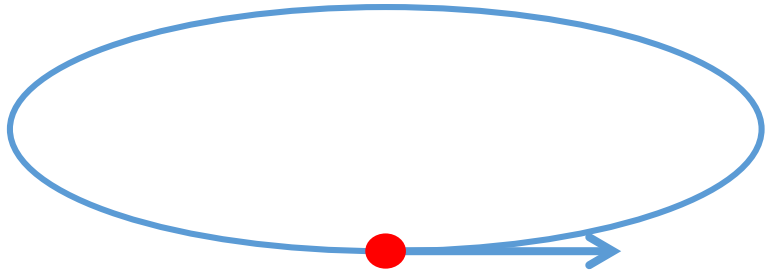
Particle on a circle

$$-\frac{\hbar^2}{2\mu R^2}\frac{\partial^2}{\partial\phi^2}\Phi = E\Phi$$



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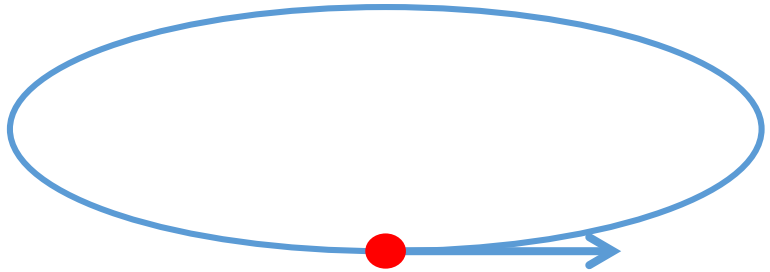

$$\Phi = \frac{1}{\sqrt{2\pi}}e^{im\phi}$$

$$m = 0, \pm 1, \pm 2, \pm 3, \ldots$$

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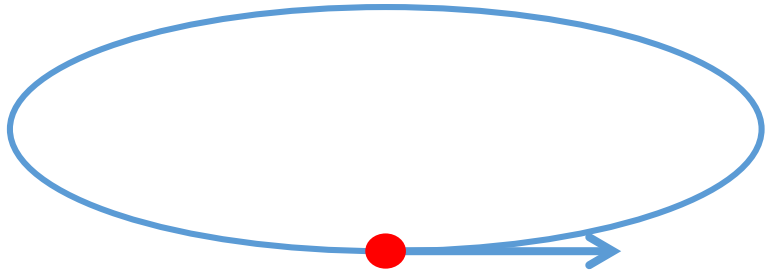

$$\Phi = \frac{1}{\sqrt{2\pi}}e^{im\phi}$$

$$m = 0, \pm 1, \pm 2, \pm 3, \ldots$$

$$E = \frac{h^2 m^2}{8\pi^2 \mu R^2}$$

Particle on a circle

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$$\Phi = \frac{1}{\sqrt{2\pi}}e^{im\phi}$$

$$E = \frac{h^2m^2}{8\pi^2\mu R^2} \qquad m = 0$$

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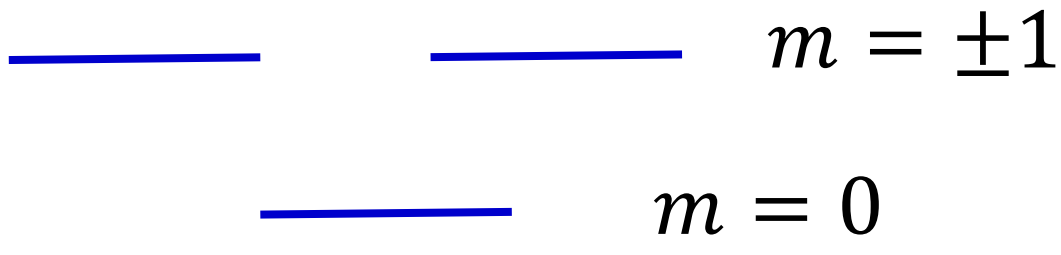

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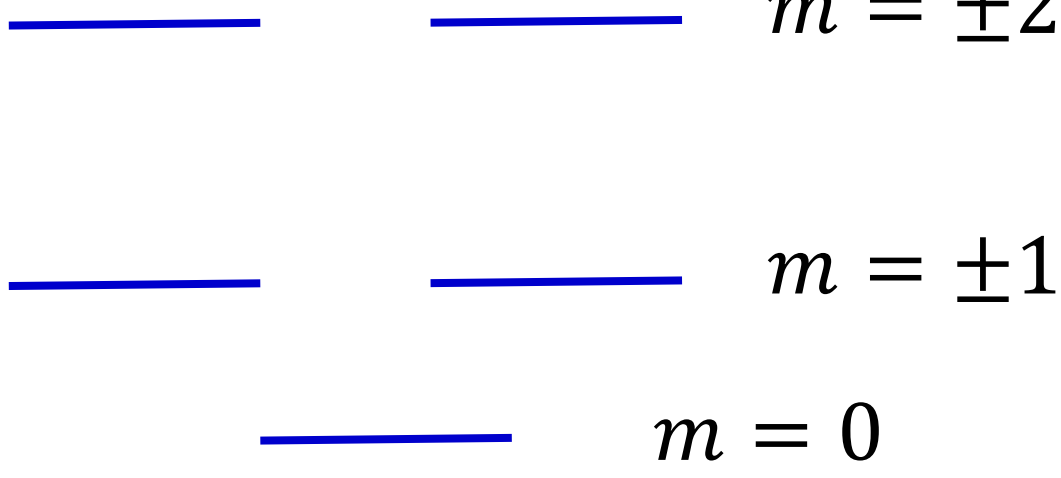

