Multiconfigurational Quantum Chemistry

Björn O. Roos as told by RL
Department of Theoretical Chemistry
Chemical Center
Lund University
Sweden

April 20, 2009

The Slater determinant

Using the spin-orbitals, we can construct anti-symmetric N-electron functions as **Slater determinants**:

$$\Phi_K = \hat{A}\{\phi_{K1}(x_1), \phi_{K2}(x_2) \cdots, \phi_{KN}(x_N)\}$$

where $x = \mathbf{r}, s$ and $\hat{A}$ is an anti-symmetrizer. The number of such determinants is

$$K = \left(\begin{array}{c} 2m \\ N \end{array} \right)$$

Weyl's Formula

Number of molecular obrtals:	n
Number of spin-orbitals:	$2n$
Number of electrons:	N
Spin qauntum number	S

The Number of configuration state functions (*CSF's*) is:

$$K(n, N, S) = \frac{2S+1}{n+1} \begin{pmatrix} n+1 \\ \frac{1}{2}N - S \end{pmatrix} \begin{pmatrix} n+1 \\ \frac{1}{2}N + S + 1 \end{pmatrix}$$

The number of singlet states

N/n	2	4	6	8	10	12	14	16	18	20
2	3	10	21	36	55	78	105	136	171	210
4	1	20	105	336	825	1716	3185	5440	8721	13300
6	-	10	175	1176	4950	15730	41405	95200	197676	379050
8	-	1	105	1764	13860	70785	273273	866320	2372112	5799465
10	-	-	21	1176	19404	169884	1002001	4504864	*	*
12	-	-	1	336	13860	226512	2147145	*	*	*
14	-	-	-	36	4950	169884	2760615	*	*	*
16	-	-	-	1	825	70785	2147145	*	*	*
18	-	-	-	-	55	15730	1002001	*	*	*
20	-	-	-	-	1	1716	273273	*	*	*
22	-	-	-	-	-	78	41405	4504864	*	*
24	-	-	-	-	-	1	3185	866320	*	*
26	-	-	-	-	-	-	105	95200	*	*
28	-	-	-	-	-	-	1	5440	2372112	*
30	-	-	-	-	-	-	-	136	197676	*
32	-	-	-	-	-	-	-	1	8721	5799465
34	-	-	-	-	-	-	-	-	171	379050
36	-	-	-	-	-	-	-	-	1	13300
38	-	-	-	-	-	-	-	-	-	210
40	-	-	-	-	-	-	-	-	-	1

The Full CI Method

We can expand the wave function in the determinants:

$$\Psi = \sum_K C_K \Phi_K$$

Inserting into the Scrödinger equation and integrating gives the Secular Equation:

$$\sum_L (H_{KL} - E\delta_{KL}) C_L = 0$$

This is called **Full CI** and becomes an exact solution in the limit of a complete basis set.

Molecular Orbitals for the H_2 Molecule

Use a minimal basis set: $(1s_A, 1s_B)$

The MO's are given by symmetry:
$\sigma_g = N_g(1s_A + 1s_B)$, $\sigma_u = N_u(1s_A - 1s_B)$

The closed shell HF configuration is: $\Phi_1 = (\sigma_g)^2 = \sqrt{\frac{1}{2}}|\sigma_g\alpha, \sigma_u\beta|$

With the spin-orbitals: $\phi_1 = \sigma_g\alpha$ and $\phi_2 = \sigma_u\beta$

Dissociation of H_2 in closed shell HF Theory

The HF function is: $\Phi_1 = \sqrt{\frac{1}{2}}|\sigma_g\alpha\sigma_g\beta| = \sigma_g(1)\sigma_g(2)\Theta_{2,0}$,

where $\sigma_g(1) = N_g(1s_A + 1s_B)$.

$$\begin{aligned}\Phi_1 &= N_g^2\{1s_A(1)1s_A(2) + 1s_B(1)1s_B(2)\\ &+ s_A(1)1s_B(2) + s_B(1)1s_A(2)\}\Theta_{2,0}.\end{aligned}$$

Thus we have for large R: $\Phi \propto \Phi(H+H) + \Phi(H^+ + H^-)$.

The energy at dissociation is:

$E(r=\infty) = \frac{1}{2}(E(2H) + E(H^+) + E(H^-)) \approx E(2H) + 6.66$ eV.

Correct Wave Function for $R = \infty$

$$\Phi_\infty = \{s_A(1)1s_B(2) + s_B(1)1s_A(2)\}\Theta_{2,0}$$

with no ionic terms. They are important at $R = R_e$ but should disappear at $R = \infty$. Now introduce a new configuration:

$$\begin{aligned}\Phi_2 &= \sqrt{\frac{1}{2}}|\sigma_u\alpha, \sigma_u\beta| = \sigma_u(1)\sigma_u(2)\Theta_{2,0} \\ \sigma_u(1) &= N_u(1s_A - 1s_B)\end{aligned}$$

$$\begin{aligned}\Phi_2 &= N_u^2\{1s_A(1)1s_A(2) + 1s_B(1)1s_B(2) \\ &- s_A(1)1s_B(2) - s_B(1)1s_A(2)\}\Theta_{2,0}.\end{aligned}$$

