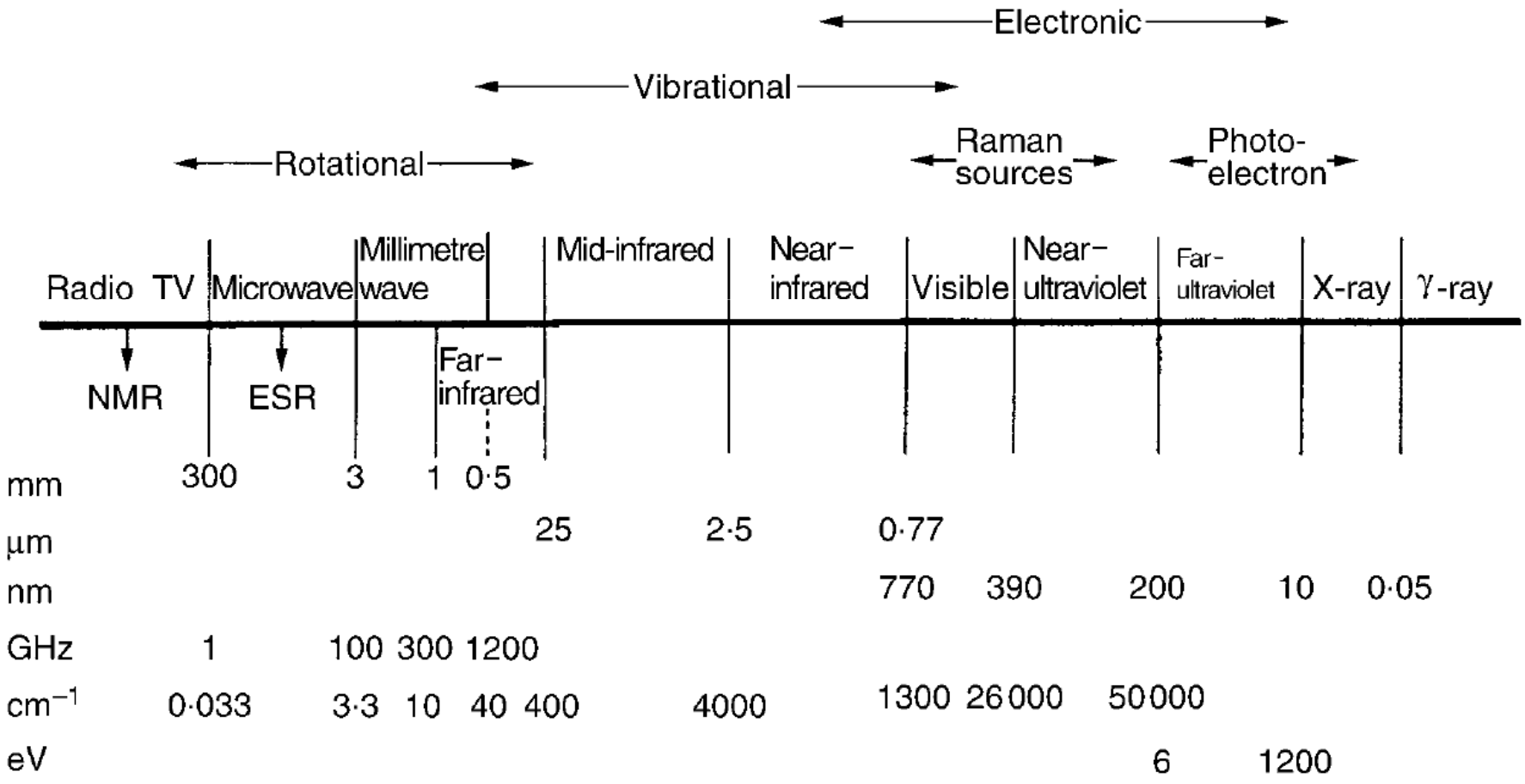
Molecular electronic spectroscopy



The states of diatomic molecules: The Hund coupling cases

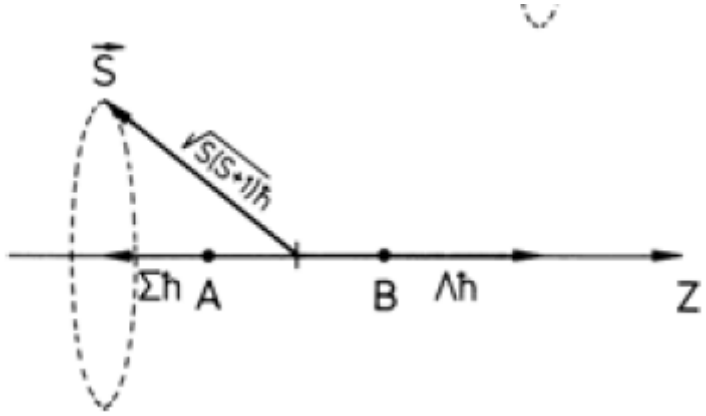
Three sources of angular momentum in a diatomic molecule:

•electron orbital angular momenta L: $\sqrt{L(L+1)}\hbar$ (1)

•the spin of the electrons S: $[S(S+1)]^{1/2}\hbar$ (2)

