Electronic, Vibrational, and Spin Structure of Excited States

Molecular Photochemistry

CHEM 4801

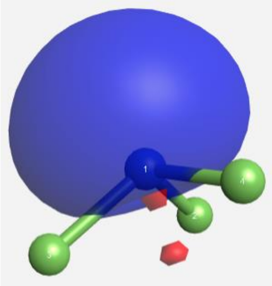
Natural Bond Orbital (NBO) Descriptions of Electrons in Organic Molecules

Electronic, Vibrational, and Spin Structure of Excited States

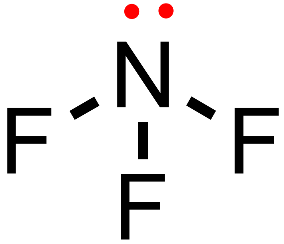
Shapes and Lewis Structural Elements

Every natural bond orbital corresponds to a visible element of Lewis structures.

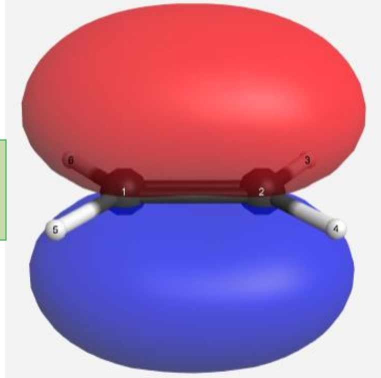
Electron Sources

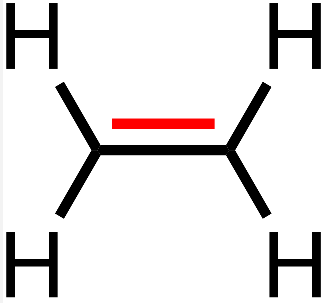


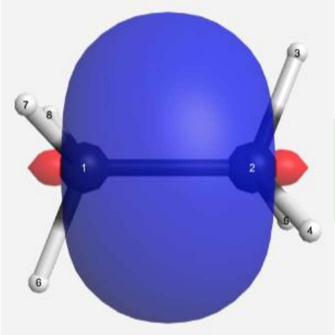
nonbonding lone pair (*n*)



pi bond (*π*)



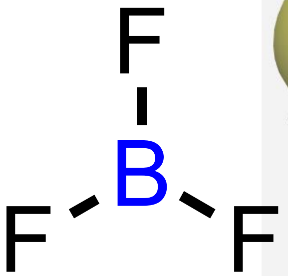


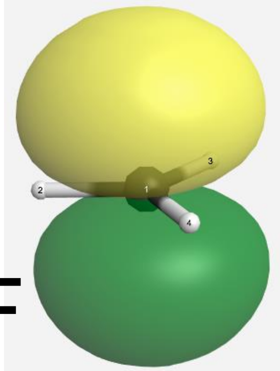


sigma bond (*σ*)

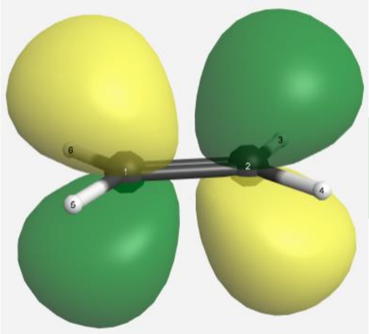
$H_3C{-}CH_3$

Electron Sinks

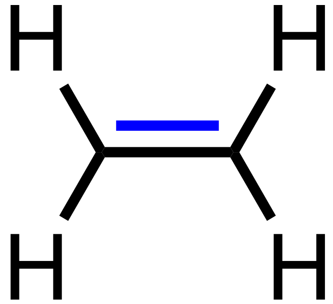




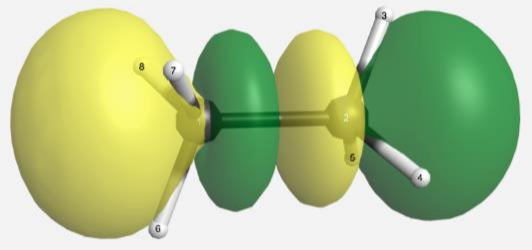
empty 2*p* orbital (*a*)



pi antibond (*π**)



