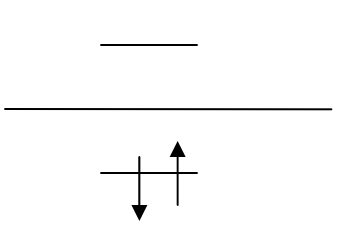
Orbital energies and excited states

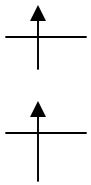


$\varepsilon_2 = \varepsilon_2' + 2J_{12} - K_{12}$

Sees both electrons in "1"

$\varepsilon_1 = \varepsilon_1' + J_{11}$

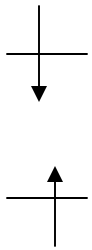
Virtual orbitals are appropriate for N+1 electron system (anion)



$E = \varepsilon_1' + \varepsilon_2' + J_{12} - K_{12}$

$= \varepsilon_1 + \varepsilon_2 - J_{11} - J_{12}$

$\Delta E = \varepsilon_2 - \varepsilon_1 - J_{12}$



$E = \varepsilon_1' + \varepsilon_2' + J_{12} + K_{12}$

$\varepsilon_1 + \varepsilon_2 - J_{11} - J_{12} + 2K_{12}$

$\Delta E = \varepsilon_1 - \varepsilon_2 - J_{12} + 2K_{12}$

Excitation energy = (orbital energy diff.) + (coul./exchange) + relaxation + correlation energy

CIS with two orbitals neglects relaxation + correlation

readwindow (RW) keyword

Generalized valence bond (GVB)

Goddard and co-workers.

A restricted type of MCSCF

Consider a water molecule and call the two occupied localized OH orbitals L and R

GVB w.f.: …..$(c_1L^2 + c_2\ L^{*2})(c_3R_2 + c_4R_2^{*2})$

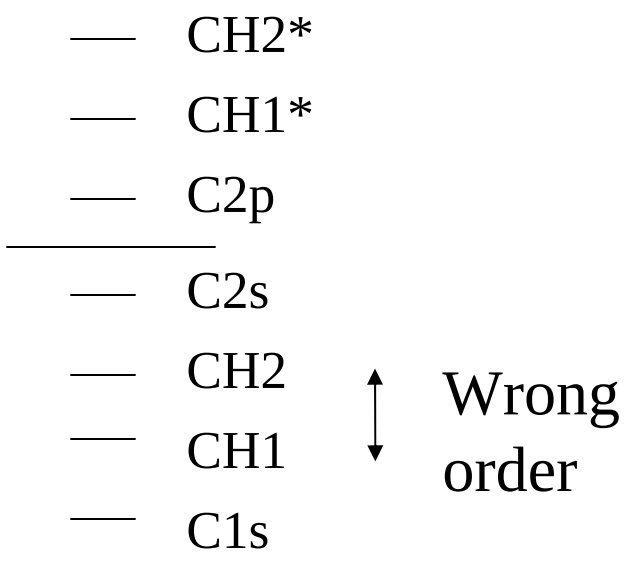
L* and R* are antibonding orbitals associated with the two bonds

If you plan to use GVB, read the G03 documentation carefully

```
# GVB(3)/6-31G(d) guess=(local, lowsymm, alter) pop=full test

GVB on CH2

**********

1 4 0 2 3 9      lowsymm info – mix (1,4) and mix (2,3)

2 3              alter info – switch order of orbitals


222              GVB info – three pairs, two orbitals each
```

G03 orders the symmetry A_1, A_2, B_1, B_2

Lowsymm drops the symmetry from C_{2v} to C_s



Guess=(local, only)

to check guess

Symm=noscf

to remove all symmetry

GVB=OSS (open shell singlet)

High-spin orbitals

Jaguar- has GVB-LMP2 capabilities.

Software at Pitt/CMMS

Gaussian 03 – HF, DFT, MP2, CASSCF, CASMP2, CCSD

Turbomole – DFT, RIMP2, RI-CC2

Spartan – HF, DFT, MP2 (more capabilities in latest release)

GAMESS – HF, DFT, MP2, CASSCF, CI, MR-MP2, QM/MM

MOLPRO – HF, DFT, MP2, LMP2, CCSD, CASSCF, CI, CASMP2, CASMP3

MOLCAS – HF, MP2, CCSD, CI, CASSCF, CASMP2

NWCHEM – HF, DFT, MP2, coupled cluster, Classical MD

- Highly parallel

Jaguar – pseudospectral HF, GVB, DFT, LMP2, GVB-LMP2

- Very fast, uses relative little disk