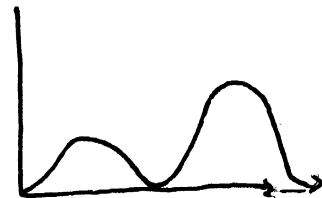
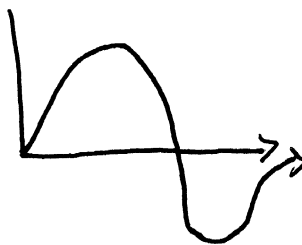
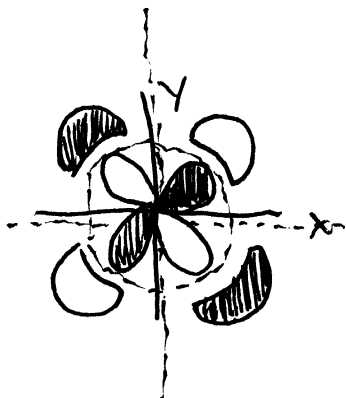
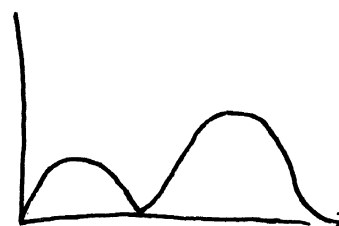
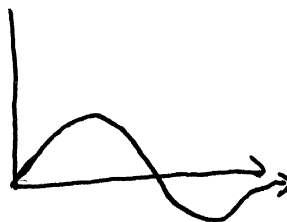
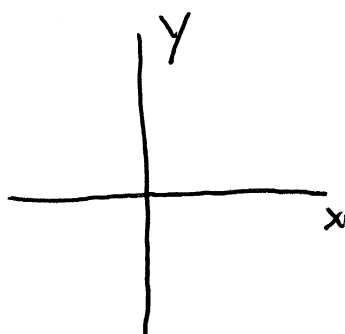


1. Provide radial wave functions, radial probability functions, and contour maps depicting wavefunction sign, all nodes, and all areas of nonnegative electron probability density on the x-y axis for the following orbitals (assume ~ 95% probability):  $4d_{xy}$ ,  $3p_z$ ,  $3p_x$  (12 points)

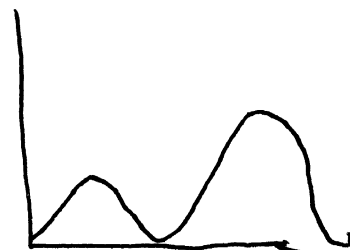
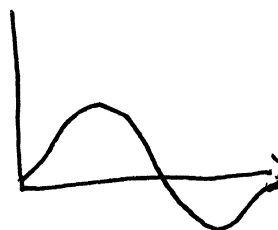
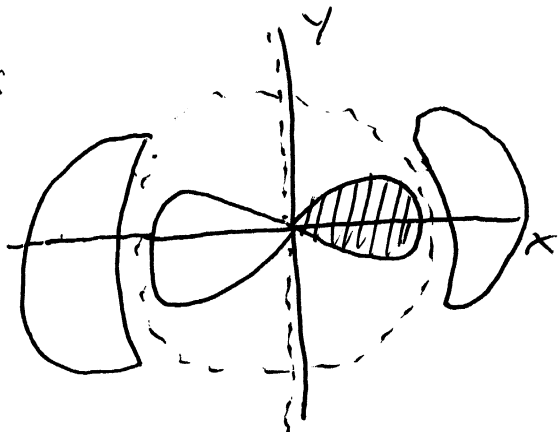
$4d_{xy}$



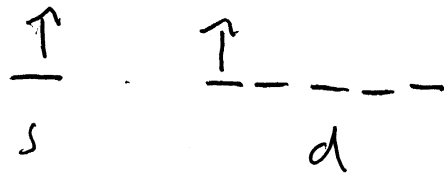
$3p_z$



$3p_x$



2. Construct a microstate table for a  $s^1 d^1$  configuration. Provide the term symbols representing the states constructed from the table. Determine which of these states represents the ground state (10 points).



