Day 9: What is $|\psi\rangle$ for two square wells?

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \underbrace{V^{sq}(x-a) + V^{sq}(x-2a)}_{V(x)}\right)|\psi\rangle = E|\psi\rangle$$

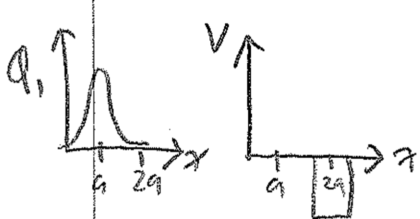
Can't solve, apply LCAO approx:

$$|\psi\rangle \cong c_1 \underbrace{\varphi(x-a)}_{|1\rangle} + c_2 \underbrace{\varphi(x-2a)}_{|2\rangle}$$ ← wave func of single sq. well

$$\hat{H}|\psi\rangle = E|\psi\rangle \Rightarrow \begin{bmatrix}\alpha & \beta \\ \beta & \alpha\end{bmatrix}\begin{bmatrix}c_1 \\ c_2\end{bmatrix} = E\begin{bmatrix}c_1 \\ c_2\end{bmatrix} \Rightarrow$$ solve for eigenvalues!

$$\alpha = \langle 1|\hat{H}|1\rangle = \langle 1|\hat{p}^2/2m + \hat{V}_{sq}(x-a)|1\rangle$$ → E_1; q-well

$$+ \langle 1|\hat{V}_{sq}(x-2a)|1\rangle$$



$$= E_1 + \int_{-\infty}^{\infty} \varphi_1^*(x-a)\, V_{sq}(x-2a)\, \varphi_1(x-a)\, dx$$

$= E_1 +$ small correction

$= \langle 2|\hat{H}|2\rangle$, by symmetry.

More important is β:

$$\beta = \langle 2|\hat{H}|1\rangle = \langle 2|\hat{H}_1 + \hat{V}_{sq}(x-2a)|1\rangle$$

$$= E_1 \underbrace{\langle 2|1\rangle}_{0} + \langle 2|\hat{V}_{sq}(x-2a)|1\rangle$$

$$= \int_{-\infty}^{\infty} \underset{\text{even func}}{\varphi^*(x-2a)}\ \underset{\text{"}-\text{ve"}}{V_{sq}(x-2a)}\ \underset{\text{even func}}{\varphi(x-a)}\, dx$$

< 0

Note: $\beta = \langle 2|\hat{H}|1\rangle = \langle 1|\hat{H}|2\rangle$, b/c $\hat{H}$ is hermitian.

Class Exercise answers:

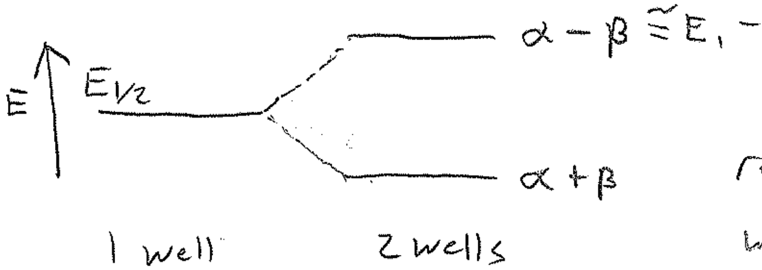
solve $H|\psi\rangle = E|\psi\rangle$ under LCAO

let $\lambda = E$

$$\Rightarrow 0 = \det(H - EI)$$

$$= (\alpha - E)^2 - \beta^2$$

$$\therefore E_{\pm} = \alpha \pm \beta, \quad \alpha \cong E_{1/2}$$



recall $\beta < 0$ for grnd state wavefunc.

What are c_1 and c_2?, (eigenvector).

Case 1 $\quad E_+ = \alpha + \beta$

$$(H - E_+ I)\begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = \begin{bmatrix} -\beta & \beta \\ \beta & -\beta \end{bmatrix}\begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0$$

$\therefore c_1 = c_2$ or $\begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = \underbrace{\frac{1}{\sqrt{2}}}_{\text{orthonormal basis}}\begin{bmatrix} 1 \\ 1 \end{bmatrix}$ or $|\psi_+\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle)$

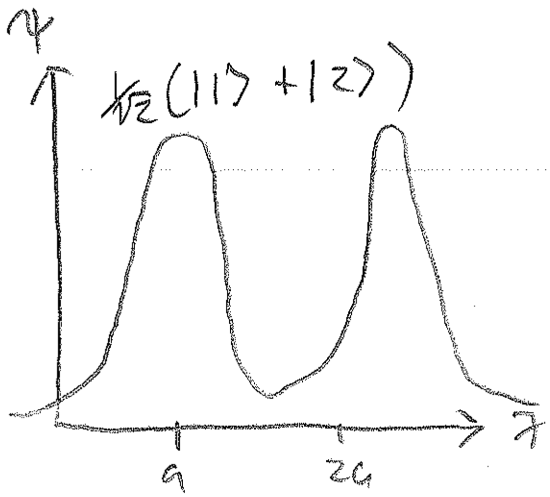
Case 2 $\quad E_- = \alpha - \beta$

$$\Rightarrow \begin{bmatrix} \beta & \beta \\ \beta & \beta \end{bmatrix}\begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \quad \Rightarrow \quad c_1 = -c_2$$

