

B. Electron Deficient (less than an octet)

e.g. BeH_2



Be does not need an octet

Total of 4 valence electrons

Not the same as unsaturated systems that achieve the $8e^-$ (octet) through the formation of multiple bonds.

C. Electron Rich (greater than an octet)

Valence shell expansion occurs with elements beyond the 2nd row

s, p, d levels are all available



$2e^-$ $6e^-$ $10e^-$ \rightarrow total of $18e^-$ possible

e.g., transition metals have expanded electron counts, typically $18e^-$

referred to as valence shell expansion

PCl_5

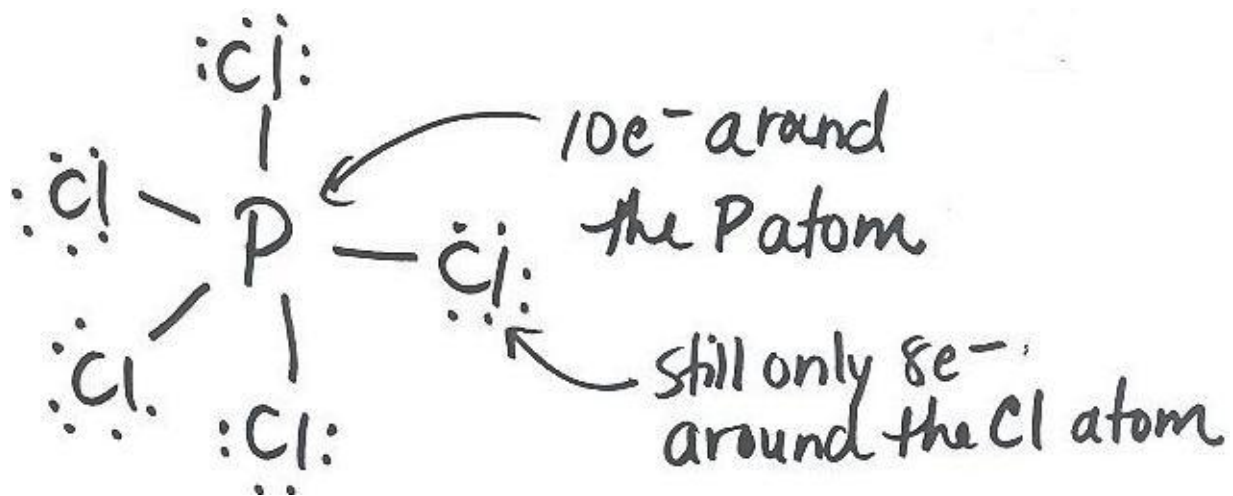
P $5e^-$

$5e^-$

Cl $7e^- \times 5 =$

$35e^-$

$40e^-$



Q. What about transition metals?

A. They tend to exhibit $18e^-$ valence shells (full s, p, d levels). They form bonds to lone pairs of molecules (called ligands) until they reach the $18e^-$ configuration.

Ex. Ni^{2+} compounds

Ni has 10 valence electrons - it needs 4 bonds to reach 18 valence electrons.

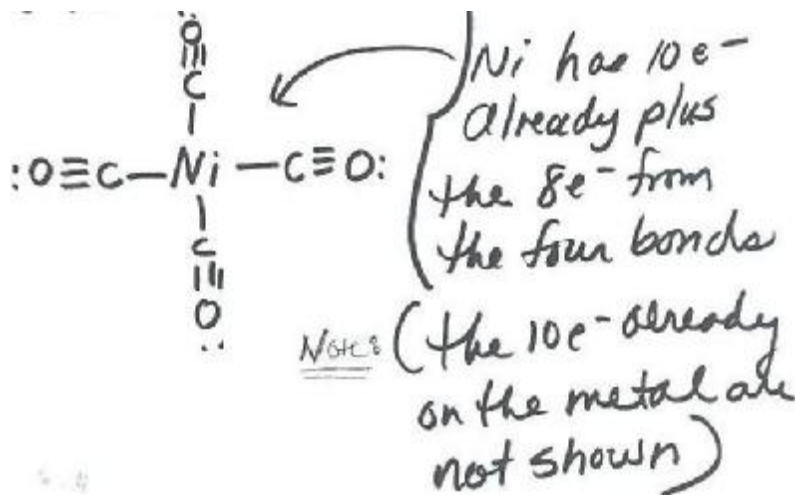
- $\text{Ni}(\text{CO})_4$ is a compound that illustrates this point.

CO valence electrons $4+6 = 10e^-$

$:\text{C} \equiv \text{O}:$
(unsaturated)

Lewis structure is this one
to allow for an octet

CO can then act as a ligand with the lone pair of C bonding to the Ni atom.*



* $\text{:C} \equiv \text{O:}$

The C lone pair is more basic (donating) than the O lone pair

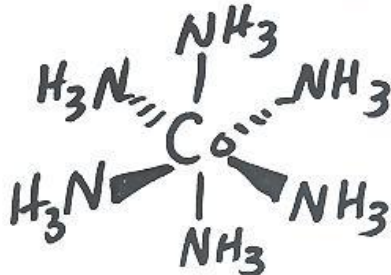
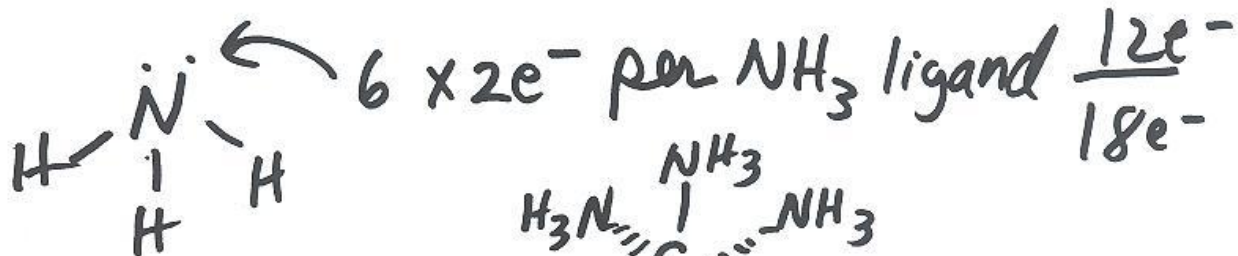
The ligand, $\text{:C} \equiv \text{O:}$, is considered to be a Lewis base (electron – pair donor) and the metal, Ni, is the Lewis acid (electron – pair acceptor).

