Electron Correlation

and how to handle it with MOLCAS

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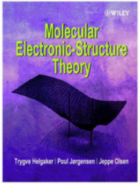
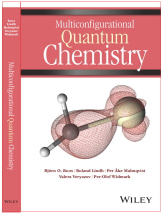
Books

Not many text books.
However, there are:

Jørgensen, Olsen, Helgaker,
Molecular Electronic-structure Theory,
Roos et al.,
Multiconfigurational Quantum Chemistry.





'The bible' (PJ-JO-TH) is the best for theory,
'The pink book' (BOR-RL-PAM-VV-POW) is the best for examples and applications

In this lecture..

Most well-known methods, old work-horses:

CASSCF	Complete Active Space SCF
MRCI	Multi-Reference Configuration Interaction
CASPT2	Complete Active Space Perturbation Theory through 2nd order

A little bit about new emerging techniques (DMRG, Stochastic CAS, etc).

What is correlation?

A relationship (usually weak), between two random variables.
Correlation coefficient.
Static and dynamic correlation.

Per-Olof Löwdin definition of correlation

$E^{exact} = E^{HF} + E^{correlation}$
under E^{HF} the Restricted Hartree Fock theory is assumed.

There are so many talks about correlation, so we might think that correlation is a very strong effect.
Spin correlation. This is really a large effect.
Correct wavefunction: $\Psi(r_1, r_2, ..., r_n)$ *vs.* Hartree product $\psi(r_1)\psi(r_2)...\psi(r_n)$
Without electrons obeying Pauli principle it will be no atoms, no chemistry.

What is electron correlation?

For **the ground state** HF reproduces 99% of the energy

Total energy for benzene molecule (in kcal/mol)

Hartree-Fock	-144791.5
CASSCF (6 orbitals)	-144837.4
CCSD(T)	-144843.8

- $E^{exact} = E^{HF} + E^{Correlation}$
- Mass of Earth$=6 * 10^{24} kg$
- Mass of all humans (est.)$= 5 * 10^{11} kg$, so can be easily neglected.
- The energy of a chemical reaction is a result of a difference between two huge numbers. So, we need to know them very precisely.

What is the source of correlation for electrons?

- In classical mechanics particles are independent
- Even with electrostatic forces, they are still independent
- Electrons are light, fast and can see each other (Coulomb), and there are some rules for fermions (Pauli principle).
- The basic principle of Quantum Mechanics: $\Psi(r_1, r_2, ..., r_n)$. They all connected

Is it possible to describe correlation approximately?

Yes, absolutely! Density Functional Theory provides many formulas and fitting for approximate treatment of correlation.

It works if electron correlation is small and can be described by a simple physical model.

It fails if electron correlation is large, and/or the electron density is rapidly changing (e.g. in strong chemical bonds and in creation/dissociation of bonds).

What exactly is missing in Hartree-Fock theory?

Hartree-Fock theory describes the wavefunction by one Slater determinant (or two in case of UHF). It corresponds to a single electron configuration. All electrons are 'sitting tight' at certain orbitals.

So, let us consider several configurations...

$\Psi = \sum C_k \psi_k$ (you probably will see this formula again)

Simple example - H_2 molecule dissociation.

Correlation in atoms, molecules and solids

Correlation is larger in a situation then electrons are "together" or changing the their status

Correlation is larger for degenerate systems

d- and f- elements and compounds with them

Creation or breaking a bond

So, in case of solids, the correlation is relatively 2̌018smaller2̌019 effect. (Unless we consider metals, superconductors, etc.)

Post HF methods

Hartree-Fock is a good reference. Single reference.
How to make excitations? Take HF orbitals and use different occupation schemes. Easy to make all single excitations, or all double excitations.

Coupled Cluster method in one slide

The main problem of S/SD/SDT method: the definition of "what is a single excitation"? depends on the circumstances.
E.g. two separated hydrogen atoms with a single excitation of each of them.
Coupled cluster method includes only "connected" excitations
Nomenclature: CCS, CCSD, CCSDT, etc..
Only CCSDTQP includes everything (it is possible to proof that no need to include more). Similar to only one- and two- electron terms in HF.
CCSD(T) is approximation to CCSDT.
Does Coupled Cluster theory a 'golden standard'? Yes, it is "the golden standard" for single reference methods. Despite many attempts, CC theory with multi-reference function is still under development.

