Experiment 19

Molecular Orbitals

Pre-Lab Assignment

Before coming to lab:

- Read the lab thoroughly.
- Answer the pre-lab questions that appear at the end of this lab exercise.

Purpose

The hybridization and bonding of a variety of diatomic molecules will be analyzed using their molecular orbital diagrams.

Background

Due to their wave-particle behavior, electrons in atoms and molecules are best described as densities. Each electron in an atom is assigned a set of four quantum numbers, (n, l, m_l, m_s) that describe its location, shape, and energy. The principal quantum number, n, describes an electron's energy level. The azimuthal, or angular momentum quantum number, l, describes the shape of an electron's orbital (s, p, d, or f). The magnetic quantum number, m_l, dictates the orientation in space of the orbital, and the spin quantum number, m_s, the direction of the electron's spin.

When atoms combine to form molecules, these atomic orbitals will average themselves into new shapes in order to match their three-dimensional VSEPR electronic geometries. These new hybrid orbitals are formed on central atoms and, while having some characteristics of their original atomic orbitals, are uniquely shaped and oriented. For example, a hybrid formed from an s-orbital and a p-orbital would make two sp-hybrids that are 180° apart that are a 50/50 mix of the s and p orbital, matching the linear VSEPR electronic geometry. The number of hybrids generated is always equal to the number of atomic orbitals used to create them and all hybrids are equivalent in shape and energy.

To bond, atoms' electronic orbitals, either atomic or hybrid, must overlap by physically occupying the same space and form new molecular orbitals. The wave-like properties of electrons mean that this overlap can be either constructive, meaning that the phases of the waves match, or destructive, meaning that the phases of the waves are exactly opposite and cancel out. Constructive overlap forms bonding molecular orbitals which are lower in energy and more stable and destructive forms antibonding molecular orbitals which are higher in energy and less stable.

The direction of the overlap determines the type of bond that is formed. If the orbitals are facing one another, the overlap is said to be direct and called a σ-bond. If the orbitals are parallel to one another, it is called a π-bond. Any type of orbitals, hybridized or unhybridized, can form a σ-bond whereas only unhybridized p or d orbitals can form π-bonds. A molecular orbital diagram is a way to pictorially represent the types of molecular orbitals and bonds that a molecule can form and where the electrons in the molecule are placed. Bond order can be determined by Eqn. 1 and is a more powerful way than Lewis structures to define the bonding present in a molecule. Bond orders greater than 0 represent stable molecules, whereas bond orders with zero or negative

values represent unstable molecules. It also explains why some respond to magnetic fields and others do not.

bond order = 1/2[(# of e^- in bonding orbitals) – (# of e^- in antibonding orbitals)] Eqn. 1

Diagmagnetic molecules have all electrons paired in their molecular orbitals and do not respond to magnetic fields. Paramagnetic molecules have at least one unpaired electron in their molecular orbitals and are attracted to magnetic fields.

Procedure

Part I: Hybridization and Molecular Orbital Theory

1. Complete the questions on your Data Sheet.

Experiment 19—Data Sheet

Name: _____

Part I: Atomic Orbitals

s-Orbitals

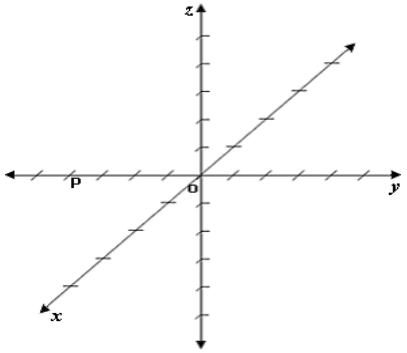
1. What is the value of l for an s-orbital? _____