$H_3C{-}CH_3$

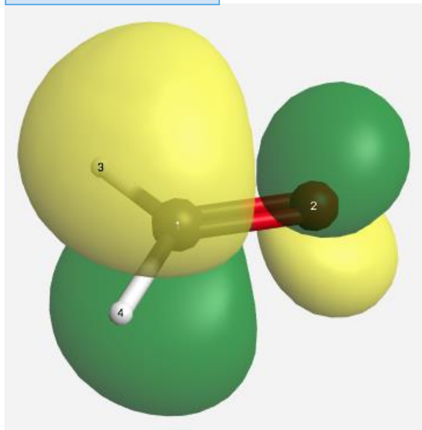


sigma antibond (*σ**)

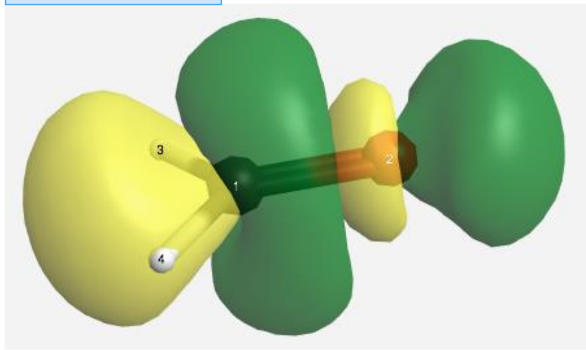
NBOs for Polarized Bonds

Filled NBOs are polarized toward the more electronegative atom in the bond.
Empty NBOs are polarized toward the less electronegative atom in the bond.

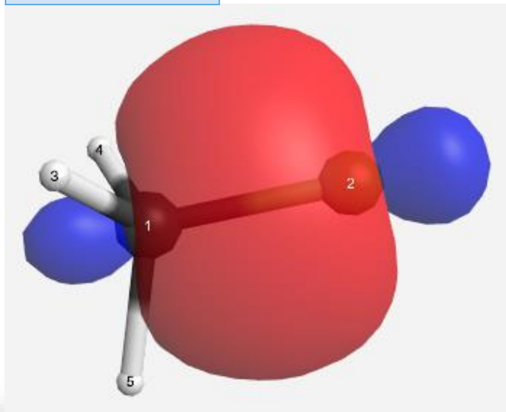
$\pi^*_{C=O}$



$\sigma^*_{C=O}$



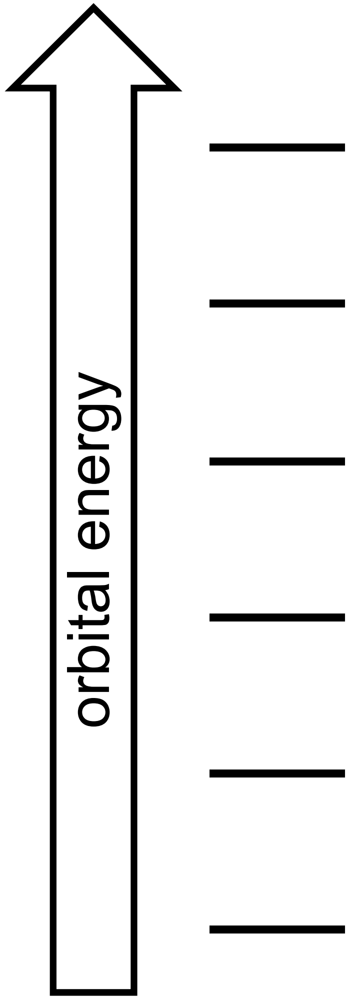
σ_{C-F}



```
  (Occupancy)   Bond orbital/ Coefficients/ Hybrids
 ---------------------------------------------------------------------------------
 1. (1.99932) BD ( 1) C   1 - F   2
              ( 26.38%)   0.5136* C   1 s( 19.94%)p 4.00( 79.68%)d 0.02(  0.39%)
                                        -0.0001 -0.4442  0.0450  0.0061  0.0000
                                        -0.0000 -0.0000  0.0000 -0.8912 -0.0509
                                        -0.0000 -0.0000  0.0000  0.0000 -0.0623
              ( 73.62%)   0.8580* F   2 s( 29.72%)p 2.36( 70.10%)d 0.01(  0.18%)
                                         0.0000 -0.5452 -0.0003 -0.0014  0.0000
                                         0.0000  0.0000  0.0000  0.8372  0.0024
                                         0.0000  0.0000  0.0000  0.0000 -0.0425
```

Trends in Relative Energies of NBOs

Within a particular molecule, NBOs tend to increase in energy as follows: σ, π, n, a, π^*, σ^*.
Highest occupied MOs (HOMOs) tend to be n, while lowest unoccupied MOs (LUMOs) tend to be a.