The limit (with a fixed basis set): Full CI

- Single reference: $\Psi = \sum_i^N C_i\psi_i$, all ψ_i made from one reference $\psi^{(0)}$.
- Full CI: $\Psi = \sum_i^\infty C_i\psi_i$
- Multireference: $\Psi = \sum_i^N \mathbf{C_i}\psi_i$, only C_i are optimized
- Multiconfigurational: $\Psi = \sum_i^N \mathbf{C_i}\psi_\mathbf{i}$, both C_i and ψ_i are optimized.

With infinity, one can choose - to optimize only C or both C and ψ. We do not want infinity, we do want a simple way to select configurations.

Active orbitals

Let us consider a system with n electrons and N orbitals. In the complete solution we have to mix all possible combinations (but take care about Pauli principle - only 2 electrons can occupy one orbital) and the total spin.

$$\Psi = \sum C_i \psi_i$$

We can use a vector form to write the configurations:
(222000) - 3 doubly occupied orbitals and 3 vacant
(22ud00),(22u0d0),(22u00d) - one electron is exited, but the total spin is still singlet.
(22uu00) - one electron is excited, but the spin is now triplet (2*(1/2+1/2)+1)

Occupation of Active orbitals

Solving this problem variationaly we will find out the coefficients (or weights) for each configuration.
E.g.
0.7(222000)+0.09(22ud00)+0.09(22u0d0)+0.09(22u00d)+....

Now we can compute an occupation number for an orbital. As in example above - first two orbitals are occupied most of the time. So, they will have occupation 2.00 (or 1.99). But some of the orbitals will have 'in between' occupation numbers.

We have now a simple criteria for the active space

If there is only one configuration with a large coefficient - the system can be described by a single configurational method

If the occupation of orbitals are close to 2.0 or to 0.0 - they don't want to be excited!

Visualization of orbitals is also important criteria.

What we need is Full CI (C)

Full CI (**with unlimited basis set**) is exact

$$\Psi = \sum_{K*All*} C_K \Phi_K,$$

where Φ_K is antisymmetric N-electron function.
Weyl's formula for the number of configuration state functions (CSF)

$$K_{n,N,S} = \frac{2S+1}{n+1} \left(\begin{array}{c} n+1 \\ N/2-S \end{array} \right) \left(\begin{array}{c} n+1 \\ N/2+S+1 \end{array} \right)$$

n - orbitals, N - electrons, S - spin.

Number of CSF for N electrons on n orbital

2	3
4	20
6	175
8	1764
10	19404
12	226512
14	2760615
16	34763300
18	449141836
...	
48	81528782754899118132297728
50	1205564663340194413152305152
...	
100	3952654378413634433811358365469701321961000000000000

Towards Full CI

- +
    - Allows to improve the results gradually
    - No parameters.
    - Variational
    - Multiconfigurational theory converges fast, usually requires only some small set of orbitals
- -
    - CASSCF (complete active space) is still far away from Full CI
    - It becomes expensive or out of reach after 14-16 orbitals
    - Full CI also requires infinite basis set
    - Interaction of different states is missing (e.g. with different spins)

How strict these restrictions?

Li atom - 1e (or 3e) - we can include 1s2s2p3s3d3p4s4d4p5s
Benzene molecule $= 3\pi + 3\pi^* =$ 6 orbitals and 6 electrons
Antracene (3 rings) = ?
Cr_2 = 3d (5*2) + s (1*2) + 4d(5*2) = 22
Larger metal clusters?
Ni:MgO - dNi (5) + pO (3*6) = 23
O5-Ni-O-Ni-O5 = ?

Mixing CASSCF with some extra rules.

RASSCF: Inactive, RAS1 (S, SD, SDT,), RAS2 (Active), RAS3 (S, SD, SDT), Virtual.
GASSCF: Any number of spaces, any rules.

Using the rules, one can model many 'historical' methods

- Closed Shell SCF (RAS1, RAS2, RAS3 empty).
- SDTQ...CI with a closed shell reference function (RAS2 empty).
- CASSCF (RAS1 and RAS3 empty).
- SDCI with a CASSCF reference (max two holes in RAS1 and max two electrons in RAS3).
- Polarization CI (max one hole in RAS1).
- Core excited states (max one electron in RAS1/3 ǎ013 which is a core orbital!).

How to select active space?