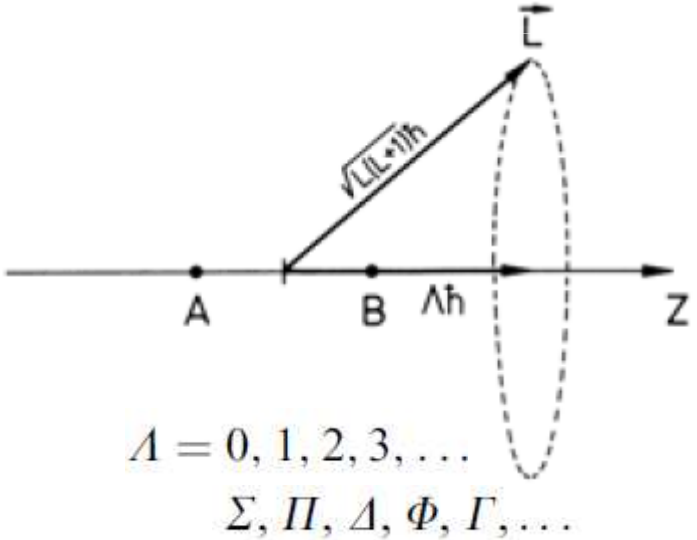
•rotation of the nuclear framework R

Total angular momentum J



$\Sigma = S, S-1, \ldots, -S$

Multiplicity: 2S+1



$\Lambda = 0, 1, 2, 3, \ldots$

$\Sigma, \Pi, \Delta, \Phi, \Gamma, \ldots$

$\Lambda > 0$: double degenerate

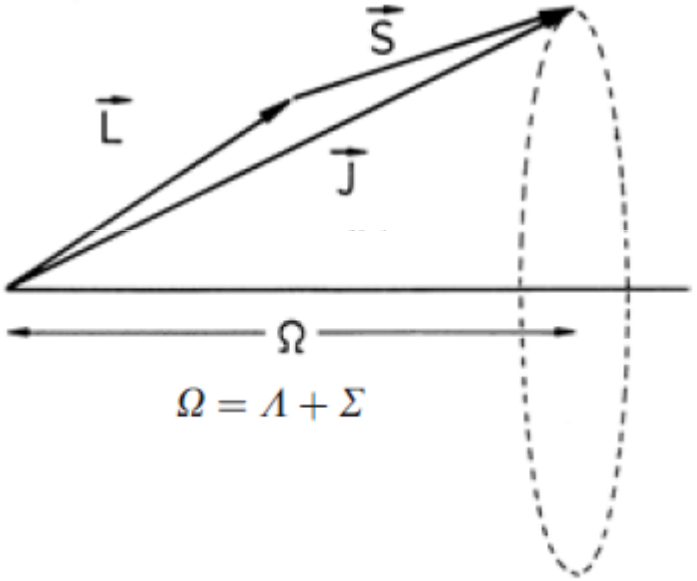
one-electron orbital momentum l_i

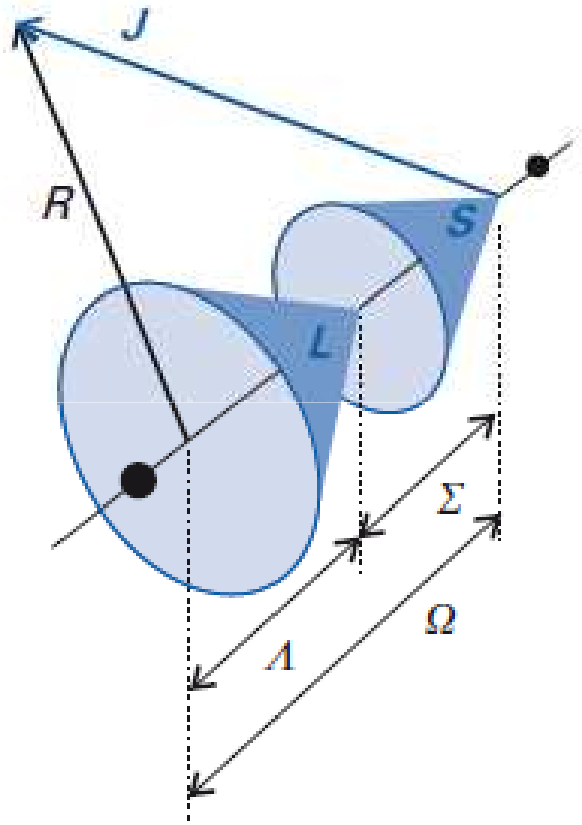
$l_{iz} = \pm\lambda_i\hbar$

λ :	0	1	2	3
Symbol :	σ	π	δ	φ

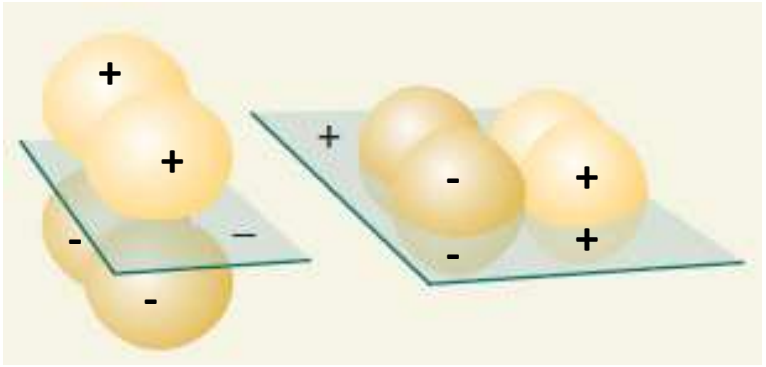
$\Lambda = |\Sigma\lambda_i|$ (3)

