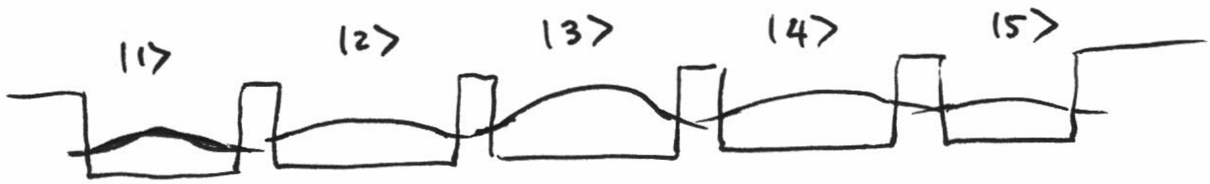
Quiz: Fill in this table that relates to the lowest energy LCAO state of a 5-well quantum system $\left(k = \frac{\pi}{6a}\right)$

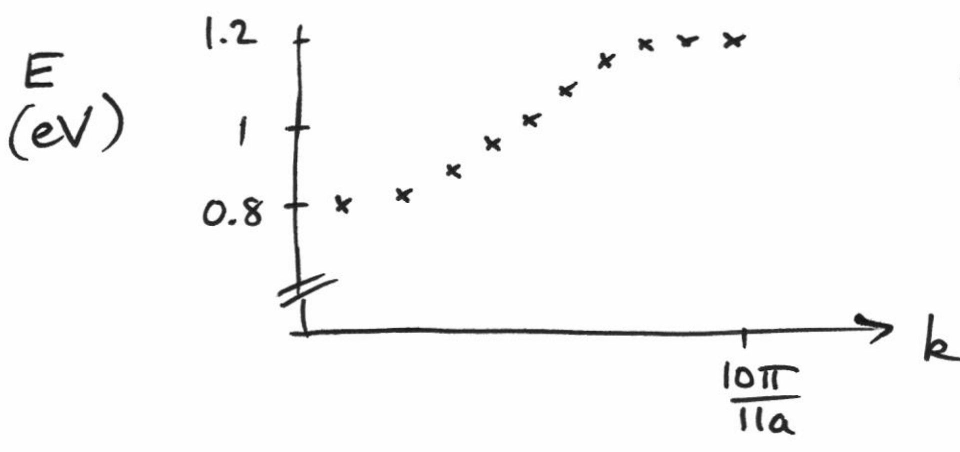
n	1	2	3	4	5
c_n	?	?	?	?	?



$$\psi = \sum_{n=1}^{5} c_n |n\rangle$$

Last time: The worksheet asked you to collect the k-values and energy eigenvalues for the 10-well system.

Let's plot these on excel



Now we will look for an analytical expression describing this curve.

As $N \to \infty$ my basis states (LCAO approx)
are $|1\rangle, |2\rangle, |3\rangle \ldots$

$$\hat{H} = \begin{bmatrix} \alpha & \beta & 0 & & \\ \beta & \alpha & \beta & 0 & \cdots \\ 0 & \beta & \alpha & \ddots & \\ & 0 & \ddots & \ddots & \\ & & \ddots & & \end{bmatrix}$$

infinite matrix

We know that

$$\hat{H} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{bmatrix} = E \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{bmatrix}$$

← An LCAO eigenstate in vector form.

The matrix eq^n is equivalent to saying

$$\alpha c_1 + \beta c_2 = E c_1$$
$$\beta c_1 + \alpha c_2 + \beta c_3 = E c_2$$
$$\beta c_2 + \alpha c_3 + \beta c_4 = E c_3$$
$$\vdots$$

All eq^{n}s (except the first) have the form

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

Is this eqn satisfied by $c_n = A \sin kna$?

$$\beta A \sin k(n-1)a + \alpha A \sin kna + \beta A \sin k(n+1)a = E A \sin kna$$