- B.O.Roos: "Sometimes trivial, sometimes more difficult, sometimes impossible"
- Depends on both: the molecule and the problem
- Chemical intuition (visualization is very helpful)
- Remember: the solution is not unique
- Follow recommendations (read the book)
- use brute force with larger RAS2 or DMRG (works occasionally)
- use RAS to detect interesting orbitals. Ideally: orbitals with occupation numbers in the range 0.02-1.98 should be active.
- use special "norms" (AutoCAS)

A short slide about DMRG

- Density Matrix Renormalization Group
- invented for a chain system
- Idea: to split entire space into small blocks, and walk through several times
- In practice:
    - implemented in QcMaquis, ChemPS2, Block
    - extremely expensive
    - depends on internal parameters
    - still restricted by ca. 40 orbitals
    - not trivial to implement PT2 on top
    - work in progress, still waiting...

A short slide about Stochastic CI

- NECI code
- Quite expensive calculations
- Manual observation is needed
- In theory - no limits, in practice - see above
- Even more expensive for excited states
- It is impossible to compute specific excited state

A short slide about MC-PDFT

- Combination of Pair-Density functional theory and multiconfigurational theory.
- Implemented in OpenMolcas
- Double counting has been resolved by definition
- Works only with the minimal active space.

Multireference methods

$\Psi = \sum C_i \psi_i$

If we have a source for reference functions, we can keep them unchanged, but optimize only coefficients. In practice, a good source of reference functions is a small CASSCF.

RASSCF

A good compromise. Not size consistent. But relatively cheap. Has PT2 (RASPT2).

Excited states

The strong side of Multiconfigurational theory is ability to optimize non only the ground state, but also excited states. They will appear as separate roots of wavefunction.

Note! the active space which was used for the ground state can be poor for excited states.

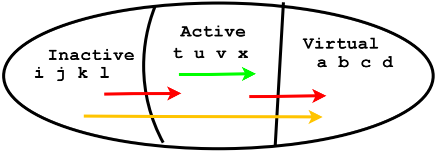
Note! Be careful with computing too many excited states!

Optimization of specific excited state is possible, but it is recommended to use average - equal weights for all states.

Flipping of states is a common problem

How far CASSCF from Full CI?

Static - Dynamic $FullCI - CAS = S + D + TQ....$



Excitation types in CASPT2:

Internal	Semi-internal	External
$\widehat{E}_{tiuv}$	$\widehat{E}_{atuv}$	$\widehat{E}_{atbu}$
$\widehat{E}_{tiuj}$	$\widehat{E}_{aitu}$ or $\widehat{E}_{tiau}$	$\widehat{E}_{aibt}$
	$\widehat{E}_{tiaj}$	$\widehat{E}_{aibj}$

Zeroth-Order Hamiltonian for CASPT2

$\widehat{H}_0$ should be

- relatively simple
- include single and double excitations
- preferably convert to MP2 for no active space

$$\widehat{H}_0 = \widehat{P}_0 \widehat{F} \widehat{P}_0 + \widehat{P}_{SD} \widehat{F} \widehat{P}_{SD} + \widehat{P}_{TQ} \widehat{F} \widehat{P}_{TQ}$$

Where $\widehat{P}_0$ is a projector into CAS space, $\widehat{P}_{SD}$ - projector into SD space

Now we have to choose F, the generalized Fock operator:

$$\widehat{F} = \sum_{p,q} F_{pq} \widehat{E}_{pq}$$

$$F_{pq} = h_{pq} + \sum_{rs} \left((pq|rs) - \frac{1}{2}(ps|rq) \right) D_{rs}$$

IPEA shift

$F_{ii} = -(IP)_i$ (ionization potential for inactive)

$F_{aa} = -(EA)_a$ (electron affinity for virtual)

thus, for active orbitals
it should in between.. $F_{tt} = -\frac{1}{2}((IP)_t + (EA)_t)$