The Two Configurational Solution

We find immediately that:

$$\Phi_\infty = \sqrt{\frac{1}{2}}\{\Phi_1 - \Phi_2\}$$

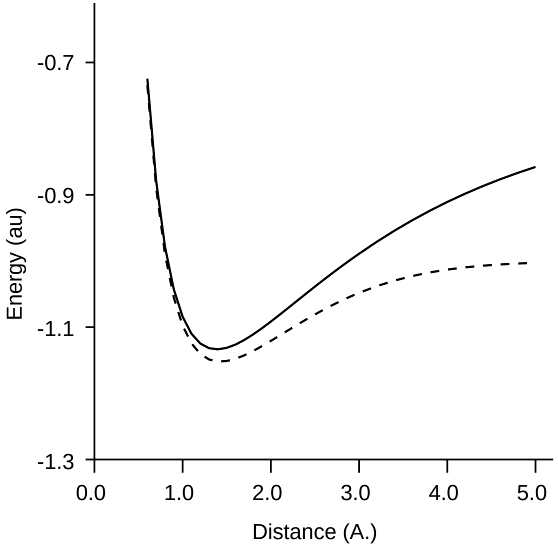
Assume now for all R:

$$\Phi = C_1\Phi_1 + C_2\Phi_2$$

The coefficients depend on R:

$R \approx R_e$	$C_1 \approx 1$	$C_2 \approx 0$
$R = \infty$	$C_1 \approx \sqrt{\frac{1}{2}}$	$C_2 \approx -\sqrt{\frac{1}{2}}$

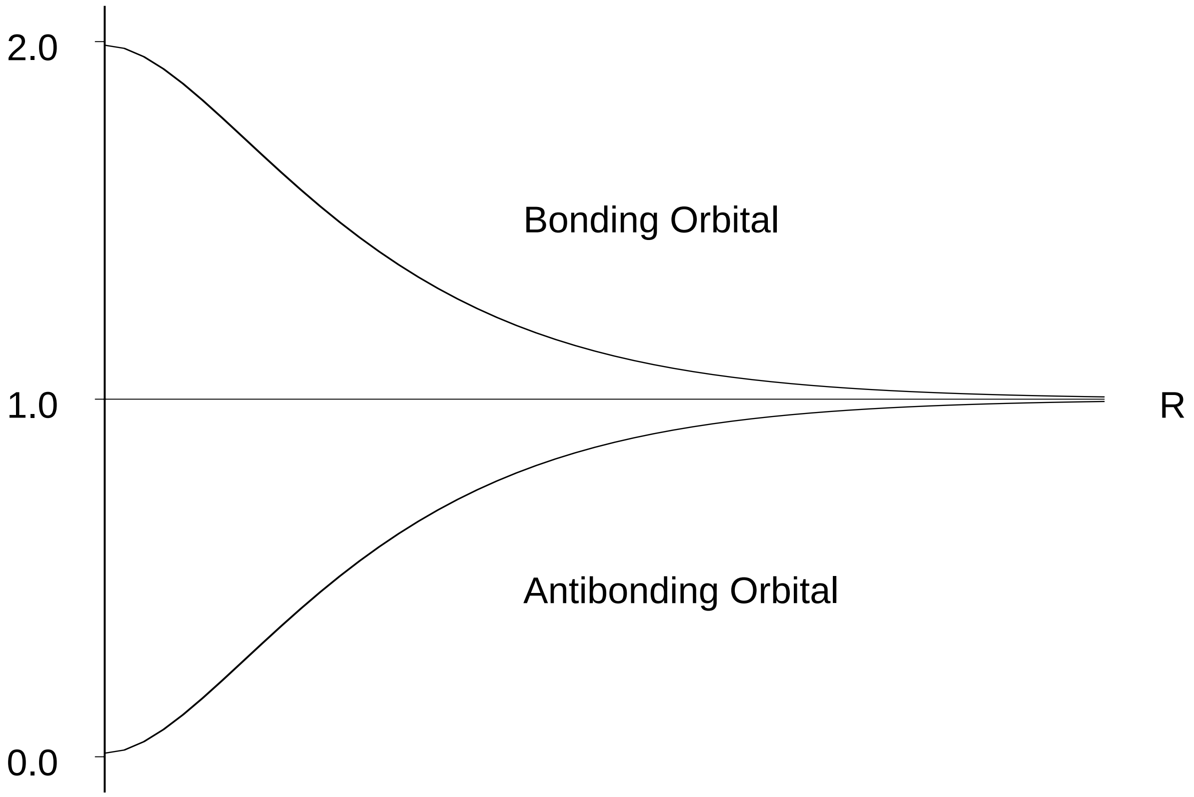
The Energy of H_2 as a Function of the Distance R



	R_e(Å)	D_e(eV)	ω_e(cm^{-1})	
SCF	0.736	3.63	4424	(Φ_1)
MCSCF	0.757	4.13	4355	$(\Phi_1,\ \Phi_2)$
Expt.	0.741	4.75	4401	

The Quantum Chemical Description of a Chemical Bond Involves both the Bonding and the Antibonding Orbital!

