

## INFOCHIMIE:

# QUANTUM CHEMICAL ELECTRONIC STRUCTURE METHODS IN A NUTSHELL

From:

<http://en.wikipedia.org/wiki/Wikipedia>

<http://ocw.mit.edu/>

## Infochimie Checklist:

- **90% of Infochimie are the practical projects!!**

**(1) oral presentation of your project (22 June, 8:15-12, BCH 4109)**

ca. 10' per group (typically 7-8 slides) plus 5' questions  
(questions concerning your projects and the underlying theory)

**(2) written reports of your project (< 30 June)**

(short, typically 10-20 pages (ask your assistant for examples of earlier reports))

### Your final marks for infochimie:

Mark of the oral presentation of your project (quality of presentation and answers to the questions) rounded by max. 1 point by your work on your projects during the semester and your written report).

## Performance HF



Relative bad performance:

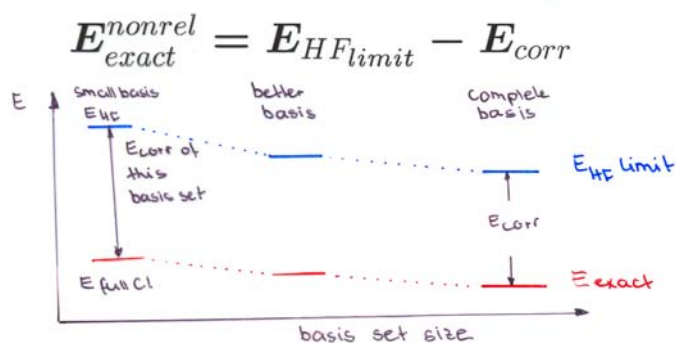
- whole PES
- vibrational frequencies:  
systematically too high (10-12 %)
- reaction energies:  
homolytic bond breaking (~ 25-40 kcal/mol off), protonations (~ 10 kcal/mol off)
- transition states
- excited states
- alkali metals (e.g. Li<sub>2</sub>, Na<sub>2</sub>..)  
transition metal complexes (e.g. ferrocene)
- systems with low lying excited states

Wrong results

- dissociation to open-shell fragments
- dispersion interactions:  
e.g. Ar<sub>2</sub> not bound
- F<sub>2</sub>

## Electron Correlation

Chemist's definition of  $E_{corr}$  (Lowdin):



→  $E_{corr}$  is basis set dependent!

### Electron Correlation: Physicist's view

Probability distribution of a system with 2 electrons is not given by the product  $\rho(1)\rho(2)$  only:

$$\rho_2(\vec{r}_1, \vec{r}_2) = \frac{1}{2}\rho(\vec{r}_1)\rho(\vec{r}_2)[1 + h(\vec{r}_1, \vec{r}_2)]$$

$h(\vec{r}_1, \vec{r}_2)$ : pair correlation function

The presence of electron(1) modifies the probability distribution for electron(2):

→ exchange-correlation hole

$$\rho_{xc}(\vec{r}_1, \vec{r}_2) = \rho(\vec{r}_2)h(\vec{r}_1, \vec{r}_2)$$

(exchange-correlation hole created by an electron at  $\vec{r}_1$ ).

→ correlated motion of electrons

→  $HF_{limit}$  is higher than the true total energy of the system

### Post-Hartree-Fock Methods

Methods use a Hartree-Fock calculation as starting point and try to improve the HF results by taking account of **electron correlation**:

- Configuration Interaction (CI)
- Møller-Plesset Perturbation (MP)
- Coupled-Cluster (CC)

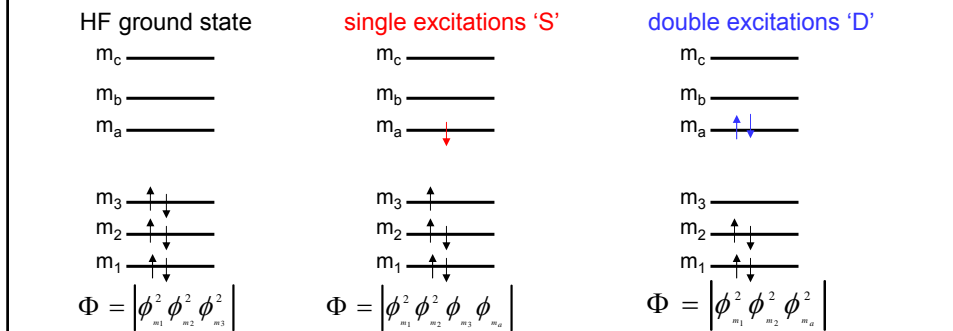
## Configuration Interaction (CI)