The Hund coupling case a





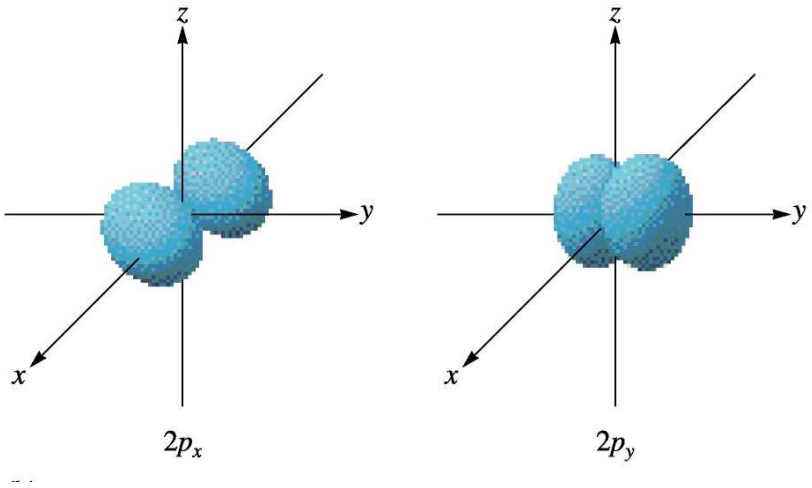
Term symbols



multiplicity $^{2S+1}\Lambda^{(+/-)}_{\Omega(g/u)}$ symmetry

parity

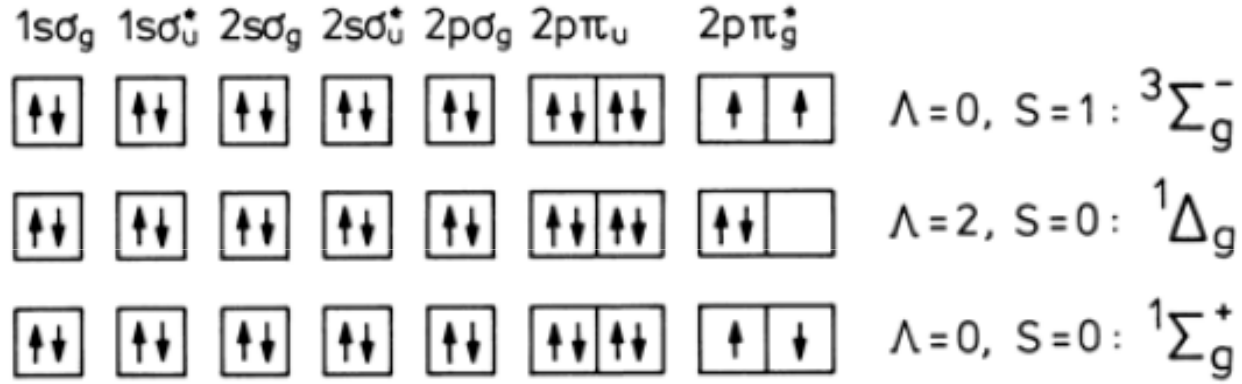
Ex: O_2 molecule $^3\Sigma_g^-$

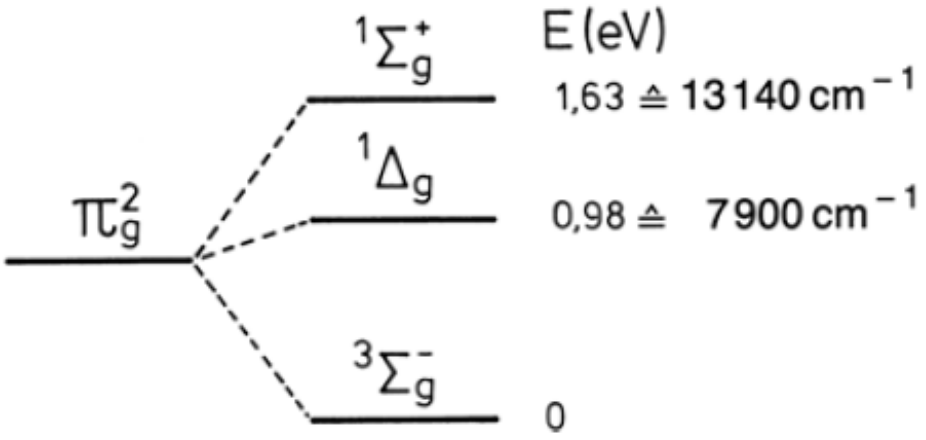


The energies:

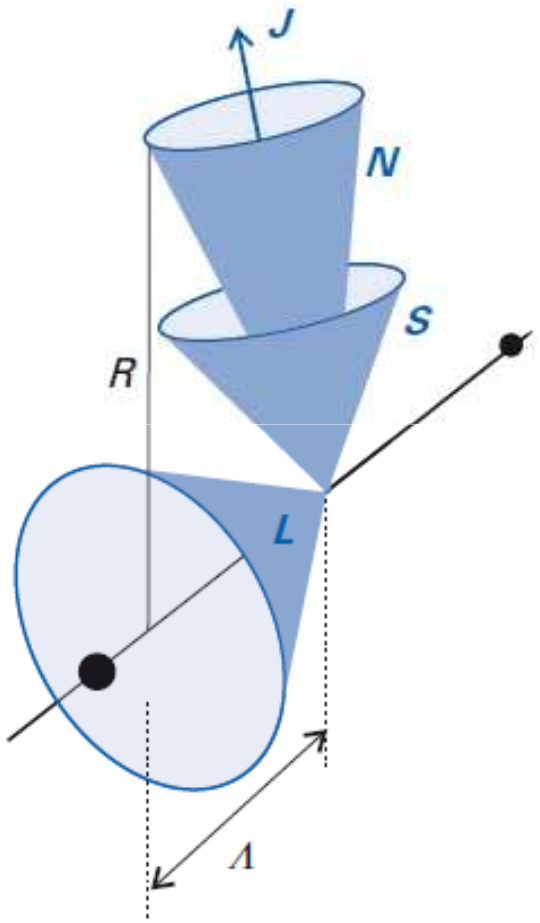
1. Pauli principle
2. The term with the maximum multiplicity lies lowest in energy.
3. For a given multiplicity, the term with the highest value of Λ lies lowest in energy.