$$g.s. = {}^3D_1$$

$$others = {}^1D_2, {}^3D_3, {}^3D_2$$

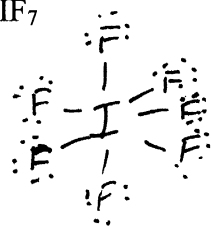
$$M_{\text{ax}} S = 1$$

$$M_{\text{ax}} L = 2$$

	1	0	-1
2	X	XX	X
1	X	XX	X
0	X	XX	X
-1	X	XX	X
-2	X	XX	X

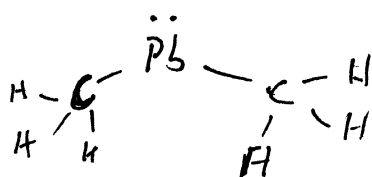
3. Draw Lewis dot structures for the following molecules and predict the geometries of the heaviest atom(s) using VSEPR theory (10 points):

a.  $\text{IF}_7$



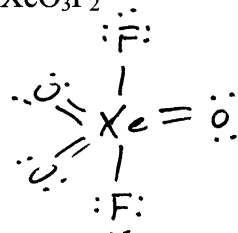
Pentagonal  
~~Trigonal~~ Bipyramidal

b.  $\text{Me}_2\text{Pb}$



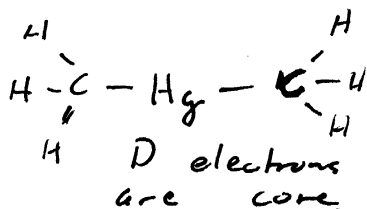
Bent ( $\text{me}-\text{Pb}-\text{me}$  ok)

c.  $\text{XeO}_3\text{F}_2$



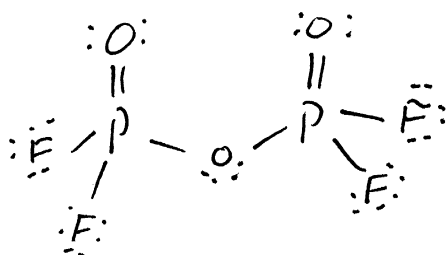
Trigonal Bipyramidal

d.  $\text{Me}_2\text{Hg}$



linear ( $\text{me}-\text{Hg}-\text{me}$  ok)

e.  $\text{P}_2\text{O}_3\text{F}_4$  (Hint: there is P-O-P bonding)



Tetrahedral

4. Calculate  $\sigma$  and  $Z_{\text{eff}}$  for the outermost electron of a neodymium and lutetium atom. Compare and contrast the shielding assigned to f-orbitals by Slater's rules with what we know about penetration and shielding (10 points).

2 options 4f for both, or 5d' for Lu & 4f<sup>4</sup> for Nd

-2 if 6s used for both (-1 Kreimer)

Lu  $Z=71$  Nd  $Z=60$

[Xe] 6s<sup>2</sup> 4f<sup>14</sup> 5d' [Xe] 6s<sup>2</sup> 4f<sup>4</sup>

Lu 5d'

Nd 4f<sup>4</sup>

$\sigma = 68$

$\sigma = 47.05$

$Z_{\text{eff}} = 3$

$Z_{\text{eff}} = 12.95$

Lu 4f<sup>14</sup>

Nd 6s<sup>2</sup>

$\sigma = 50.55$

$\sigma = 57.15$

$Z_{\text{eff}} = 20.45$

$Z_{\text{eff}} = 2.85$

Lu 6s<sup>2</sup>

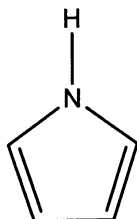
$\sigma = 68$

$Z_{\text{eff}} = 3$

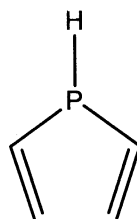
Nd  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} \underline{4f^4} 5s^2 5p^6 5d^0 5f^0 \underline{6s^2}$

Lu  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} \underline{4f^{14}} 5s^2 5p^6 \underline{5d^1} 5f^0 \underline{6s^2}$

5. The phosphorous analogue of pyrrole (A) is called phosphole (B). Pyrrole is considered an aromatic compound because the nitrogen atom is able to delocalize its lone pair into the ring quite well. Phosphole, however, is not very aromatic. This is reflected in its higher reactivity (10 points).