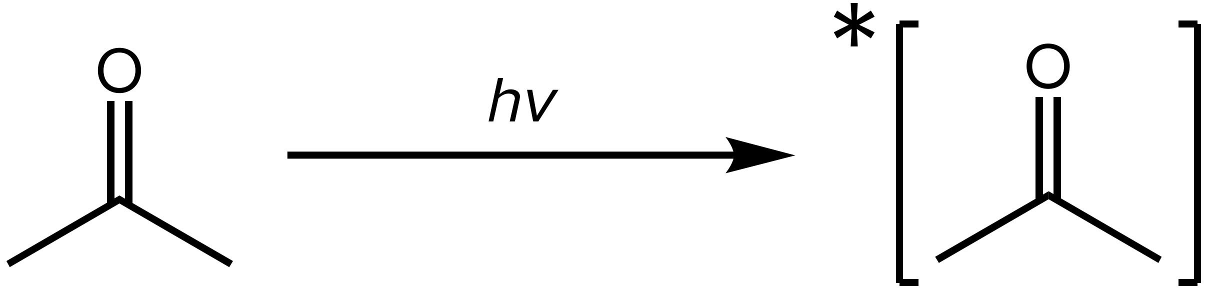
Beware delocalization effects!

Excitation as Electron Promotion

Electronic, Vibrational, and Spin Structure of Excited States

NBO Descriptions of Excited States

We can briefly describe an excited state using its half-filled NBOs. The lower-energy orbital is typically listed first. This assumes minimal structural change from the ground state and no mixing of NBOs.



$n \longrightarrow \pi^*$ excitation

$\pi \longrightarrow \pi^*$ excitation

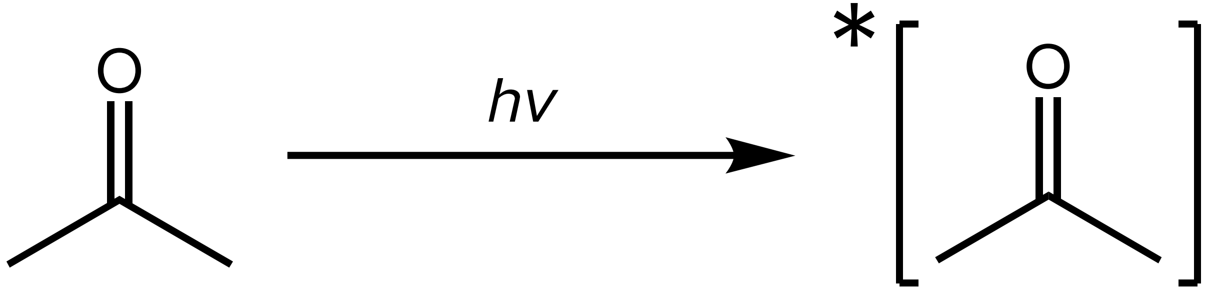
Enhancement of Redox Reactivity

Excited states are *both* stronger reductants *and* stronger oxidants than their corresponding ground states. This paradoxical result is easily understood using the electron promotion picture of excitation.

Ground state	Excited state
LUMO	SOMO (H)
HOMO	SOMO (L)

Lewis Structures of Excited States

We can work backwards from an NBO description of an excited state to its ***natural Lewis structure (NLS)*** based on the shapes and occupancies of the NBOs.



