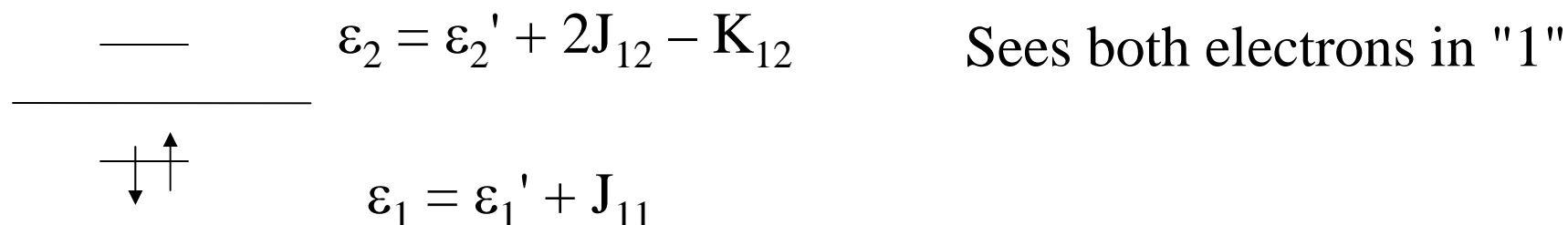
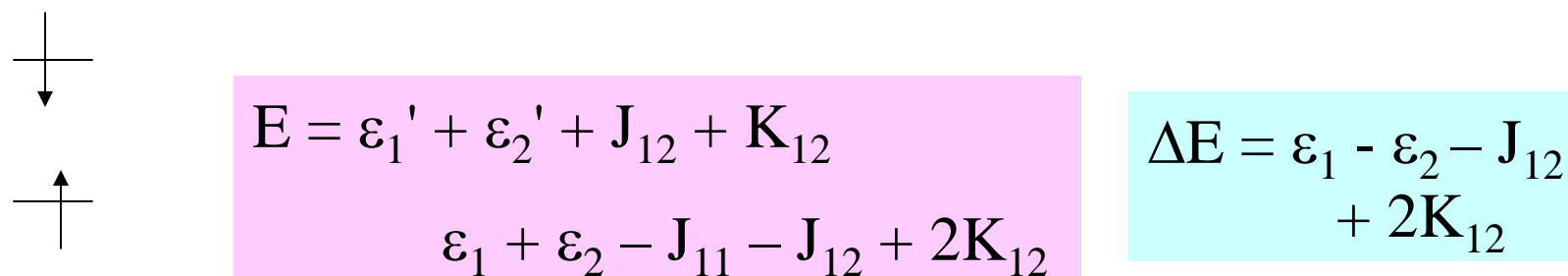
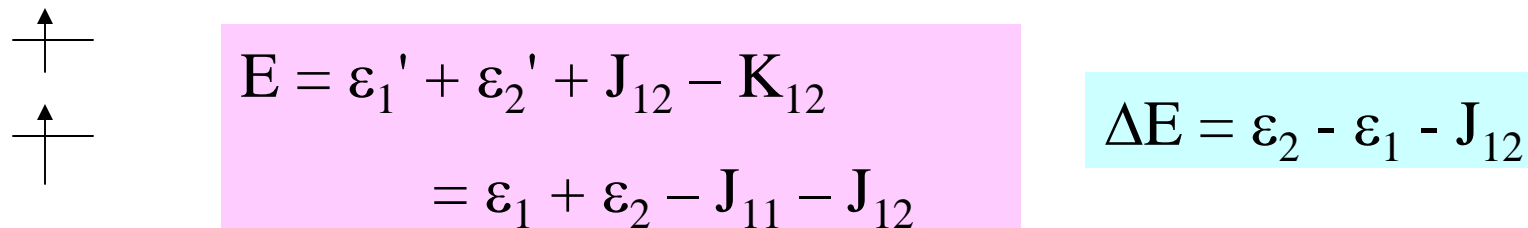


## Orbital energies and excited states



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



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  $C_s$

— CH2\*  
— CH1\*  
— C2p  
————  
— C2s  
— CH2  
— CH1  
— C1s

↑ Wrong  
↓ order

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