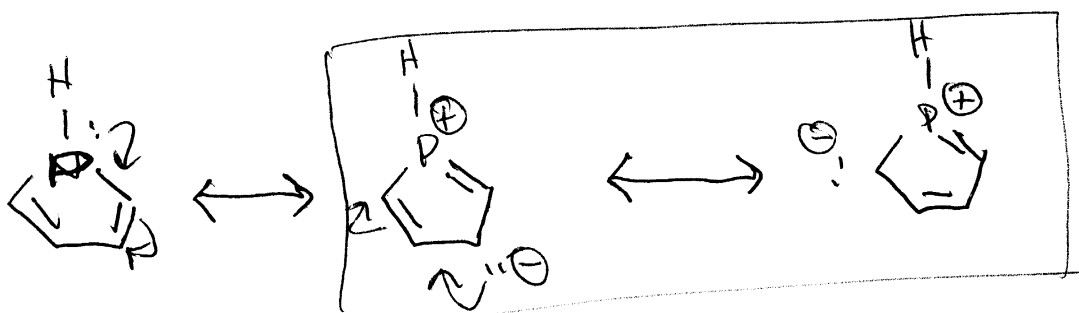
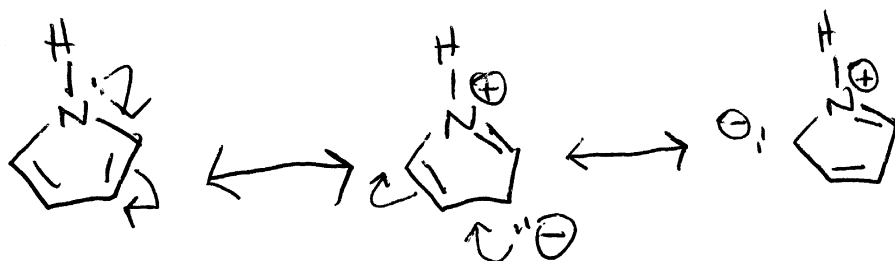


A



B

- a) Draw 3 resonance structures each for pyrrole and phosphole. (5 pt)



Must have formal charges to have credit.

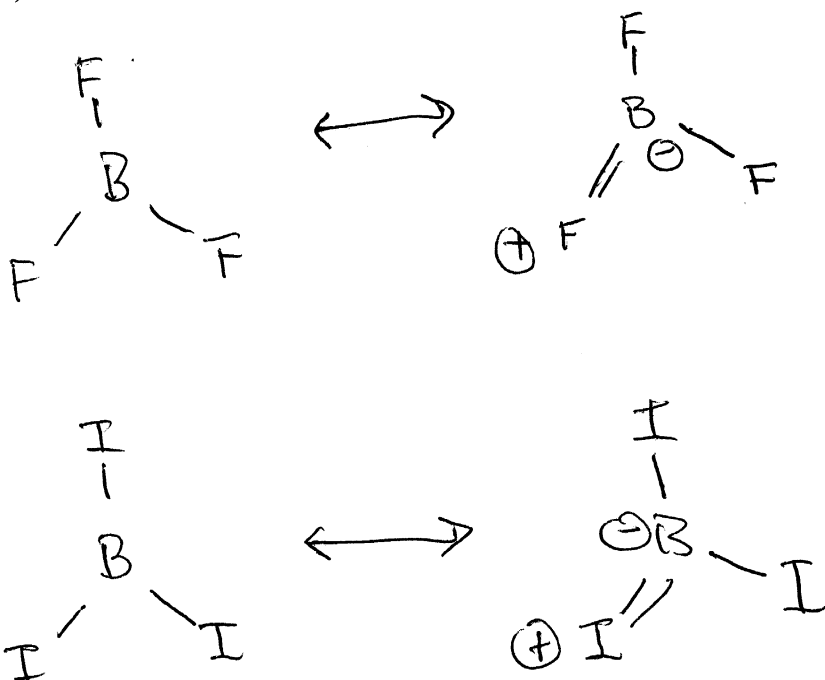
- b) Circle the resonance structures of phosphole which are least stable. Explain in 3 sentences or less why you chose those structures.

- Yes, these are less stable because of charge separation, but this is an incomplete explanation.
- The 3p orbital of P does not overlap well with the 2p orbitals of carbon so it does not want to form double bonds