(n,π^*) state

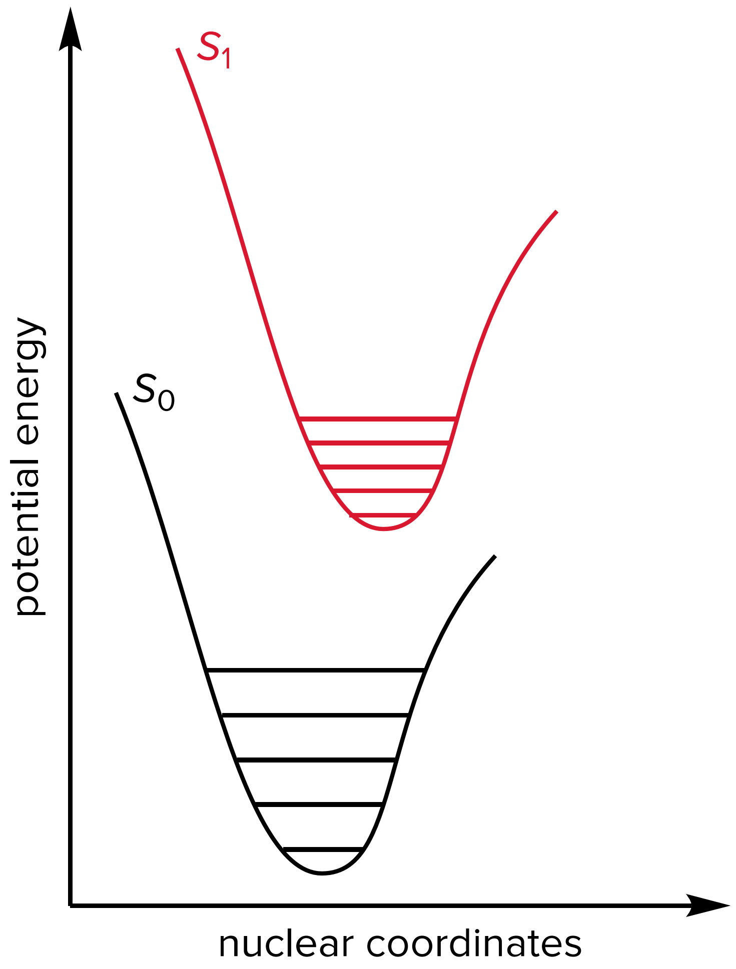
(π,π^*) state

Vibrational Structure of Excited States

Electronic, Vibrational, and Spin Structure of Excited States

Excited States Have Vibrational Modes

Vibrational relaxation in excited states is generally very rapid. Conversion of an excited state into a “hot” vibrational level of a lower state (or *vice versa*) is called ***internal conversion***.

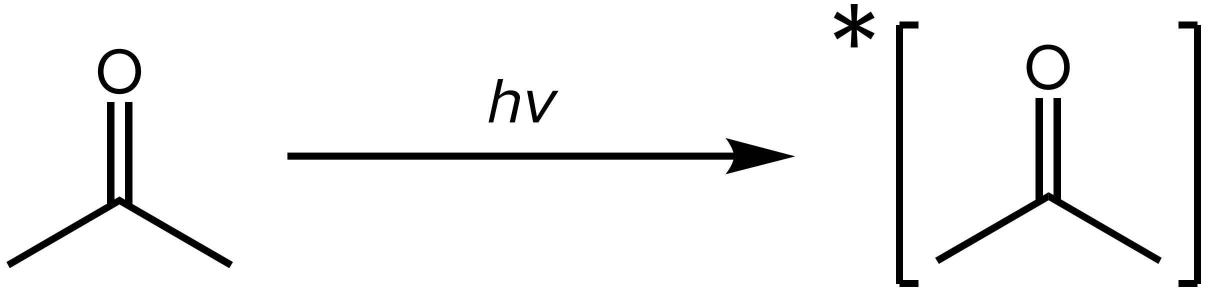


A Vectoral Model for Electron Spins

Electronic, Vibrational, and Spin Structure of Excited States

Singlet and Triplet States

Singlet states have net zero total spin and unpaired electrons with opposing spins. *Triplet* states have unpaired electrons with parallel spins and three magnetic "sub-states" (more soon).

