Solving a 2x2 Hamiltonian:

basis: φ_1, φ_2 : $\langle\varphi_1|\varphi_1\rangle = \langle\varphi_2|\varphi_2\rangle = 1$; $\langle\varphi_1|\varphi_2\rangle = \langle\varphi_2|\varphi_1\rangle = 0$

$\langle\varphi_1|H|\varphi_1\rangle = 0$; $\langle\varphi_2|H|\varphi_2\rangle = \Delta$

$\langle\varphi_1|H|\varphi_2\rangle = \langle\varphi_2|H|\varphi_1\rangle = t$.

Schrödinger eq.: $H\psi = E\psi$; $\psi = \alpha\varphi_1 + \beta\varphi_2$; $\alpha^2+\beta^2 = 1$

$$H = \begin{bmatrix} 0 & t \\ t & \Delta \end{bmatrix}, \quad \psi = \begin{bmatrix} \alpha \\ \beta \end{bmatrix}, \quad \varphi_1 = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \quad \varphi_2 = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

$$\begin{bmatrix} 0 & t \\ t & \Delta \end{bmatrix}\begin{bmatrix} \alpha \\ \beta \end{bmatrix} = E\begin{bmatrix} \alpha \\ \beta \end{bmatrix} \rightarrow \begin{bmatrix} -E & t \\ t & \Delta-E \end{bmatrix}\begin{bmatrix} \alpha \\ \beta \end{bmatrix} = 0 \rightarrow \begin{vmatrix} -E & t \\ t & \Delta-E \end{vmatrix} = 0 \rightarrow$$

$$-E(\Delta-E)-t^2=0 \rightarrow E^2-\Delta E-t^2=0 \rightarrow E_\pm = \frac{\Delta \pm \sqrt{\Delta^2+4t^2}}{2}$$

$*\ t=0 \rightarrow E_-=0 \rightarrow \begin{pmatrix} 0=0 \\ \Delta\beta=0 \end{pmatrix} \rightarrow \beta=0 \rightarrow \alpha=1 \rightarrow \psi_- = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \varphi_1$

$E_+=\Delta \rightarrow \begin{pmatrix} -\Delta\alpha=0 \\ 0=0 \end{pmatrix} \rightarrow \alpha=0 \rightarrow \beta=1 \rightarrow \psi_+ = \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \varphi_2$

$*\ \Delta=0 \rightarrow E_-=-t \rightarrow \begin{pmatrix} t\alpha+t\beta=0 \\ t\alpha+t\beta=0 \end{pmatrix} \rightarrow \alpha=-\beta \rightarrow \psi_- = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}$

$E_+=t \rightarrow \begin{pmatrix} -t\alpha+t\beta=0 \\ t\alpha-t\beta=0 \end{pmatrix} \rightarrow \alpha=\beta \rightarrow \psi_+ = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$

- "bonding state" $= \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$, $E_+=t$ to be lowest $\rightarrow$ t = negative
- if t = positive $\rightarrow$ define $\varphi_2^* = -\varphi_2$ $\rightarrow$ use φ_1, φ_2^* as basis $\rightarrow$

  $\langle\varphi_1|H|\varphi_2^*\rangle = \langle\varphi_1|H|-\varphi_2\rangle = -t$

  define $t^* = -t$, thus t^* is negative.

$*\ |t| \ll |\Delta| \rightarrow \sqrt{\Delta^2+4t^2} = \Delta\sqrt{1+4t^2/\Delta^2} \approx \Delta(1+2t^2/\Delta^2) = \Delta + 2t^2/\Delta$

$\rightarrow E_- \approx \frac{\Delta-(\Delta+2t^2/\Delta)}{2} = -t^2/\Delta$; $E_+ \approx \frac{\Delta+(\Delta+2t^2/\Delta)}{2} = \Delta + t^2/\Delta$

$\rightarrow E_-: \frac{t^2}{\Delta}\alpha + \beta t \approx 0 \rightarrow \beta \approx -\frac{t}{\Delta}\alpha \rightarrow \beta^2 \approx \frac{t^2}{\Delta^2}, \alpha^2 \approx 1-\frac{t^2}{\Delta^2}$

$E_+: t\alpha - \frac{t^2}{\Delta}\beta \approx 0 \rightarrow \alpha = \frac{t}{\Delta}\beta \rightarrow \alpha^2 \approx \frac{t^2}{\Delta^2}, \beta^2 \approx 1-\frac{t^2}{\Delta^2}$.

energy gain $\approx -t^2/\Delta$, admixture $\approx t^2/\Delta^2$.

2x2 Hamiltonian : addendum

$$H = \begin{bmatrix} 0 & t \\ t & \Delta \end{bmatrix} \quad \psi = \begin{bmatrix} \alpha \\ \beta \end{bmatrix} \quad \varphi_1 = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad \varphi_2 = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

$$H\psi = E\psi, \quad \psi = \alpha\varphi_1 + \beta\varphi_2, \quad \alpha^2 + \beta^2 = 1, \quad E_\pm = \frac{\Delta \pm \sqrt{\Delta^2 + 4t^2}}{2}$$

$$\Rightarrow \alpha \equiv \cos\theta, \ \beta \equiv \sin\theta, \quad 0 \le \theta \le \frac{\pi}{2}$$

$$\tan 2\theta = \frac{\sin 2\theta}{\cos 2\theta} = \frac{2\sin\theta\cos\theta}{\cos^2\theta - \sin^2\theta} = \frac{2\alpha\beta}{\alpha^2 - \beta^2}$$

$$\begin{bmatrix} -E & t \\ t & \Delta - E \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = 0 \longrightarrow -E\alpha + t\beta = 0 \longrightarrow \beta = \frac{E}{t}\alpha$$

$$\tan 2\theta = \frac{2 \cdot \frac{E}{t} \cdot \alpha^2}{\alpha^2 - \left(\frac{E}{t}\right)^2 \alpha^2} = \frac{2\, E/t}{1 - (E/t)^2} = \frac{2tE}{t^2 - E^2} = \frac{t\left(\Delta \pm \sqrt{\Delta^2 + 4t^2}\right)}{t^2 - \frac{1}{4}\Delta^2 - \frac{1}{4}\left(\Delta^2 + 4t^2\right) \pm \frac{1}{2}\Delta\sqrt{\Delta^2 + 4t^2}}$$

$$= t\left(\Delta \pm \sqrt{\Delta^2 + 4t^2}\right) \Big/ \left(-\frac{1}{2}\Delta^2 \pm \frac{1}{2}\Delta\sqrt{\Delta^2 + 4t^2}\right) = -\frac{2t}{\Delta}$$

If $t < 0$ then ground state is $\psi = \cos\theta \cdot \varphi_1 + \sin\theta\, \varphi_2$
with $0 \le \theta \le \frac{\pi}{2}$

Bonding state

$$\Rightarrow \tan 2\theta = \frac{2|t|}{\Delta}$$