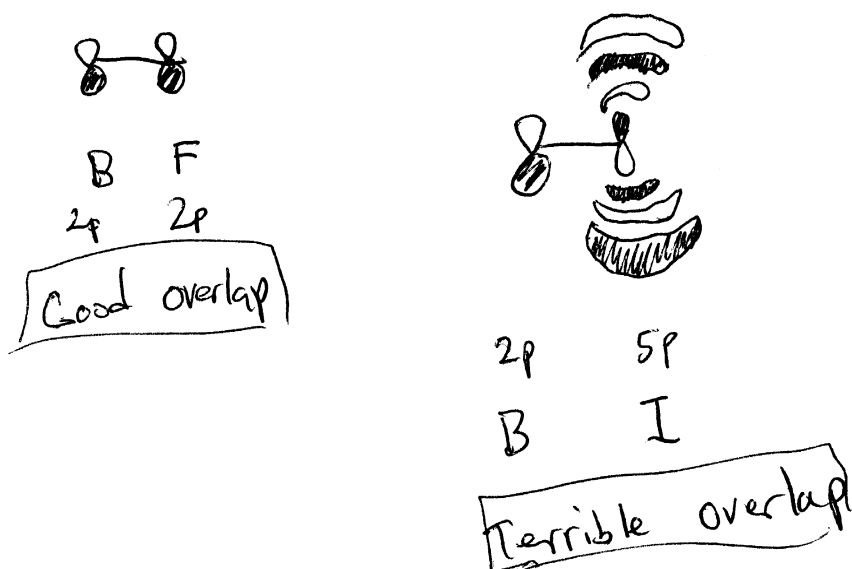


6. Boron trifluoride ( $\text{BF}_3$ ) is less electrophilic at boron than boron triiodide ( $\text{BI}_3$ ) even though fluorine is more electronegative than iodine (8 points).

a) Draw 2 resonance structures each for  $\text{BF}_3$  and  $\text{BI}_3$ .



b) Draw the orbital interactions for the B-F and B-I  $\pi$ -bond and use this to explain in 3 sentences or less why  $\text{BF}_3$  is less electrophilic at boron than  $\text{BI}_3$ .



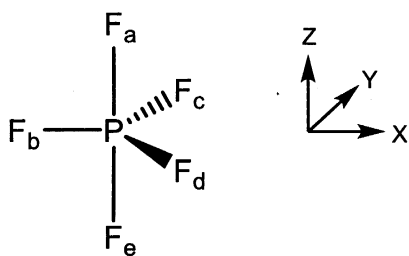
- ~~The~~ - Since there is good p-p interaction in  $\text{BF}_3$ , there is a lot of double bond character.  
 - This quenches the empty p orbital of Boron.  
 - So it does not want  $e^-$  as much (less electrophilic)

7. Noble gases were once thought to be inert, but in the last century compounds of noble gases have been made. Compounds such as  $\text{XeF}_2$  and  $\text{KrF}_2$  can be easily made and stored; however, compounds of Ne and Ar are either unknown or extremely unstable (6 points).

Based on periodic table trends, explain in 3 sentences or less why stable compounds of  $\text{XeF}_2$  and  $\text{KrF}_2$  exist while  $\text{NeF}_2$  and  $\text{ArF}_2$  do not. Your answer should include the terms "electronegativity" and "ionization energy".

In general, noble gases ~~are hard to~~ have high ionization energy, but moving down the group reduces the I.E. enough so that F, a very electronegative element, is able to ~~form~~ remove electrons from Xe and Kr to form bonds

8. (28 points) Consider the molecule,  $\text{PF}_5$ , with fluorine atoms labeled a-e:



A. List all symmetry elements in the molecule (10 pts):

~~Handwritten scribbles~~  
 $E, C_3, C_3^2, 3\sigma_d, 3C_2, S_3, S_3^5$  ( $2C_3 + 2S_3$  ok)

B. Which pair(s) of atoms, if any, get interchanged by each series of operations? What single, net symmetry operation has been performed? (5 pts):

i.  $C_3, \sigma_h, \sigma_{v(xz)}, C_3$   $\text{F}_c, \text{F}_d$ ;  $\text{F}_a, \text{F}_e - C_2$

ii.  $S_3, C_3^{-1}$ :  $\text{F}_a, \text{F}_e - \sigma_h$

iii.  $\sigma_h, C_3^2, S_3$ : None -  $\bar{E}$

iv.  $C_{2(x)}, C_3$ :  $\text{F}_a, \text{F}_e$ ;  $\text{F}_c, \text{F}_d - C_2$

v.  $S_3^2, C_3$ : None -  $\bar{E}$

C. Give a symmetry element which interchanges only the given set(s) of atoms. If this is not possible, write "not possible" (3 pts):