Natural Occupation Numbers for the Orbital Pair:



A More Complicated Example: Cr_2

The chromium atom has six unpaired electrons, $(3d)^5(4s)$, ^6S

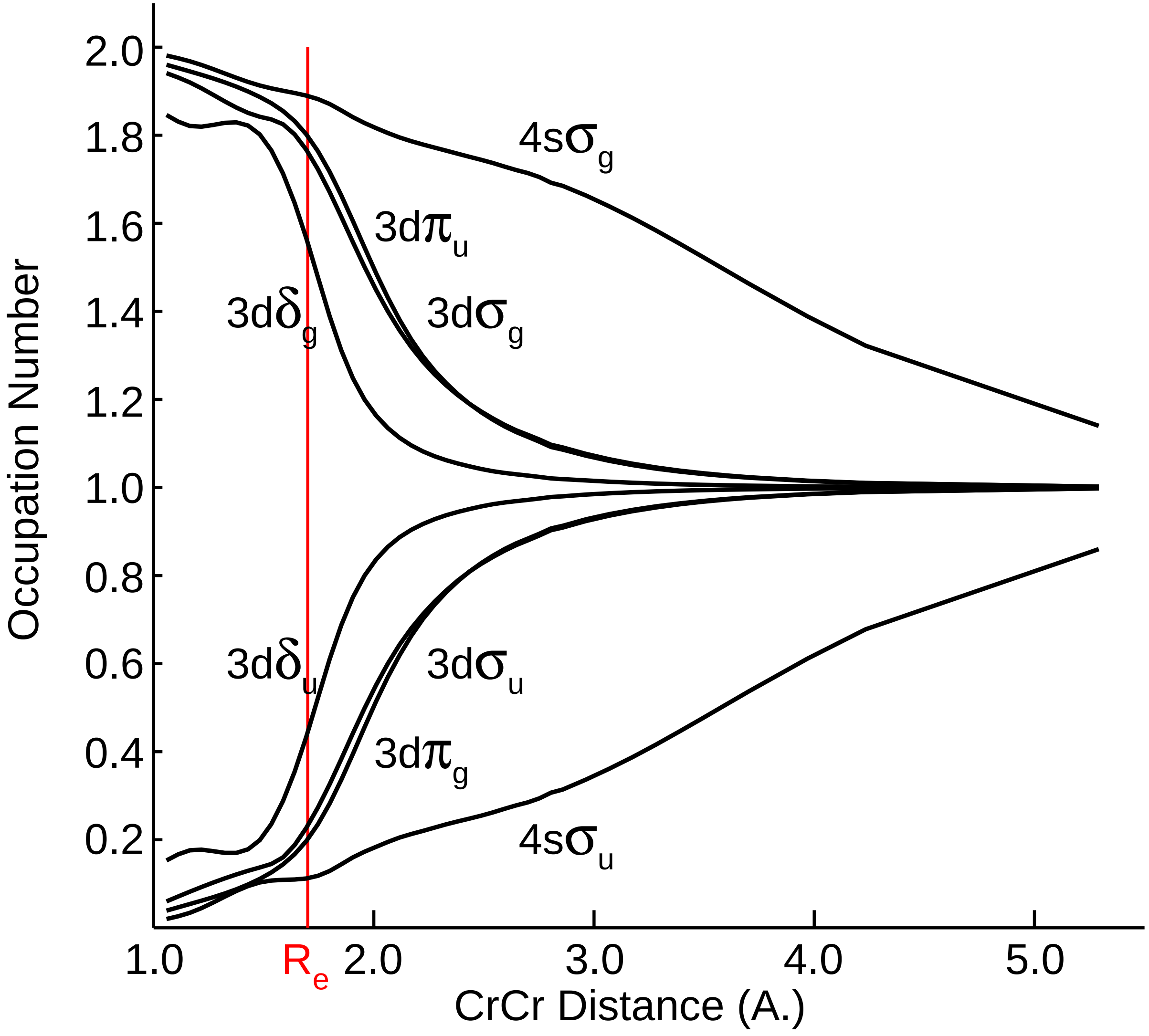
These atomic orbitals can be used to construct the following molecular orbitals:

bonding: $4s\sigma_g$, $3d\sigma_g$, $3d\pi_u$, $3d\delta_g$
antibonding: $4s\sigma_u$, $3d\sigma_u$, $3d\pi_g$, $3d\delta_u$

A sextuple bond can be formed!

Around 3000 configurations are needed for a correct description of the dissociation process.

