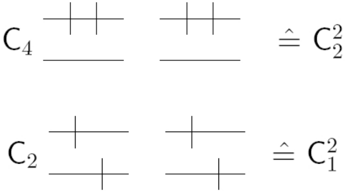
recommendation : use CI with caution !

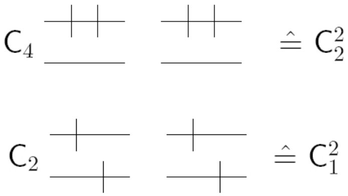
improving configuration interaction



$C_4 \triangleq C_2^2$

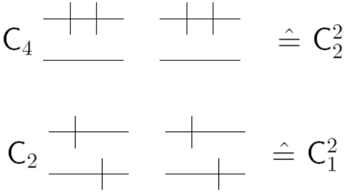
$C_2 \triangleq C_1^2$

improving configuration interaction



not only include C_1, C_2 but also **products** of excitations
C_1^2, C_2^2 for FCI result !

improving configuration interaction



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instead of a linear ansatz, a product separable ansatz
is required for size extensivity

coupled cluster theory

ansatz :
instead of linear expansion, use exponential expansion !

$$|\Psi_{CC}\rangle = e^{\hat{T}}\,|\Psi_0\rangle$$

coupled cluster theory

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cluster operator $\hat{T}$ analogous to CI-Operator

$$\hat{T} \quad = \quad \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \ldots$$

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$$\hat{T} \quad = \quad \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \ldots$$

coefficients are called amplitudes:

$$e^{\hat{T}} = 1 + \hat{T} + \frac{1}{2!}\hat{T}^2 + \frac{1}{3!}\hat{T}^3 + \ldots$$

coupled cluster theory

product terms resulting from exponential expansion

$$
\begin{aligned}
|\Psi_{CC}\rangle = (1 &+ \hat{T}_1 + \frac{1}{2!}\hat{T}_1^2 + \frac{1}{3!}\hat{T}_1^3 + \ldots \\
&+ \hat{T}_2 + \frac{1}{2!}\hat{T}_2^2 + \frac{1}{3!}\hat{T}_2^3 + \ldots \\
&+ \hat{T}_1\hat{T}_2 + \frac{1}{2!}\hat{T}_1^2\hat{T}_2 + \frac{1}{2!}\hat{T}_1\hat{T}_2^2 + \ldots \\
&+ \ldots)\,|\Psi_0\rangle
\end{aligned}
$$

coupled cluster theory

Energy equations :

$$\langle\Psi_0|\, e^{-\hat{T}}\hat{H}e^{\hat{T}}\, |\Psi_0\rangle = E$$

Amplitude equations :

$$\langle\, \Psi_{ij..}^{ab..}|e^{-\hat{T}}\hat{H}e^{\hat{T}}\, |\Psi_0\rangle = 0$$

energy as expectation value of similarity transformed Hamiltonian

"projection trick" to derive amplitude equations

iterative solution of nonlinear set of equations !

state selective (ground state)

quite expensive !

coupled cluster theory

- CI based method with inclusion of higher excitations
- strictly size consistent
- faster convergence towards FCI
- highly accurate !

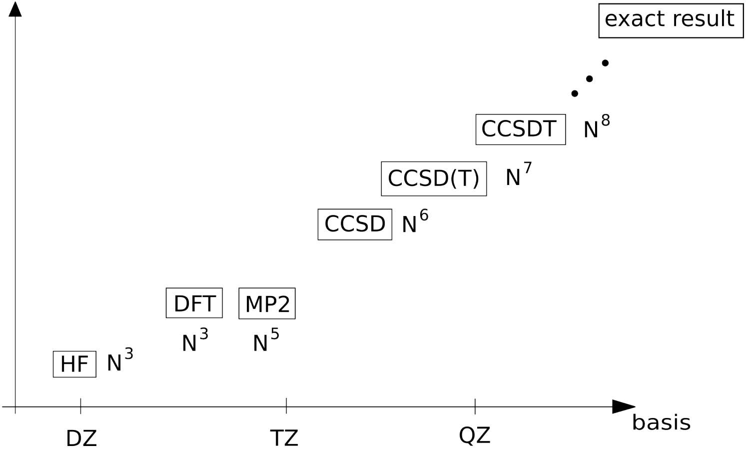
approximate methods :
CCSD : Coupled Cluster Singles and Doubles
CCSD(T):Singles, Doubles + perturbative approximation to Triples
CCSDT : Singles, Doubles and Triples
...