Ex: O_2 molecule



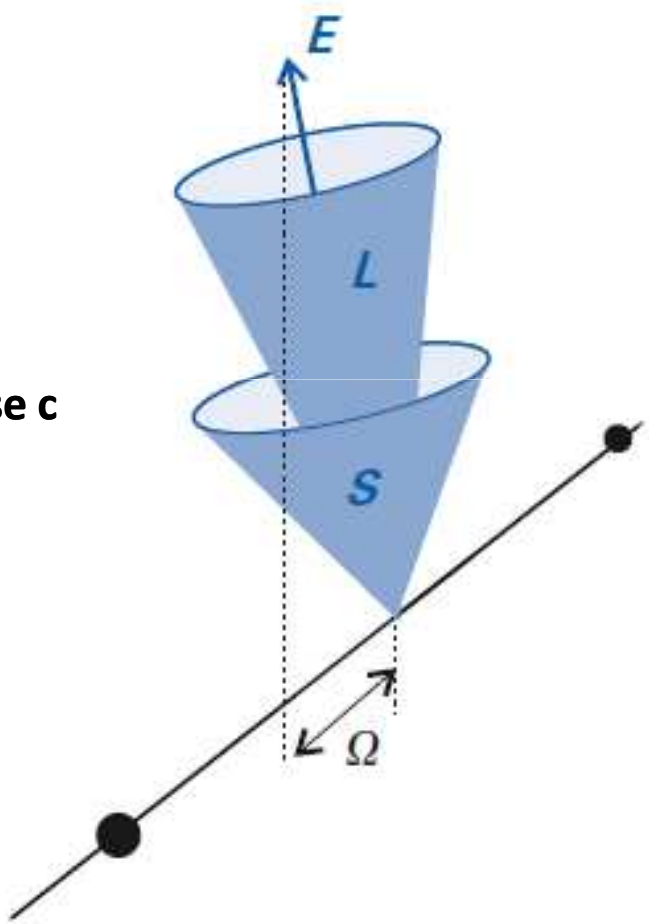


The Hund coupling case b

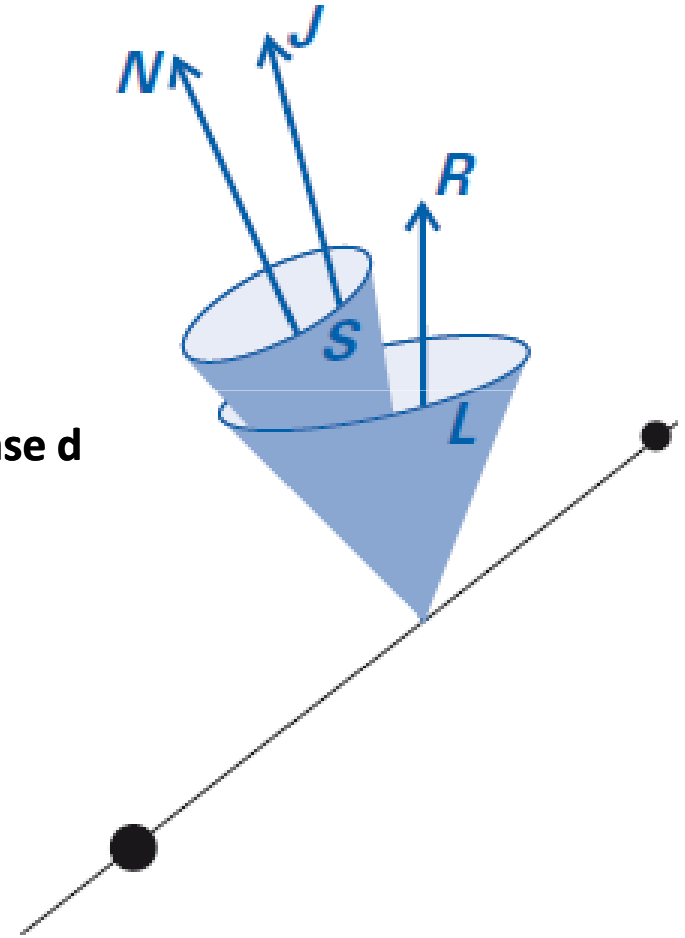