2. How many nodes does an s-orbital have? _____

3. What is the value of m_l for an s-orbital? _____

4. How many s-orbitals are there in each n-level? _____

5. Sketch an s-orbital below. Shade in regions of different phase as applicable.



p-Orbitals

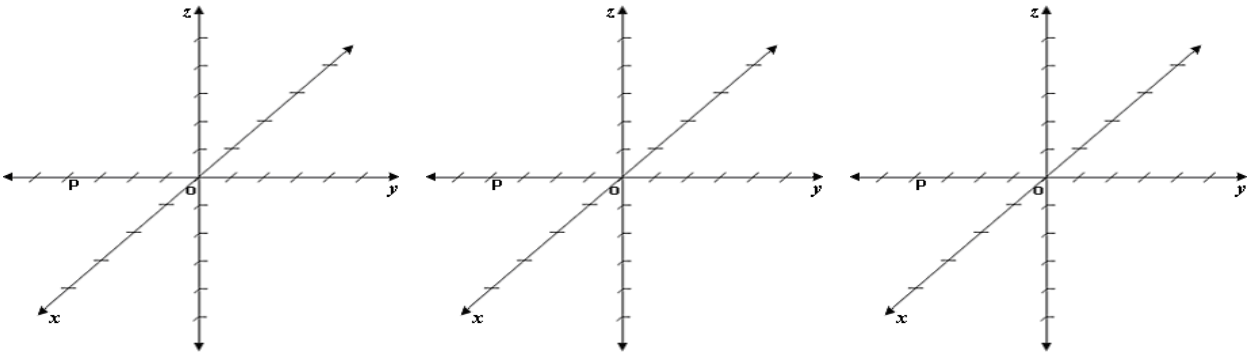
6. What is the value of l for a p-orbital? _____

7. How many nodes does a p-orbital have? _____

8. What is the value of m_l for a p-orbital? _____

9. How many p-orbitals are there in each n-level? _____

10. Sketch the p-orbitals below. Shade in regions of different phase as applicable.



d-Orbitals

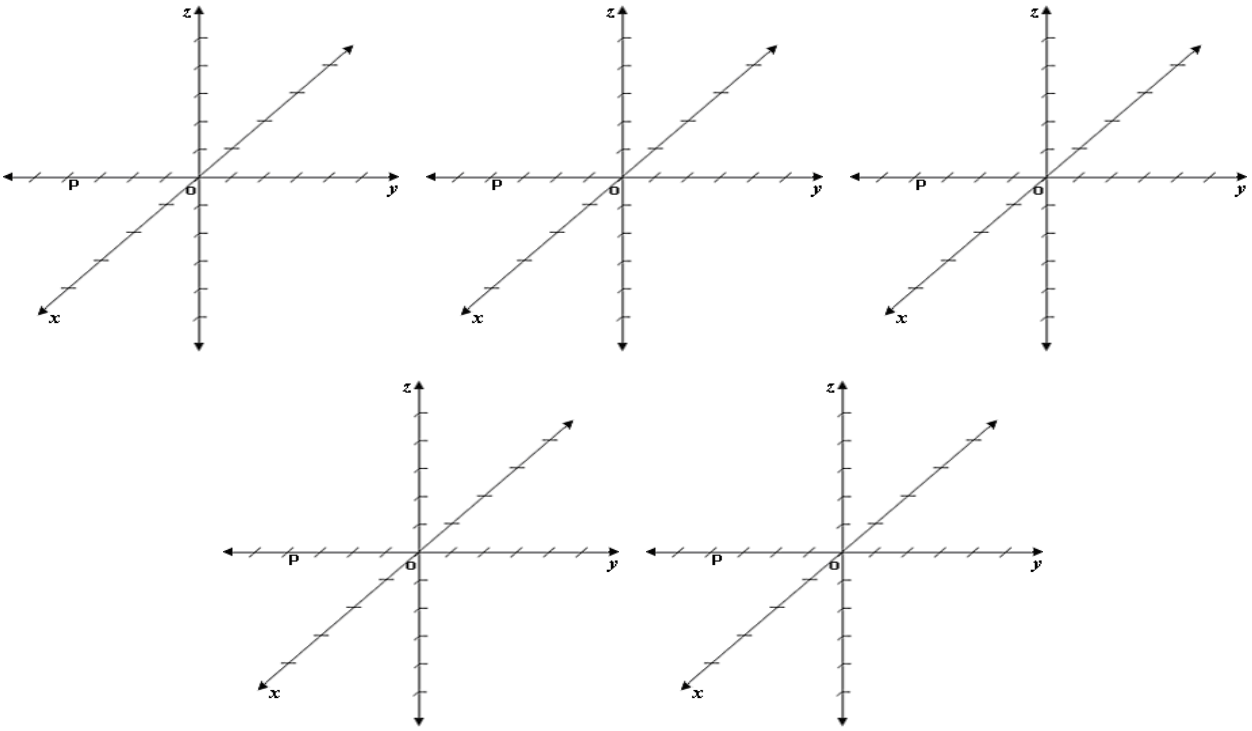
11. What is the value of l for a d-orbital? _____

