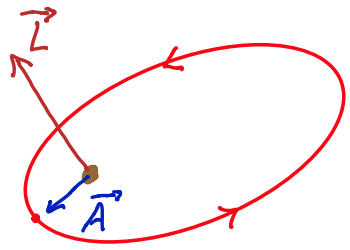
Coulomb degeneracy



Classical Laplace-Runge-Lenz vector

$\vec{A} = \vec{p} \times \vec{L} - m e^2 \hat{r}$ $\quad |\vec{A}|$ = eccentricity

$\hat{A}$ = perihelion

Conservation of $\vec{A}$ $\Rightarrow$ closed orbit (Kepler)

Quantum: $[\vec{A}, H] = 0$ but $[A_x, L_z] \neq 0$

Let $H\psi_{klm} = E_{kl}\psi_{klm} \Rightarrow HA_x\psi_{klm} = A_x H\psi_{klm} = E_{kl} A_x \psi_{klm}$

$\therefore$ $A_x\psi_{klm}$ is eigenvector of H but $A_x\psi_{klm} \neq c\,\psi_{klm}$

↑ since A_x, L_z do not commute

Conservation of $\vec{A}$ causes "accidental" degeneracy

Side note: Conservation of $\vec{A}$ and $\vec{L}$ reflects rotational symmetry in 4D!

Hybrid orbitals: linear combinations of degenerate states

Example: $\varphi_{n1\pm1} = \mp\sqrt{\frac{3}{8\pi}} R_{n1}(r) \sin\theta\, e^{\pm i\varphi}$

$\varphi_{n10} = \sqrt{\frac{3}{4\pi}} R_{n1}(r) \cos\theta$

$x = r\sin\theta\cos\varphi$

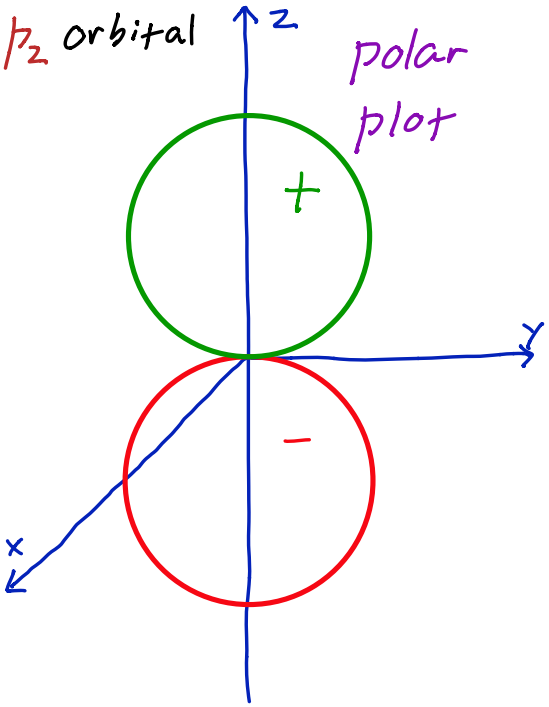
Let $\varphi_{np_x} = \frac{-1}{\sqrt{2}}[\varphi_{n11} - \varphi_{n1-1}] = \sqrt{\frac{3}{4\pi}} R_{n1}(r) \cdot \frac{x}{r}$

$\varphi_{np_y} = \frac{i}{\sqrt{2}}[\varphi_{n11} + \varphi_{n1-1}] = \sqrt{\frac{3}{4\pi}} R_{n1}(r) \cdot \frac{y}{r}$

$\varphi_{np_z} = \varphi_{n10} = \sqrt{\frac{3}{4\pi}} R_{n1}(r) \cdot \frac{z}{r}$