methods and basis sets

“Pople Diagram”

quality of method

computational effort



exact result

CCSDT N^8

CCSD(T) N^7

CCSD N^6

DFT N^3

MP2 N^5

HF N^3

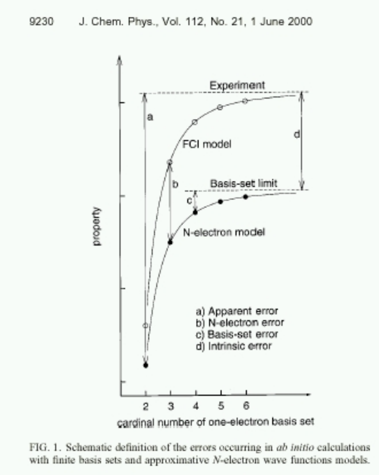
DZ

TZ

QZ

basis

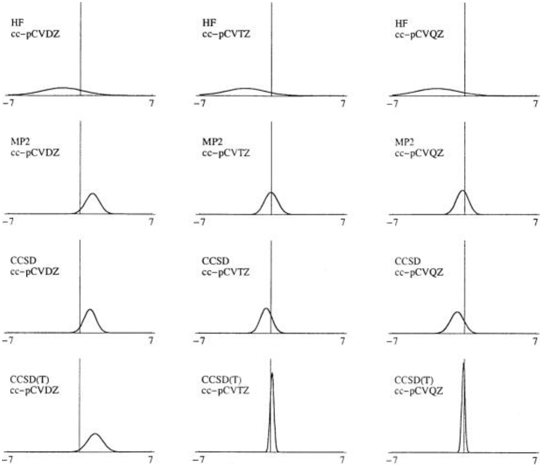
benchmark studies



9230 J. Chem. Phys., Vol. 112, No. 21, 1 June 2000

FIG. 1. Schematic definition of the errors occurring in *ab initio* calculations with finite basis sets and approximative *N*-electron wave functions models.

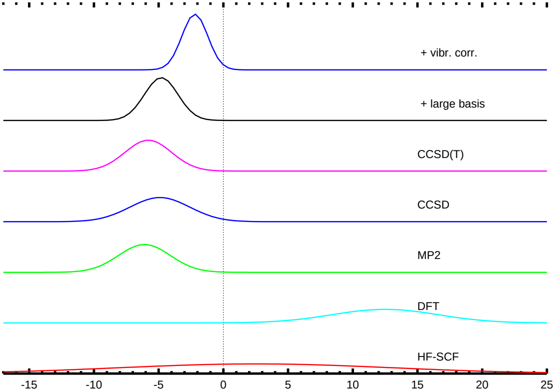
benchmark studies



K. Bak, et. al *J. Chem. Phys.* **114**, 6548 (2001).

benchmark studies

^{13}C-NMR chemical shifts - benchmark study on 16 small organic compounds, deviation and standard deviation from experiment [ppm]



A.A.Auer, J.Gauss, J.F.Stanton *J. Chem. Phys.*, **118**, 10407 (2003)

a detective story : Cyclopropane

	r_e (CC)	r_e (CH)
rotational spectroscopy	1.5101 (23)	1.0742 (29)
electron diffraction	1.501 (4)	1.083 (5)

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rot. data - vibr.corr.	1.5030 (10)	1.0786 (10)

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discrepancy due to empirical force field data
in analysis of rotational data !!

J. Gauss, D. Cremer and J. F. Stanton, *J. Phys. Chem. A*, **104**, 1319 (1999)

pitfalls in electronic structure methods

up to now all methods based on orbital expansions
(ground state wavefunction or density represented by a single slater determinant)

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consider Ozone :
$\cdot\ \mathbf{O}\ \text{-}\ \mathbf{O}\ \text{-}\ \mathbf{O}\ \cdot \qquad \mathbf{O} = \mathbf{O}^{+}\ \text{-}\ \mathbf{O}^{-} \qquad \mathbf{O}^{-}\ \text{-}\ \mathbf{O}^{+} = \mathbf{O}$

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$\cdot\,\mathbf{O}$ - $\mathbf{O}$ - $\mathbf{O}\,\cdot$ $\quad$ $\mathbf{O} = \mathbf{O}^+$ - $\mathbf{O}^-$ $\quad$ $\mathbf{O}^-$ - $\mathbf{O}^+ = \mathbf{O}$

more than one determinant needed to describe electronic structure even qualitatively !