### Improved Ansatz for the Many-Body Wavefunction:

$$\Psi(x_1, x_2, x_3 \dots x_N) = \sum_m C_{m_1, m_2, m_3 \dots m_N} \left| \phi_{m_1}(x_1) \phi_{m_2}(x_2) \phi_{m_3}(x_3) \dots \phi_{m_N}(x_N) \right|$$

where  $x_i = (\vec{r}_i, s)$ .

Instead of describing the wavefunction with a single Slater determinant (like in HF) we describe it with a linear combination of Slater determinants. Each Slater determinant corresponds to a different electronic configuration (therefore the name CI) that is generated by creating excited state configurations from the ground state Hartree-Fock wavefunction.



If we include all possible excited state configuration where one electron is promoted from the occupied to the unoccupied orbitals, the method is called **CIS**, if we include all possible single and double excitation it is **CISD** etc.. (**CISDT**, **CISDTQ**...). By allowing for this increased flexibility of wavefunction, we are able to capture the modifications of the electronic distribution caused by correlation effects. If we include all possible excited state configurations, the method is called **full CI** and the results is exact.

So in theory we now how to solve a many-electron Schrodinger equation exactly!

**In practice: the number of determinants we have to include to do a full CI calculations is intractable in most cases!**

$$\# \text{ of determinants} \approx \binom{N_{SO}}{N_{electrons}} = \frac{N_{SO}!}{N_{el}!(N_{SD} - N_{el})!}$$

Ex.: Benzene with 6-311G\*\* basis:

$$\binom{288}{42} \approx 10^{52}$$

Full CI calculations have been performed as benchmarks studies for very small molecules. CIS is sometimes used for approximated excited state calculations. Otherwise CI is not used very often because it is simply too expensive and other correlated methods give results of comparable quality for a lower cost.

**Percentage of Correlation energy:**

Molecule	Basis Set	CISD	CISDT	CISDTQ
BH	DZP	94.91	n/a	99.97
H <sub>2</sub> O (R <sub>e</sub> )	DZ	94.70	95.47	99.82
H <sub>2</sub> O (1.5 R <sub>e</sub> )	DZ	89.39	91.15	99.48
H <sub>2</sub> O (2.0 R <sub>e</sub> )	DZ	80.51	83.96	98.60
NH <sub>3</sub>	DZ	94.44	95.43	99.84
HF	DZP	95.41	96.49	99.86
H <sub>7</sub> <sup>+</sup>	DZP	96.36	96.87	99.96

- **doubles** contribute most to gs correlation energy
- **quadruples** are more important than triples (at least for energy)
- at stretched geometries CISD and CISDT markedly poorer, CISDTQ ok

**Number of CSF's:**

Molecule	Basis set	CISD	CISDT	CISDTQ
BH	DZP	568	n/a	28 698
H <sub>2</sub> O	DZ	361	3 203	17 678
NH <sub>3</sub>	DZ	461	4 029	19 925
HF	DZP	552	6 712	48 963
H <sub>7</sub> <sup>+</sup>	DZP	1 271	24 468	248 149

(Handy et al., CPL 95, 386 (1983)  
Schaefer et al., JCP 100, 8132 (1994))

**Many-Body Perturbation Theory (MBPT)**

**General idea:**

in case correlation effects are relatively small → HF solutions  $|\Psi_i\rangle_{HF}$  and  $\{E_i\}_{HF}$  are already close approximations to the exact  $|\Psi_i\rangle$  and  $\{E_i\}$

→ correlation effects can be considered as perturbation to the HF solutions and treated via perturbation theory

**Perturbation Theory:**

**Given:** Hamiltonian  $\mathcal{H}^0$   
with eigen functions  $|\Psi_i^0\rangle$   
and eigen values  $E_i^0$

True Hamiltonian  $\mathcal{H}$  partitioned into:

$$\mathcal{H} = \mathcal{H}^0 + \lambda \mathcal{H}' = \mathcal{H}^0 + \lambda \mathcal{V} \quad (\mathcal{V} \ll \mathcal{H}^0)$$