The bonds formed in this way are coordinate covalent bonds.

→ The ligand supplies both electrons of the metal – ligand bond.

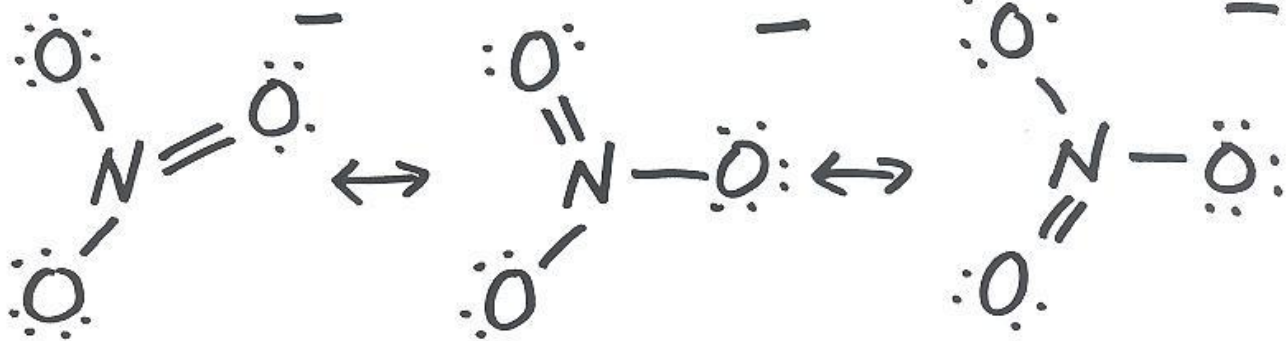


Co^{3+} 6 valence electrons $6e^-$



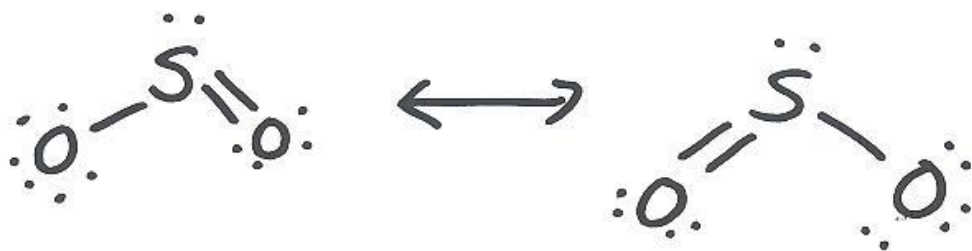
Resonance

Recall NO_3^- :



the real structure is a "resonance hybrid"

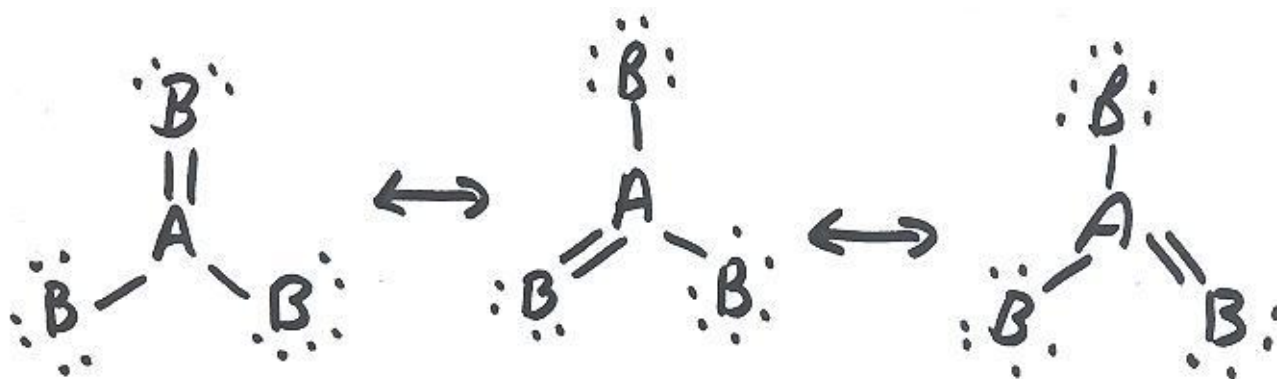
SO_2



Q. How did we justify the concept of resonance?

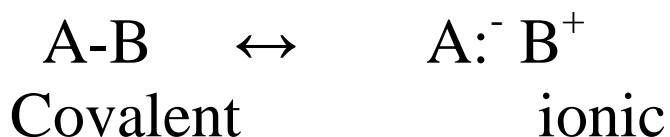
A. Experimental evidence says that all the bonds are the same length in these molecules.
→ more of a delocalization model.

Summary of Resonance Hybrids



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- (a.) None of these “canonical forms” is an actual representation of the real structure. These structures don’t really exist, but their average corresponds to the real structure.
- (b.) Experiment shows that all bonds A-B are equal in length so theory and experiment correlate.
- (c.) The average “hybrid” structure has a lower energy than any of the contributing structures.

A special case of resonance
is covalent \leftrightarrow ionic resonance



- A is more electronegative than B
- A-B bond enthalpy is a combination of the two contributing structures.

Consequently

A-B $\Delta H_{\text{A-B}}$ (bond energy) is greater than the average of $\Delta H_{\text{A-A}}$ & $\Delta H_{\text{B-B}}$ due to the ionic contribution.

In the end, however, Lewis structures are not enough to describe localized bonding in molecules.

Q. Besides Lewis structures, what other localized bond theories do we need?

A. VSEPR and Hybridization

Q. Why do we need to go further than the concept of Lewis?

A. Because there are numerous issues that Lewis structures do not address such as:

(a). How is the electron – pair bond shared?

