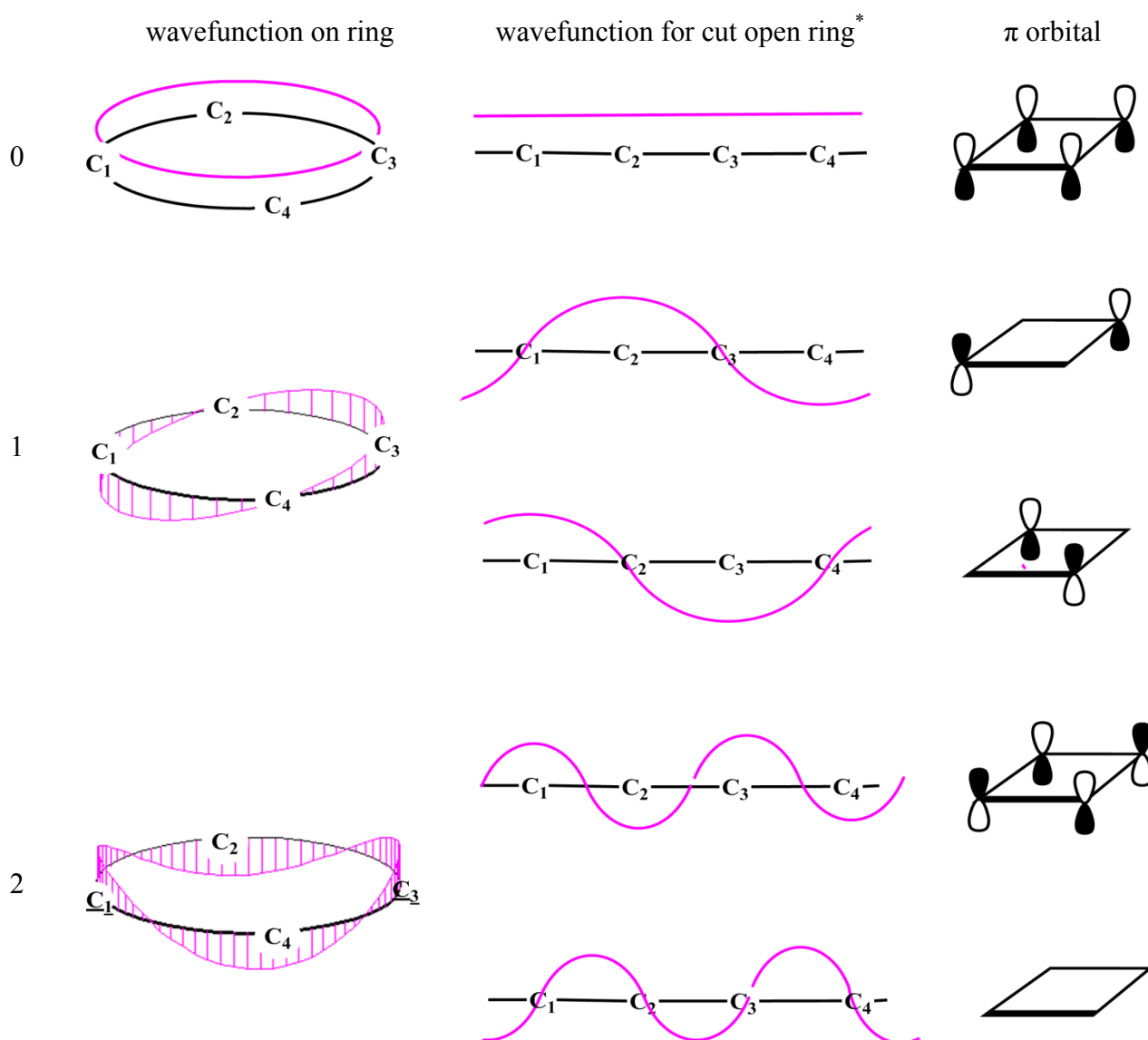


(a) Using the analogy between the particle on a ring waves and the π -orbitals on slide 17, draw the four π molecular orbitals for C_4H_4 and the six π molecular orbitals for C_6H_6 .

For C_4H_4 , there are 4 π orbitals corresponding to $j = 0$ (singly degenerate), $j = 1$ (doubly degenerate) and $j = 2$ (singly degenerate). Although $j = 2$ is doubly degenerate for a particle on a ring, one of the solutions has the nodes of the wavefunction passing through the atoms on the ring giving wavefunction which is zero everywhere.