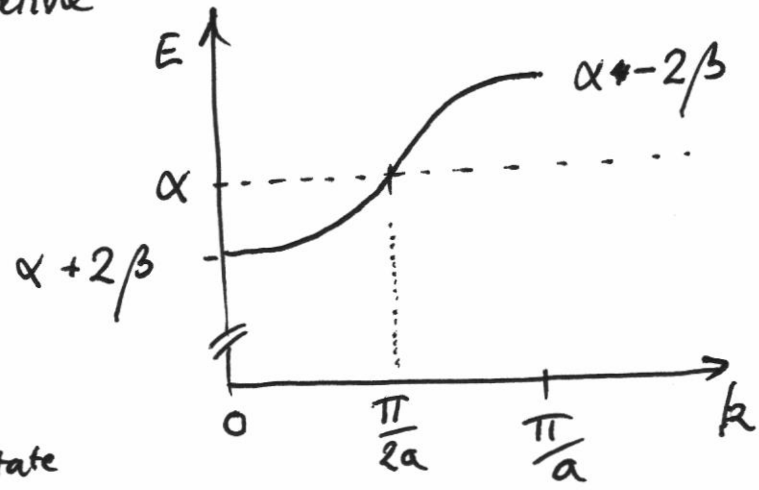
$$\Rightarrow \beta e^{i(k(n-1)a)} + \alpha e^{ikna} + \beta e^{ik(n+1)a} = E e^{ikna}$$

⇧ Check that you agree the imaginary terms from the complex ~~component of the~~ exponentials say the same thing as the first eqn that used sine functions.

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

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

If β is negative

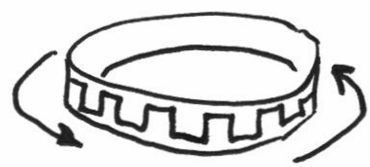


Recall $\alpha \approx E_{gnd\,state}$

Boundary conditions

The computer used fixed-end B.C.s.
Electron cannot escape from either end

Compare to periodic B.C.s where we allow the electron to tunnel from the last well to the first well



Such a system should support traveling waves.

Let's check:

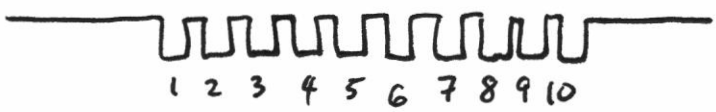
Ansatz $c_n = Ae^{ikna}$

satisfies $\beta c_{n-1} + \alpha c_n + \beta c_{n+1} = E c_n$?

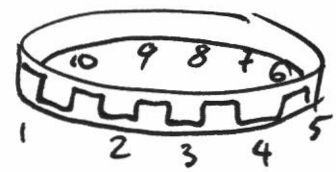
Yes.

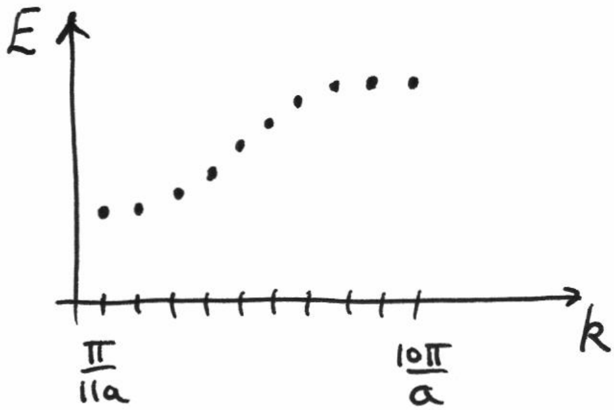
You can easily check for yourself. The eqn is satisfied as long as $E = \alpha + 2\beta \cos ka$

Fixed end

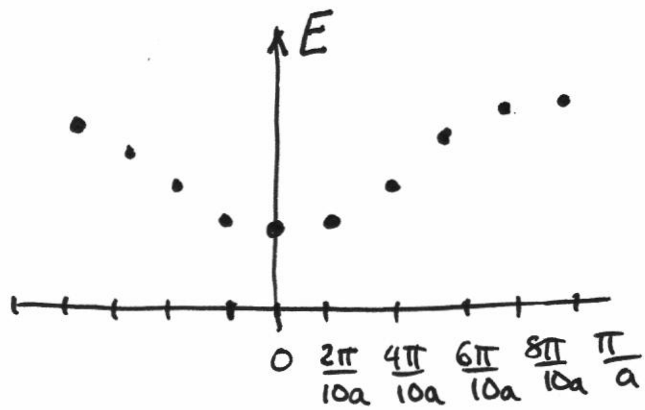


Periodic





Standing waves



Traveling waves

In both cases there are 10 eigenstates, but B.C.s affect which k-values are allowed.