(b). Which orbitals are involved in the bonding?

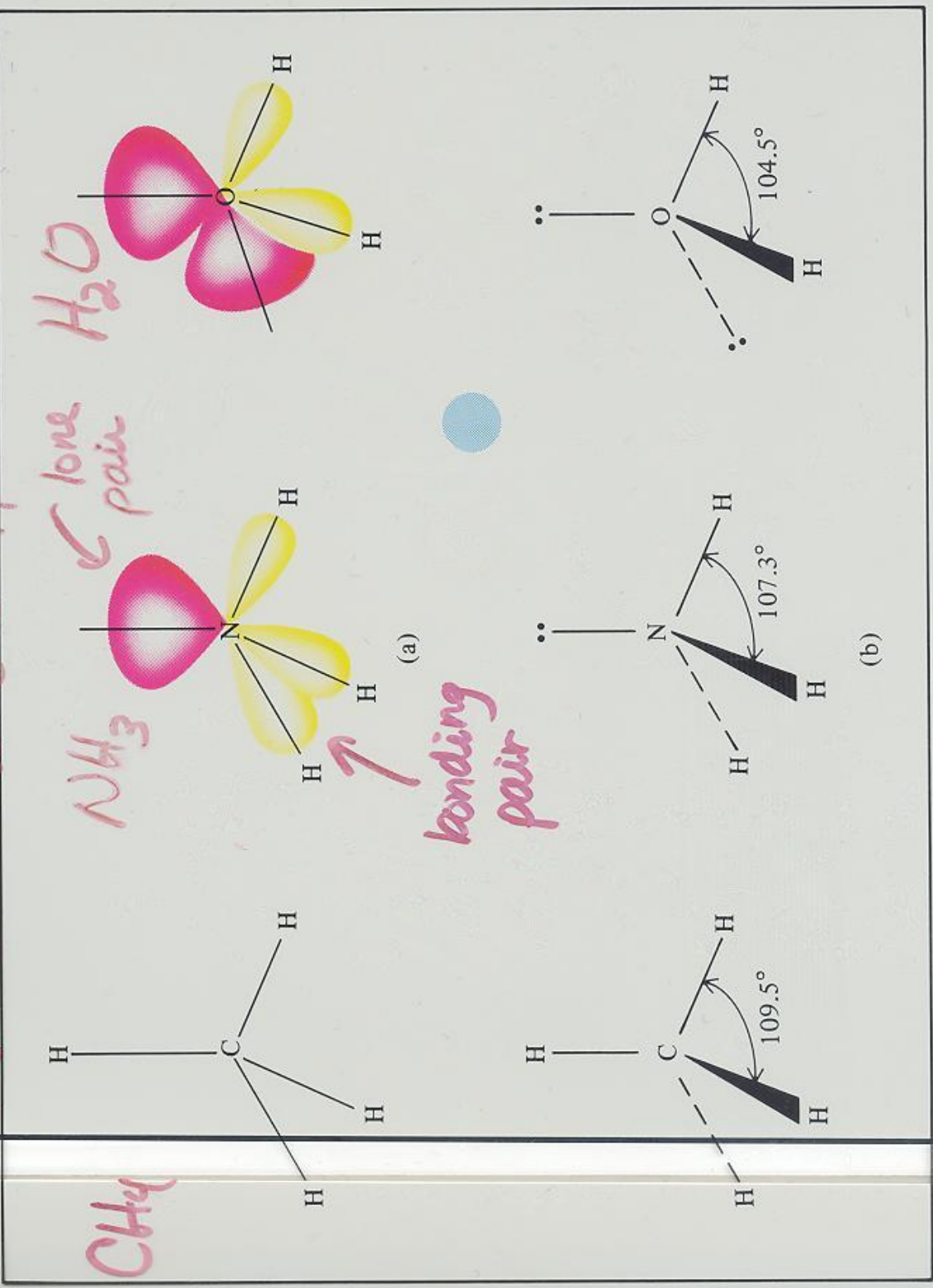
(c). What geometry should one assign to the molecule? (bonds, angles?)

(d). Why does sharing electrons lead to stability for a molecule?

IN LOCALIZED BONDING THEORY, WE USE EITHER VSEPR OR HYBRIDIZATION TO ANSWER THESE QUESTIONS.

Figure 10.1

We need to be able to explain these structures



2. Hybridization Theory or Model

For this, we need the concept of valence state

Ex: H-Be-H

X – Be – X

X = halogen

How does one explain the linear shape?

(a.) Be $1s^2 2s^2$

- $2s^2$ is the valence shell

If we promote an e^- to the 2p level it is now possible to pair the two unpaired electrons with those of incoming group H or X (halide)

- $2s^1 2p^1$ valence state requires 323 kJ/mol (this doesn't explain the shape, only how it happens)

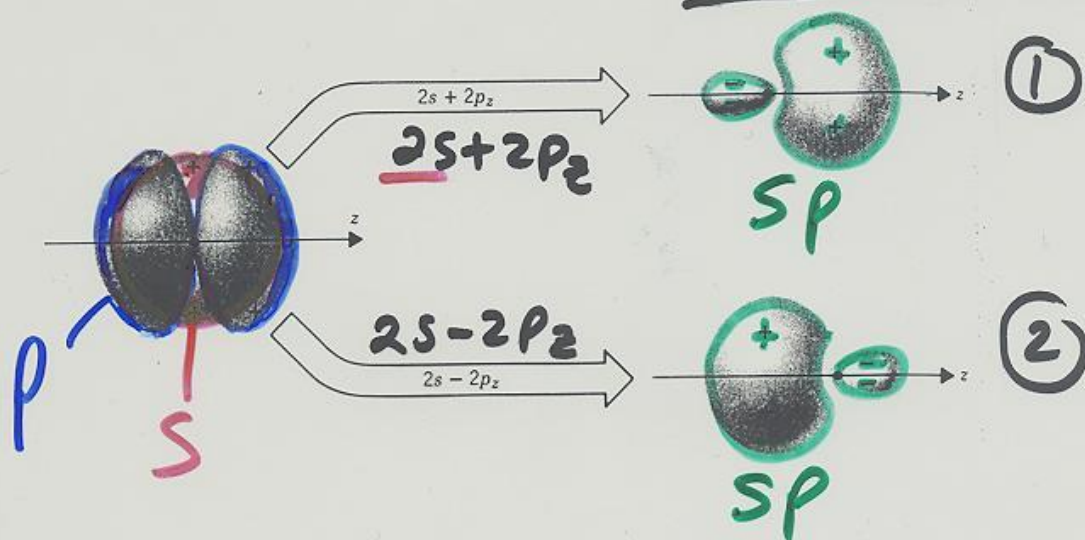
(b.) Hybridization occurs between the s and p orbitals