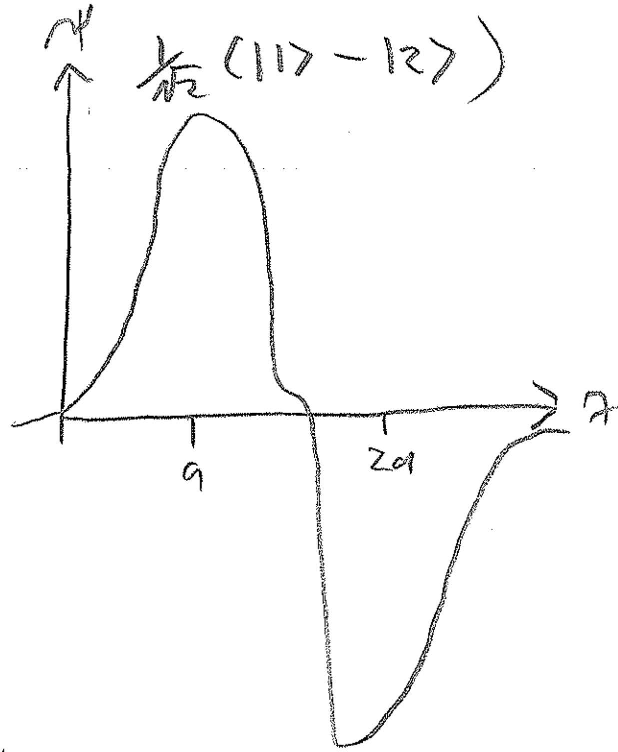
OR $\begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ -1 \end{bmatrix}$ or $|\psi_-\rangle = \frac{1}{\sqrt{2}}(|1\rangle - |2\rangle)$

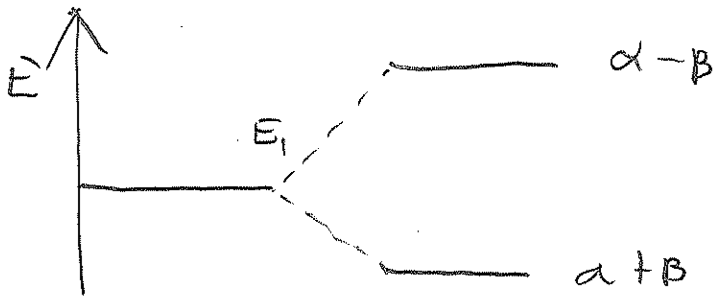
DONE! You completely described the quantum state of 2-well (i.e. two atom molecule) under LCAO.

Graph results of LCAO wave functions

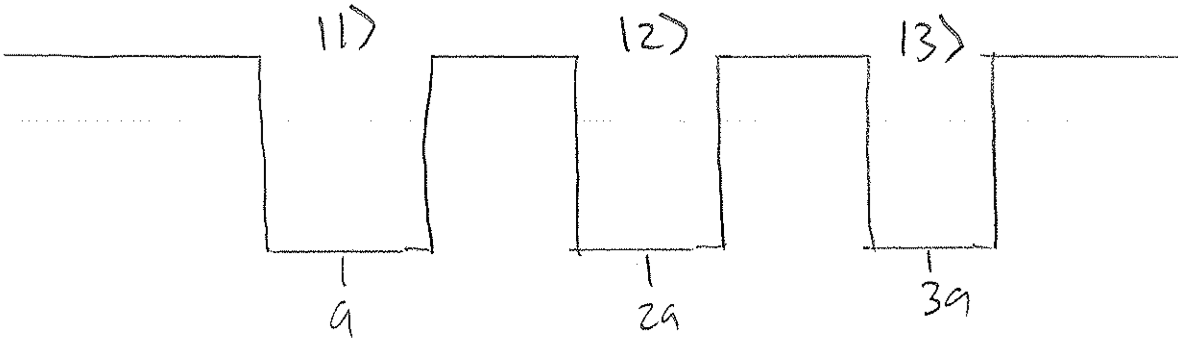


bonding





Problem Set Do it for a 3×3 matrix.