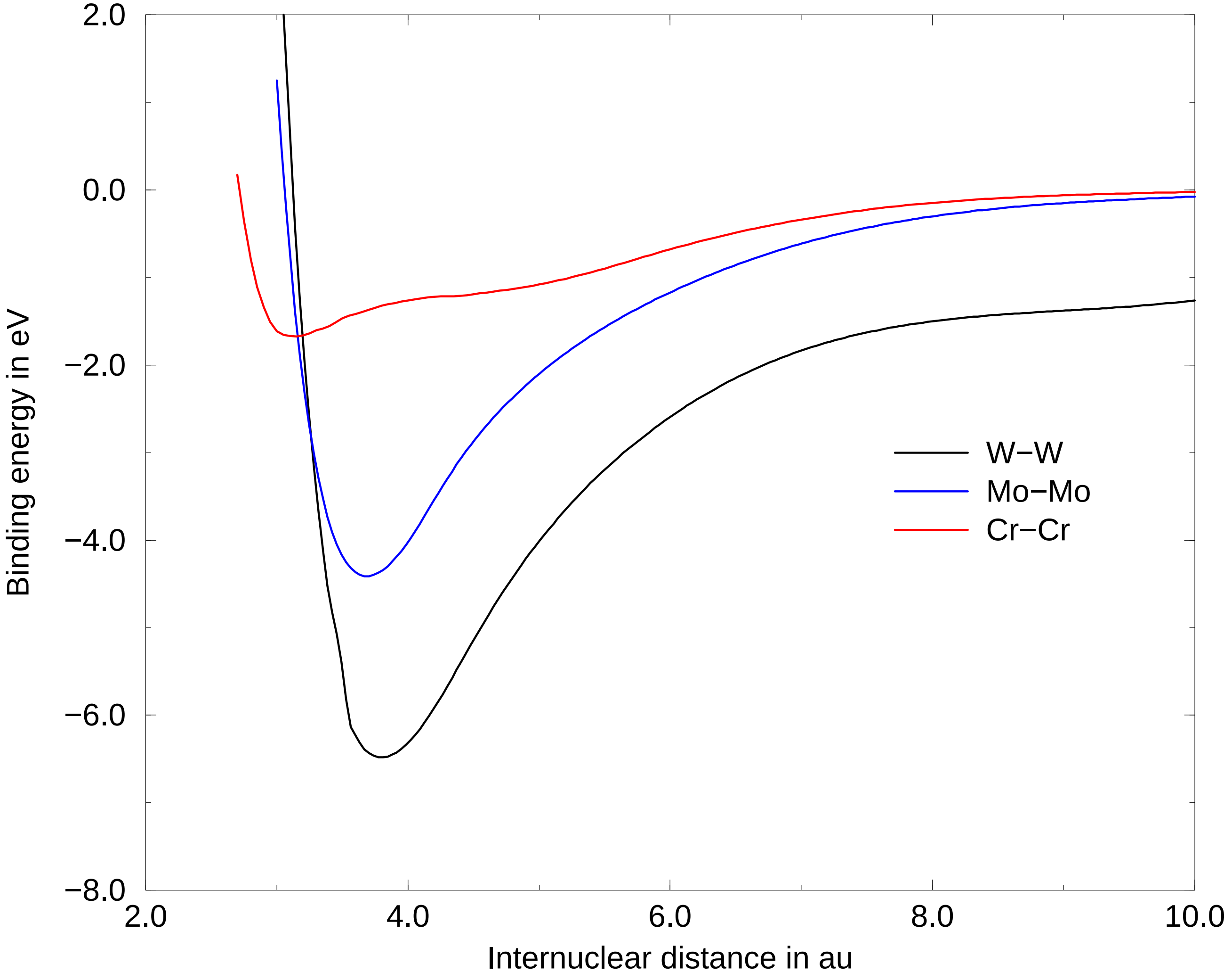
The Natural Orbital Occupation Numbers for Cr_2



Comparing Cr_2, Mo_2, and W_2

	Cr	Mo	W
sσ_g	1.90	1.92	1.93
sσ_u	0.10	0.08	0.07
dσ_g	1.77	1.89	1.88
dσ_u	0.23	0.11	0.12
dπ_u	1.81	1.90	1.91
dπ_g	0.19	0.10	0.09
dδ_g	1.58	1.78	1.81
dδ_u	0.42	0.22	0.19
Bond order	4.46	5.17	5.19
D_0 (eV)	1.65(1.53±0.06)	4.41(4.48)	5.37(5±1)
R_e (Å)	1.66(1.68)	1.95(1.94)	2.01()
ω_e (cm^{-1}	413(452)	459(477)	322(337)

Potential curves for Cr_2, Mo_2, and W_2



Active Orbitals and the Complete Active Space

Construction of the MCSCF wave function:
Divide the occupied MO's into two groups:

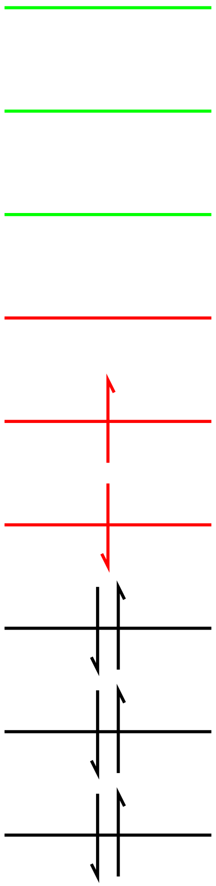
Inactive Orbitals	Occ.No. 2
Active Orbitals	Occ.No. Varies

Include all electronic configurations that can be obtained by distributing the active electrons among the active orbitals ion all possible ways consistent with a given overall spin and space symmetry.

This is the Complete Active Space (CAS) wave function

The CASSCF method: Optimize the CI coefficients and the MO's for a CAS wave function.

Orbital Spaces for CAS Wave Functions



Unoccupied Orbitals

Active Orbitals

Inactive Orbitals

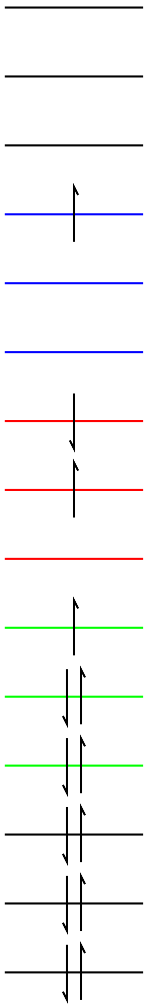
The Restricted Active Space (RAS) SCF Method

Divide the occupied MO's into four groups:

Inactive Orbitals	Occ.No. 2
RAS1 Orbitals	Max number of holes
RAS2 (Active) Orbitals	Occ.No. Varies
RAS3 Orbitals	Max number of electrons

This is thus a CAS with the additional possibility to excite out of some doubly occupied orbitals and into some virtual orbitals.