The Hund coupling case c and d

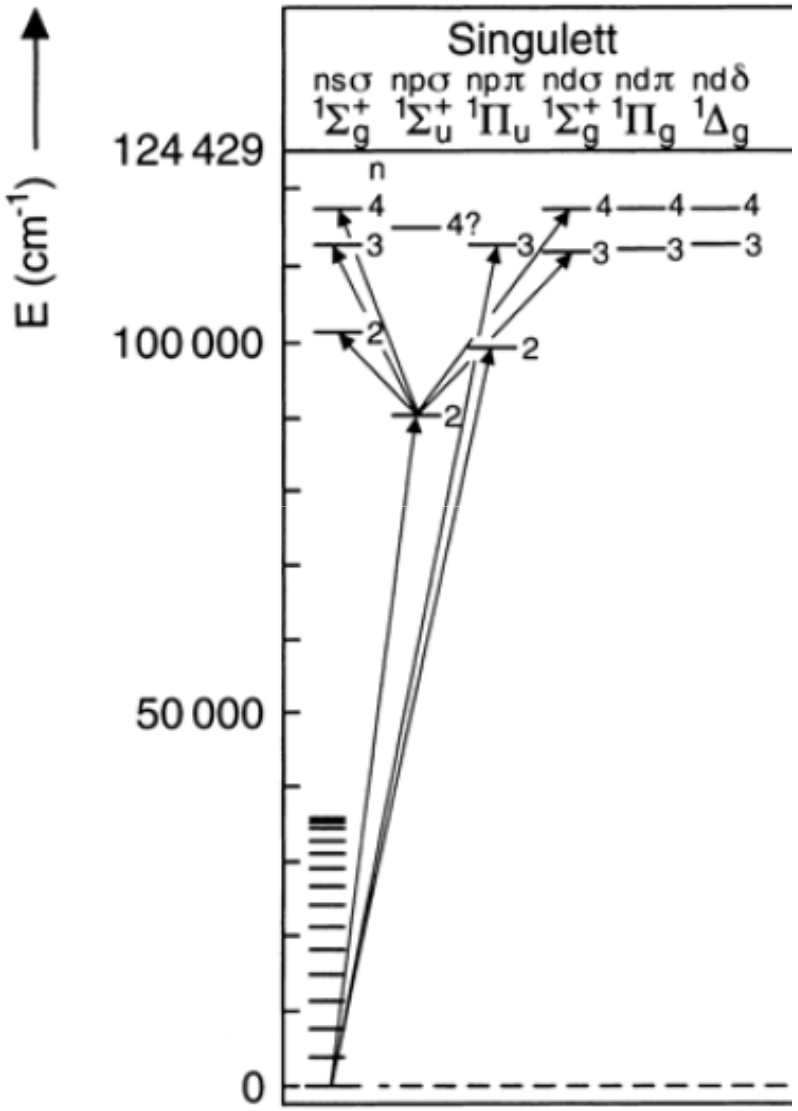
case c



case d



Electronic terms of the H_2 molecule (singlet)