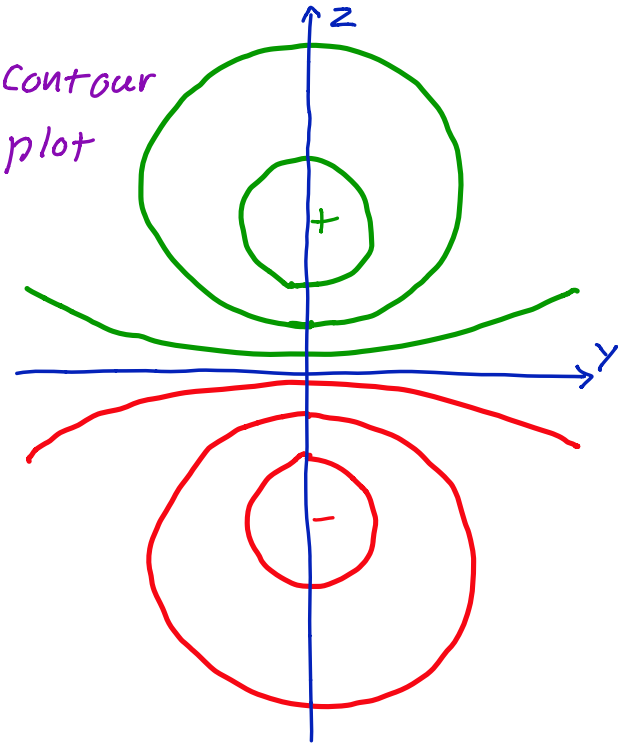
Pictures of orbitals

p_z orbital

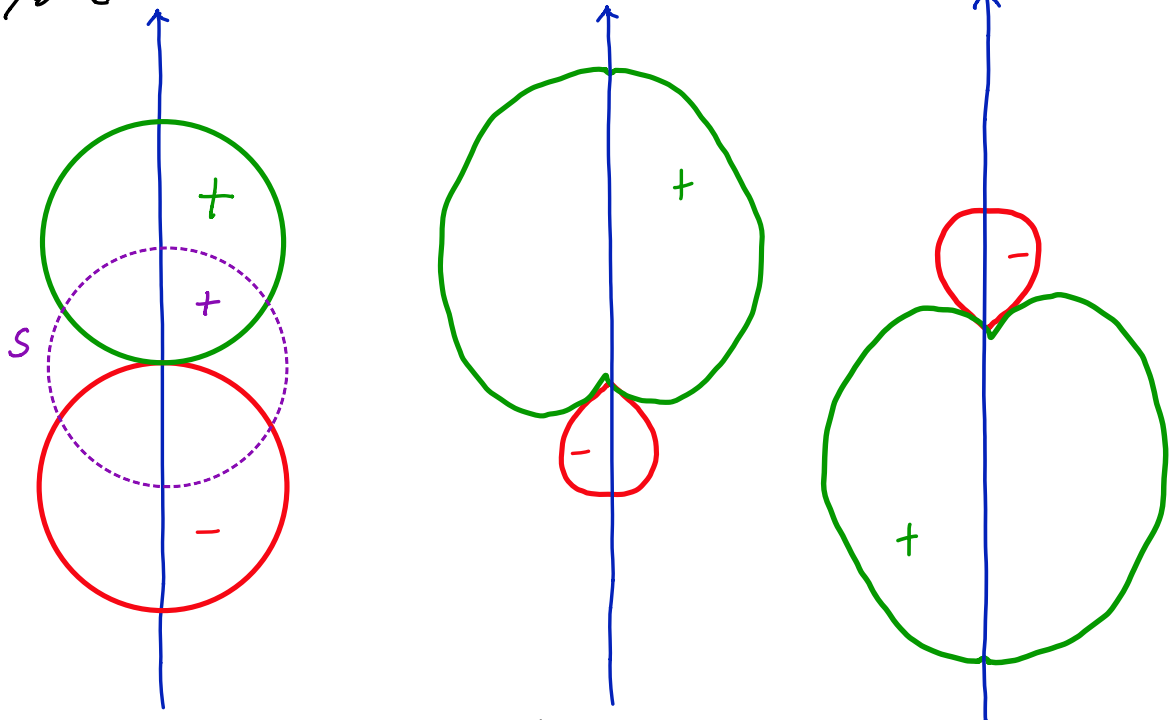


polar plot

contour plot