RAS Orbital Spaces



Unoocupied Orbitals

RAS 3 Orbitals

RAS 2 Orbitals

RAS 1 Orbitals

Inactive Orbitals

Some Typical Ras Wave Functions

- 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).
- RASSCF is useful to determine active spaces and input orbitals for CASSCF.

The zeroth order Hamiltonian in CASPT2

In second order perturbation theory you solve a set of linear equations:

$$(\hat{H}_0 - E_0)\Psi_1 = \hat{V}\Psi_0$$

The zeroth order Hamiltonian $\hat{H}_0$ is defined in terms of a one-electron Hamiltonian (usually) $\hat{F}$:

$$\hat{H}_0 = \hat{P}_0\hat{F}\hat{P}_0 + \hat{P}_I\hat{F}\hat{P}_I$$

where $\hat{P}_0$ and $\hat{P}_I$ are projection operators onto the reference function and the interacting configuration space, respectively.

The generalized Fock operator

The *generalized* Fock operator:

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

where the matrix elements are defined as:

$$F_{pq} = h_{pq} + \sum_{r,s} D_{rs}[(pq|rs) - \frac{1}{2}(ps|rq)]$$

for inactive, i, half-occupied ,t, and virtual, a, orbitals we have:

$$\begin{aligned} F_{pp} &= -(IP)_p \\ F_{aa} &= -(EA)_a \\ F_{tt} &= -\frac{1}{2}((IP)_t + (EA)_t) \end{aligned}$$

The new H_0-IPEA

The diagonal of the Fock matrix for active orbitals:

$$F_{pp} = -\frac{1}{2}\left(D_{pp}(IP)_p + (2 - D_{pp})(EA)_p\right) \tag{1}$$

Shift for exciting into this orbital:

$$\sigma_p^{(EA)} = \frac{1}{2} D_{pp}((IP)_p - (EA)_p) \tag{2}$$

Shift for exciting out of this orbital:

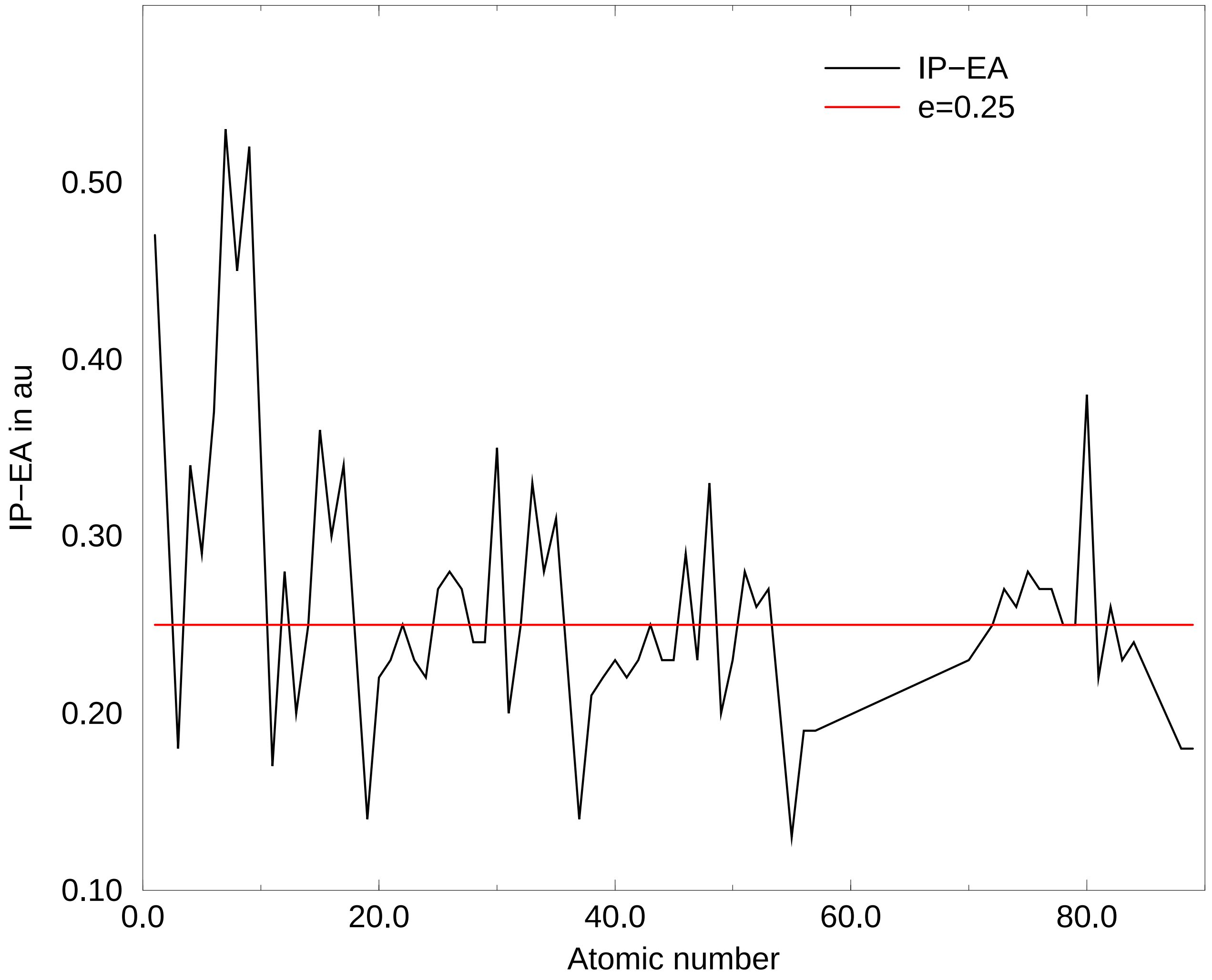
$$\sigma_p^{(IP)} = -\frac{1}{2}(2 - D_{pp})((IP)_p - (EA)_p) \tag{3}$$

