Day 10 molecular eigenvalues to electronic bands

Step ① LCAO; $|\psi\rangle \cong c_1|1\rangle + c_2|2\rangle + \dots + c_n|n\rangle + \dots + c_N|N\rangle$

N atoms (or wells)

$$\hat{H}|\psi\rangle = E|\psi\rangle \Rightarrow \begin{bmatrix} \alpha & \beta & 0 & 0 & \dots \\ \beta & \alpha & \beta & 0 & \\ 0 & \beta & \alpha & \beta & \\ \vdots & & & & \ddots \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{bmatrix} = E \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{bmatrix}$$

1st row: $\alpha c_1 + \beta c_2 = E c_1$

2nd row: $\beta c_1 + \alpha c_2 + \beta c_3 = E c_2$

nth row: $\beta c_{n-1} + \alpha c_n + \beta c_{n+1} = E c_n$

Step ② In PhET lab you'll show the $|\psi\rangle$ oscillates only in "normal modes" $k = \frac{2\pi}{\lambda}$ hence,

$$|\psi_k\rangle = \sum_{n=1}^{N} A e^{ikna} \phi_n(x - na, t) \leftarrow \text{atomic or q-well w.f.}$$

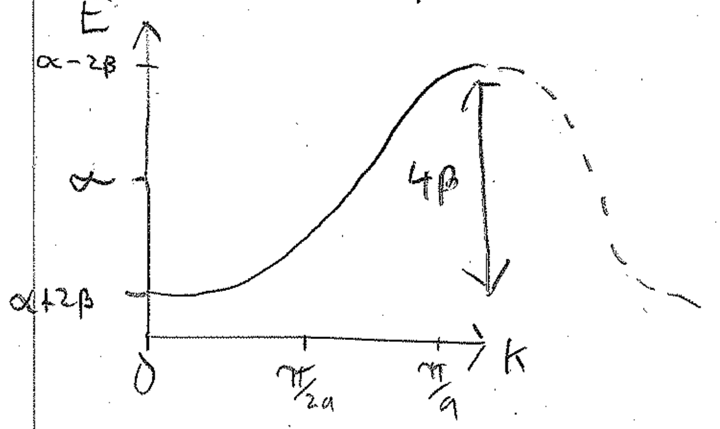
$e^{-iEt/\hbar}$ $\therefore$ $c_n = Ae^{ikna}$ gives the amplitude (eigenvector coefficient) of each atomic orbital wavefunction

Sub in nth row;

$$\Rightarrow (\beta e^{-ika} + \alpha + \beta e^{ika}) e^{ikna} = E e^{ikna}$$

$$E = \alpha + \beta(e^{-ika} + e^{ika})$$

$$= \alpha + 2\beta \cos ka$$



Valence band electronic dispersion relation (band structure);

$$\boxed{E(k) = \alpha + 2\beta \cos ka}$$

Bandwith: 4β

$E(k)$ is continuous for all k, but we claim we require only the 1st Brillouin zone (i.e. 0 to π/a) to obtain all eigenstates and eigenenergies.

Proof suppose there exists another k' such that

$k' = k + 2\pi/a$

$$\Rightarrow c_{n,k'} = Ae^{ik'na}$$
$$= Ae^{ikna}e^{i2\pi n}$$
$$= Ae^{ikna}$$
$$= c_{n,k}$$

$\therefore c_{n,k+2\pi/a} = c_{nk}$. This proof is called Bloch's theorem

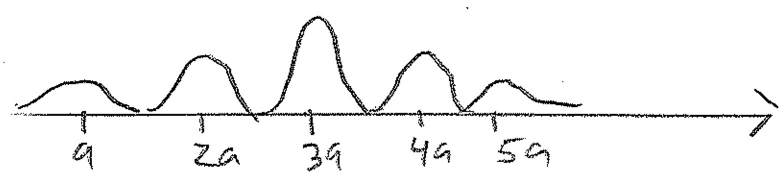
PhET Lab finite wells and electronic structure

$$|\psi_k\rangle = \sum_n Ae^{ikna}\,\phi_n(x-na, t) \text{ still works?}$$

What is k? $k = 2\pi/\lambda$

Example: What are the eigenvector coefficients for the lowest energy state of 5-well system?