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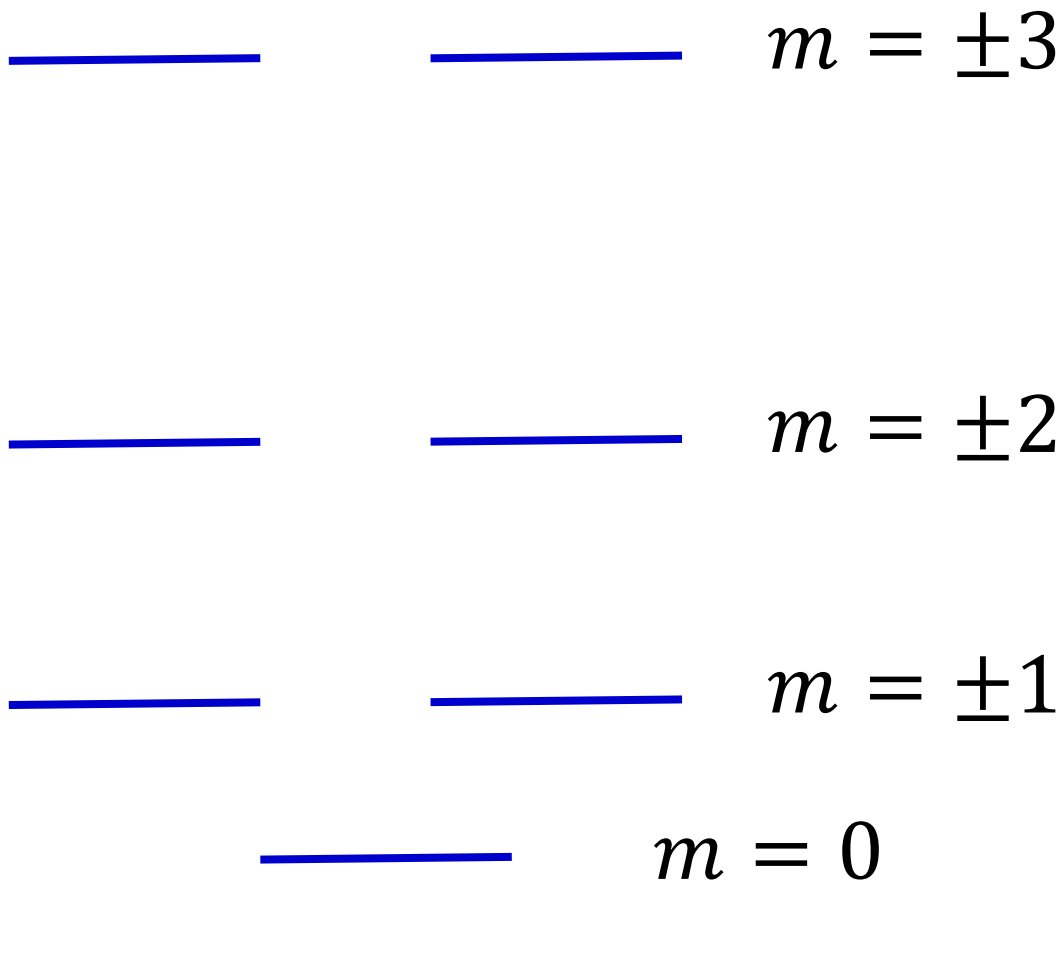