Replace $((IP)_p - (EA)_p)$ with an average value: ϵ:

$$\sigma_p^{(EA)} = \frac{1}{2} D_{pp}\epsilon \tag{4}$$

$$\sigma_p^{(IP)} = -\frac{1}{2}(2 - D_{pp})\epsilon \tag{5}$$

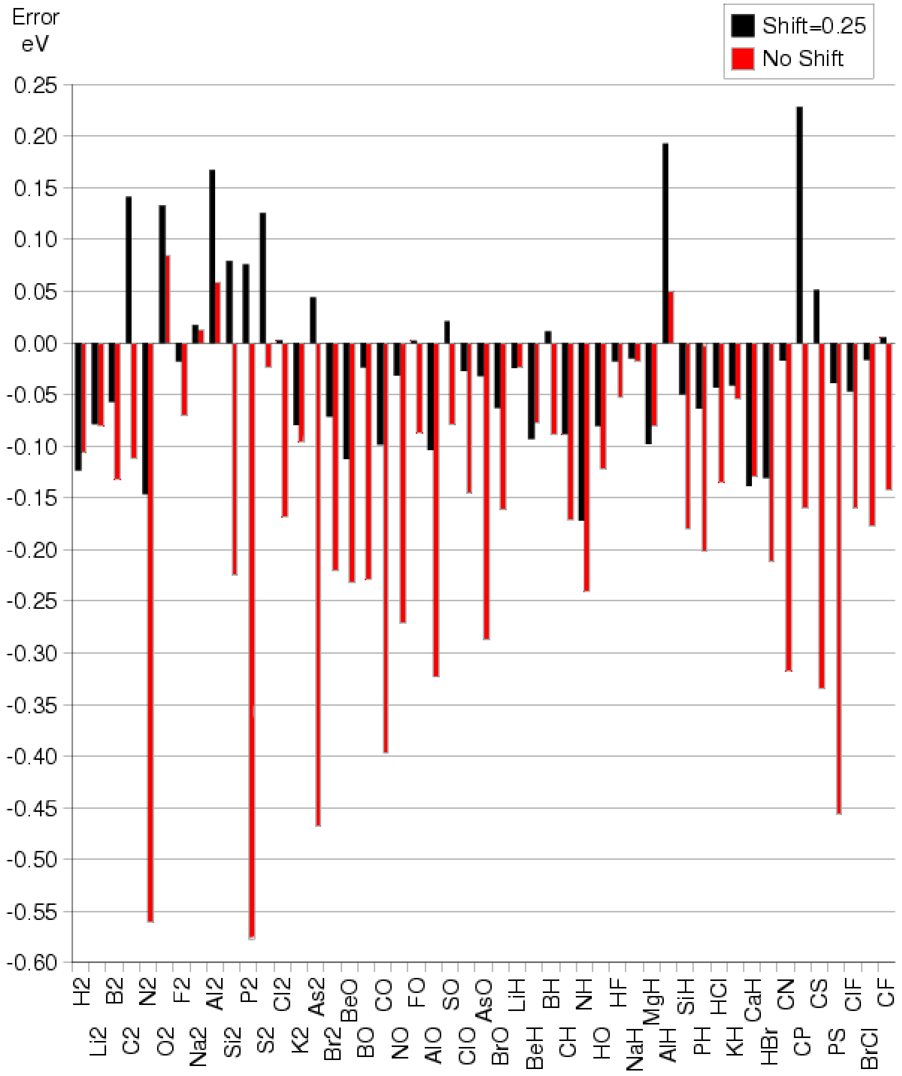
IP-EA for the Atoms



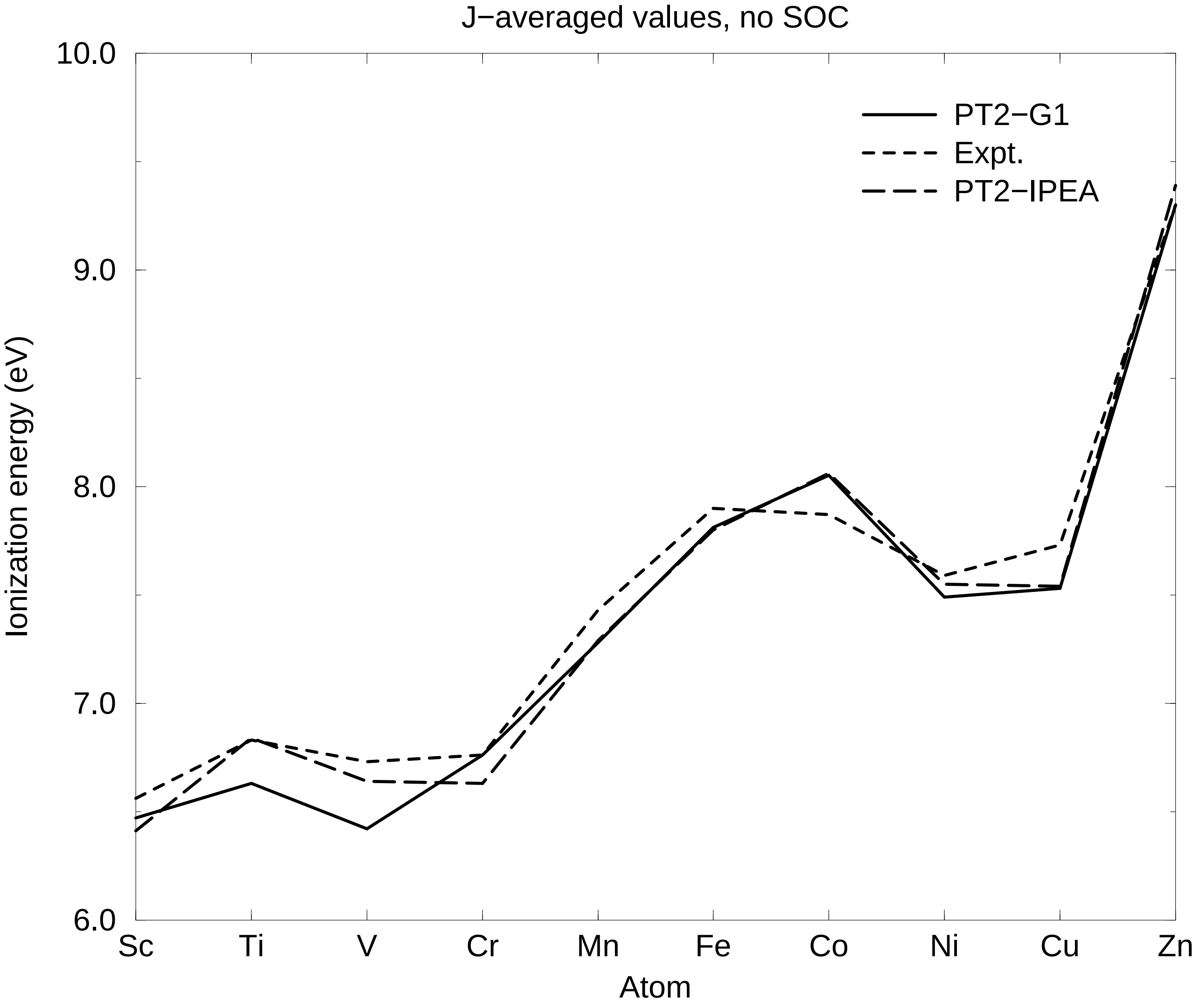
The new H_0-IPEA, determining ϵ

- Calculations of 49 diatomic molecules, all over the periodic table.
- The RMS error in D_e is reduced from 0.2 to 0.1 eV.
- For the molecules N_2, P_2, and As_2 was reduced from 0.45 eV to less than 0.15 eV.
- Similar improvements were obtained for excitation and ionization energies.
- The Optimial value for ϵ is 0.25 au.
- **H_0-IPEA is the standard option in MOLCAS-6.4**

Dissociation energies for diatomic molecules



Ionization energies for transition metal atoms



Multi-state CASPT2

- Treats several states simultanously at the CASPT2 level.
- Useful when there are states of the same symmetry close in energy.