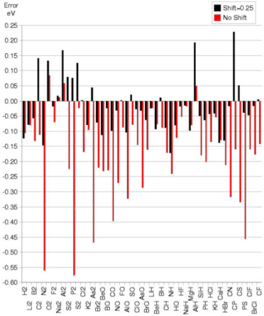
The correction for excitation into active orbital
$\frac{1}{2}D_{tt}((IP)_t - (EA)_t)$
and for exciting out $-\frac{1}{2}(2 - D_{tt})((IP)_t - (EA)_t)$
The Fock operator used in the definition of the zeroth order Hamiltonian is

$$\begin{aligned}\hat{F} &= \sum_{pq} f_{pq}\hat{E}_{pq}, \\ f_{pq} &= h_{pq} + \sum_{rs} D_{rs}\left((pq|rs) - \frac{1}{2}(ps|rq)\right)\end{aligned}$$

the effect of IPEA shift

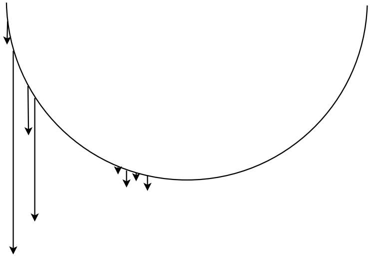
Now we consider $\epsilon = (IP)_t - (EA)_t$ as a constant.
We set ϵ to 0.25, as an average value for atoms.
Dissociation energies for two-atomic molecules.

(Error bars are red for the standard CASPT2 and black for IPEA shift)



an empirical correction, if you wish.... For some organic molecules the results are better without IPEA.

PT2 and variational methods



Second order perturbation theory is always pushing energy down.

Closer to the minimum the correction is smaller.

Test question: complete the picture by adding PT3 here...

Intruders!

Diagnosis:
Large difference between reference (CASSCF) and the final (CASPT2) energies.
Small (almost zero!) reference weight.
The cause:
division by 0
The treatment:
Change the Hamiltonian, trying to make a small change
IPEA (side effect), level shift technique, or imaginary shift.

To simulate an intruder state we set up a "CAS" calculation for H_2 molecule (with H-H distance= 20Å) as containing 1(!) active orbital, and 2 electrons.

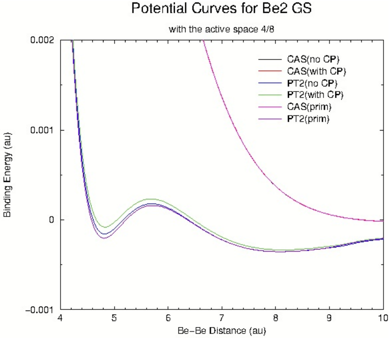
CAS energy	= -0.726970
CASPT2 energy	= -1.9131454
Reference weight	= 0.04376
if we include imaginary shift:	
CASPT2 energy	= -0.9045727
Reference weight	=0.89060

Can CASPT2 do magic?

Wrong question! Full CI with infinite basis set can.
Other methods could give you an illusion.

CASPT2 with small active space

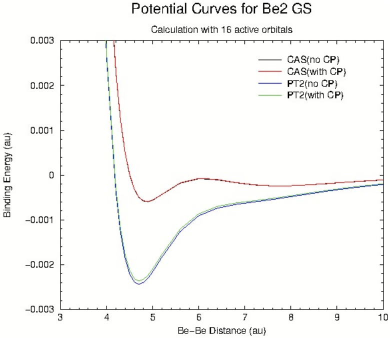
Ground state of Be_2 molecule is repulsive in HF and in small CAS. But CASPT2 shows a minimum!



CASPT2 was trying to recover some missing correlation.

same with larger active space

Same effect can be achieved by increasing the active space in CASSCF (to 16 orbitals).



again, Static vs Dynamic

Alternatives to CASPT2

CASPT2 is not a parameter-free method. The choice of zero-order Hamiltonian, IPEA-shift, selection of frozen orbitals, etc.
There are many alternative ways to correct dynamic correlation:

- XMS-CASPT2
- RMS-CASPT2
- NEVPT2
- XMCQDPT2

Mixing the states. RASSI

RASSI is the code, which can take WFs (at CASSCF, RASSCF, etc. level) and mix them.

$\Psi = \sum C_i \psi_i$

The states can corresponds to different spins. RASSI also can mix CASPT2 states.

If states are not interacting - the resulting energy remains the same.

RASSI also can include spin-orbit coupling and compute oscillators strenghts for the transitions.

Molcas and CASSCF

- Calculation without control of the active space is rubbish: both before the calculation and after.
- Specification of the number of the active orbitals is not sufficient.
- GuessOrb orbitals (default for ANO-type basis set) might be better than SCF orbitals.
- CASPT2 is a black box, but RASSCF is not.

Ways to select Active space in Molcas

- use FileOrb keyword in RASSCF (you also can link the file as INPORB)
- use Alter keyword
- use TypeIndex in Orbital file or resort orbitals
- visual detection of orbitals vs analysis of coefficients