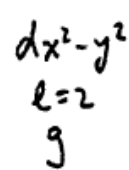
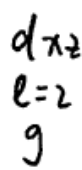
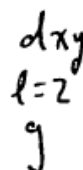
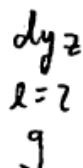
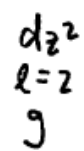
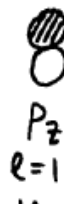
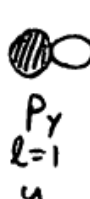
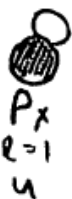
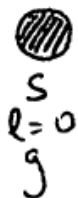
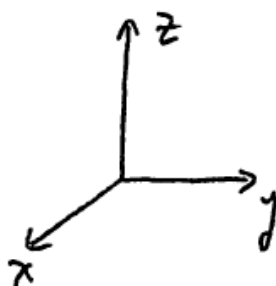


CHEM-457 PS1 Solutions

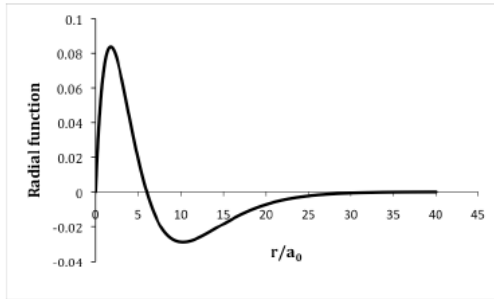
1.



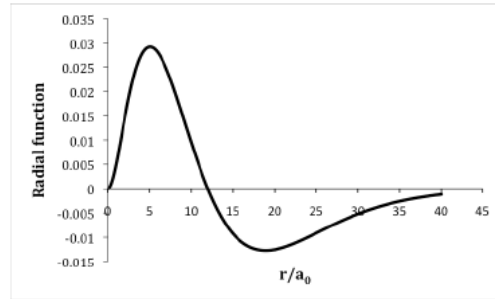
2.  
MF&T #2.9

a.

$3p_z$

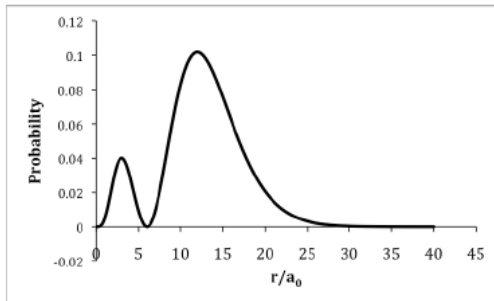


$4d_{xz}$

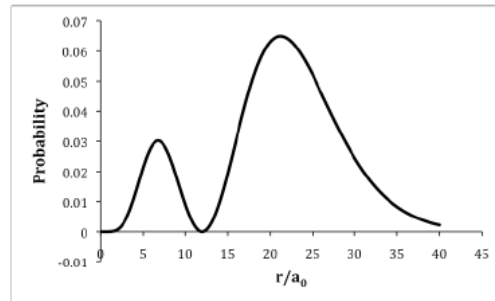


b.

$3p_z$



$4d_{xz}$

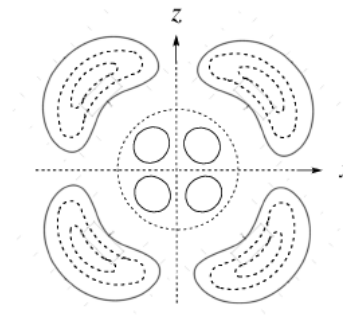


c.

$3p_z$

For contour map, see Figure 2.8.

$4d_{xz}$



MF&T #2.9

a.	Z	(1s <sup>2</sup> ) 1	(2s <sup>2</sup> 2p <sup>6</sup> ) 0.85	(3s <sup>2</sup> 3p <sup>n</sup> ) 0.35	Z*	r
P	15	- (2 × 1 + 8 × 0.85 + 4 × 0.35) =			4.8	106 pm
S	16	- (2 × 1 + 8 × 0.85 + 5 × 0.35) =			5.45	102 pm
Cl	17	- (2 × 1 + 8 × 0.85 + 6 × 0.35) =			6.1	99 pm
Ar	18	- (2 × 1 + 8 × 0.85 + 7 × 0.35) =			6.75	98 pm

The size of the atoms decreases slightly as Z increases, even though the number of electrons in the atom increases, because Z\* increases and draws the electrons closer. Ar has the strongest attraction between the nucleus and the 3p electron, and the smallest radius.

