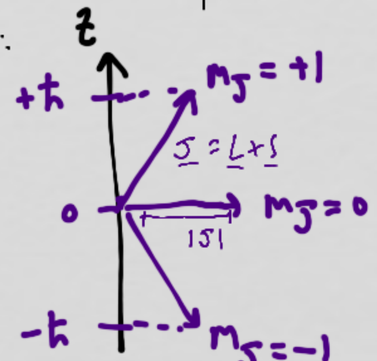
Degeneracy in Molecular Term Symbols

- Note in atoms, $2S+1$ degeneracy arises from $2S+1$ possible projections of $\vec{S}$ onto the space-fixed axis:



- But, in molecules we do not define projections this way. Instead we project to the internuclear axis:

this is ∵ $\vec{S}$ is not a good quantum # when the system is not spherically symmetric

↓

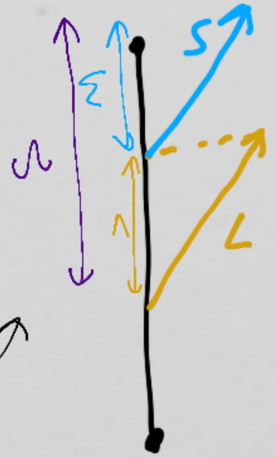
$\hat{S}$ does not commute with $\hat{H}$ in this case

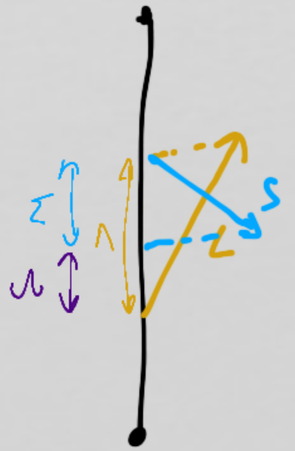
see Zare "Angular Momentum" p. 66 :)

$\rightarrow \Omega = |\Lambda + \Sigma|$

- So, there is no analogue of $\vec{S}$, only of m_S (Ω). So cannot specify the # of projections with $2S+1$. Instead, for given Λ, specify the possible values of Σ. $\Sigma = S, S-1, \ldots |-S|$ ← $2S+1$ values of Σ.

- So, the number of states in a given term (the degeneracy) $= 2S+1$





For a fixed Λ, i.e. in a $^2\Pi$ state $g = 2S+$