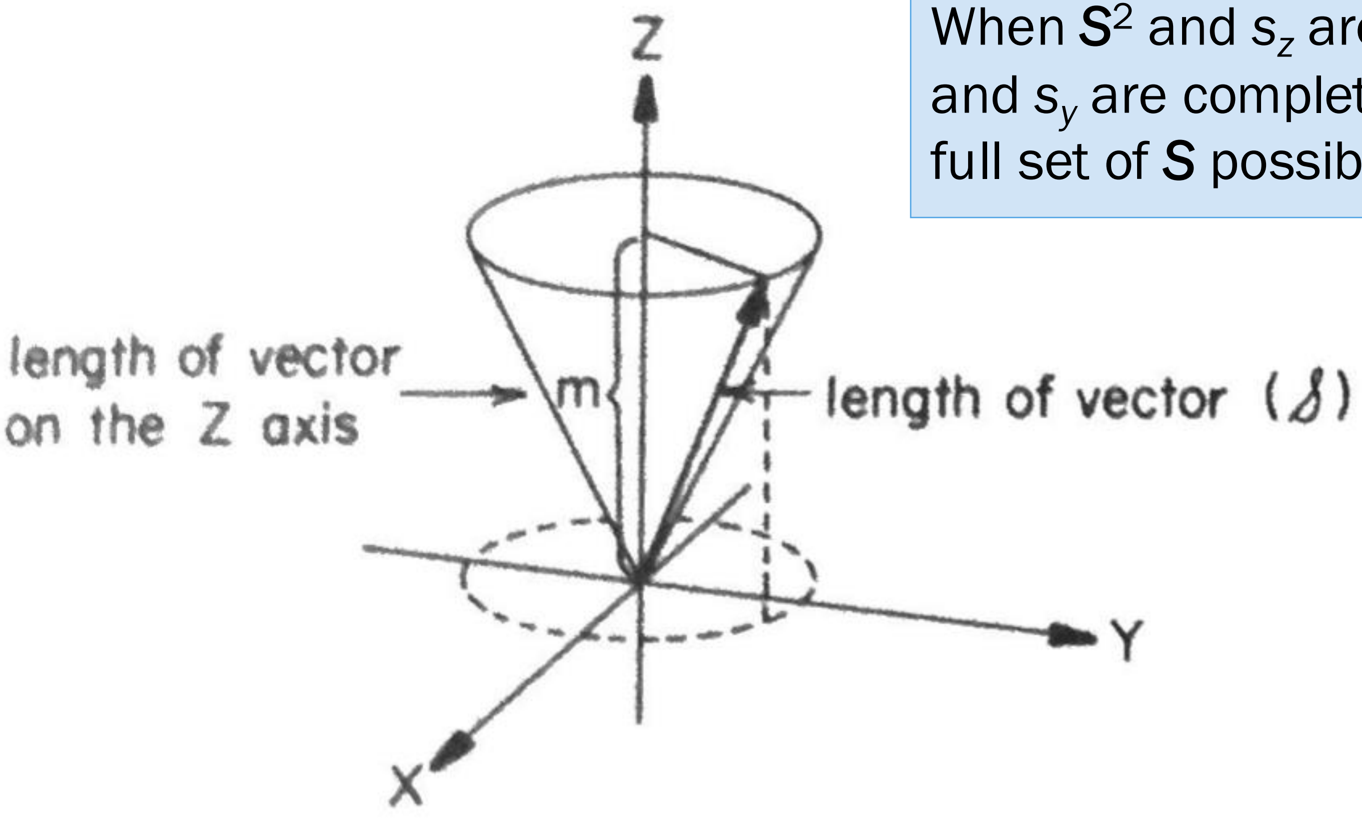


$^1(n,\pi^*)$ $^3(n,\pi^*)$ $^1(\pi,\pi^*)$ $^3(\pi,\pi^*)$

Electron Spin as a Vector

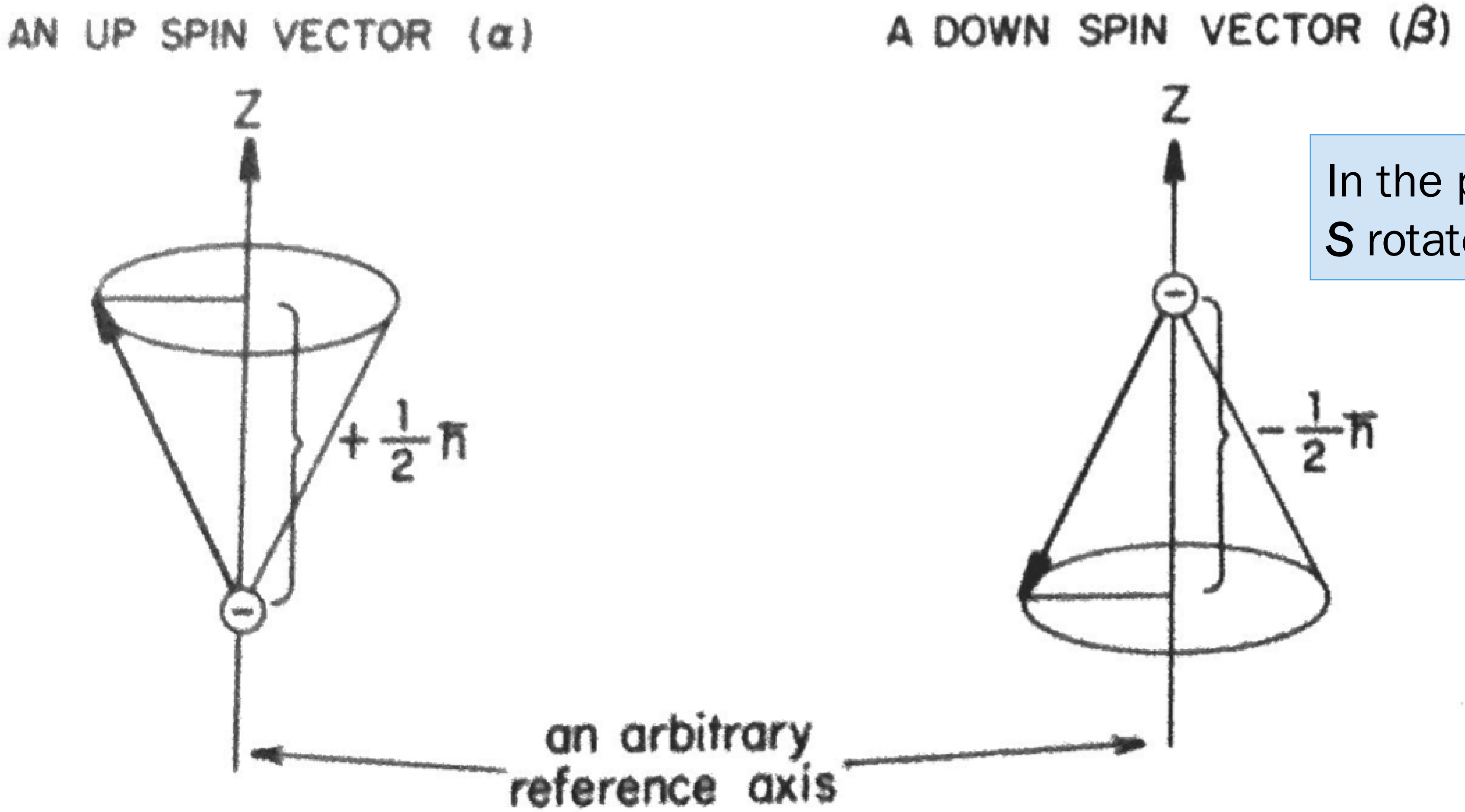
Elementary descriptions of spin consider only its *z* component. However, spin behaves as a vector with components in all three directions.

