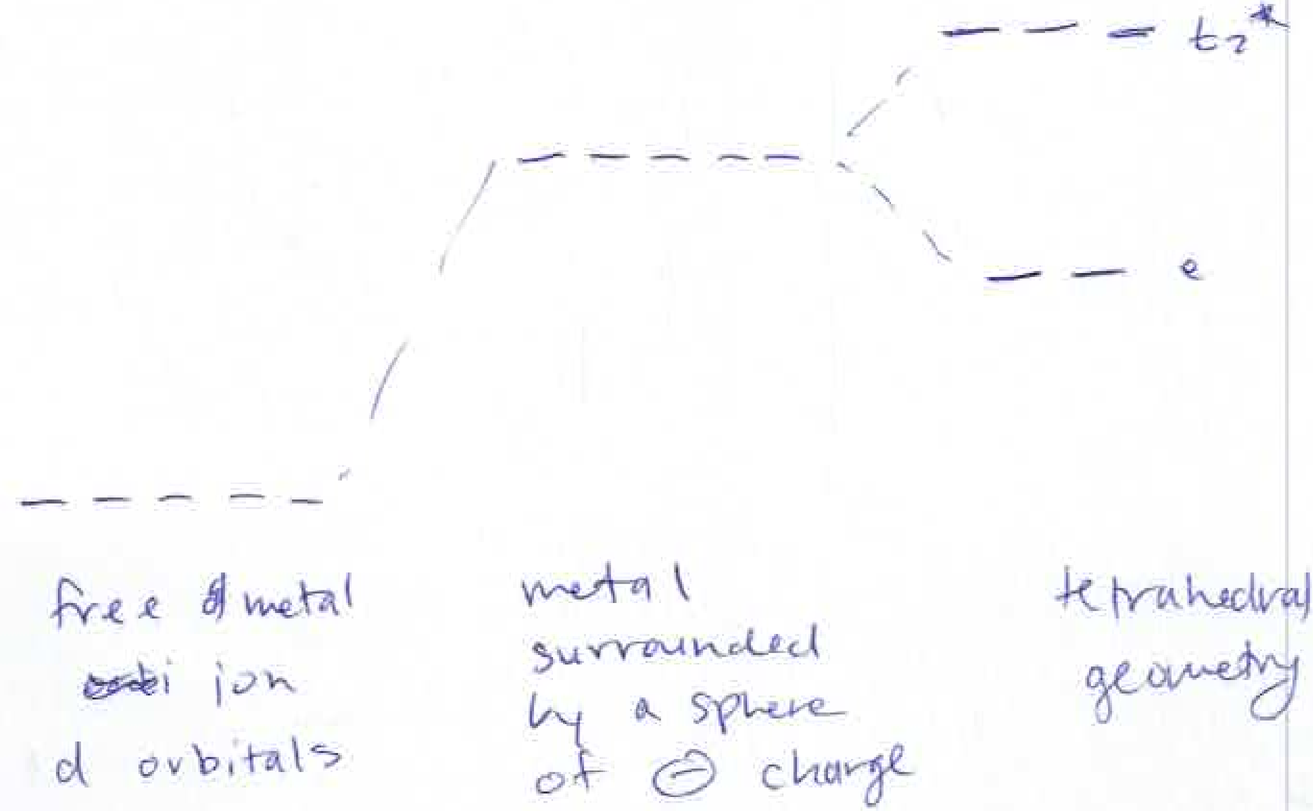
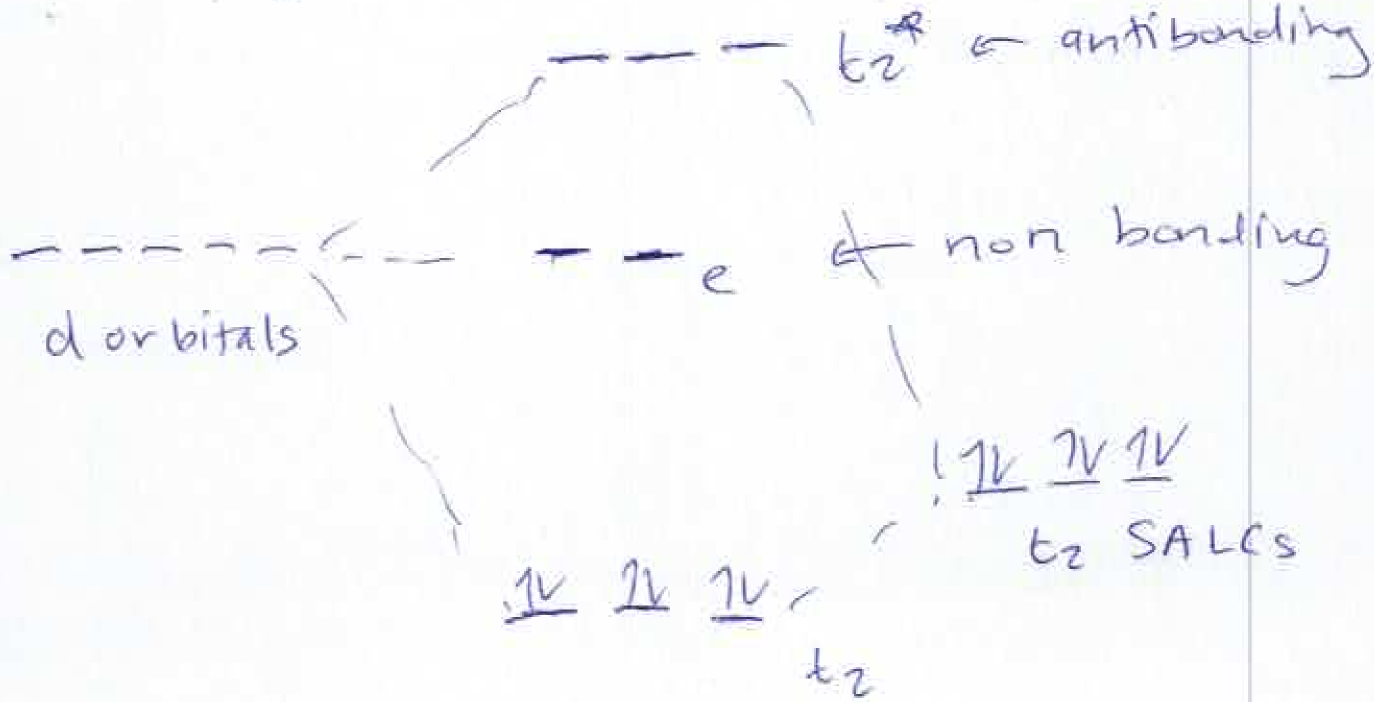
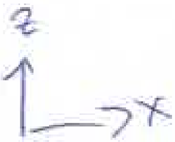
CH431 Lecture ~~a~~17 10/25/16