12. How many nodes does a d-orbital have? _____

13. What is the value of m_l for a d-orbital? _____

14. How many d-orbitals are there in each n-level? _____

15. Sketch the d-orbitals below. Shade in regions of different phase as applicable.



f-Orbitals

16. What is the value of l for an f-orbital? _____

17. How many nodes does an f-orbital have? _____

18. What is the value of m_l for an f-orbital? _____

19. How many f-orbitals are there in each n-level? _____

Part II: Hybridized Orbitals

sp-Hybrids

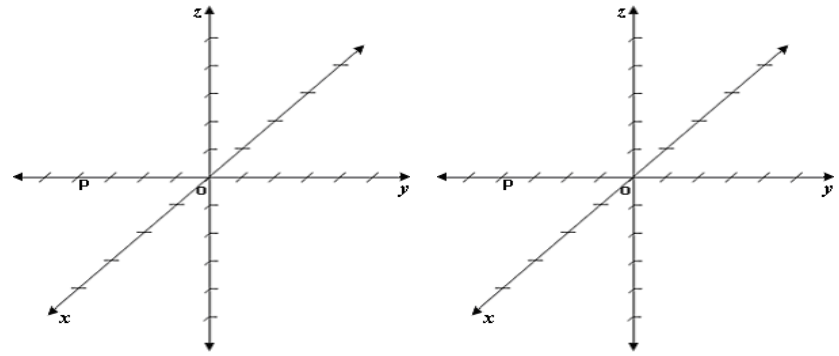
1. What atomic orbitals combine to form sp-hybrids? _____

2. How many sp-hybrids are formed? _____

3. What electronic geometry do sp-hybrids match? _____

4. How many unhybridized p-orbitals remain? _____

5. Sketch the sp-hybrids below.



sp^2-Hybrids

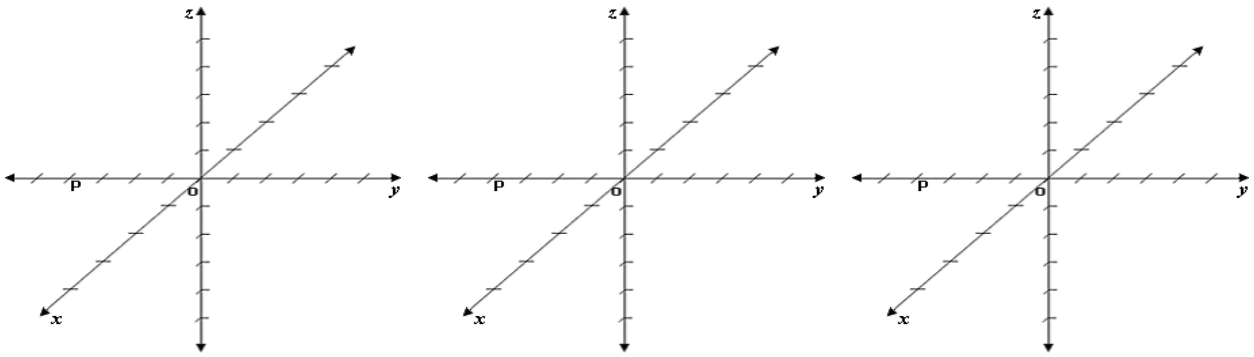
6. What atomic orbitals combine to form sp^2-hybrids? _____