↑ exact Hamiltonian
↑ unperturbed system
↑ scaled perturbation
λ=0 →  $\hat{H} = \hat{H}_0$ 
λ=1 →  $\hat{H} = \hat{H}_0 + \hat{H}$

⇒ Taylor expansion of  $E_i$  and  $|\Psi_i\rangle$  around  $\lambda = 0$

$$E_i = \lambda^0 E_i^{(0)} + \lambda^1 E_i^{(1)} + \lambda^2 E_i^{(2)} + \dots$$

$$|\Psi_i\rangle = \lambda^0 |\Psi_i^{(0)}\rangle + \lambda^1 |\Psi_i^{(1)}\rangle + \lambda^2 |\Psi_i^{(2)}\rangle + \dots$$

$$H |\Psi_i\rangle = E_i |\Psi_i\rangle$$

Indices (0),(1),(2)..(n): refer to the unperturbed system (0th order correction), the 1st order correction, 2nd order correction...nth order correction → MP2,MP3, MP4 etc...

Series does not necessarily converge!

### Møller-Plesset Perturbation Theory

unperturbed system:

$$\mathcal{H}^0 |\Psi^{(0)}\rangle = E_0^{(0)} |\Psi^{(0)}\rangle$$

$\mathcal{H}^0$ : Hartree-Fock Hamiltonian

$$\mathcal{H}^0 = \sum_i \hat{f}(i)$$

Note: First nontrivial energy correction at second order MP2

perturbation:

$$\mathcal{V}' = \mathcal{H} - \mathcal{H}^0 = \left( \sum_i \hat{h}(i) + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \right) - \sum_i \hat{f}(i)$$

$$= \left( \sum_i \hat{h}(i) + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \right) - \left( \sum_i \hat{h}(i) + \sum_i \hat{v}_{HF}(i) \right)$$

$$= \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} - \sum_i \hat{v}_{HF}(i)$$

→ total e-e repulsion minus Hartree-Fock e-repulsion

## Coupled Cluster (CC)

Yet another Ansatz for the Many-Body Wavefunction:

$$|\Psi\rangle = e^{\hat{T}} |\Phi_0\rangle$$

where  $|\Phi_0\rangle$  is a reference wavefunction. e.g. the Hartree-Fock determinant and  $\hat{T}$  is the cluster operator

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \dots$$

$\hat{T}_1$  is the one-particle excitation operator which generates singly excited configurations.

$\hat{T}_2$  is the two-particle excitation operator which generates doubly excited Slater determinants.

Etc..

In analogy to the terminology used in case of CI calculations, coupled clusters are labelled according to the order of excitations that is included e.g. CCD, CCSD, CCSDT, CCSDTQ etc..

Acronyms of the type CCSD(T) refer to a coupled cluster calculation including singles and doubles and a perturbatively treatment to include the effects of triple excitations.

Calculations of the coupled cluster time are nowadays one of the most popular approaches for very high accuracy calculations.

## Overview

### Some Important Features of QC Calculations:

- what is the Ansatz for the **wavefunction**?
- how are **exchange and correlation** treated?
- is the method **variational** (i.e. is  $E \geq E_{\text{true}}$ )?
- is the method **size consistent** (i.e. is the energy of two noninteracting systems the sum of the single systems?)
- can **excited states** be treated with the same method?
- what is the **scaling** of the method (i.e. how does the computational cost grow if I double the system size?)

## Overview

Method	wavefunction	exchange	correlation	variational?	Size-consistent?	Excited states?	Scaling
<b>HF</b>	1 determinant	exact	none	yes	yes	no	$N^2$ - $N^4$
<b>Truncated CI</b>	selected determinants	exact	some	yes	no	yes	e.g. CISD $N^6$
<b>MPn</b>	contributions from excited determinants through perturbation	exact	some	no	yes	CAS-PT2	MP2 $N^5$ MP3 $N^6$ MP4 $N^7$ MP5 $N^8$
<b>CC</b>	contribution of selected excitations through infinite order	exact	some	no	yes	EOM-CC CC2	CCSD $N^6$ CCSD(T) $N^7$ CCSDT $N^8$ CCSDTQ $N^{10}$
<b>Full CI</b>	exact wf within basis set, linear combination of all possible excited determinants	exact	all	yes	yes	yes	$N!/N_{\text{el}}!(N-N_{\text{el}})!$
<b>DFT</b>	1 determinant	approximate	approximate	no	yes	TDDFT	$N^2$ - $N^3$