$Re(\psi) \rightarrow$

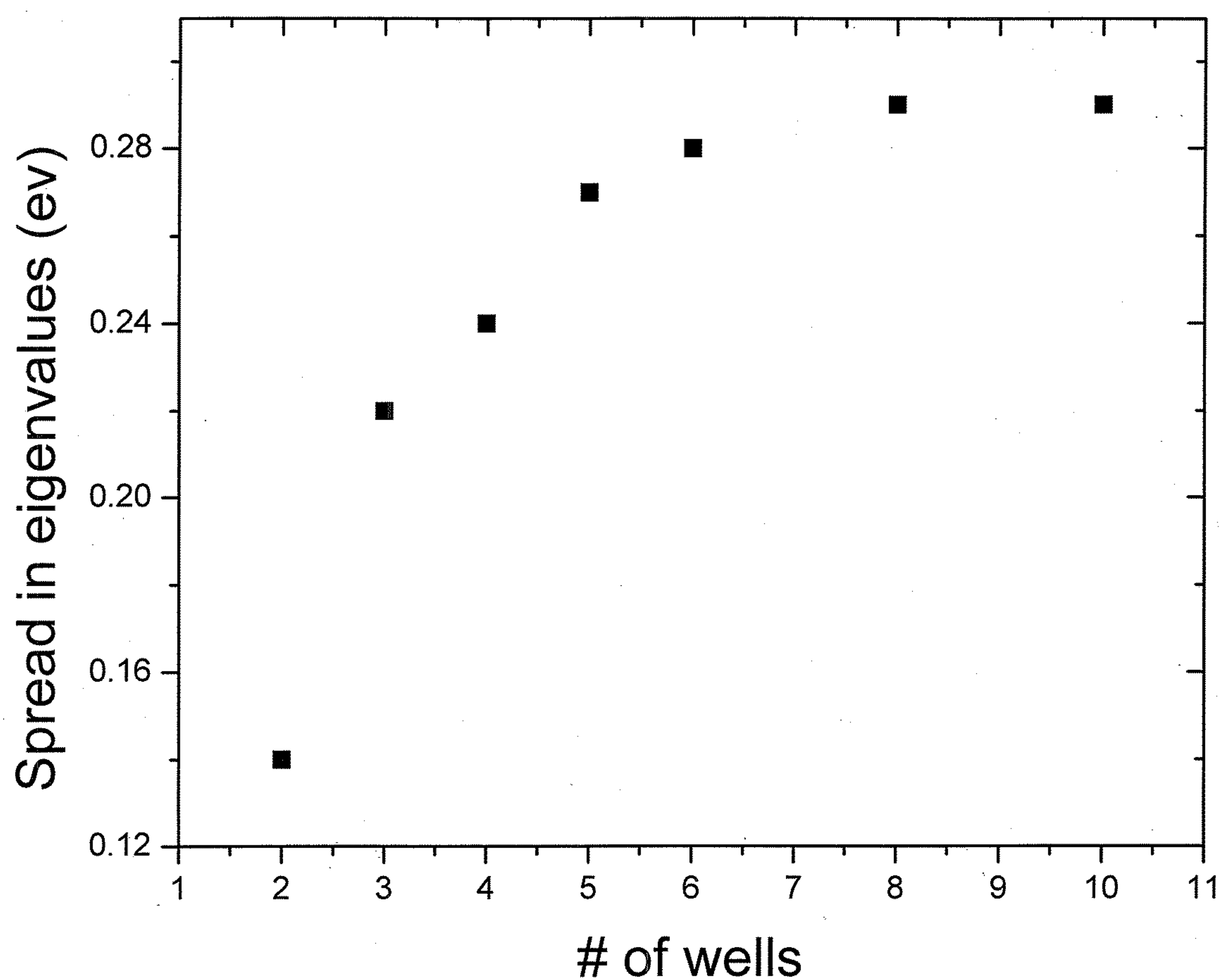


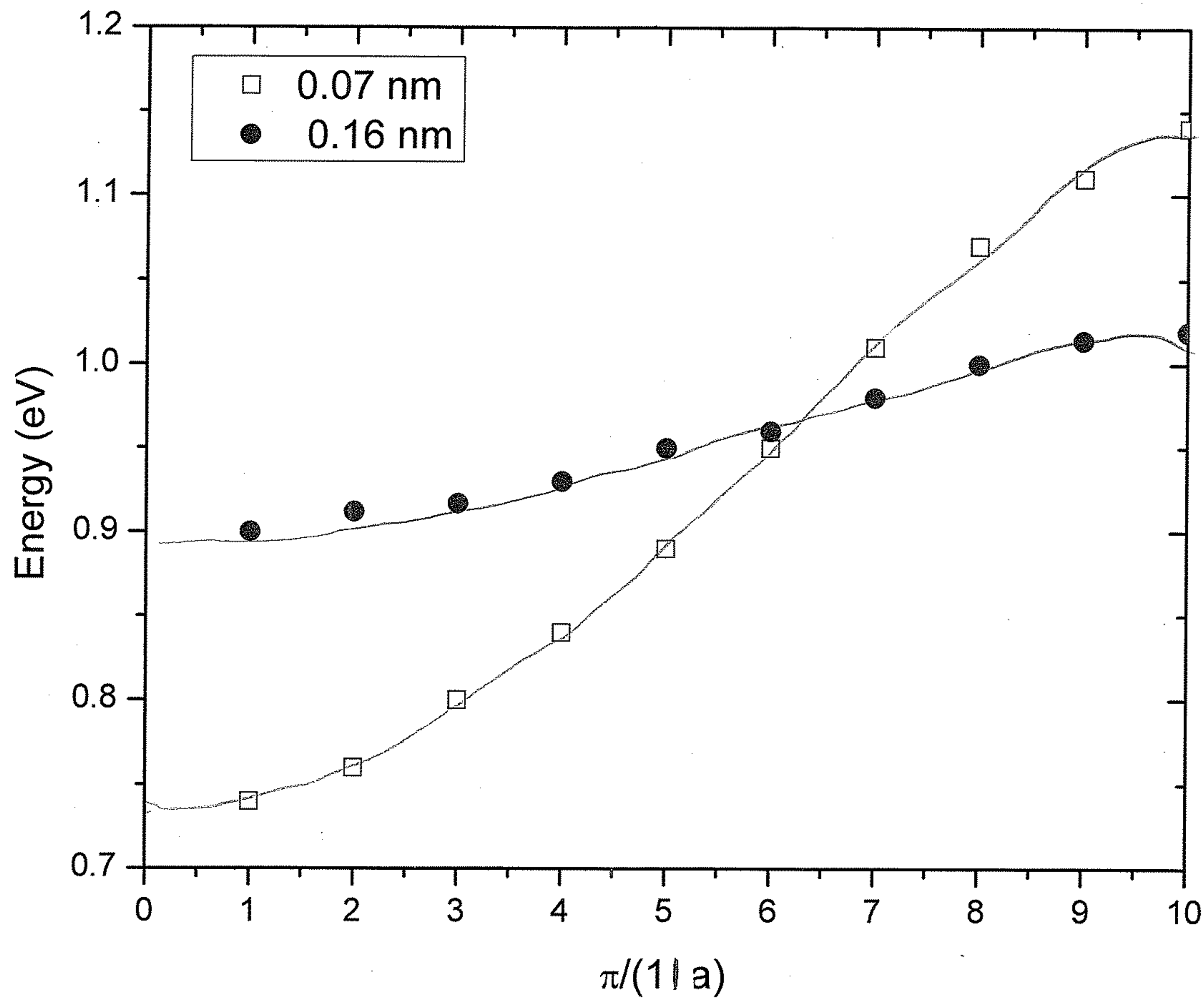
$$|\psi_{k_1}\rangle = \sum_{n=1}^{5} Ae^{ik_1na}\phi(x-na)$$

$$\lambda_{long} = 2\times(6a) = 12a$$

$$k_1 = \pi/6a$$

n	1	2	3	4	5
$A\,c_n$	$e^{i\pi/6}$	$e^{i\pi/3}$	$e^{i\pi/2}$	$e^{i2\pi/3}$	$e^{i5\pi/6}$


Spread in eigenvalues (ev)
0.12
0.16
0.20
0.24
0.28
1
2
3
4
5
6
7
8
9
10
11
# of wells


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