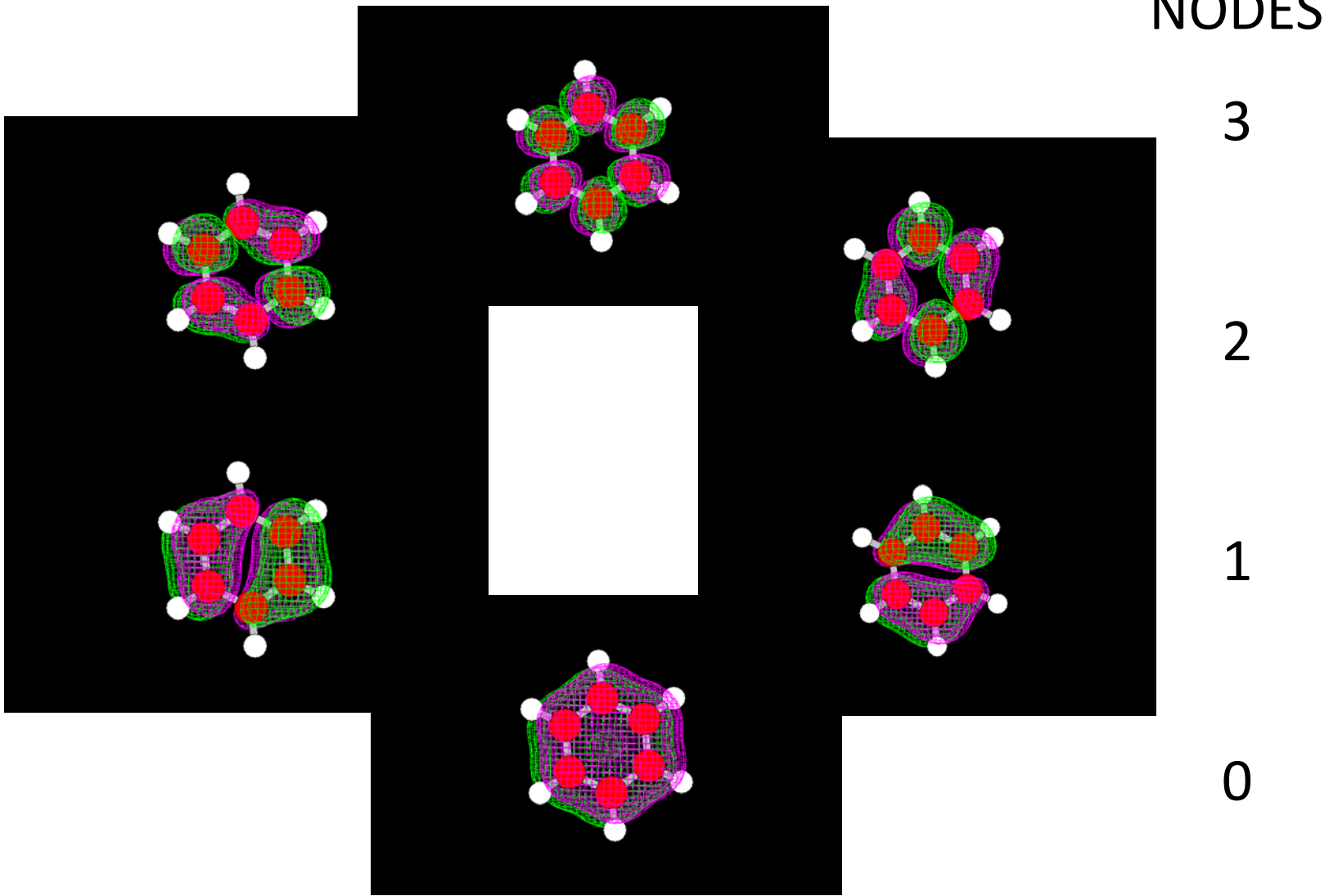
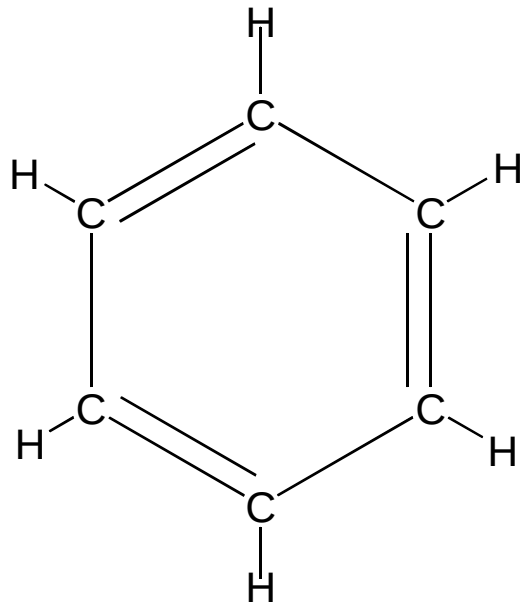