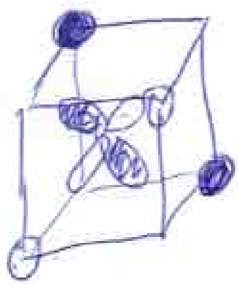
Crystal field approach




MO diagram

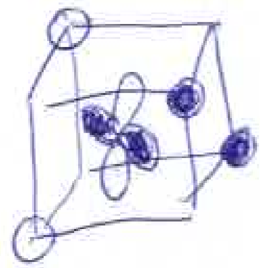




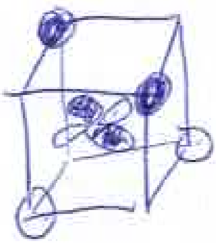
$d_{xz}$

+ SALC (bonding)



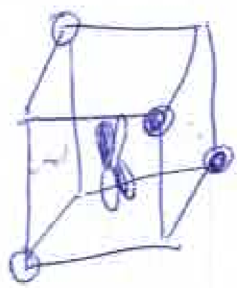
$d_{yz}$

+ SALC (bonding)

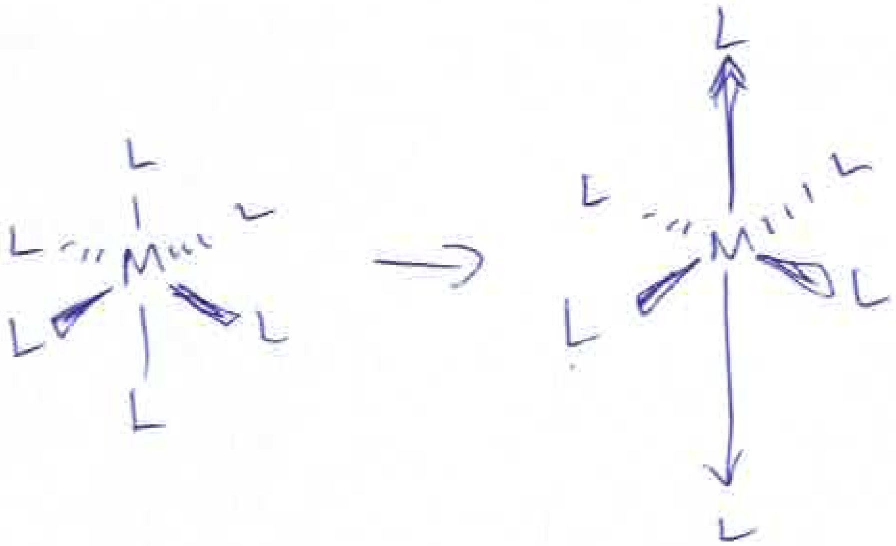


$d_{xy}$

+ SALC (bonding)