When $\boldsymbol{S}^2$ and s_z are known with certainty, s_x and s_y are completely uncertain. Thus, the full set of $\boldsymbol{S}$ possibilities sweeps out a cone.



“Up” and “Down” Spins as Vectors

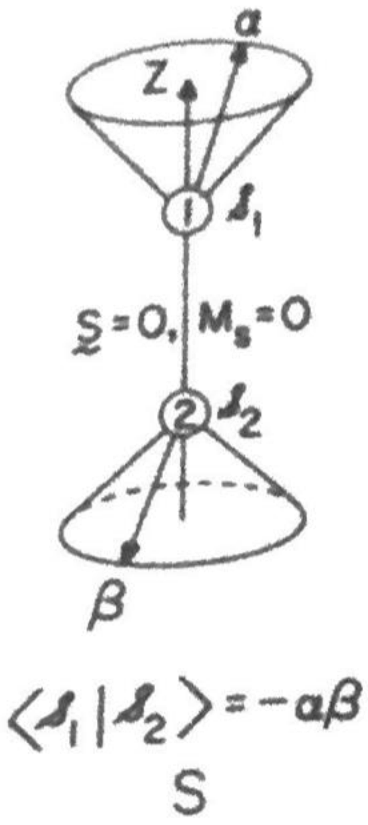
↑ and ↓ electron spins sweep out cones pointing in opposite directions.
The z component may be +1/2 or –1/2 in units of $h/2\pi$.

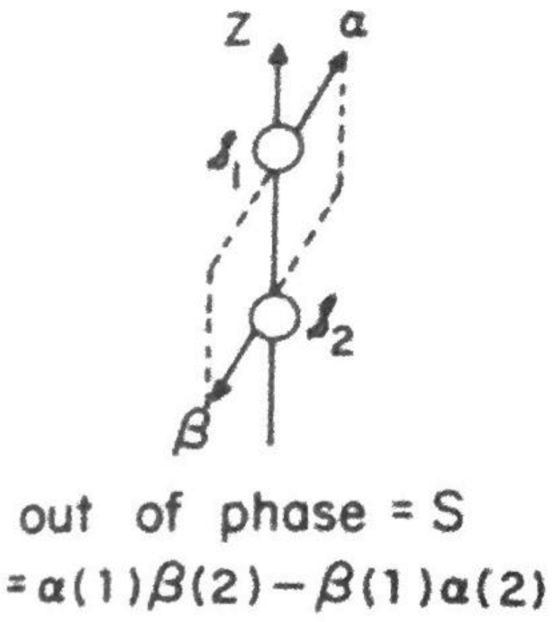


In the presence of a magnetic field *S* rotates about the axis of the field.

