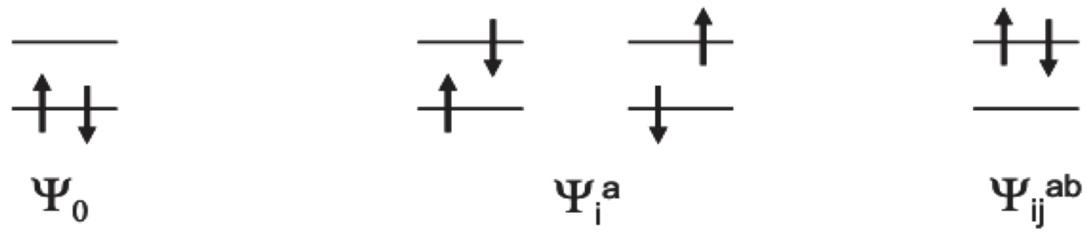
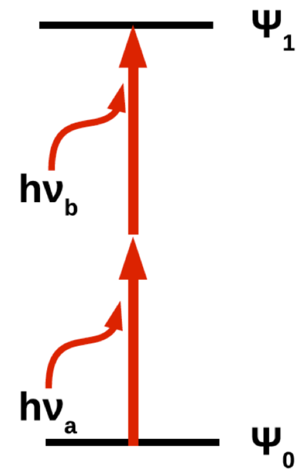
# EOM-EE calculation of 2PA (butadiene)

**EOM-EE:** $\Psi(M_s=0) = R(M_s=0)\Psi_0(M_s=0)$



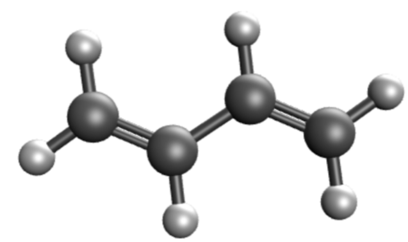

**Two-Photon Absorption**

**Example:** EOM-EE/6-31+G* calculations of 2PA cross-sections

2PA transition probability and selection rules are different from 1PA probability. The calculation involves computing initial and final states and calculation of the cross section

Trans-butadiene has C2h point group. Ag, Bg, Au, Bu irreps.

Ag transitions are dark in 1PA but bright in 2PA



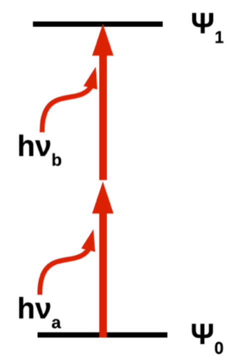
**Exercise:** Compute 4 excited states of Ag symmetry and their 2PA cross-sections. Assign state characters. Which state is the brightest in 2PA?

# EOM-EE calculation of 2PA (butadiene)

- Import geometry (butadiene.xyz) into IQmol
- Use singlet reference (charge=0, multiplicity=1)
- Request 5 singlet states of Ag symmetry using EE_SINGLETS
- Request 2PA calculation: CC_EOM_2PA = 1 (set manually in IQmol)
- Look at the EOM amplitudes and MOs to assign state character
- Summarize excitation energies and 2PA cross sections (report parallel cross-section):

'2PA cross section for parallel linearly polarized light:
sigma_par = 2*del_f + 2*del_g + 2*del_h = 1.058690e+03 a.u.'

- Assign state characters by looking at leading amplitudes and respective MOs



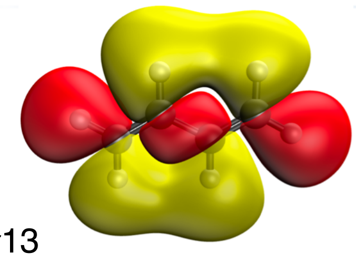

Two-Photon Absorption

```
$rem
   JOBTYPE = SP
   GUI = 2
   METHOD  = EOM-CCSD
   EE_SINGLETS =    [5,0,0,0]
   BASIS =  6-31+g*
   CC_EOM_TRANSITION_PROPERTIES = 1
   CC_EOM_2PA = 1
$end
```

**Note:** One can also compute 2PA Natural Transition Orbitals that reveal the nature of the "virtual state". For large systems, 2PA calculations can be performed with Cholesky decomposition and in single precision.

# EOM-EE 2PA of butadiene

| State | $E_{ex}$, eV | MOs | Sigma (par), a.u. |
|---|---|---|---|
| 1Ag | 7.18 | 1bg(#15)-2bg(#21) | 1.06E+03 |
| 2Ag | 8.24 | 1au(#14)-2au(#18) | 1.42E+02 |
| **3Ag** | **9.02** | **1bg(#15)-3bg(#25)** | **2.01E+03** |
| 4Ag | 9.90 | 7ag(#13)-8ag(#16) | 1.77E+02 |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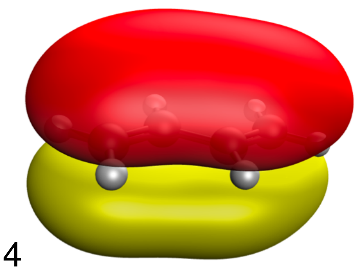
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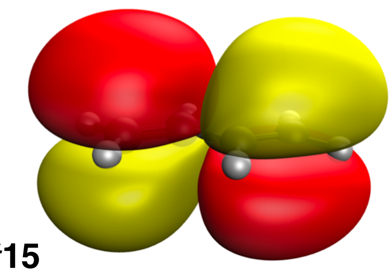
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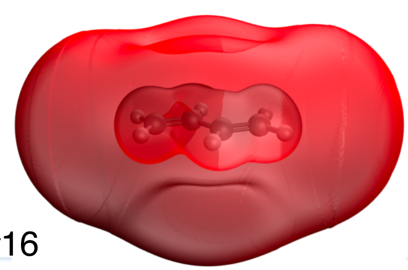
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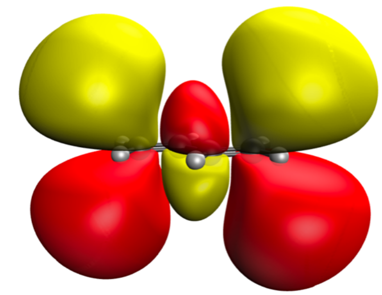
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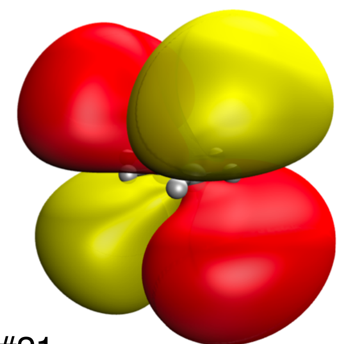
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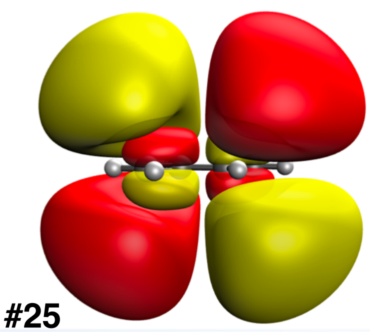
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