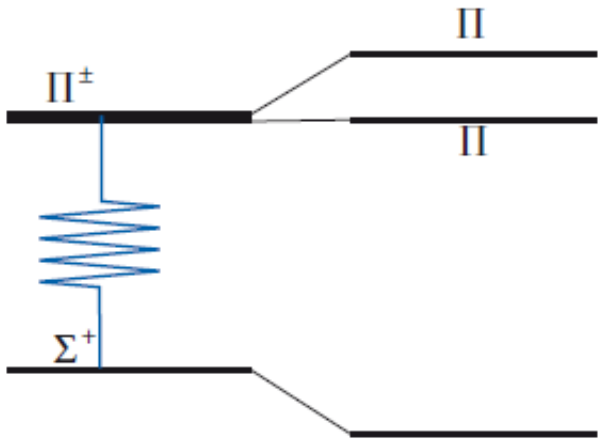


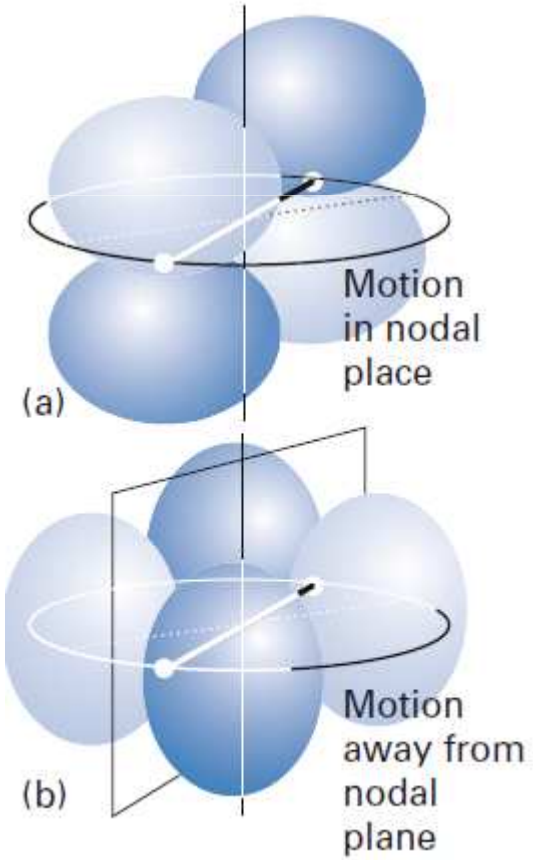
Decoupling and Λ-doubling

Correct scheme: $\left\langle n_i, \Lambda_i, S_i, \Omega_i, v_i \middle| \hat{H}' \middle| n_j, \Lambda_j, S_j, \Omega_j, v_j \right\rangle$: minimum (0), i ≠ j

Decoupling: the tendency of one coupling scheme to be contaminated by another.

Electron slip: $C_2\ (1\sigma_g^2\, 1\sigma_u^2\, 1\pi_u^3\, 2\sigma_g^1\, {}^1\Pi_u)$





Second order perturbation theory:

$$\Delta E^{(2)} = \frac{2(hcB)^2 L(L+1)J(J+1)}{E(\Pi) - E(\Sigma_g^+)}$$

Selection rules

Changes in the angular momentum:

$$\Delta\Lambda = 0, \pm 1 \qquad \Delta S = 0 \qquad \Delta\Sigma = 0 \qquad \Delta\Omega = 0, \pm 1 \tag{4}$$

Changes in symmetry:

$$\Sigma^+ \rightarrow \Sigma^+, \Sigma^- \rightarrow \Sigma^- \tag{5}$$

$$\mathrm{g} \rightarrow \mathrm{u} \text{ but not } \mathrm{g} \rightarrow \mathrm{g}, \mathrm{u} \rightarrow \mathrm{u} \tag{6}$$

Allowed $\mathrm{g} \rightarrow \mathrm{g}$ and $\mathrm{u} \rightarrow \mathrm{u}$: **vibronic transitions**