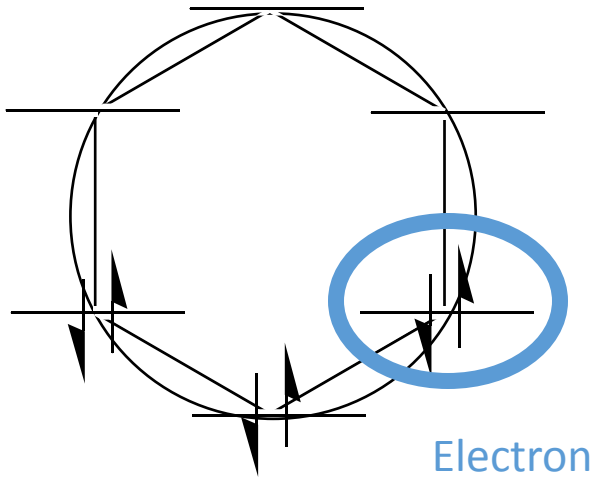
Benzene molecular orbitals



We can construct molecular orbitals of benzene using the six electrons in π orbitals



Benzene Structure

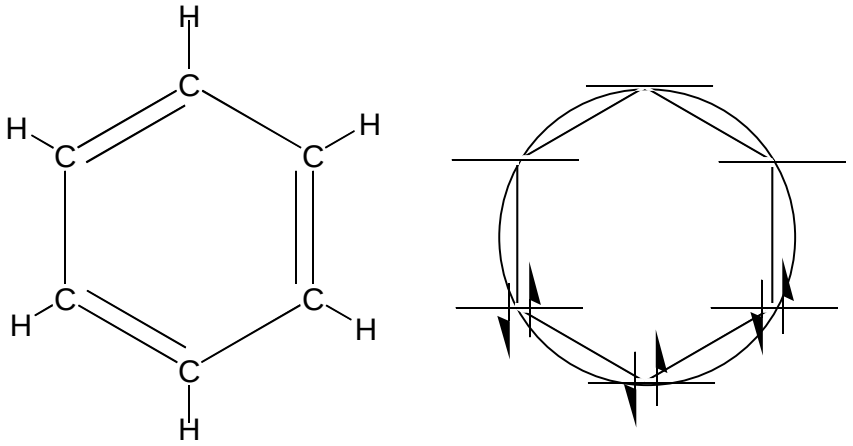


Electrons are spin-paired

Electronic Energy Levels

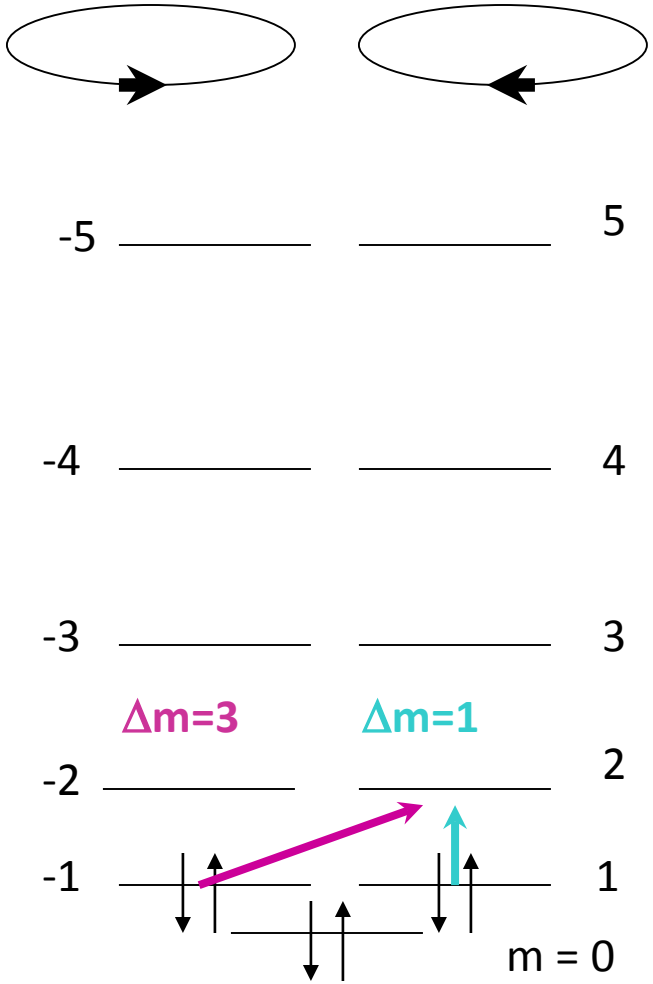
Free electron model applied to benzene

The π system approximates circular electron path.



$$-\frac{\hbar^2}{2\mu R^2}\frac{\partial^2}{\partial\phi^2}\Phi = E\Phi \qquad \Phi = \frac{1}{\sqrt{2\pi}}e^{im\phi}$$

$$m = 0, \pm1, \pm2, \pm3, \ldots$$



Energy levels calculated by particle on a circle model

The energies for the circle model differ in that they come in pairs. Since the quantum numbers can be both positive and negative:

$$m = 0, \pm 1, \pm 2, \pm 3, \ldots$$

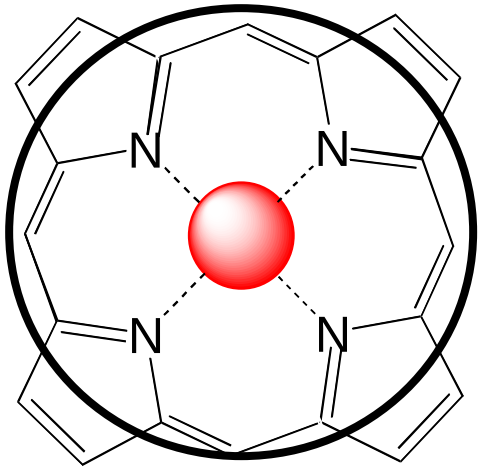
The energies can be calculated using:

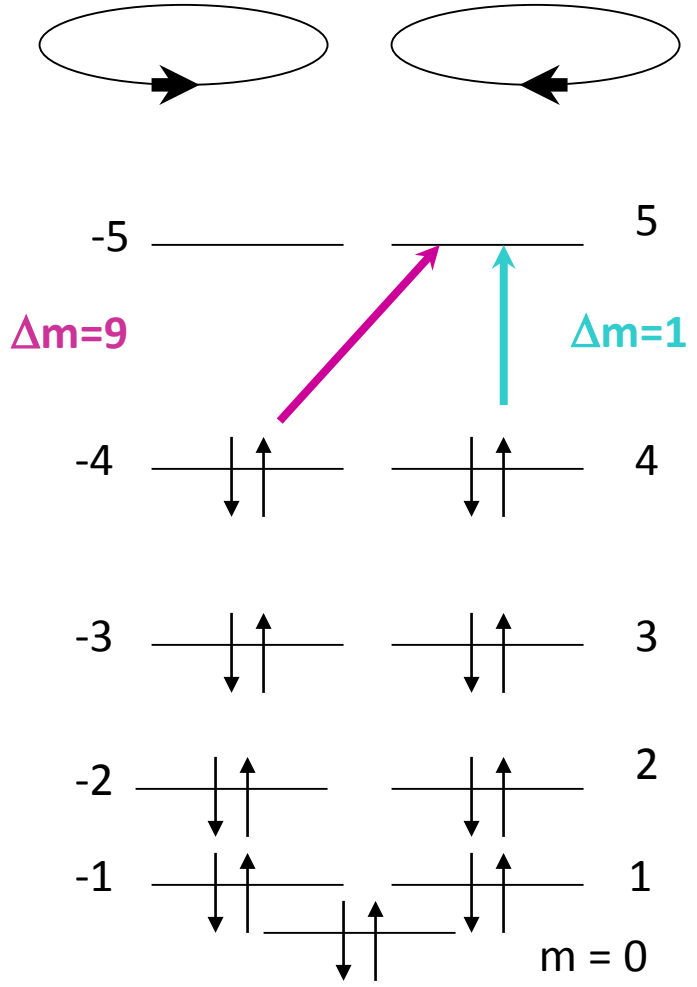
$$E = \frac{h^2 m^2}{8\pi^2 \mu R^2}$$

The analogy with the particle in a box is quite strong except for this pairing of the levels (above m = 0). The length L is replaced by πR.

The perimeter model applied to porphyrin

The aromatic ring has 18 electrons.
The π system approximates circular electron path.