$2s+2p_z$

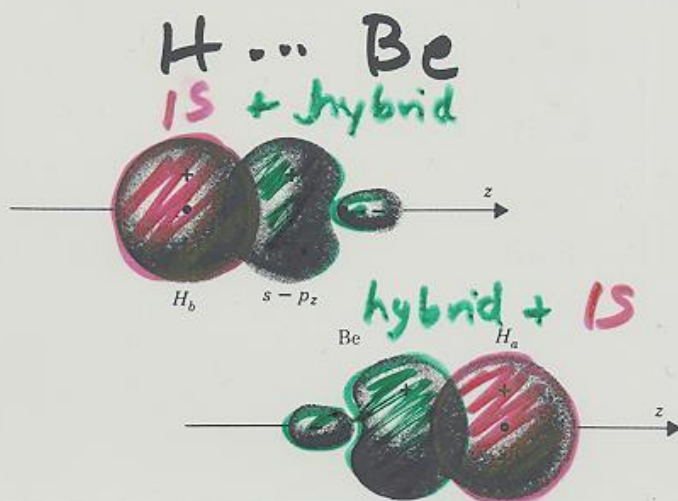
$2s-2p_z$



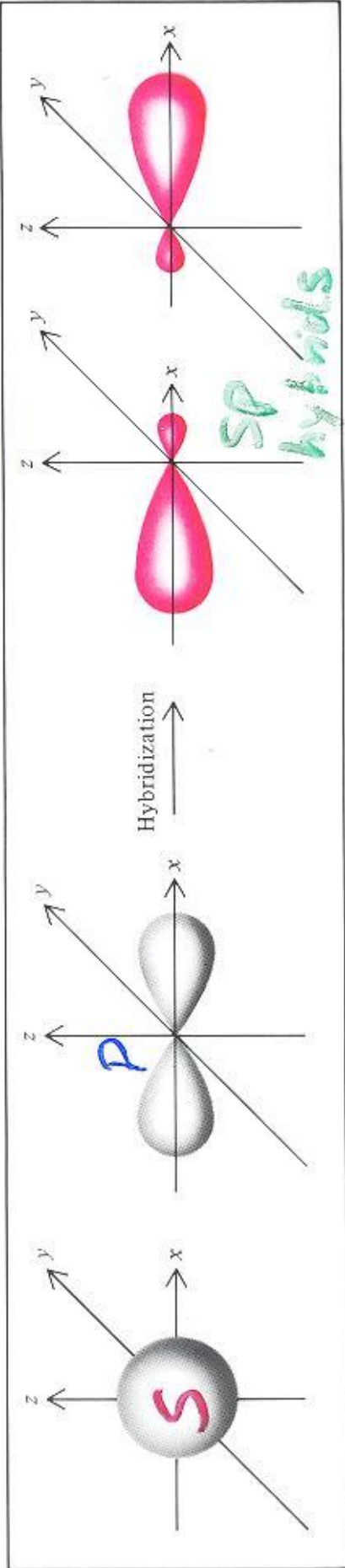
Two HYBRIDS



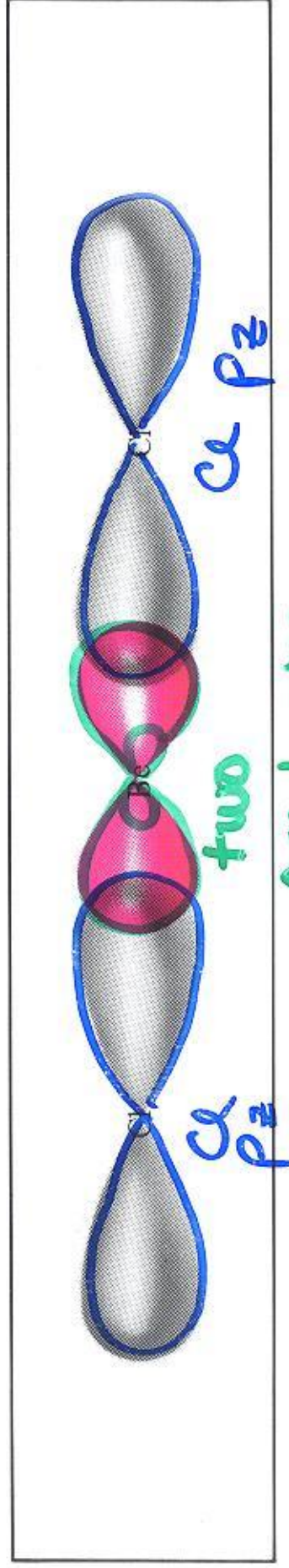
OVERLAP OF HYBRIDS WITH H atoms



So, the linear shape of the $\text{H} - \text{Be} - \text{H}$ molecule is due to best overlap with H $1s$ orbitals and sp hybrid



