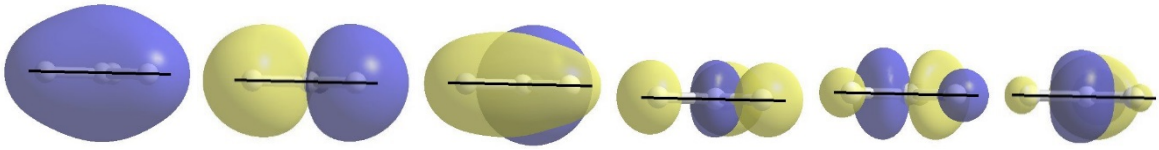
Exercise 2.1
Sigma and Pi Symmetry

What are sigma and pi?

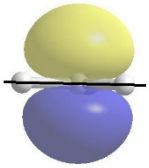
Sigma (σ) and pi (π) are different types of symmetry. Whether an orbital is σ-symmetric or π-symmetric is determined by the shape of the molecule and the nodes of the orbital.

First, imagine a plane passing through every atom in the molecule. The picture below shows a side view of BH_3, a trigonal planar molecule; the plane through all four atoms is shown using a black line:

Then look at the orbital in question. Do any of the lobes of the orbital cross your imaginary plane? If so, the orbital is σ-symmetric. Six examples are shown below:



If, instead, the orbital has a node that lies along that plane, the orbital is probably π-symmetric:[1]



Note that the only nodes affecting the orbital's symmetry are those that lie along the plane passing through all atoms in the molecule. Other nodes do *not* affect the orbital's symmetry! Instead, they relate to whether the orbital is bonding, nonbonding or antibonding.

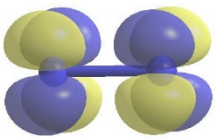
Why does symmetry matter?

Atomic orbitals can only combine to make molecular orbitals if they have the same type of symmetry. Atomic orbitals with different kinds of symmetry do not interact with each other.

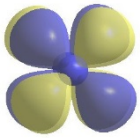
---

[1] Orbitals with delta(δ) symmetry also meet this requirement. A δ-symmetric orbital has a node along your imaginary plane and another one perpendicular to that. Imagine two d orbitals approaching each other so that all four lobes line up. δ-symmetric orbitals are not typically discussed in first year classes, and orbitals cannot be δ-symmetric if they have been made from (or are) s or p orbitals.

Side view of a δ-symmetric orbital:



Looking down the bond at a δ-symmetric orbital:



Convention for labeling axes

It is important to remember that the *z* axis is always "the one that's different".

- If two p orbitals have σ symmetry and one has π symmetry, p_z has the π symmetry.
- If two p orbitals have π symmetry and one has σ symmetry, p_z has the σ symmetry.

As a result, in linear molecules, all atoms lie along the *z* axis. Conversely, in planar molecules, all atoms lie along the *xy* plane (and the *z* axis points perpendicular to the plane of the molecule).

1. Identify each of the following atomic orbitals as σ-symmetric or π-symmetric in a linear molecule. To help you, draw the orbital on an atom in a linear molecule.

(a) s (b) p_x (c) p_y

(d) p_z (e) d_{xz} (f) d_{yz}

(g) d_{z^2}

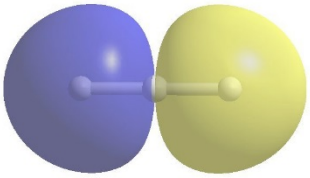
2. Identify each of the following atomic orbitals as σ-symmetric or π-symmetric in a trigonal planar molecule. To help you, draw the orbital on an atom in a trigonal planar molecule.

(a) s (b) p_x

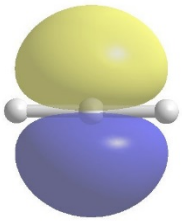
(c) p_y (d) p_z

3. Identify each of the following molecular orbitals of BeH_2 as σ-symmetric or π-symmetric.

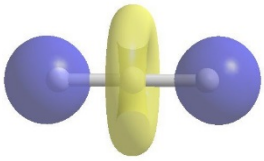
(a)



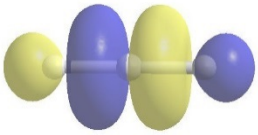
(b)



(c)

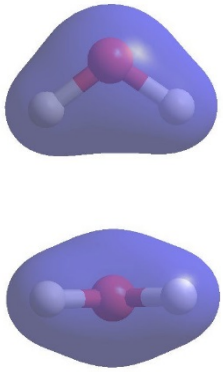


(d)

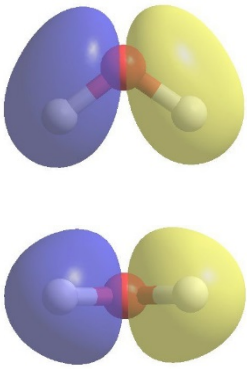


4. Identify each of the following molecular orbitals of H_2O as σ-symmetric or π-symmetric. Both top view and side view of each molecular orbital are provided.

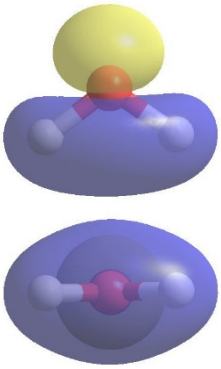
a)



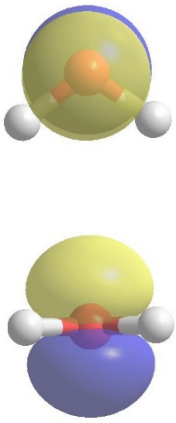
b)



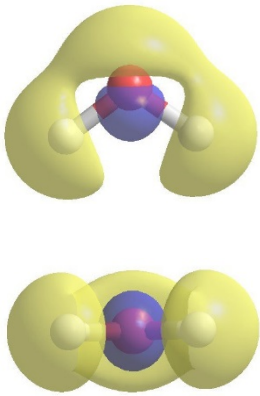
c)



(d)



e)



f)