7. How many sp^2-hybrids are formed? _____

8. What electronic geometry do sp^2-hybrids match? _____

9. How many unhybridized p-orbitals remain? _____

10. Sketch the sp^2-hybrids below.



sp^3-Hybrids

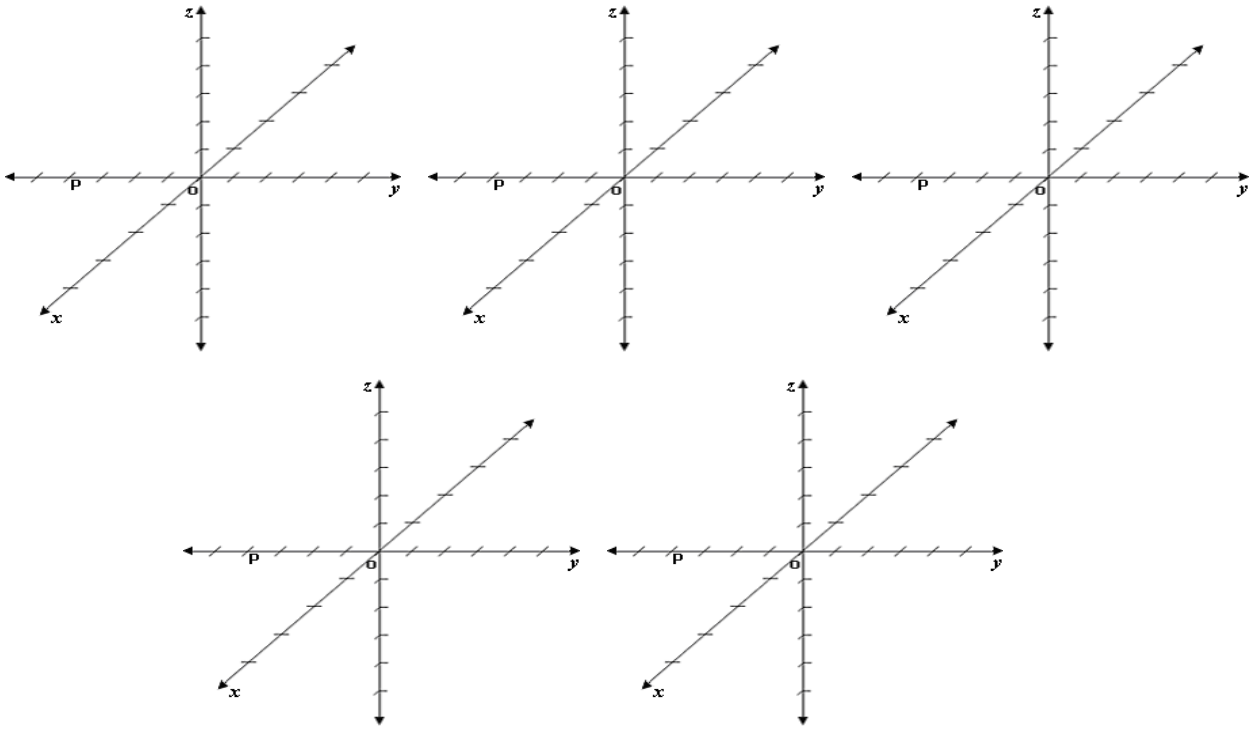
11. What atomic orbitals combine to form sp^3-hybrids? _____

12. How many sp^3-hybrids are formed? _____

13. What electronic geometry do sp^3-hybrids match? _____

14. How many unhybridized p-orbitals remain? _____

15. Sketch the sp^3-hybrids below.



sp^3d-Hybrids

16. What atomic orbitals combine to form sp^3d-hybrids? _____

17. How many sp^3d-hybrids are formed? _____

18. What electronic geometry do sp^3d-hybrids match? _____

sp^3d^2-Hybrids

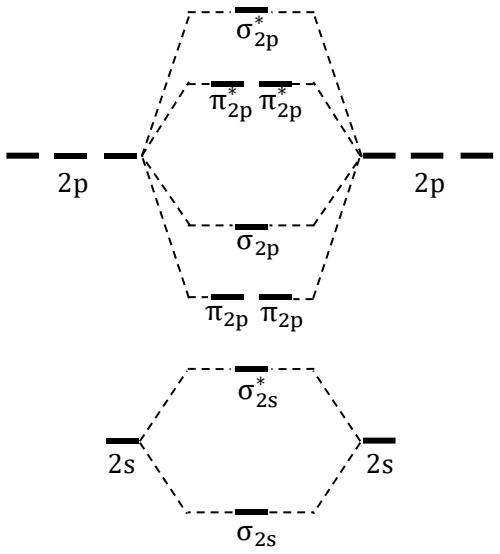
19. What atomic orbitals combine to form sp^3d^2 hybrids? _____