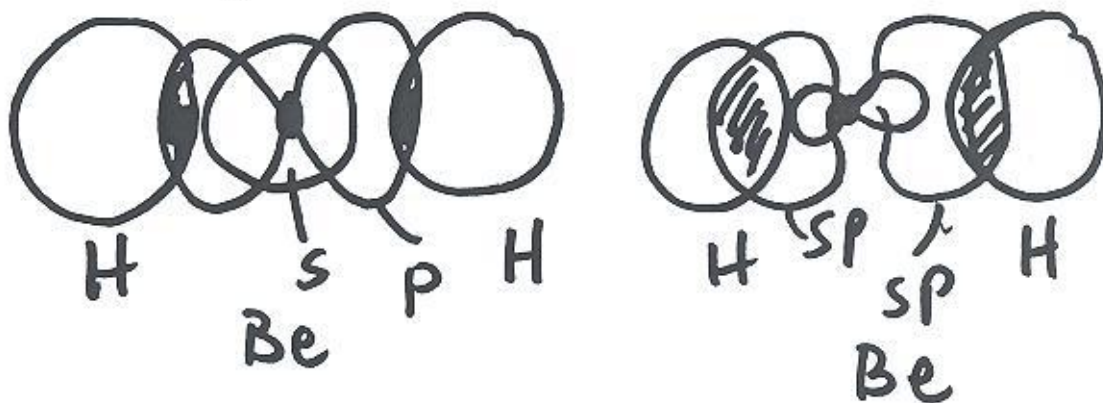
BeCl₂ molecule



two overlapping
sp hybrids

Main Point about Hybrid Orbitals

- They have a huge lobe pointed in a particular direction that can overlap strongly with an atom along that direction.
- Calculations show that the extent of overlap obtained with the hybrid orbitals of H-Be-H (sp) is much greater than it would be with pure s and p orbitals on Be