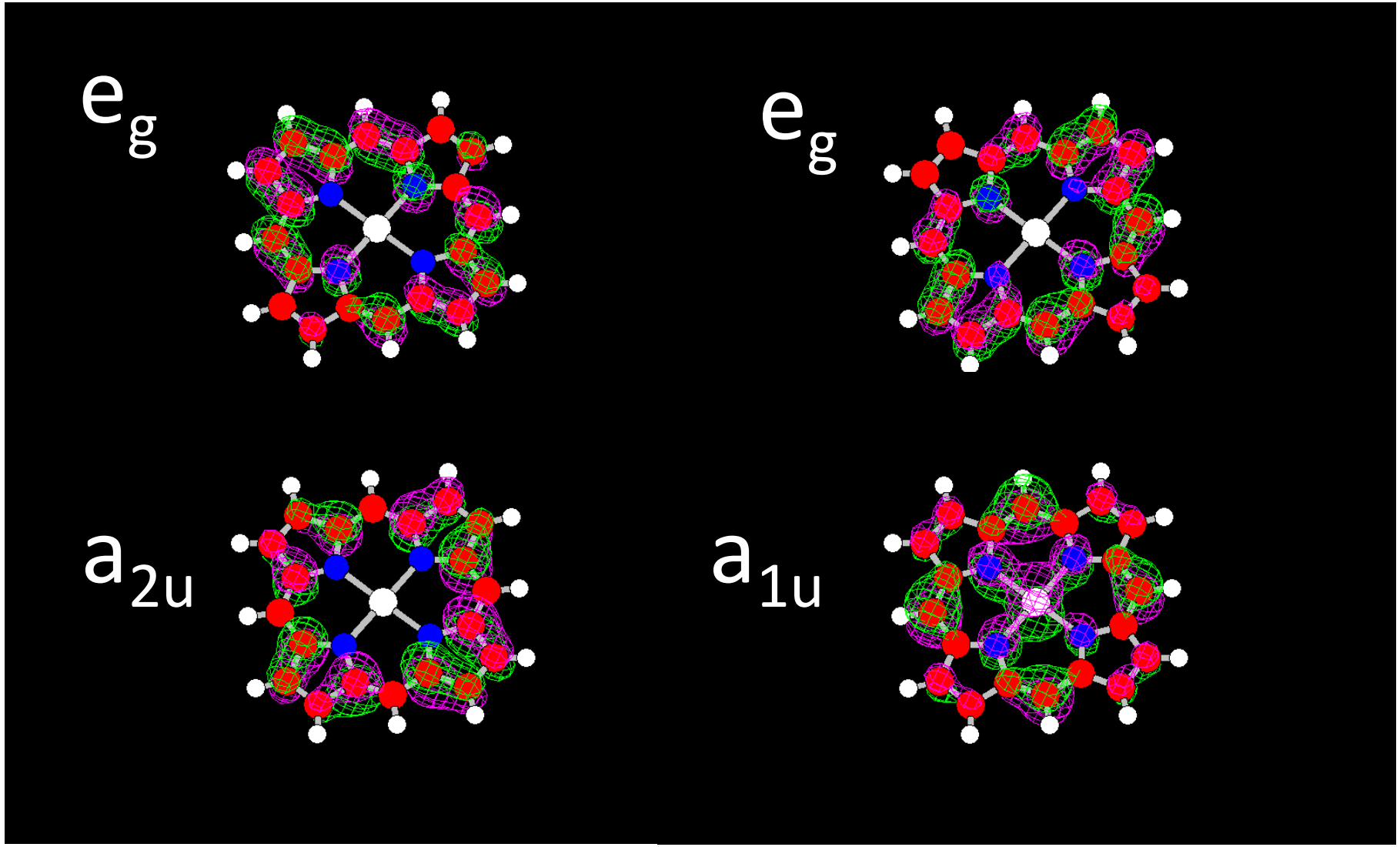




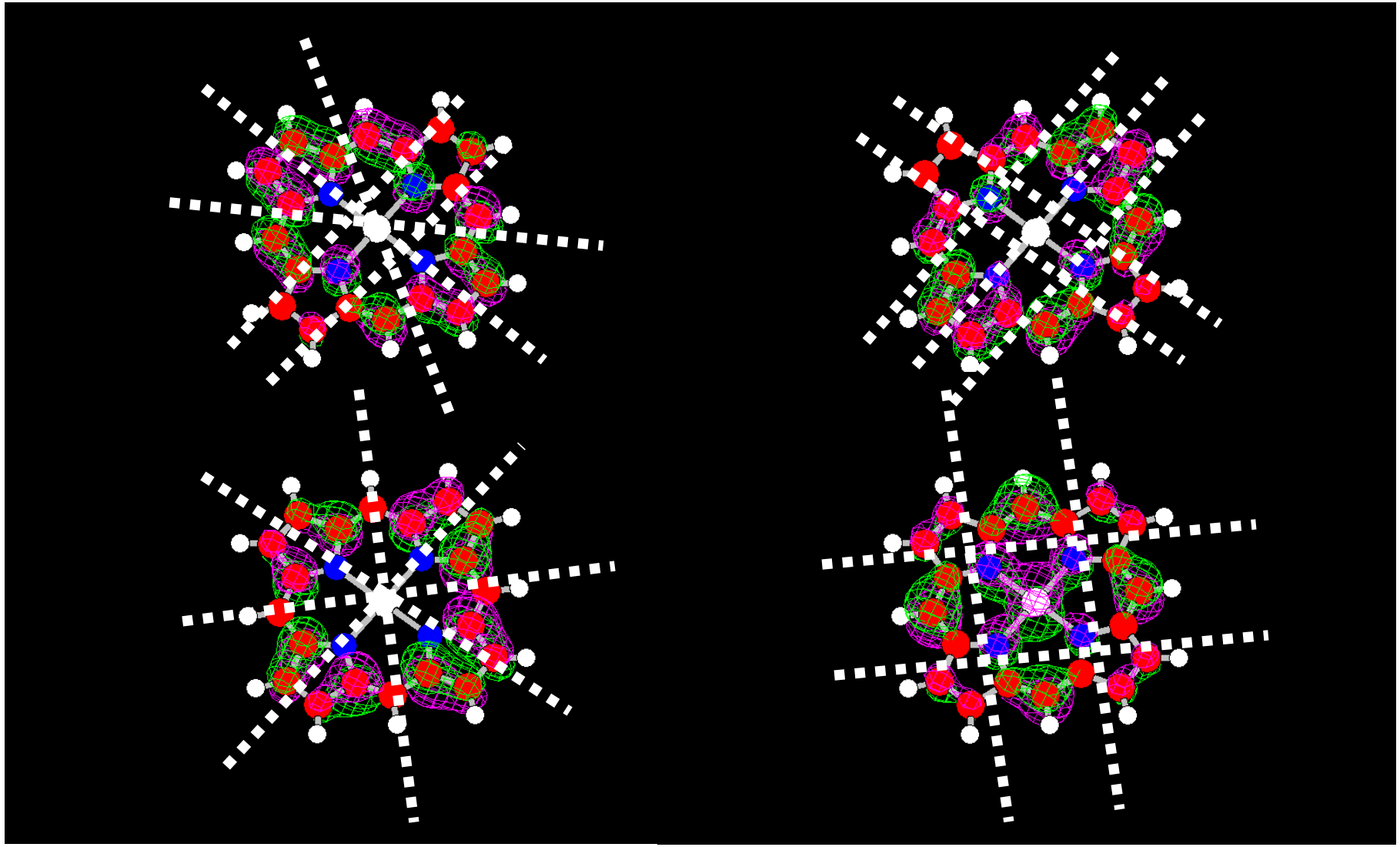
$$-\frac{\hbar^2}{2\mu R^2}\frac{\partial^2}{\partial\phi^2}\Phi = E\Phi \qquad \Phi = \frac{1}{\sqrt{2\pi}}e^{im\phi}$$