20. How many sp^3d^2-hybrids are formed? _____

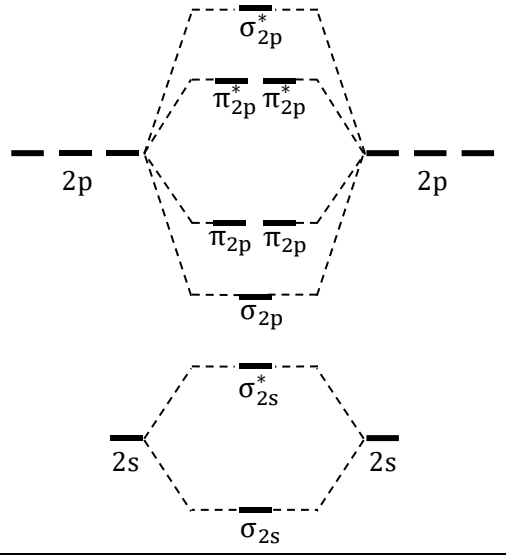
21. What electronic geometry do sp^3d^2-hybrids match? _____

Part III: Molecular Orbitals

1. Complete the molecular orbital diagram for N_2 below. Calculate the bond order and determine whether the molecule is paramagnetic or diamagnetic.

Molecule	Molecular Orbital Diagram	Bond Order
N_2		*Circle one:* Paramagnetic Diamagnetic

2. Complete the molecular orbital diagram for N_2 below. Calculate the bond order and determine whether the molecule is paramagnetic or diamagnetic.

Molecule	Molecular Orbital Diagram	Bond Order
O_2		*Circle one:* Paramagnetic Diamagnetic

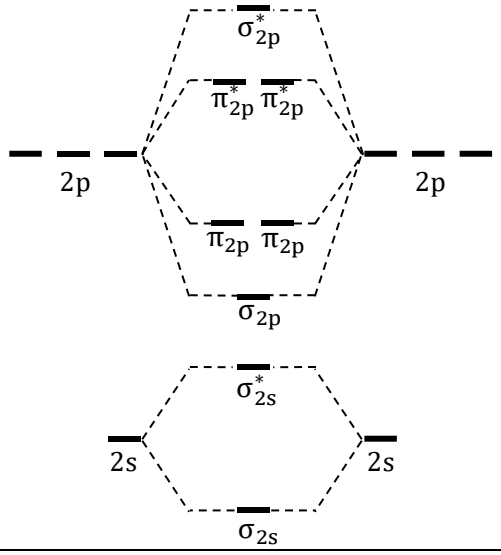
3. Which molecular orbitals have been flipped between N_2 and O_2? Why?

4. Sketch and label each of the molecular orbitals in N_2. Use shading to illustrate orbital lobes with opposite phases. If a set of orbitals are degenerate and have the same shape, draw only one orbital in the set.

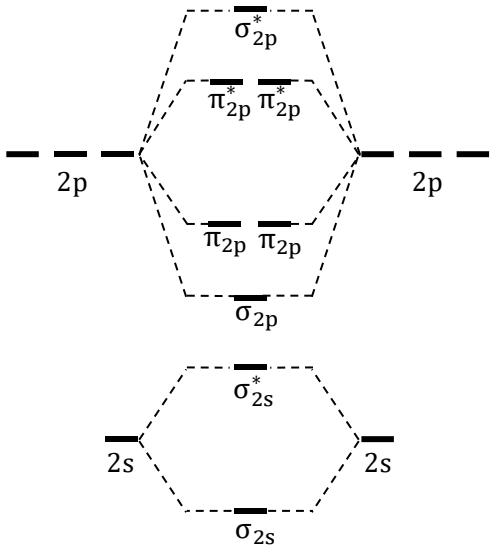
Orbital Name	**Sketch**

5. Will the sketches for the molecular orbitals look the same for O_2? Why or why not?

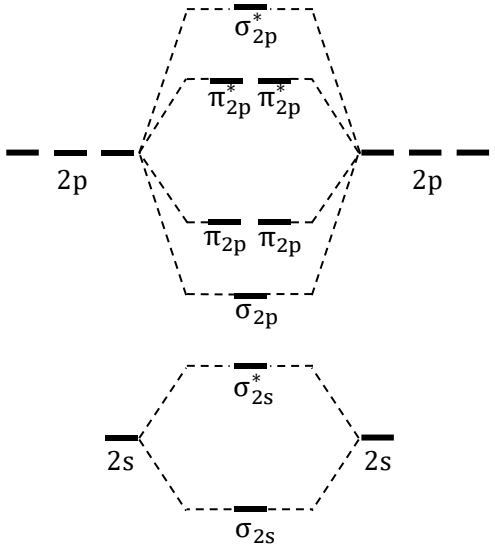
6. Complete the molecular orbital diagram for F_2 below. Calculate the bond order and determine whether the molecular is paramagnetic or diamagnetic.