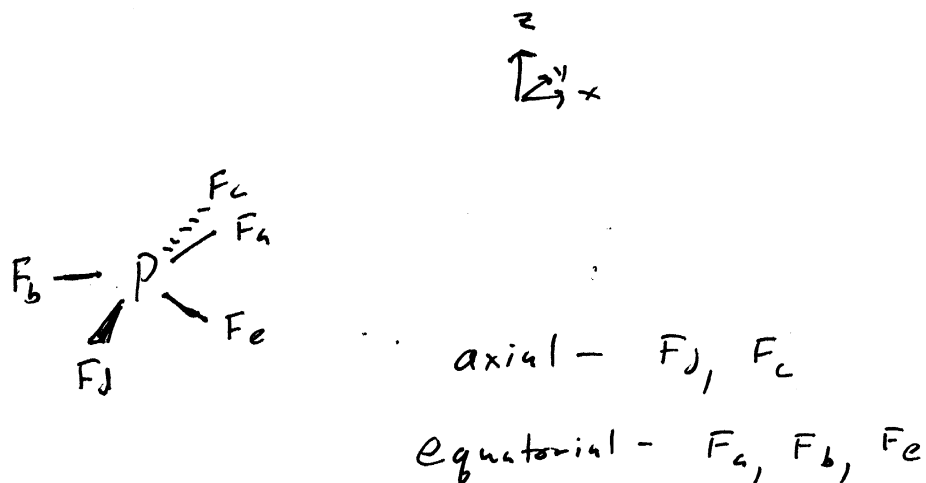
i.  $\text{F}_b/\text{F}_d$   $\sigma_v$

ii.  $\text{F}_a/\text{F}_c$  Not possible

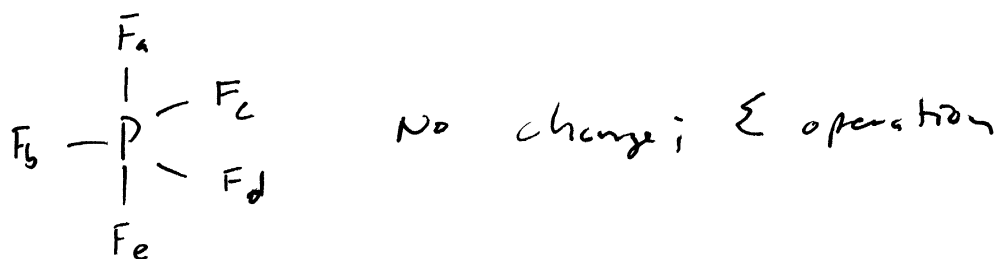
iii.  $\text{F}_a/\text{F}_e; \text{F}_c/\text{F}_d$   $C_2$



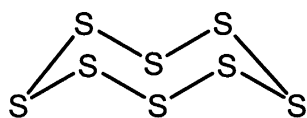
- D. Draw the result of a single Berry pseudorotation that results in the placement of the axial ligands on the y axis of the given coordinate system. Which fluorine atoms are now equatorial? Which are axial? (5 pts):



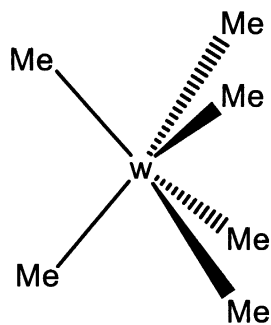
- E. Draw the result of the following operations performed in series:  $S_3^2$ ,  $\sigma_{v(xz)}$ ,  $C_3^{-1}$ ,  $\sigma_h$ ,  $C_{2(x)}$ :



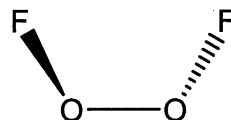
9. State the highest order proper rotation in the following molecules (6 points):



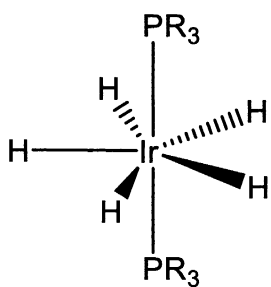
$C_4$



$C_3$

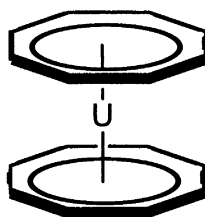


$C_2$

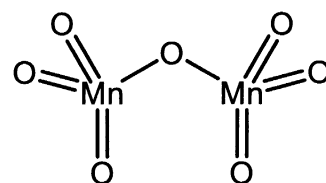


All hydride ligands coplanar

$C_5$



$C_2$



$C_2$