b.	Z	(1s <sup>2</sup> ) 0.85	(2s <sup>2</sup> 2p <sup>6</sup> ) 0.35	Z*	r
O <sup>2-</sup>	8	- (2 × 0.85 + 7 × 0.35) =		3.85	126 pm
F <sup>-</sup>	9	- (2 × 0.85 + 7 × 0.35) =		4.85	119 pm
Na <sup>+</sup>	11	- (2 × 0.85 + 7 × 0.35) =		5.85	116 pm
Mg <sup>2+</sup>	12	- (2 × 0.85 + 7 × 0.35) =		6.85	86 pm

These values increase directly with Z, and parallel the decrease in ionic size. Increasing nuclear charge results in decreasing size for these isoelectronic ions, although the change between F<sup>-</sup> and Na<sup>+</sup> is smaller than might be expected.

c.	Cu	(1s <sup>2</sup> )	(2s <sup>2</sup> 2p <sup>6</sup> )	(3s <sup>2</sup> 3p <sup>6</sup> )	(3d <sup>10</sup> )	(4s <sup>1</sup> )				
4s	S =	2	+	8	+	(8 × 0.85)	+	(10 × 0.85) =	25.3	Z* = 29 - 25.3 = 3.7
3d	S =	2	+	8	+	(8 × 1.00)	+	(9 × 0.35) =	21.15	Z* = 29 - 21.15 = 7.85

The 3d electron has a much larger effective nuclear charge and is held more tightly; the 4s electron is therefore the first removed on ionization.

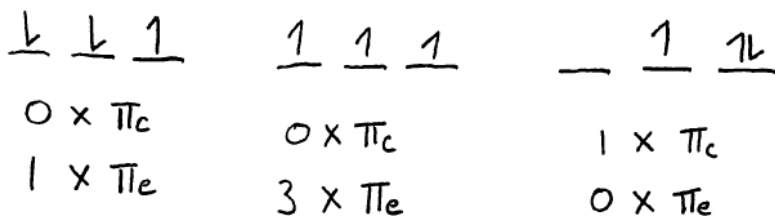
d.		(1s <sup>2</sup> )	(2s <sup>2</sup> 2p <sup>6</sup> )	(3s <sup>2</sup> 3p <sup>6</sup> )	(3d <sup>10</sup> )	(4s <sup>2</sup> 4p <sup>6</sup> )	(4d <sup>10</sup> )	(4f <sup>n</sup> )							
Ce	S =	2	+	8	+	8	+	10	+	8	+	10	= 46	Z* = 58 - 46 = 12	
	[Xe]	6s <sup>2</sup> 4f <sup>1</sup> 5d <sup>1</sup>						4f <sup>1</sup>							
Pr	S =	2	+	8	+	8	+	10	+	8	+	10	+	(2 × 0.35) = 46.7	Z* = 59 - 46.7 = 12.3
	[Xe]	6s <sup>2</sup> 4f <sup>2</sup>						4f <sup>2</sup>							
Nd	S =	2	+	8	+	8	+	10	+	8	+	10	+	(3 × 0.35) = 47.05	Z* = 60 - 47.05 = 12.95
	[Xe]	6s <sup>2</sup> 4f <sup>4</sup>						4f <sup>4</sup>							

The outermost electrons experience an increasing Z\*, and are therefore drawn in to slightly closer distances with increasing Z and Z\*.

3.

Electron Affinities ( $M + e^- \rightarrow M^-$ ) are usually negative. If an element has less electron affinity, the incoming  $e^-$  feels a lower  $Z^*$  + the exothermicity is reduced, which makes the value closer to zero. For K, the incoming  $e^-$  will occupy the 4s orbital where it will experience a high  $Z^*$  because it is not shielded well by the other 3s  $e^-$ . For Ca, 4s is full so the incoming  $e^-$  will enter 3p which is well shielded by 4s.  $\therefore$  Despite the general trend of increased EA across a period, Ca should exhibit a lower EA than Na.

4.

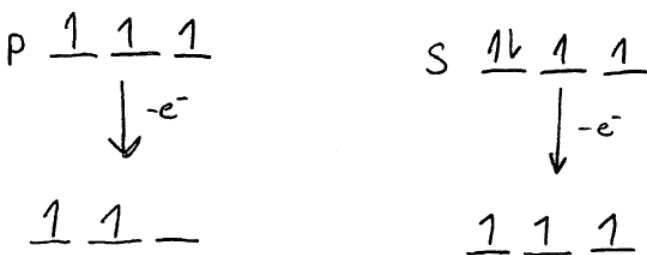


↑  
Ground State Configuration.

5.

Phosphorus should have a higher IE for 3 reasons:

- ① Decrease of  $\pi_c$  upon P oxidation
- ② Increase of  $\pi_e$  upon S oxidation
- ③ Elimination of  $\pi_c$  upon S oxidation



6.