$$m = 0, \pm 1, \pm 2, \pm 3, \ldots$$

Porphine orbitals



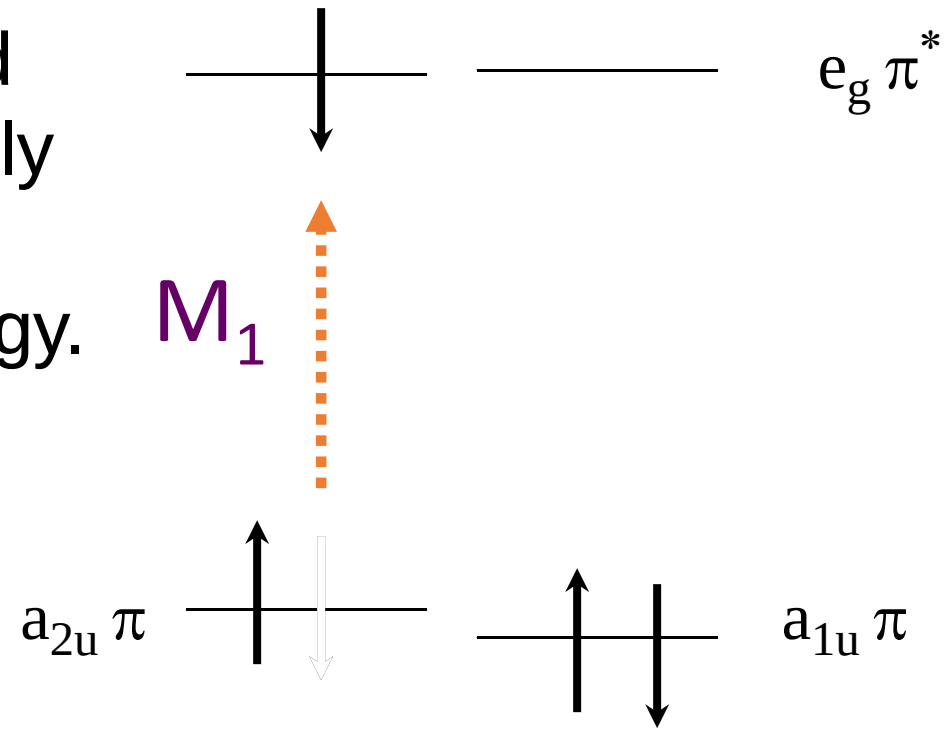
Nodes in Porphine orbitals



The four orbital model represents the highest occupied and lowest unoccupied MOs of porphyrins

The two highest occupied orbitals (a_{1u},a_{2u}) are nearly equal in energy. The e_g orbitals are equal in energy. Transitions occur from:

$a_{1u} \rightarrow e_g$ and $a_{2u} \rightarrow e_g$.



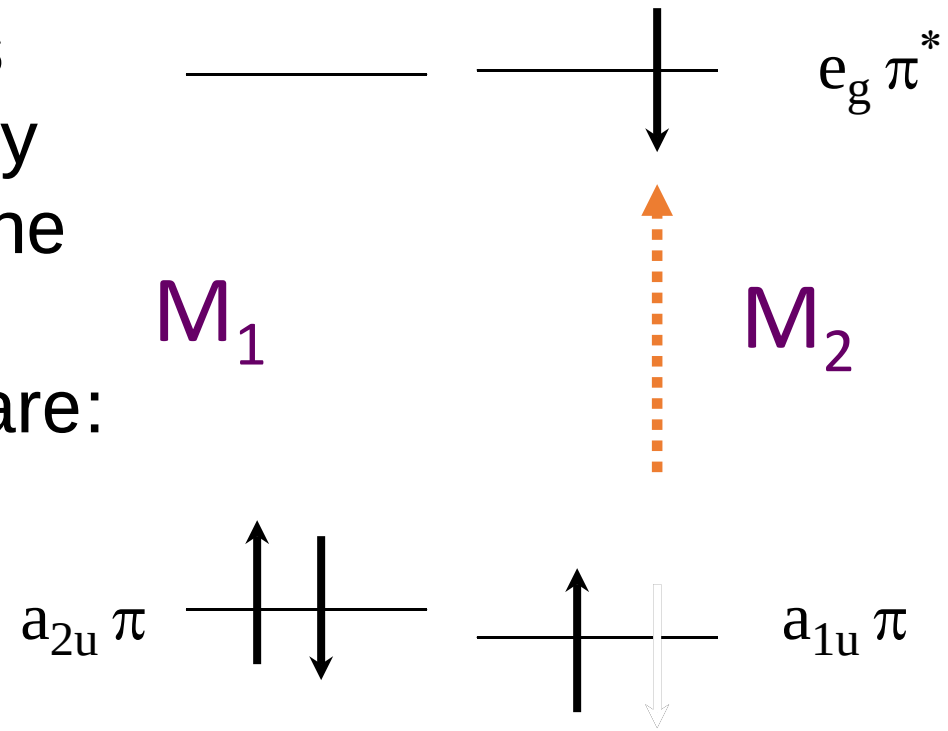
The transitions from ground state π orbitals a_{1u} and a_{2u} to excited state π^* orbitals e_g mix by configuration interaction