- Separate Rydberg and valence excited states.
- Compulsory when studying avoided crossings, conical intersections, etc.

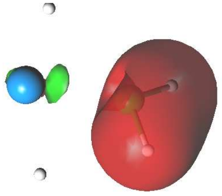
Two excited states of Ethene

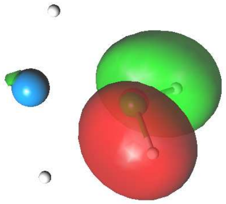
	CASPT2	MS-PT2	Expt.
The V-state:			
dE (eV)	8.45	7.98	8.0
$< x^2 >$	52.0	20.1	-
The 3dπ state:			
dE (eV)	8.93	9.40	9.33
$< x^2 >$	50.1	81.7	-

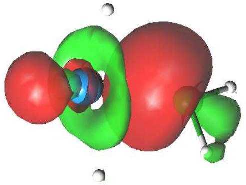
Choosing the active space

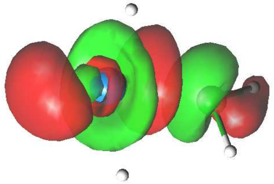
- Sometimes trivial, sometimes more difficult, sometimes impossible.
- It is necessary to know something about the electronic structure!
- Two problems must be solve: The number of active orbitals in each symmetry and the shape of them (the input orbitals)
- Use MOLCAS-GV to identify the orbitals in the active space.
- In difficult cases, run RASSCF calculations with larger active space
- Ideally: orbitals with occupation numbers in the range 0.02-1.98 should be active.