Step ① apply LCAO approximation to $|\psi\rangle$

$$|\psi\rangle = c_1|1\rangle + c_2|2\rangle + c_3|3\rangle$$

$$\hat{H}|\psi\rangle = E|\psi\rangle \quad \text{or} \quad \langle\psi|\hat{H}|\psi\rangle = E$$

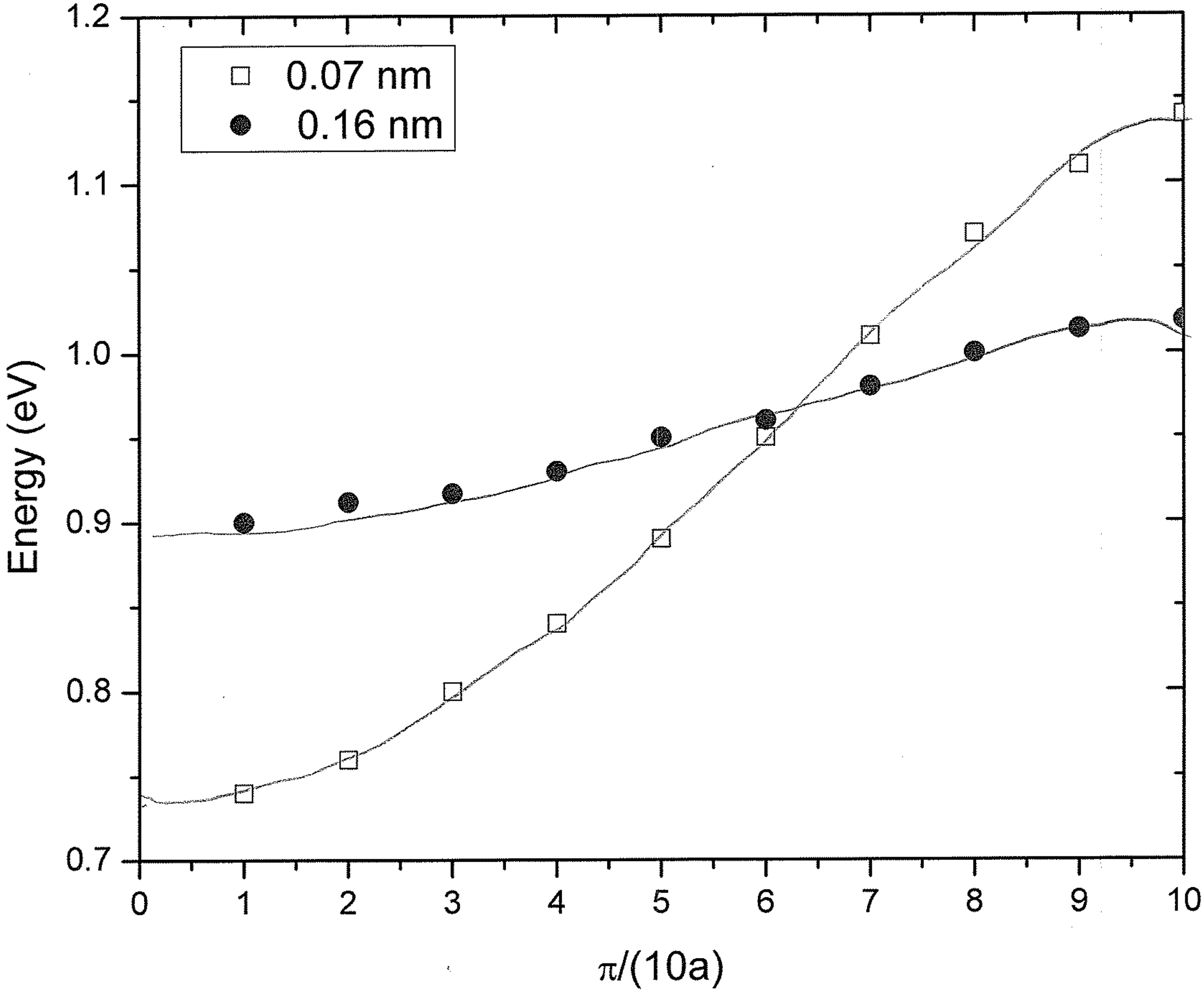
$$H = \begin{bmatrix} \alpha & \beta & 0 \\ \beta & \alpha & \beta \\ 0 & \beta & \alpha \end{bmatrix} \qquad \begin{aligned} \alpha &= \langle 1|\hat{H}|1\rangle = \ldots \\ \beta &= \langle 1|\hat{H}|2\rangle \\ &= \langle 2|\hat{H}|3\rangle \end{aligned}$$

assume; $\langle 1|\hat{H}|3\rangle \cong 0$

Step ② Find eigenvalues, $E = E_1, E_2, E_3$

Step ③ Find eigenvectors for E_1, E_2, E_3

write out wavefunctions of each energy state.


0.07 nm
0.16 nm
1.2
1.1
1.0
0.9
0.8
0.7
Energy (eV)
0
1
2
3
4
5
6
7
8
9
10
π/(10a)