Two electronic transitions are observed. One is very strong (B or Soret) and the other is weak (Q).

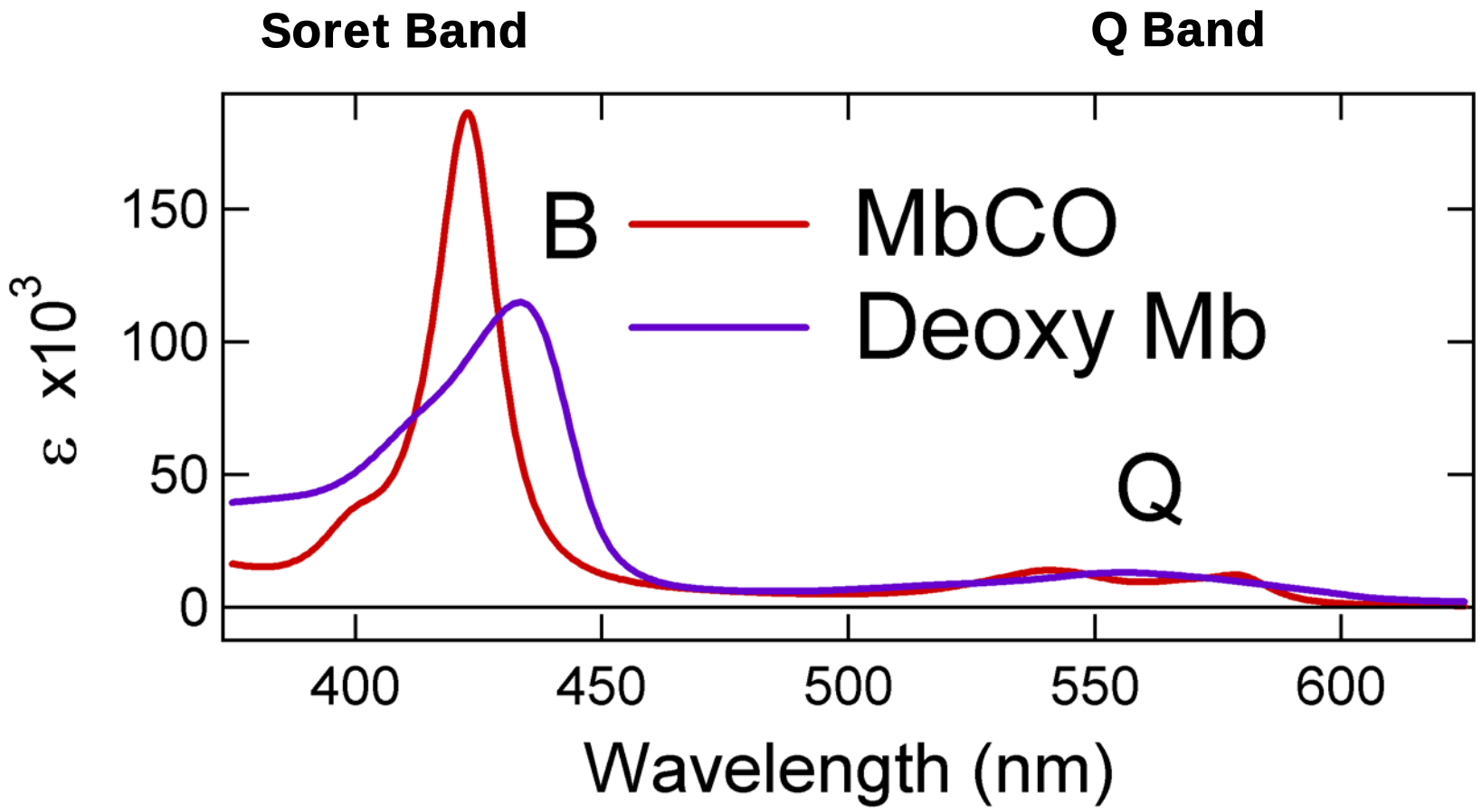
The transition moments are:

$M_B = M_1 + M_2$

$M_Q = M_1 - M_2 \approx 0$



Absorption spectra for MbCO and deoxy Mb



The spectrum of the heme has two bands. The B band or Soret band is allowed and therefore intense. The Q band is forbidden. It is observed because of vibronic coupling with the Soret band.