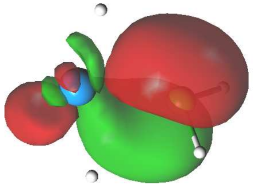
The active space for the molecule H_2CUH_2

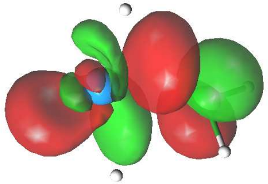

CH(2.00)

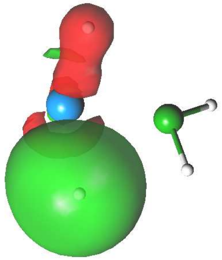

CH(2.00)

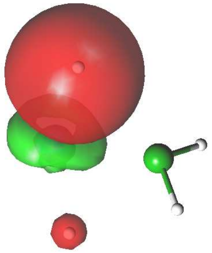

CUσ(1.97)

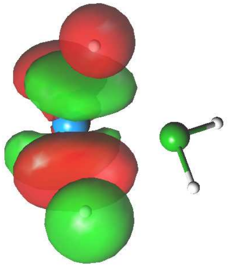

CUσ^*(0.03)

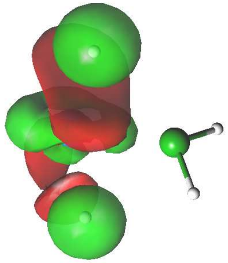

CUπ(1.94)

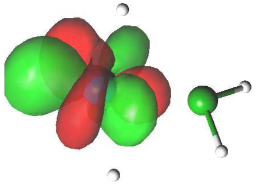

CUπ^*(0.06)

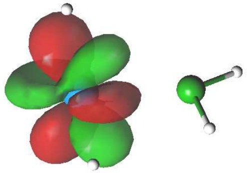

UH(1.97)


UH(1.06)


UH*(0.03)


UH*(0.04)


5f(1.00)


5f(1.00)

Main group molecules

- For Li, B, C: choose 2s,2p as active (four orbitals).
- For N, O, F: 2s can be left inactive (three orbitals).
- A molecule like S_3O needs twelve active orbitals (16in 12). This allows all transformations to be studied.
- CH bonds can often be left inactive. A molecule like butadiene (C_4H_6) then needs 12 active orbitals (12in 12). You can now break all CC bonds.
- A long alkyl chain with an active end group only needs orbitals there to be active.
- The choice of active space does not limit the size of molecules that can be studied.

Excited states of planar unsaturated molecules

- All $\pi-$ orbitals should be active, if possible. Otherwise select by energy criteria. Also depends on how large fraction of the spectrum shall be computed.
- Add Rydberg orbitals, when needed (above 5 eV for first row). Don't describe Rydberg states with diffuse orbitals on each atom!!
- Defined the charge center of the ion. Place specially selected Rydberg basis functions there.
- A large library of calculations exists. Consult the literature.

Transition metal compounds

- This is a more difficult case.
- For Cr-Cu one needs to account for the *double shell effect*, at least if the d-orbital occupation changes in the process studied.
- This is less important for second and third row atoms. In general they are easier than the crowded first row.
- The general rule is that all orbitals that have d-character should be included. For example: the molecules Cr(CO)$_6$, Fe(CO)$_5$ and Ni(CO)$_4$ needs that active space 10in10.
- High oxidation numbers need more active orbitals because bonds become very covalent (large charge transfer): Example MnO$_4^-$: 24in17 (all 3d and O(2p)./sbin/ifconfig)
- Recommended reading: K. Pierloot, Mol. Phys. 101, 2083 (2003).

The Nickel atom in 1992
(K. Andersson and B. O. Roos, CPL, 191, 507 (1992))

CASSCF/CASPT2 calculations with different active spaces. Empirical addition of relativistic effects. State specific CASSCF calculations.

CASPT2 results for excitation from d^{9}s^1,^{3}D (in eV)

State	SCF	3d,4s	3d,4s,4p	3d,3d',4s,4p	with 3p corr.	expt.
d^{8}s^2,^{3}F	-1.62	0.47	0.22	-0.18	-0.08	0.03
d^{10},^{1}S	4.35	0.40	0.42	1.87	1.77	1.74
d^{9}s^1,^{1}D	0.33	0.33	0.32	0.25	0.32	0.33

Lanthanides and Actinides

Lanthanides

The 4f shell is inert but has to be kept active.

5d,6s (6p) the most important orbitals.

Often very ionic complexes. Only 4f active.

Covalent bonds difficult because large demands on the active space.

High spin in the f-shell helps (ex: Gd_2, S=7).

Actinides

In principle: 5f,6d,7s active (13 orbitals).

But: actinides are often highly charged: only 5f active.

But: covalent bonding is not unusual. Example uranyl, UO_2^{2+}, which needs a 12in12 active space.

Beware: nothing is trivial in actinide chemistry.

The RASSCF State Interaction Method, RASSI (P.-Å. Malmqvist, 1986)

- Assume a set of RASSCF(CASSCF) wave functions have been computed.
- For each pair of wave functions, transform to a set of bi-orthonormal orbitals. Transform the corresponding CI wave functions to the new basis.
- It is now easy to compute transition density matrices (1- and 2-). Routinely used to compute transition dipole moments.
- Use them to compute the Hamiltonian matrix elements. Solve the CI problem.
- Can be used to mix many RAS(CAS) states (more than 200 have been used).

The RASSCF State Interaction Method with Spin-Orbit Coupling, RASSI-SO (P.-Å. Malmqvist et al., 2000)

- Perform CASSCF/CASPT2 calculations on the electronic states that are expected to interact via SO coupling.
- Set up the SO Hamiltonian using AMFI integrals and (eventually) CASPT2 energies. Compute the total interaction matrix with RASSI-SO.
- Diagonalize to obtain the final energies and wave functions.