→ antibonding will have opposite shading




axial ligands along z-axis are further away that other ligands

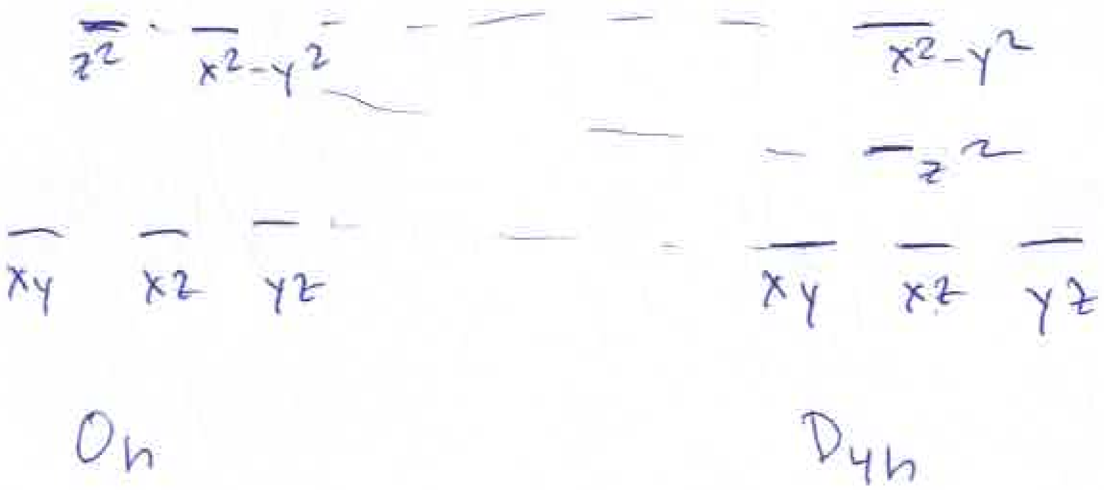
$e_g$ — $z^2$ — $x^2-y^2$

1) $dz^2$ will go down in energy (less interaction w/ axial ligands along z axis

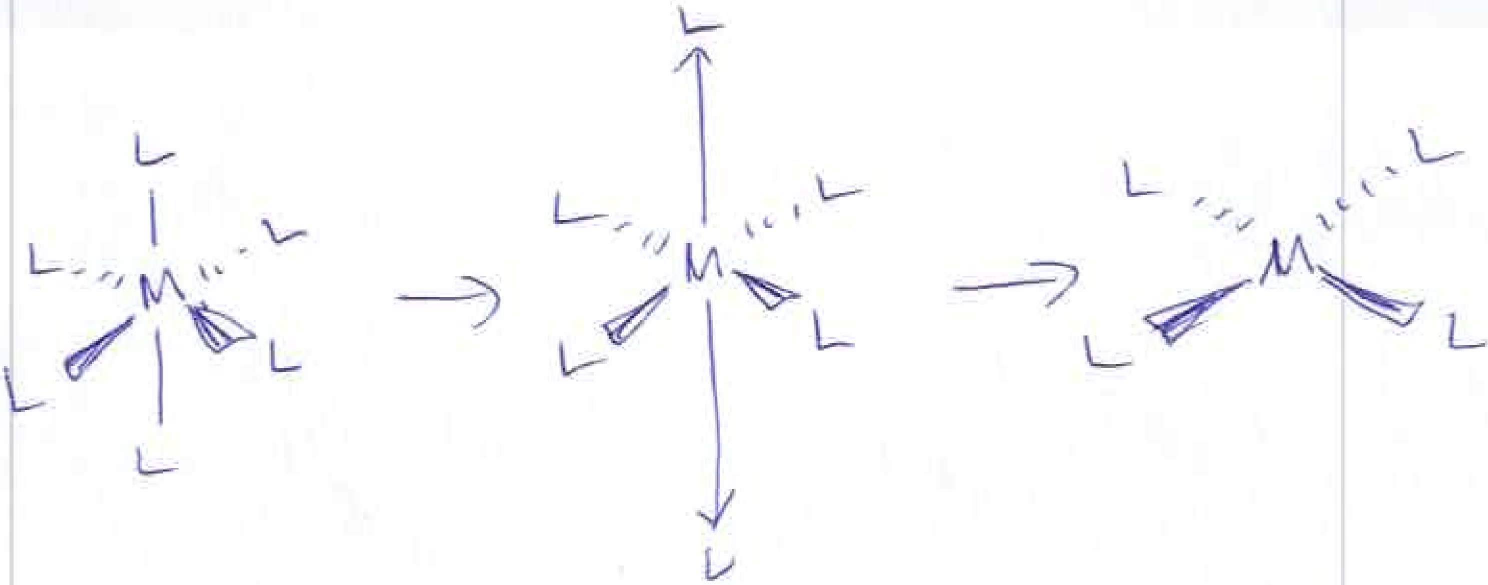
$t_{2g}$ — $xy$ — $xz$ — $yz$

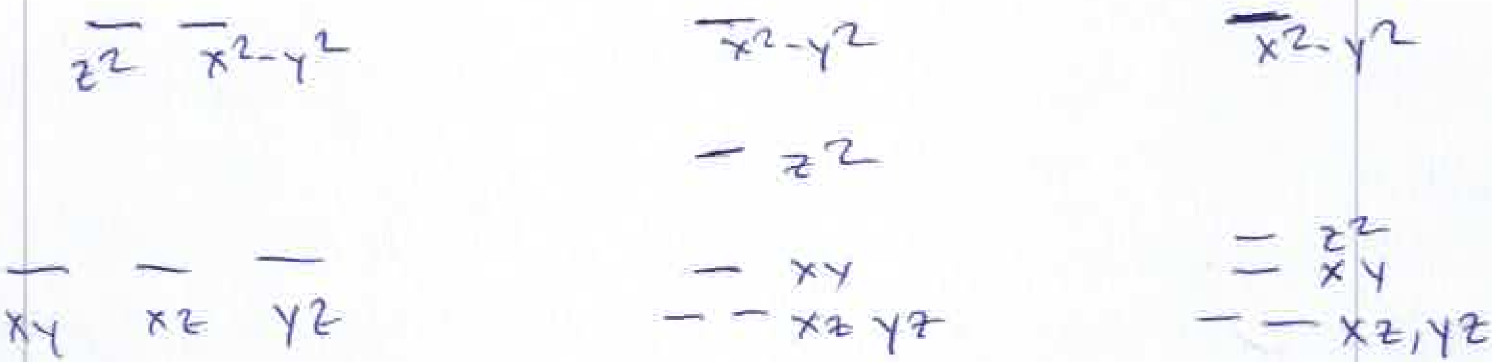
2) $d_{x^2-y^2}$ will have same energy level, not affected by z-axis ligand changes