sp² Hybridization

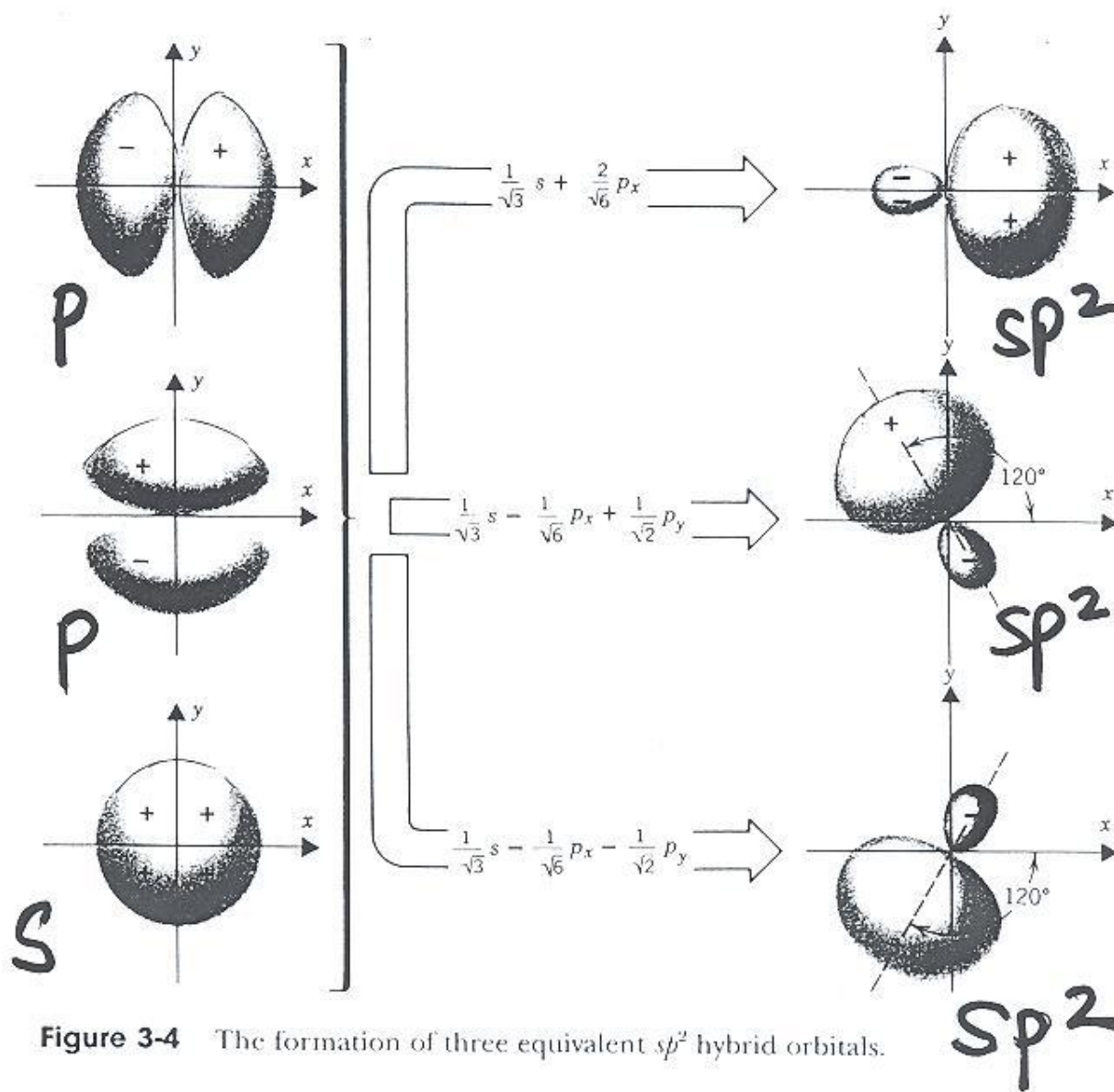
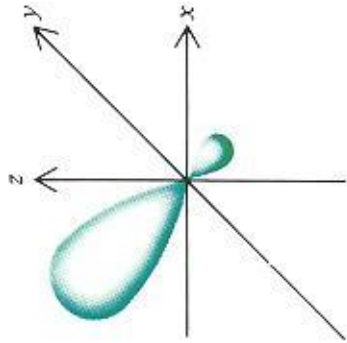
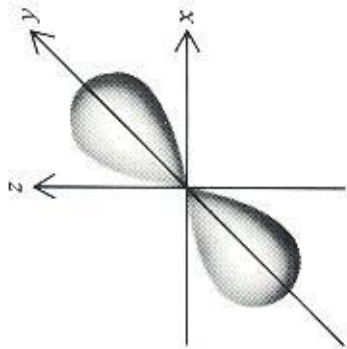
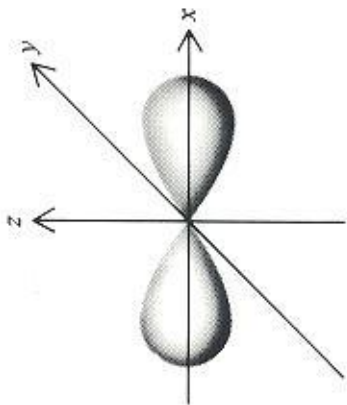
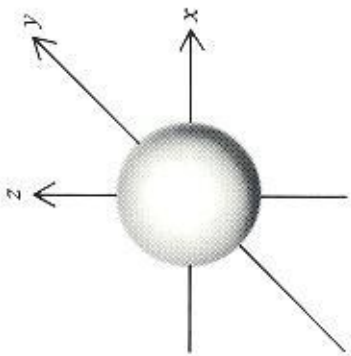
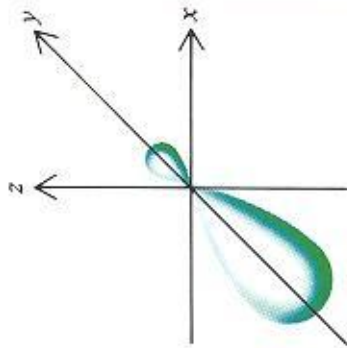
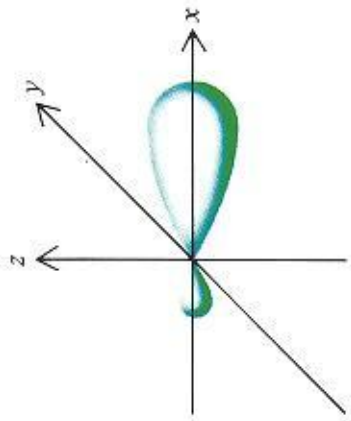


