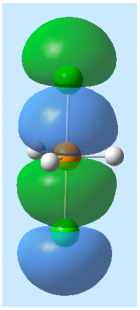
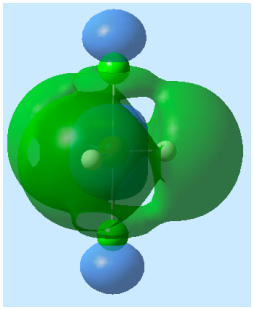
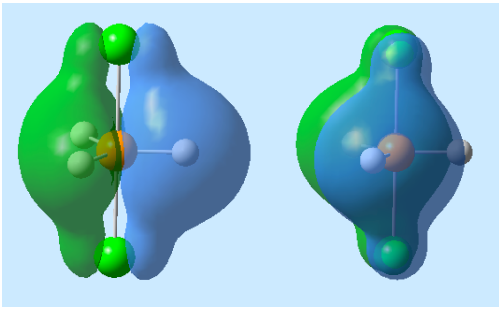
After carrying out a calculation on $PH_3Cl_2$ with the π-donor ligand in the axial position, the following MOs were obtained. Construct a MO diagram for this molecule. Hint, because P and H have very similar electronegativity, the best molecular fragments to use are $PH_3$ + $Cl_2$.



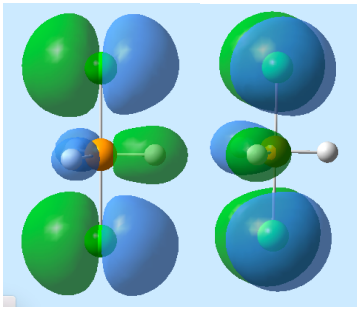
MO21



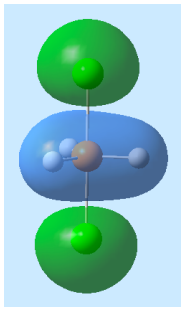
MO27: LUMO



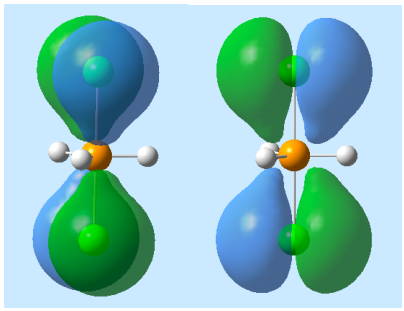
MO19 & MO20



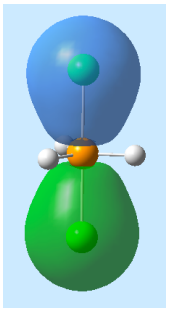