First approximation:

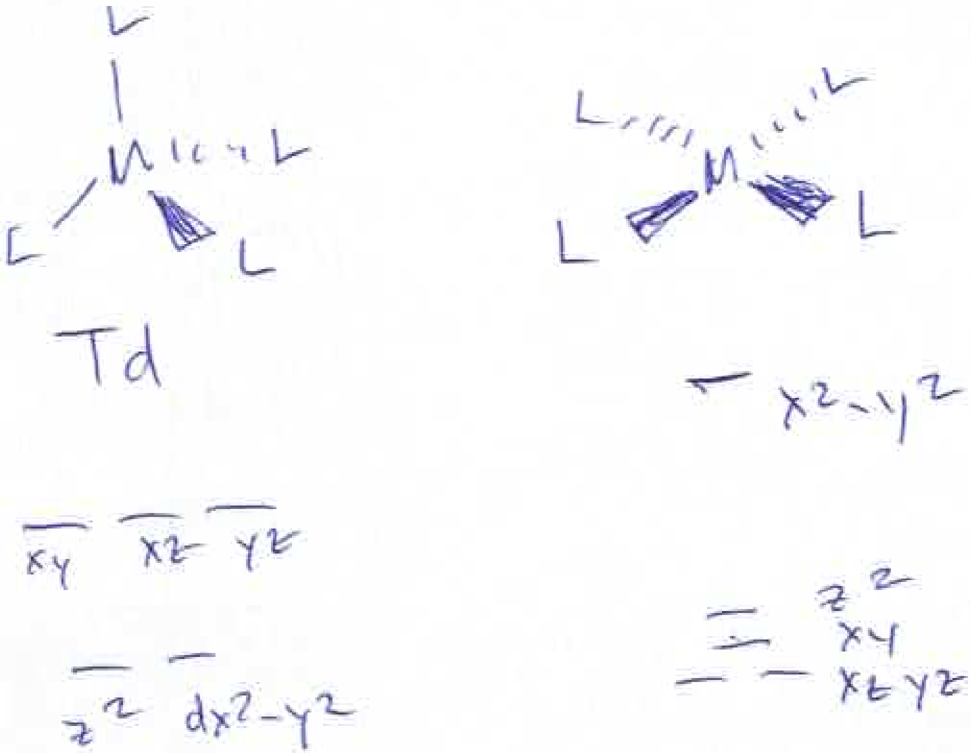



2nd approximation




In square planar complexes, $d_{x^2-y^2}$ is very destabilized relative to all the other orbitals since this is the only orbital w/ significant interactions with the ligands.