The Singlet State

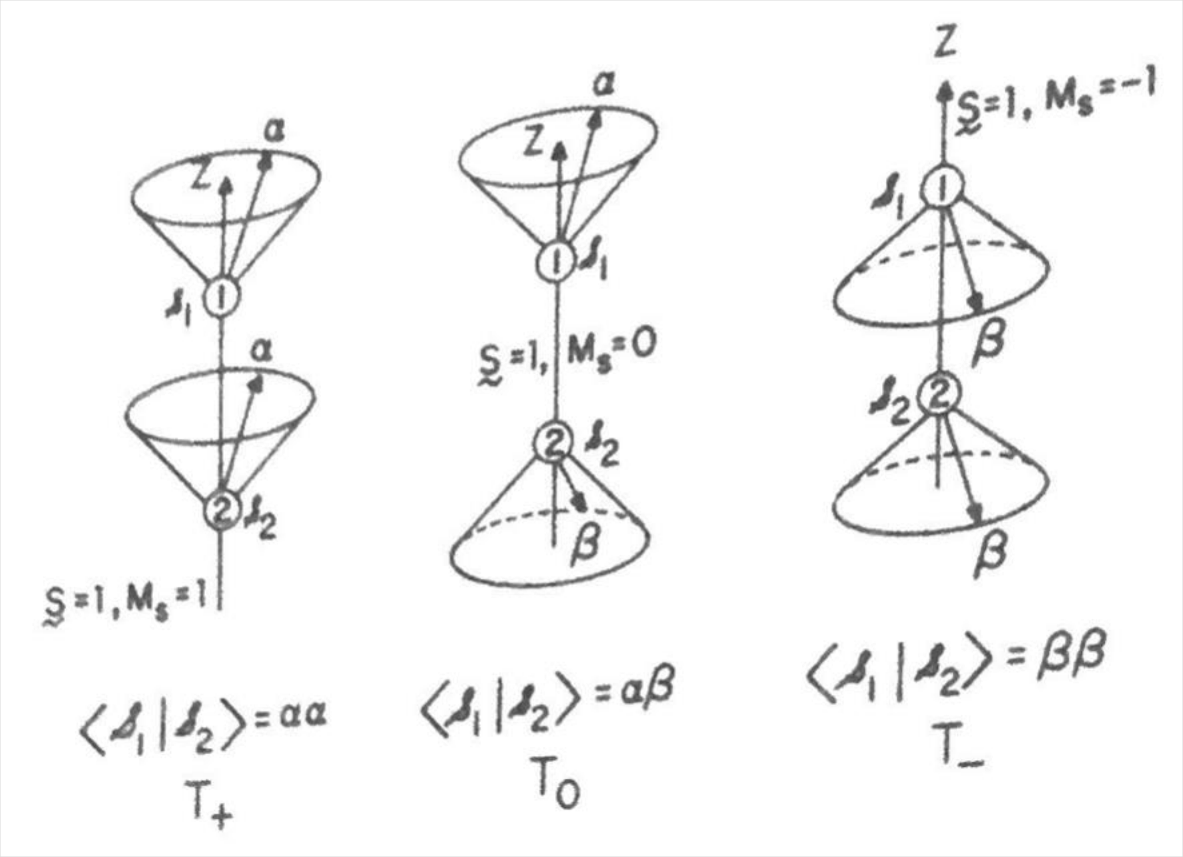
In the singlet state, the unpaired electron spins are exactly antiparallel so that their resultant is *S* = 0. There is only one way this result can be achieved.

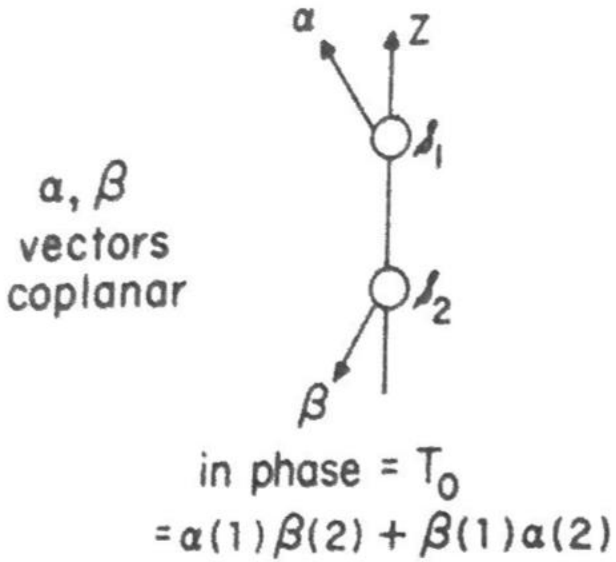




The Triplet State

In the triplet state, the unpaired electron spins are aligned so that their resultant is S = 1. There are three ways this can be achieved, with s_z = +1, 0, or –1.