Matching the form of the wavefunction to the phase and amplitude of the contributions from the carbon p -orbitals of the ring gives the 4 solutions below. For clarity, the particle on a ring wavefunctions are also displayed as 'cut open'. The ring wavefunction can be remade by joining the two ends back together.

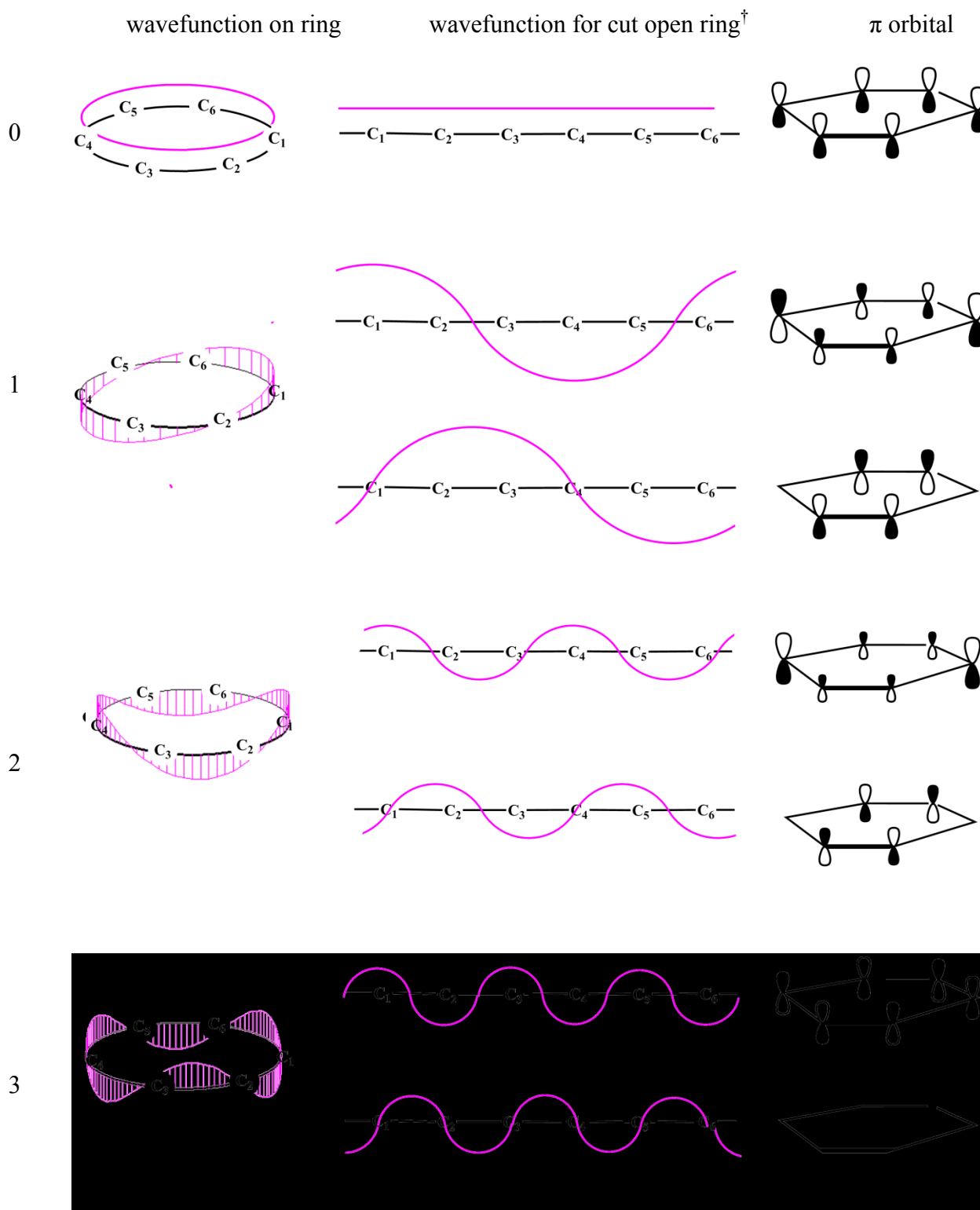


For a particle on a ring, the $j = 0$ solution is singly degenerate and the solutions with $j > 0$ are doubly degenerate corresponding to sine and cosine solutions with j waves fitting around the ring. Note however that one of the $j = 2$ solutions has nodes on each of the atoms so gives no wavefunction.