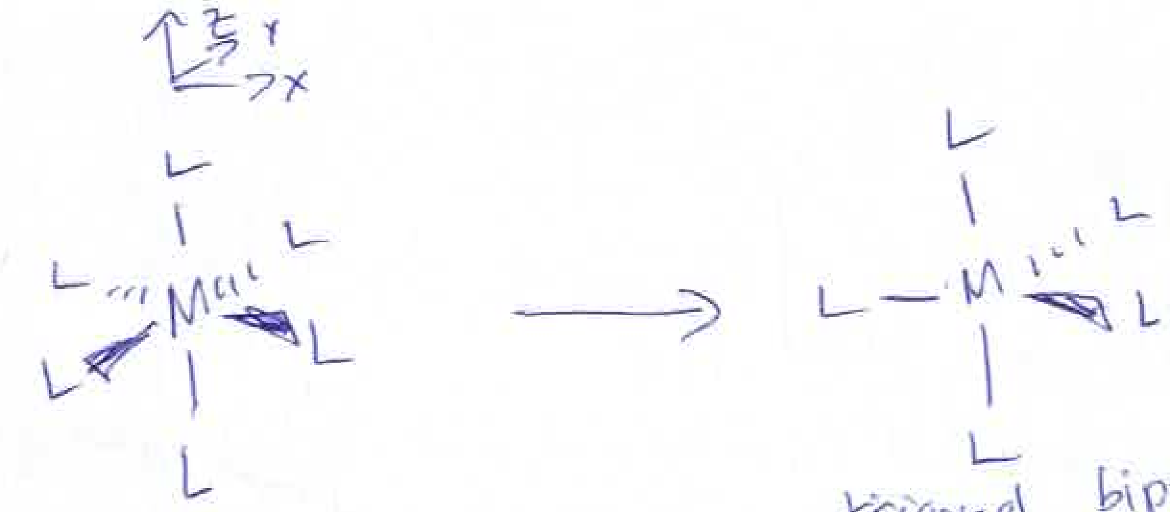

If a metal ion only has 8 d electrons, it will often favor square planar because no electrons go into highly antibonding orbitals

$d^8$ in Td

$d^8$ in square planar

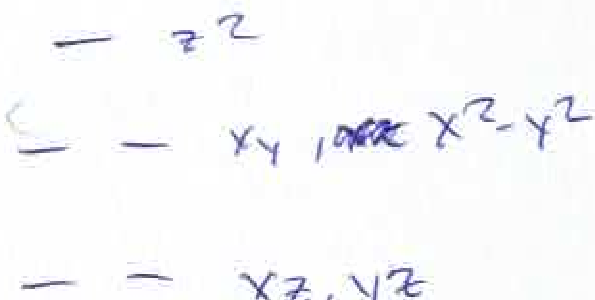
→ no electrons go into $d_{x^2-y^2}$ ⇒ low spin

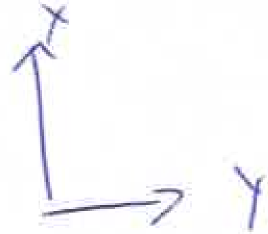
* especially true for 4d and 5d metals w/ 8 d electrons
* 3d metals w/ 8 d electrons and pi acceptor ligands

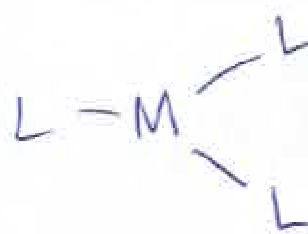

z
y
x
L
M
L
trigonal bipyramidal
D3h

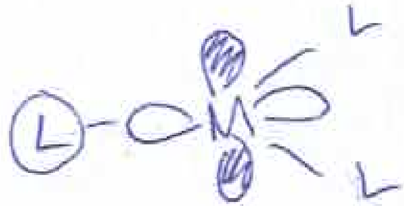

z2
x2-y2
xy
xz
yz
very (antibonding)
z2
xy
x2-y2 (slightly less antibonding)
xz, yz
(non bonding)


L
M
pentagonal bipyramid

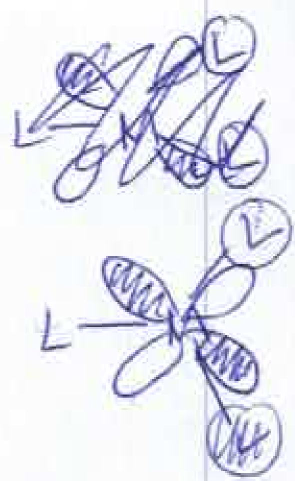

z2
xy, x2-y2
xz, yz


$d_{x^2-y^2}$



$d_{xy}$