MO25 & MO26: HOMO



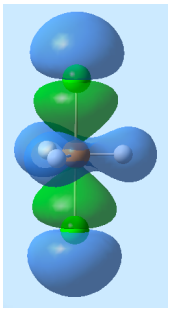
MO18



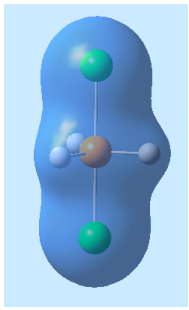
MO23 & MO24



MO17

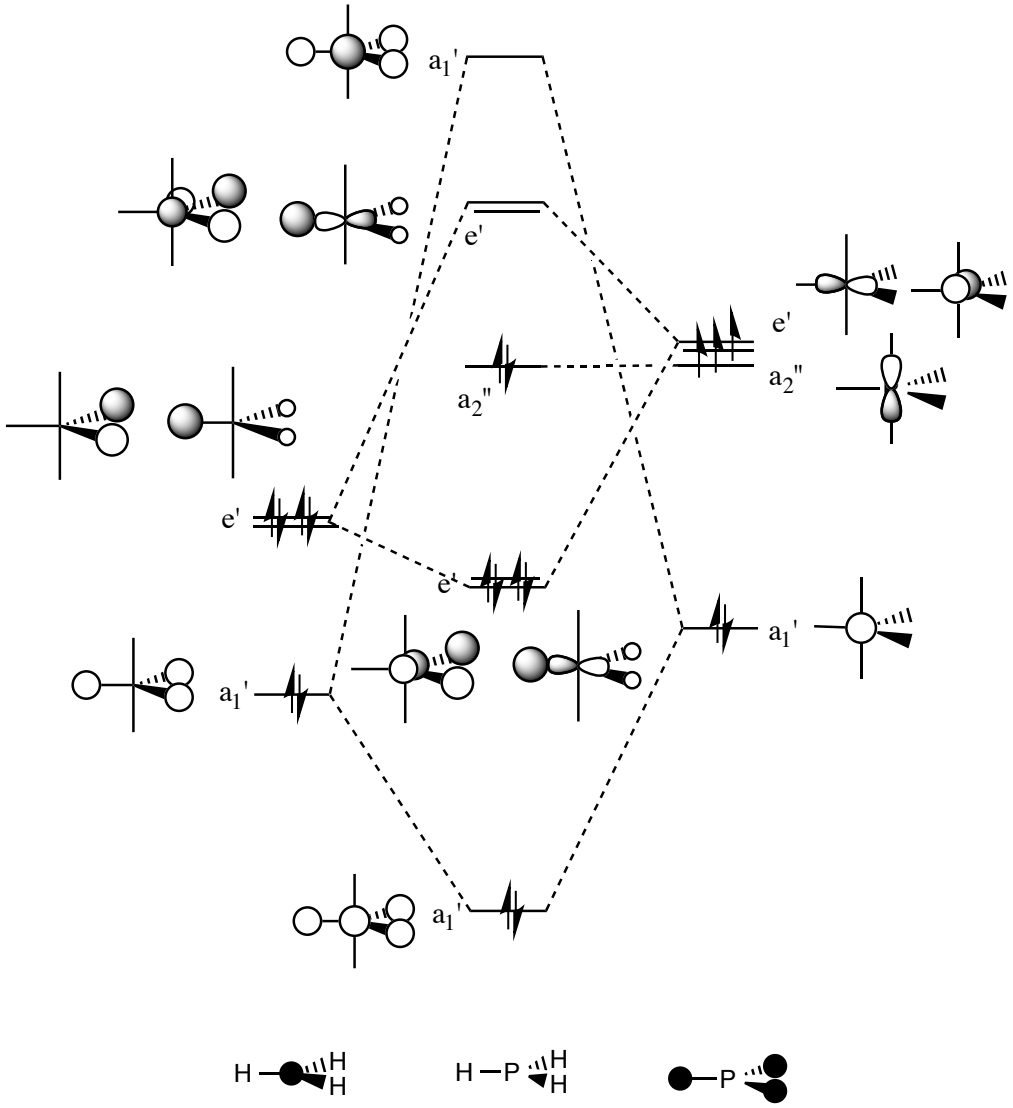


MO22

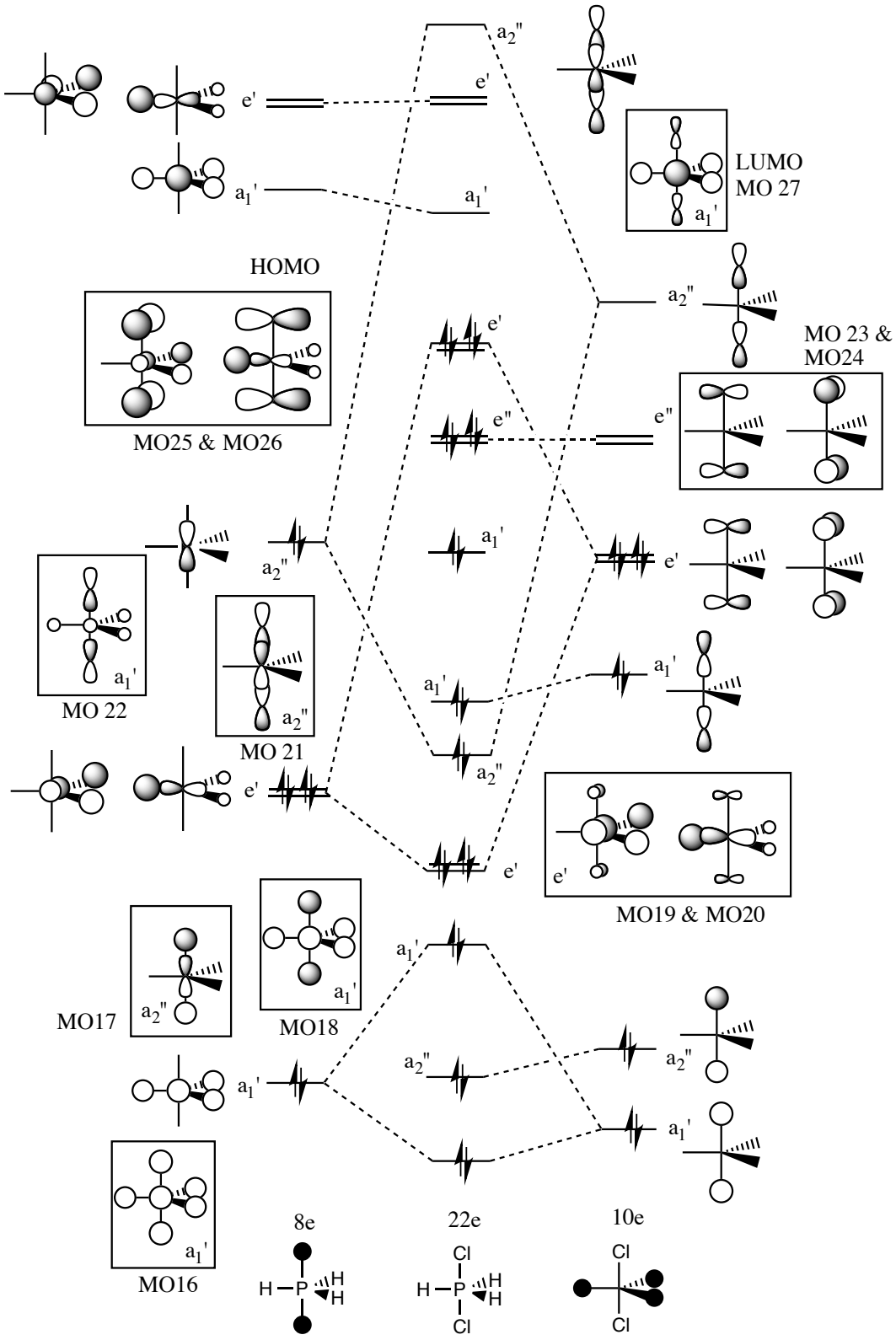


MO16

- first construct the $PH_3$ fragment orbitals, the $Cl_2$ fragment orbitals should be well known and can be added directly to the final MO diagram




- then next concern is where to position the $Cl_2$ FOs relative to the $PH_3$ orbitals, we can obtain hints from the molecule MOs, we tend to look for MOs that show minimal interaction
    - MOs 16 and 18 are essentially a bonding antibonding combination, so the lowest energy $a_1$' of $PH_3$ and the lowest energy of the Cl must be close enough to intract
    - but MOs 17 $a_2$" is essentially non-interacting, but has a small amount of PpAO mixed in.
    - MOs 19 and 20 are essentially pure $PH_3$ e' MOs, so these must lie much lower in energy than the e' combination of $Cl_2$.
    - MO 22 is very much the pAOs on $Cl_2$ with a small amount of $PH_3$ $a_1$' mixed in
    - from this information we can roughly position the fragment orbitals.


a2"
e'
a1'
LUMO
MO 27
HOMO
MO25 & MO26
e"
MO 23 &
MO24
MO 22
MO 21
MO19 & MO20
MO17
MO18
MO16
8e
22e
10e
H
P
Cl