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→ **multireference problem !**

often observed :

excited states, radicals, multiply charged ions, non-minimum structures, bond formation and breaking of chemical bonds ...

typical multireference case

H_2O molecule - at minimum geometry and at stretched geometry

	$r=R_e$		$r=2R_e$	
	$E-E_{FCI}$	W	$E-E_{FCI}$	W
RHF	0.2178	0.9410	0.3639	0.5897
CISD	0.0120	0.9980	0.0720	0.9487
CISDT	0.0090	0.9985	0.0561	0.9591
CISDTQ	0.0003	0.9999	0.0058	0.9987
CISDTQ5	0.0001	0.9999	0.0022	0.9999

multireference problems

multireference treatment : optimize determinant coefficients and orbitals parameters at the same time !

multireference problems

multireference treatment : optimize determinant coefficients and orbitals parameters at the same time !

artificial distinction :

CI - dynamic correlation MR - static correlation

Methods :

MCSCF multi configuration SCF

CASSCF complete active space SCF

CASPT2 CASSCF + 2nd order PT

NEV-PT or NEV-CI

MRCI multi reference CI

hierarchy of post-HF *ab-initio* methods

MP2 / CC2 : noniterative / iterative N^5

CCSD : iterative $N_{occ}^2 N_{vrt}^4$ (formal N^6)

CC3, CCSD(T) : iterative / noniterative $N_{occ}^3 N_{vrt}^4$ (formal N^7)

CCSDT : iterative $N_{occ}^3 N_{vrt}^5$ (formal N^8)

CCSDTQ : iterative $N_{occ}^4 N_{vrt}^6$ (formal N^{10})

....

hierarchy of post-HF *ab-initio* methods

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....

dilemma of high level *ab-initio* methods:
high scaling of computational cost !

CC and CI theory - computational effort

amplitude equations

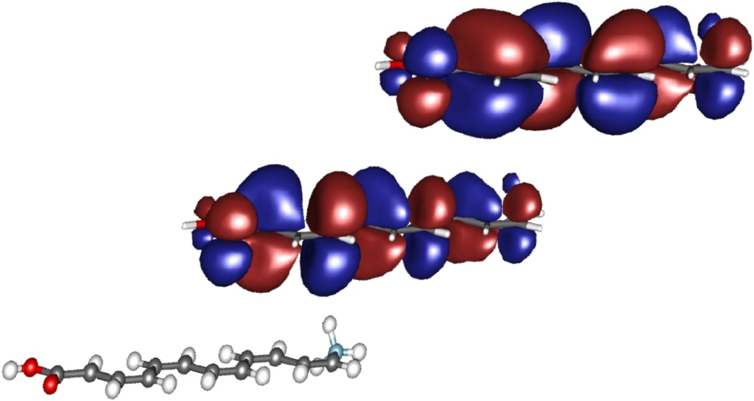
$$\langle \Psi_{ij..}^{ab..} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Psi_0 \rangle = 0$$

example of T_2 equations for CCD:

$$T_{ij}^{ab} \leftarrow v_{ij}^{ab} - f_i^m t_{mj}^{ab} - f_e^b t_{ij}^{ea} + \frac{1}{2} t_{mn}^{ab} v_{ij}^{mn} + t_{nj}^{ea} v_{ie}^{nb} + \color{red}{\frac{1}{2} t_{ij}^{ef} v_{ef}^{ab}}$$

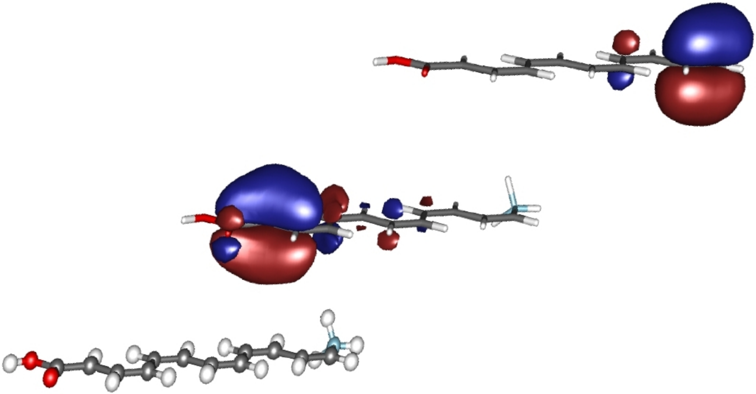
$$+ \frac{1}{2} t_{ij}^{eb} t_{mn}^{fa} v_{ef}^{mn} + \frac{1}{4} t_{ij}^{ef} t_{mn}^{ab} v_{ef}^{mn} - \frac{1}{2} t_{mi}^{ab} t_{nj}^{ef} v_{ef}^{mn} - t_{mi}^{eb} t_{nj}^{fa} v_{ef}^{mn}$$

Classical theory based on canonical orbitals



T_{ij}^{ab}

Rotation among occupied yields localized orbitals



$T_{mn}^{\gamma\delta}$

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