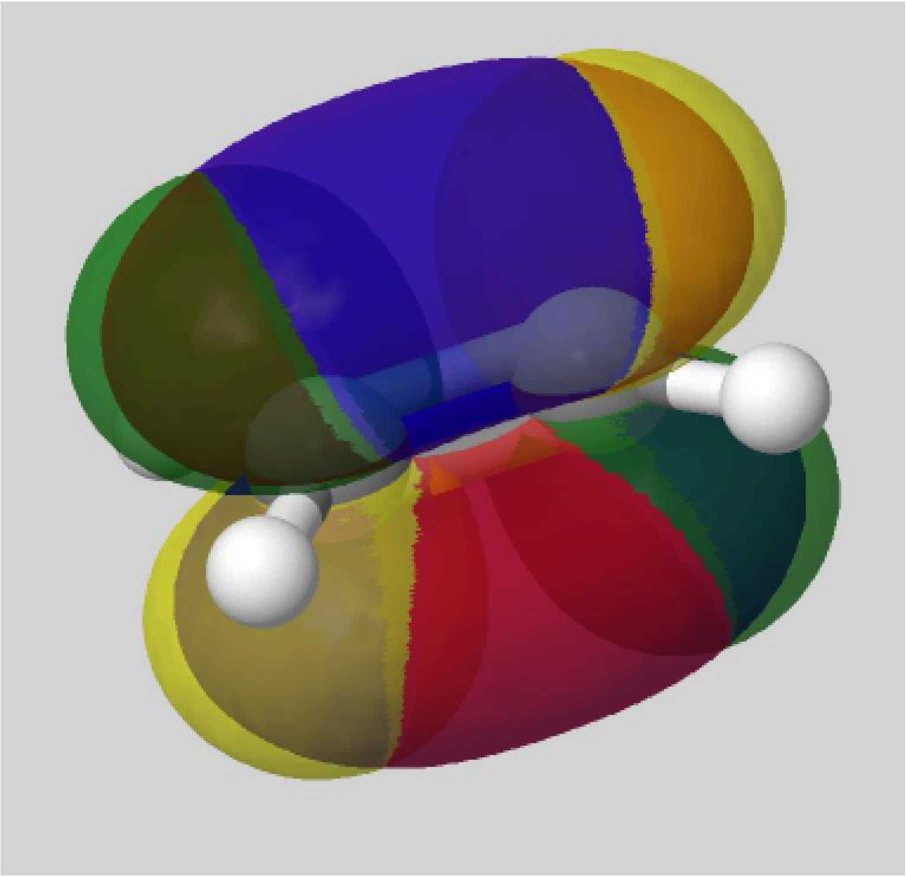
Energy Differences Between Singlet and Triplet States

Electronic, Vibrational, and Spin Structure of Excited States

Correlated Electron Motion in S and *T* States

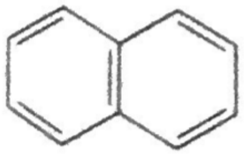
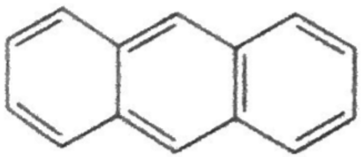
In a triplet state, electrons with identical spin "avoid" one another due to the Pauli principle. Greater distance between triplet electrons leads to reduced *e-e* repulsion in the triplet state.

Exchange interaction



Examples of ΔE_{ST}

Table 2.1 Singlet-Triplet Splittings

Molecule	Configuration ($S_1 - T_1$)	ΔE ($S_1 - T_1$) in kcal/mole
$CH_2{=}CH_2$	π, π^*	70
	π, π^*	40
	π, π^*	35
	π, π^*	30
$CH_2{=}O$	n, π^*	10
$(CH_3)_2C{=}O$	n, π^*	7
$Ph_2C{=}O$	n, π^*	7

Overlap of SOMOs and ΔE_{ST}

The greater the overlap between the singly occupied MOs in an excited state, the larger the magnitude of ΔE_{ST} due to stronger exchange interaction J.