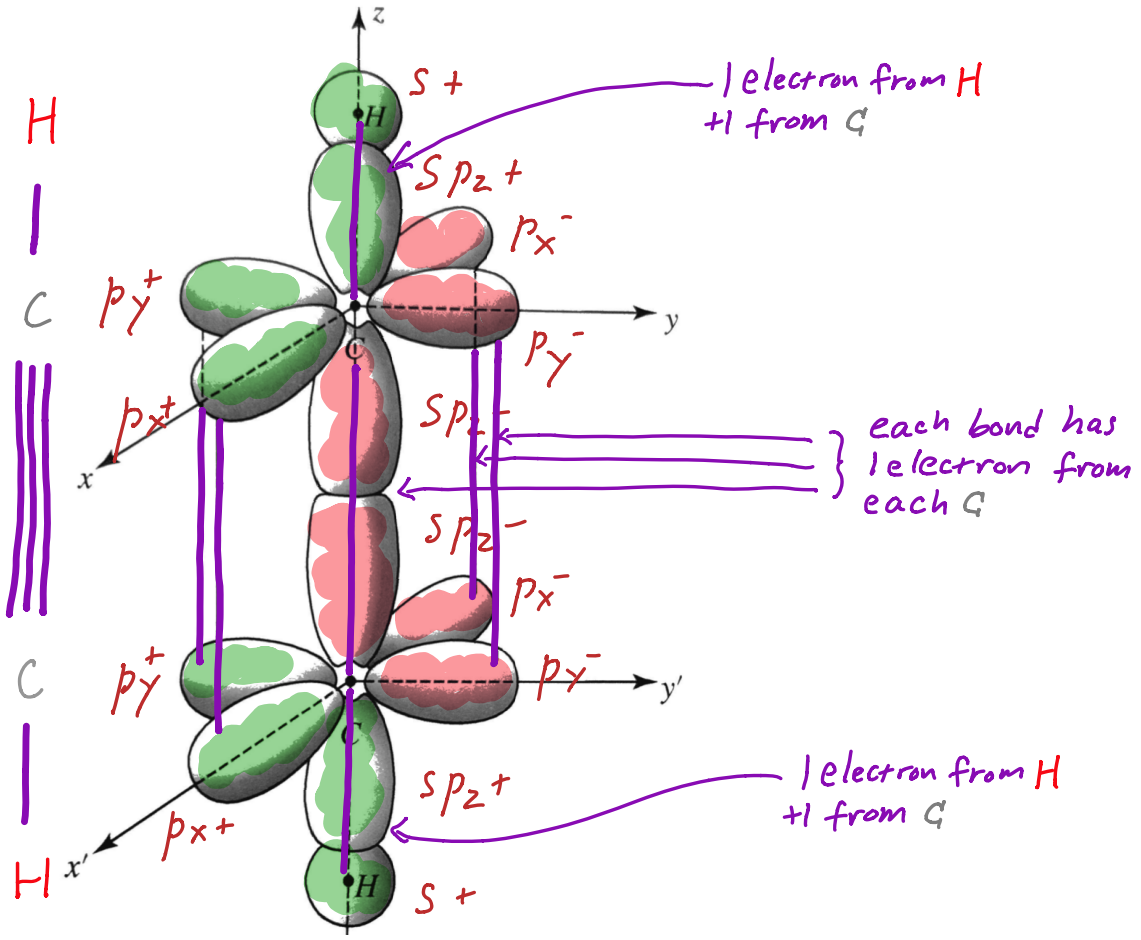


sp hybrid



$\varphi = \frac{1}{\sqrt{2}}(\varphi_{ns} + \varphi_{np_z})$ $\varphi = \frac{1}{\sqrt{2}}(\varphi_{ns} - \varphi_{np_z})$

