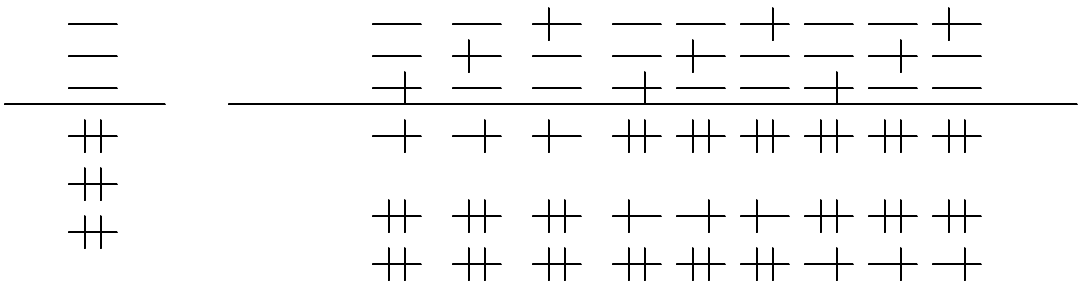
CIS = “Configuration Interaction Singles”



HF ground state → use these orbitals to do single excitation CI calculation on excited state

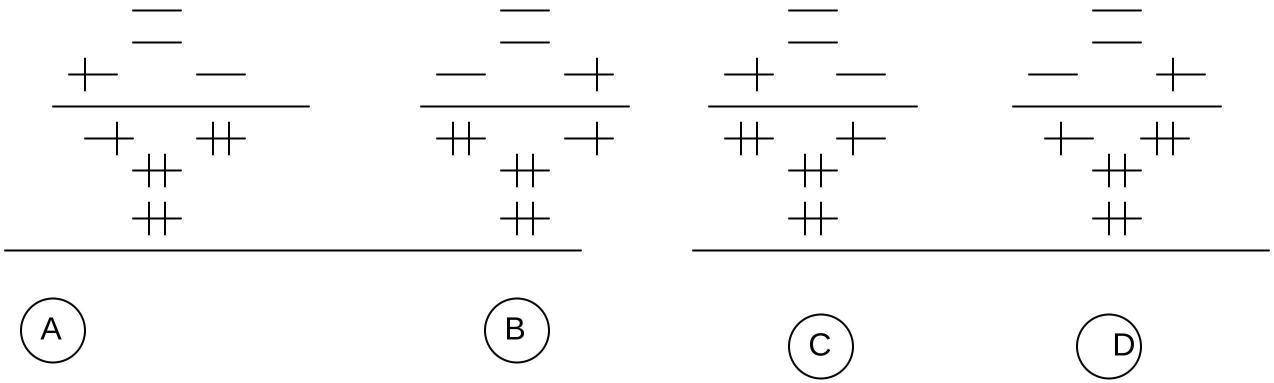
CIS is not really treating electron correlation

It is essentially an HF calculation on the excited state, allowing for single excitation degeneracies.

It properly handles spin in excited singlet states.

A ± B

Now consider benzene



degenerate

degenerate

Proper wavefunctions go like A ± B and C ± D

CIS properly handles this sort of degeneracy

CIS = singlets
triplets
root = N – root for geometry opt.
(default N = 1)
direct (if over 200 basis functions)

Nstates = M (default is 3)

CIS calculations give:

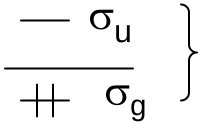
- excited state energies
- excitation energies
- transition moments ~ $|\langle 0|\tilde{r}|i\rangle|$
- oscillator strengths ~ $|\langle 0|\tilde{r}|i\rangle|^2$
- dipole moments, etc. (using density = current or density = all)

CASSCF (N, M)
- N = # electrons
- M = # orbitals

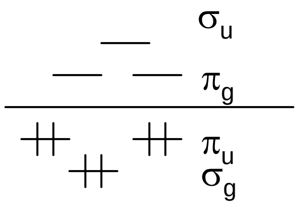
All arrangements
of N electrons
in M orbitals

Examples

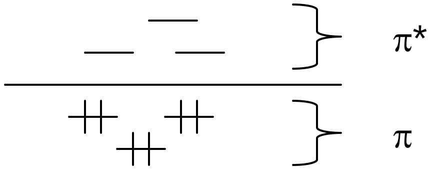
H_2 – CAS (2,2)



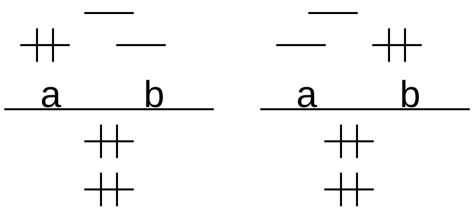
active space



N_2 – CAS(6,6)



Benzene – CAS (6,6)



← CAS(2,2) ← especially important for diradicals

$\psi = a^2 - b^2 = (L + R)^2 - (L - R)^2$

$= LF + RL$ ← two unpaired electrons singlet diradical.

Some “tricks” of CASSCF calculations

- Need correct orbitals occupied in initial guess (might need alter)
- #P to get eigenvalues and eigenvectors printed
- NROOT = 1 – optimize the ground state
- CASMP2 – add multireference MP2 correction to CASSCF
- stateguess = k – starting vector for Lanczos method
- Maximum # active orbitals = 12 (fairly expensive)
- Careful – does not use symmetry in setting up the CAS CI matrix

$$\psi = C_1 \left|1\sigma_g^2\right| + C_2 \left|1\sigma_u^2\right|$$

CASSCF – optimize orbitals + coefficients

lowest possible energy for this type of wavefunction

CI – Fix orbitals, vary coefficients

– Linear variational princ.

– Matrix eigenvalue problem

Full CI grows factorially

possible for only small systems, e.g., H_2O with 3-21G basis set

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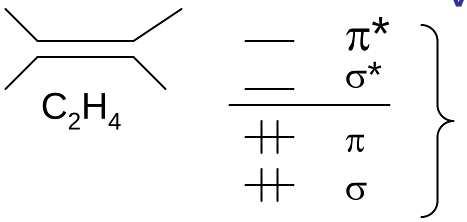
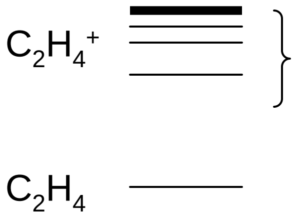
Valence *vs.* Rydberg states



$\sim 1/n^2$ progression → Rydberg series



$\pi \rightarrow \pi^*$, $\sigma \rightarrow \pi^*$, $\pi \rightarrow \sigma^*$
valence transitions

$\pi\rightarrow$3s, $\pi\rightarrow$4s, $\pi\rightarrow$5s,
$\pi\rightarrow$3p, $\pi\rightarrow$4p, $\pi\rightarrow$3d

Observations

- In some cases, lowest valence transitions below lowest Rydberg transitions
- But in some molecules, Rydberg states overlap low-lying valence states
- In fact, molecules such as H_2O, and CH_4 lack valence excited states.