* Note that one wave is $\sin(j\theta)$ and the other is $\cos(j\theta)$. They differ by 90° ($\pi/2$ radians).

For C_6H_6 , there are 6 π orbitals corresponding to $j = 0$ (singly degenerate), $j = 2$ (doubly degenerate) and $j = 3$ (doubly degenerate) and $j = 4$ (singly degenerate). Although $j = 4$ is doubly degenerate for a particle on a ring, one of the solutions has the nodes of the wavefunction passing through the atoms on the ring giving wavefunction which is zero everywhere.

Matching the form of the wavefunction to the phase and amplitude of the contributions from the carbon p -orbitals of the ring gives the 6 solutions below.



Note again that one of the $j = 3$ solutions has nodes on each of the atoms so gives no wavefunction.

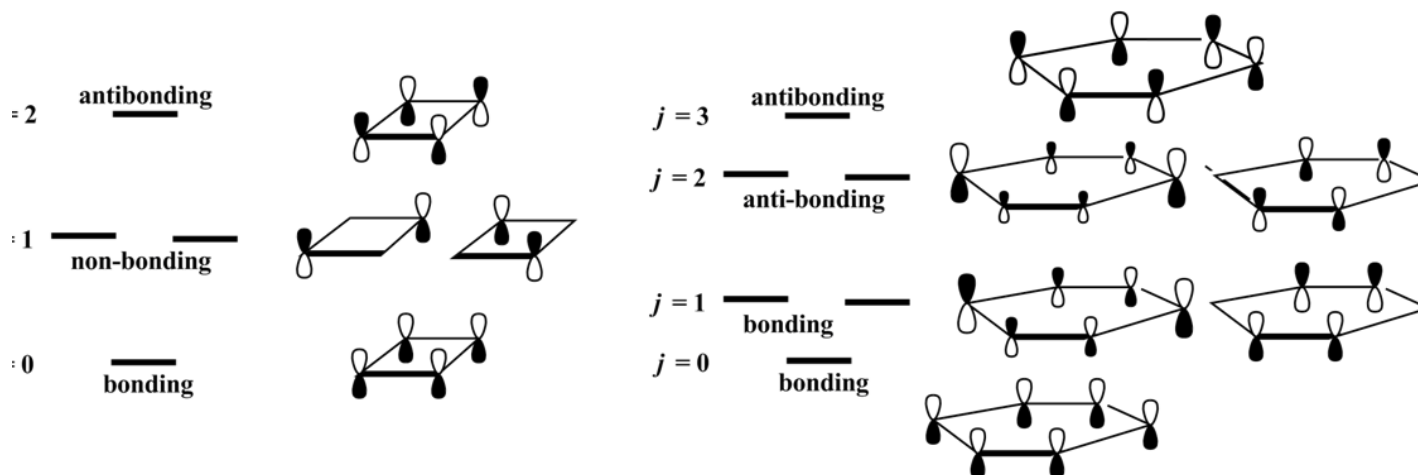
[†] Note that one wave is $\sin(j\theta)$ and the other is $\cos(j\theta)$. They differ by 90° ($\pi/2$ radians).

(b) Using *qualitative* arguments (based on the number of nodes and/or the number of in-phase or out-of-phase interactions between neighbours) construct energy level diagrams and label the orbitals as bonding, non-bonding or antibonding.

The energy increases with the number of nodes.

For C_4H_4 , $j = 0$ is bonding and $j = 2$ is antibonding. The two orbitals with $j = 1$ are *non-bonding* as there are no contacts between orbitals on adjacent atoms.

For C_6H_6 , $j = 0$ and $j = 1$ are bonding and $j = 2$ and $j = 3$ are antibonding.



(c) Based on your answer to (b), why is C_6H_6 aromatic and C_4H_4 antiaromatic?

C_6H_6 has 6 π electrons so has the $j = 0$ and $j = 1$ levels full. All of these levels are bonding with the lowest, $j = 0$, level more bonding than it would be in a straight chain hexatriene:

C_4H_4 has 4 π electrons so has the $j = 0$ level full and $j = 1$ levels half full. The lowest, $j = 0$, level is more bonding than it would be in a straight chain butadiene. However, the $j = 1$ levels are non-bonding whereas in butadiene all of the electrons are in bonding orbitals (see lecture 2).