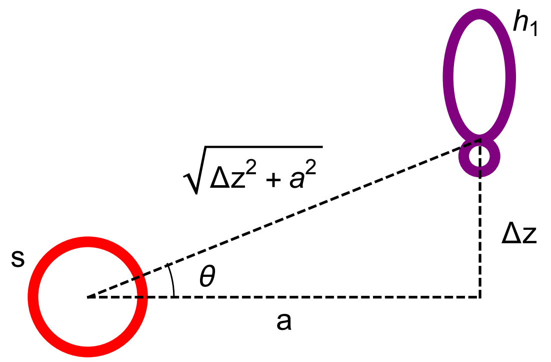
Construction of sp_Z Hybrids

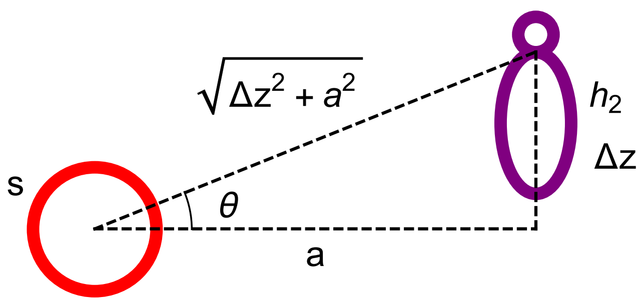
$$|h_1\rangle = \frac{1}{\sqrt{2}}(|s\rangle + |p_z\rangle) \qquad |h_2\rangle = \frac{1}{\sqrt{2}}(|s\rangle - |p_z\rangle)$$

Derivation of hybridization between s-orbital and sp_Z-orbital



$$t_{\text{up}} = \langle s|H|h_1\rangle = \frac{1}{\sqrt{2}}(\langle s|H|s\rangle + \langle s|H|p_z\rangle)$$

$$= \frac{1}{\sqrt{2}}(V_{ss\sigma} + \sin\theta V_{sp\sigma}) = \frac{1}{\sqrt{2}}(V_{ss\sigma} + \frac{\Delta z}{\sqrt{a^2+\Delta z^2}}V_{sp\sigma})$$



$$t_{\text{down}} = \langle s|H|h_2\rangle = \frac{1}{\sqrt{2}}(\langle s|H|s\rangle - \langle s|H|p_z\rangle)$$

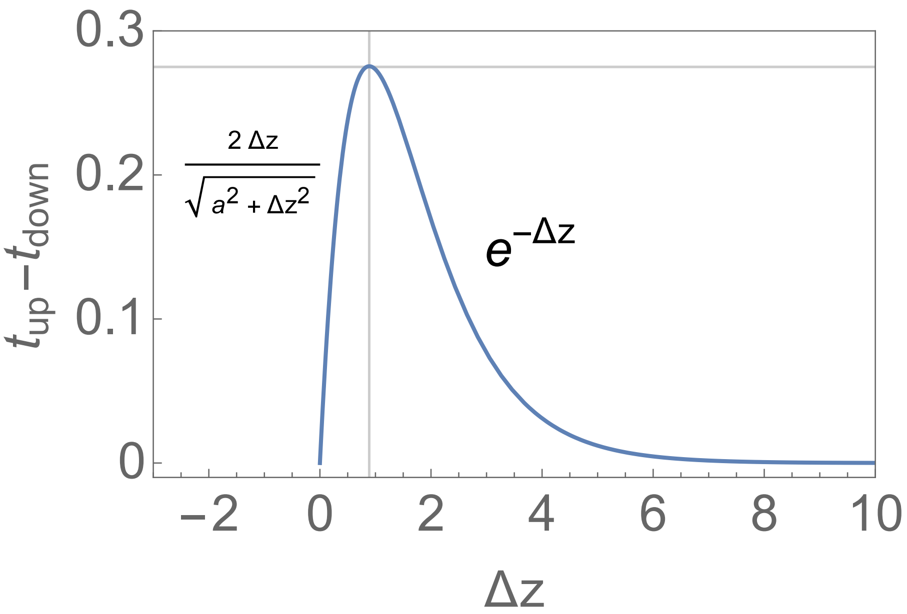
$$= \frac{1}{\sqrt{2}}(V_{ss\sigma} - \sin\theta V_{sp\sigma}) = \frac{1}{\sqrt{2}}(V_{ss\sigma} - \frac{\Delta z}{\sqrt{a^2+\Delta z^2}}V_{sp\sigma})$$

$$t_{\text{up}} - t_{\text{down}} = \frac{2\Delta z}{\sqrt{a^2 + \Delta z^2}} V_{sp\sigma} \qquad \Delta z \approx a$$

In the limit of $\Delta z \gg a$

$$\langle s|H|p_z(\Delta z)\rangle \sim V_{sp\sigma} e^{-\Delta z}$$

So, we can plot



Thus we have formula for optimal :

$$\frac{\partial}{\partial \Delta z}\left(\frac{2\Delta z}{\sqrt{a^2 + \Delta z^2}} e^{-\Delta z}\right) = 0$$

$$\Delta z = -\frac{\frac{2}{3}^{1/3} a^2}{(9a^2 + \sqrt{3}\sqrt{27a^4 + 4a^6})^{1/3}} + \frac{(9a^2 + \sqrt{3}\sqrt{27a^4 + 4a^6})^{1/3}}{2^{1/3} 3^{2/3}}$$

For example

BiAg (111)

$a = 5.088$ Å, $\Delta z = 0.69$ Å

$$= a = 2.544;\ N\left[-\frac{\left(\frac{2}{3}\right)^{1/3} a^2}{\left(9 a^2+\sqrt{3}\sqrt{27 a^4+4 a^6}\right)^{1/3}}+\frac{\left(9 a^2+\sqrt{3}\sqrt{27 a^4+4 a^6}\right)^{1/3}}{2^{1/3}\, 3^{2/3}}\right]$$

$= 0.890785$

similar value?