Molecule	Molecular Orbital Diagram	Bond Order
F_2		*Circle one:* Paramagnetic Diamagnetic

7. Complete the molecular orbital diagram for F_2^{2+} below. Calculate the bond order and determine whether the molecule is paramagnetic or diamagnetic.

Molecule	Molecular Orbital Diagram	Bond Order
F_2^{2+}		*Circle one:* Paramagnetic Diamagnetic

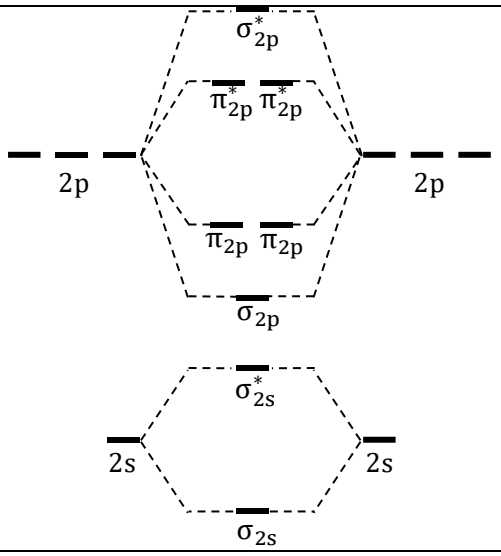
8. Complete the molecular orbital diagram for F_2^{2-} below. Calculate the bond order and determine whether the molecule is paramagnetic or diamagnetic.

Molecule	Molecular Orbital Diagram	Bond Order
F_2^{2-}		*Circle one:* Paramagnetic Diamagnetic

9. Which is the most stable: F_2, F_2^{2+}, or F_2^{2-}? Why?

10. Complete the molecular orbital diagram for NO+ below. Calculate the bond order and determine whether the molecule is paramagnetic or diamagnetic.

Molecule	Molecular Orbital Diagram	Bond Order
NO^+ Assume molecular orbitals fill like O_2.		*Circle one:* Paramagnetic

		Diamagnetic

Experiment 19—Post-Lab Assignment

1. Complete the following molecular orbital diagrams by adding the correct electrons for Si_2 and SO^+. For each, determine the bond order and whether the molecule is paramagnetic or diamagnetic.

Si_2

Atomic Orbitals	Molecular Orbitals	Atomic Orbitals
	σ^*_{3p} _____	
	π^*_{3p} _____ _____	
3p _____ _____ _____		_____ _____ _____ 3p
	σ_{3p} _____	
	π_{3p} _____ _____	
	σ^*_{3s} _____	
3s _____		_____ 3s
	σ_{3s} _____	

SO^+

Atomic Orbitals	Molecular Orbitals	Atomic Orbitals
	σ^*_{3p} _____	
	π^*_{3p} _____ _____	
2p _____ _____ _____		_____ _____ _____ 3p
	π_{3p} _____ _____	
	σ_{3p} _____	
	σ^*_{3s} _____	
2s _____		_____ 3s
	σ_{3s} _____	

Experiment 19—Pre-Lab Assignment

Name: _____

1.For each of the following sets of quantum numbers (n, l, m_l, m_s), decide if the set is valid or invalid. For valid sets, identify the type of orbital (i.e., 2p) that the set describes. For invalid sets, explain why the set cannot exist.

a. n = 2, l = 1, m_l = 0, m_s = ½

b. n = 0, l = 0, m_l = 0, m_s = ½

c. n = 3, l = 2, m_l = -2, m_s = - ½

d. n = 3, l = -2, m_l = 3, m_s = ½

2. Explain the difference between Schrödinger's orbitals and Bohr's electron orbits.

3. For each quantum number, list the symbol and give a brief description.

a. Principal

b. Angular Momentum or Azimuthal

c. Magnetic

d. Spin

4. Complete the following table to indicate the total number of orbitals in each energy level (n). In the remaining columns, specify how many of those orbitals are s, p, d, and f.

Level n	Total # of Orbitals	# of s-orbitals	# of p-orbitals	# of d-orbitals	# of f-orbitals
1					
2					
3					

4					