Acetylene C_2H_2 $H-C\equiv C-H$



Each H: $1s^1$: 1 electron shared with C in σ bond

Each C: $2s^2 2p^2$: 1 electron shared with H in σ bond

1 electron shared with other C in σ bond

\+ 2 electrons shared with other C in π bonds

4 ✓

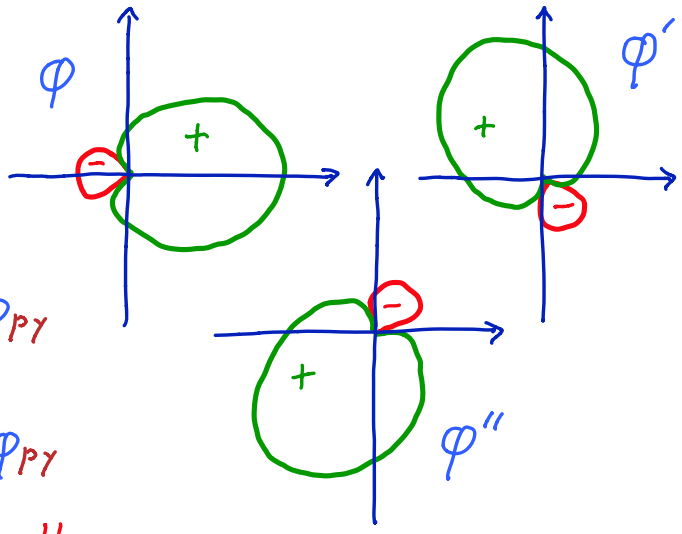
C≡C triple bond : $\sigma_z + \pi_x + \pi_y$

sp^2 hybrids

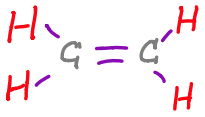
$$\varphi_{sp_xp_y} = \frac{1}{\sqrt{3}}\varphi_s + \sqrt{\frac{2}{3}}\varphi_{p_x}$$

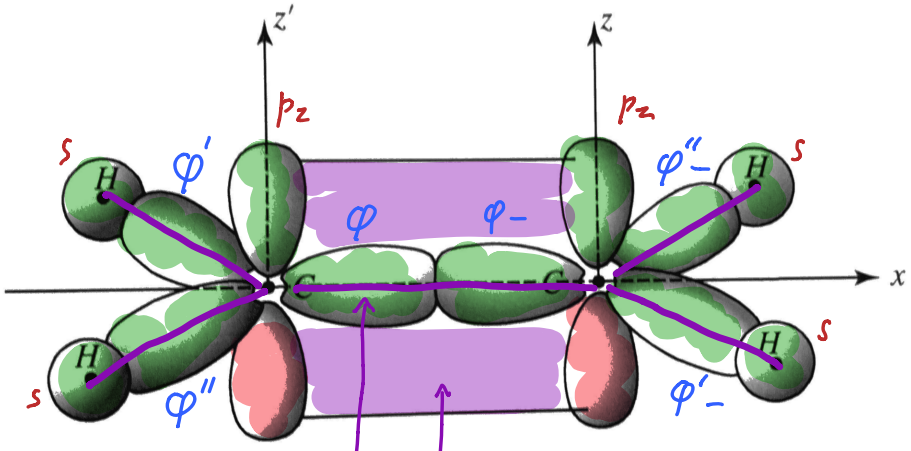
$$\varphi'_{sp_xp_y} = \frac{1}{\sqrt{3}}\varphi_s - \frac{1}{\sqrt{6}}\varphi_{p_x} + \frac{1}{\sqrt{2}}\varphi_{p_y}$$

$$\varphi''_{sp_xp_y} = \frac{1}{\sqrt{3}}\varphi_s - \frac{1}{\sqrt{6}}\varphi_{p_x} - \frac{1}{\sqrt{2}}\varphi_{p_y}$$



Ethylene: C_2H_4





C=C double bond: $\sigma + \pi_z$

sp^3 hybrid Methane CH_4