Figure 3-4 The formation of three equivalent sp² hybrid orbitals.

B $1s^2 2s^2 2p^1$ is the starting, standard electron config.
 B tends to form BX_3 if the bonding configuration is $1s^2 2s^1 2p^2$, this allows for three decoupled spins, $2s^1 2p^2$, to form three bonds with $H\cdot$, $X\cdot$.



Hybridization \rightarrow



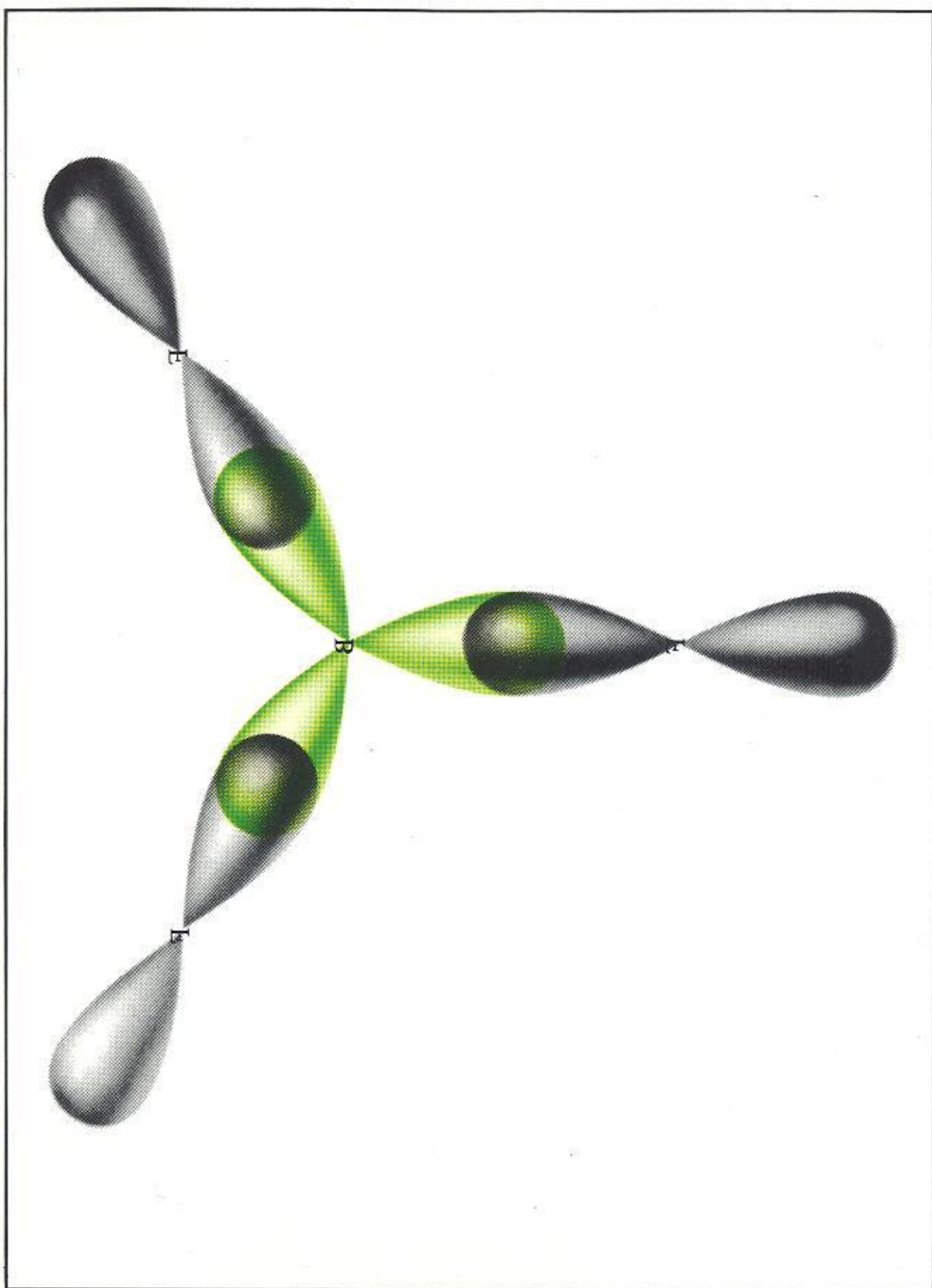
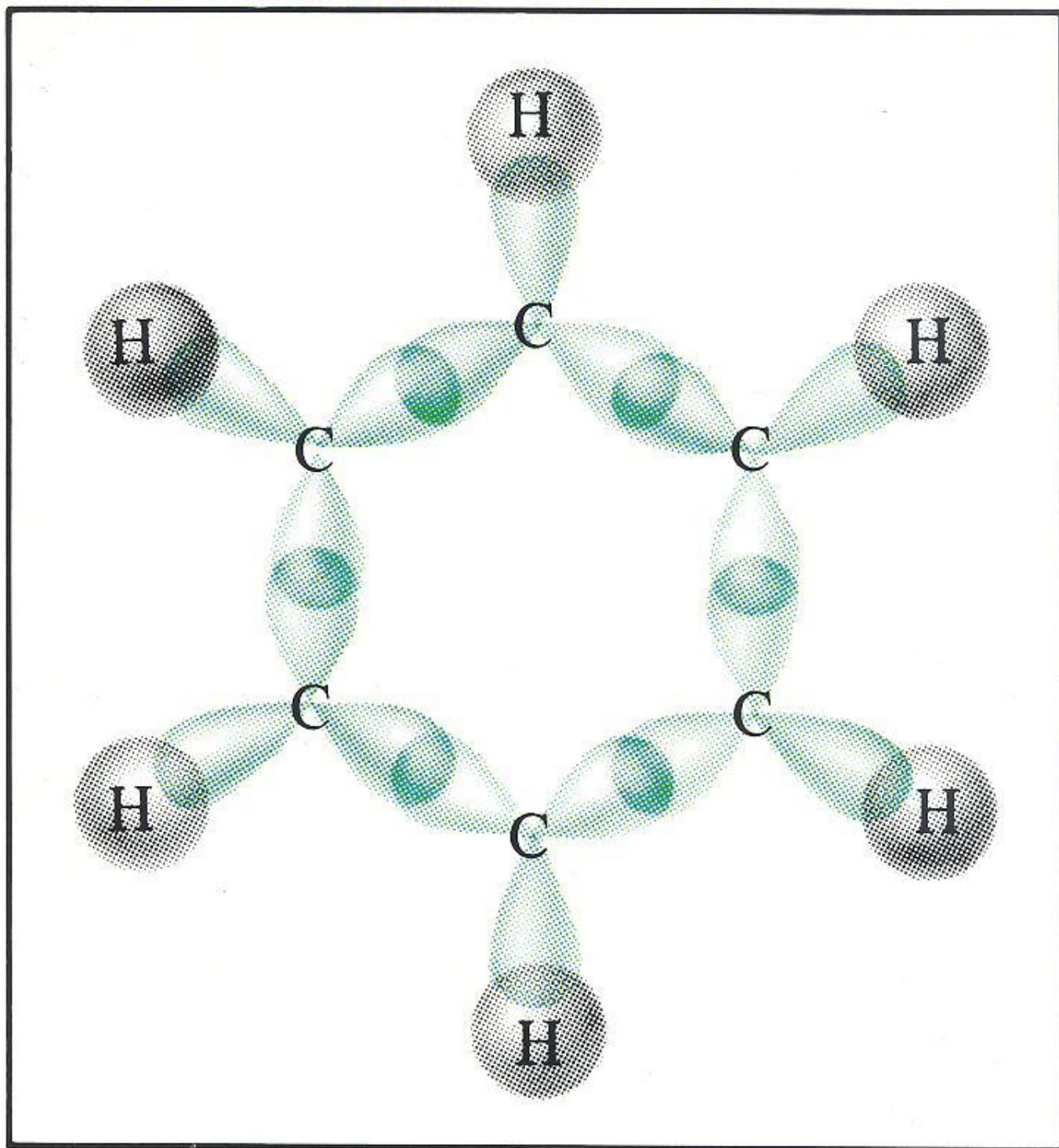


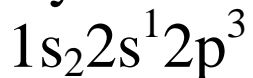
Fig. 10.13

Sigma bond framework
in benzene based on sp^2 hybrids





For hybridization:



4 uncoupled spins

now we can hybridize these orbitals

sp^3 hybridization

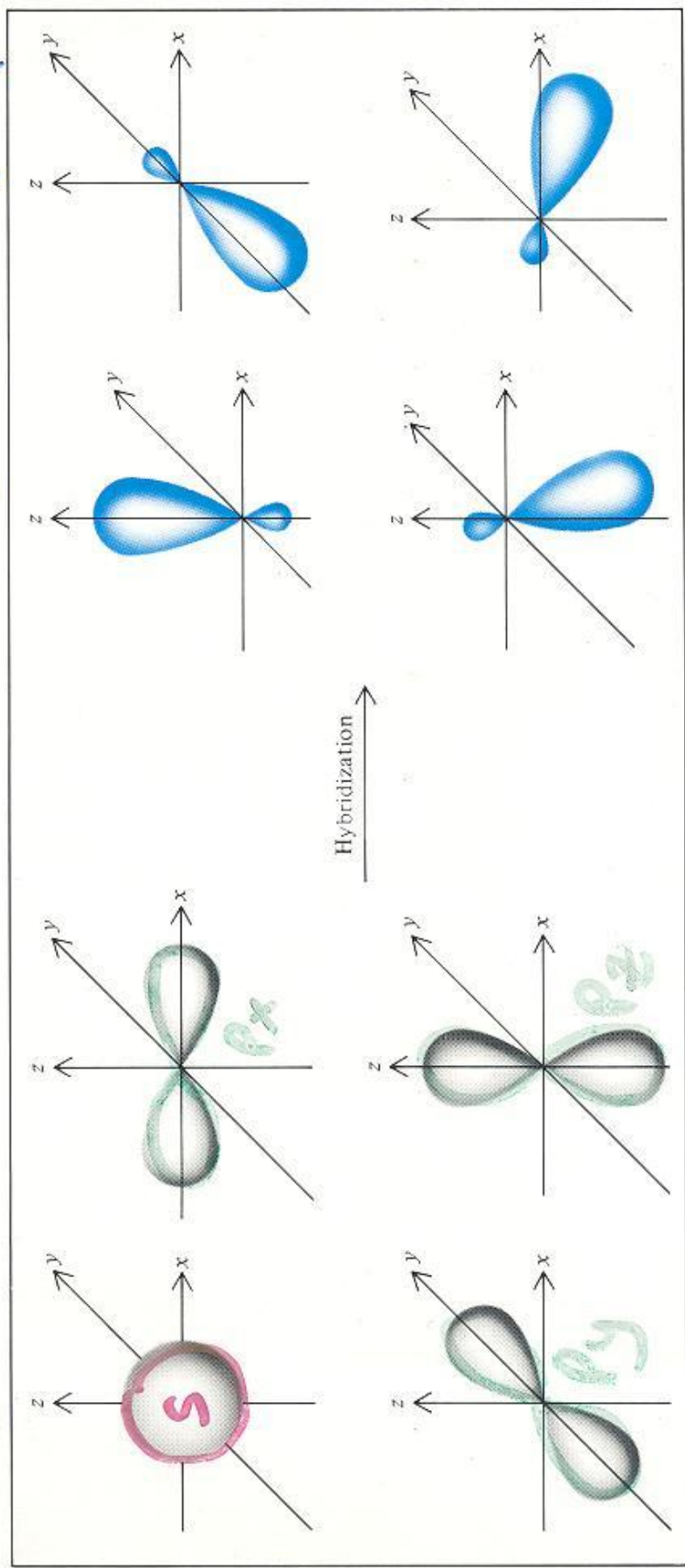
Summary s, p Hybridization

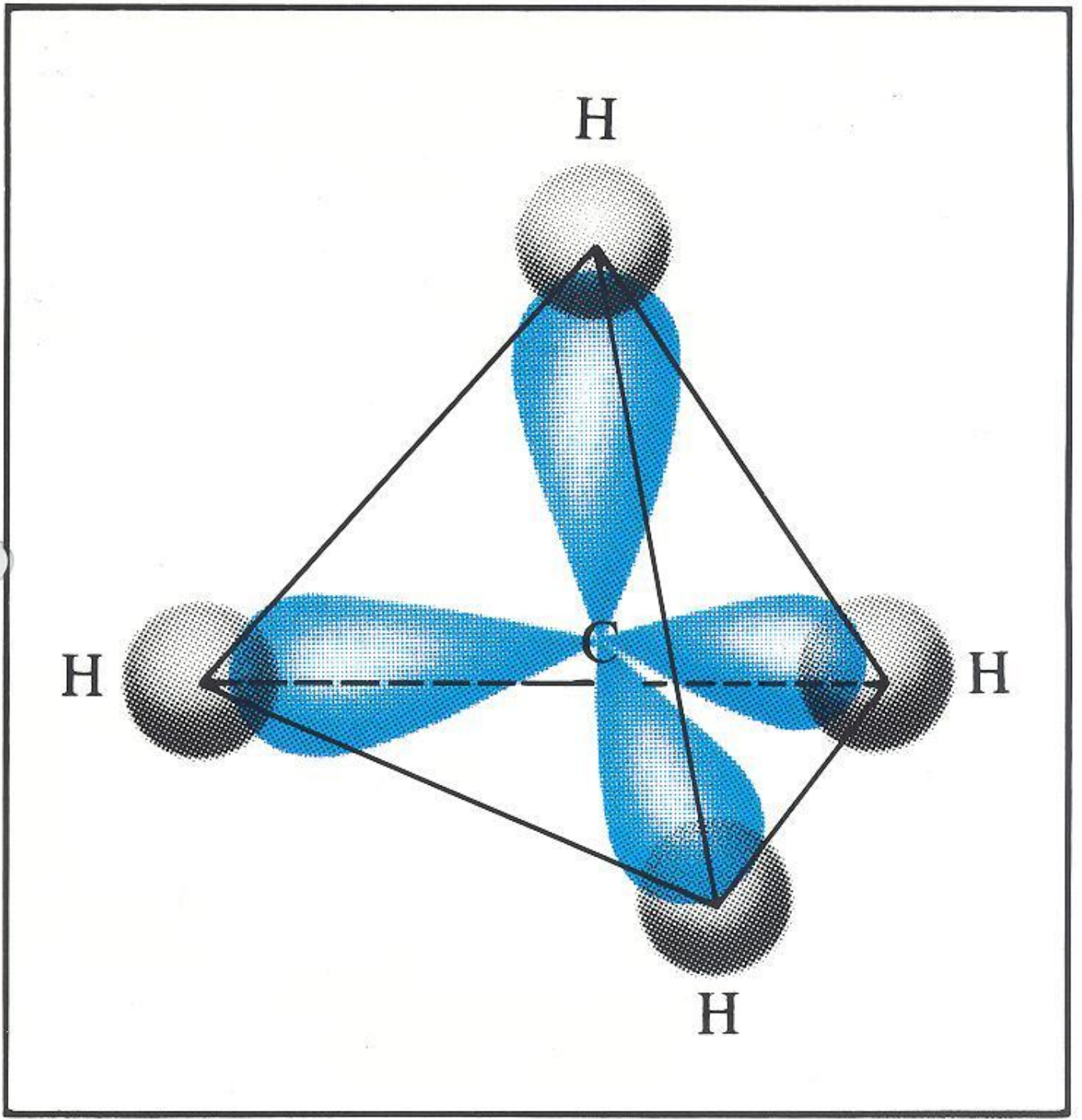
| | |
|--------|----------------------------|
| sp | linear molecule |
| sp^2 | planar triangular molecule |
| sp^3 | tetrahedral molecule |

The geometries arise from maximum overlap along these directions (sp , sp^2) and from the algebra of the hybridization for sp^3 (it also happens to be the maximum distance from each other in each case)

Figure 10.7

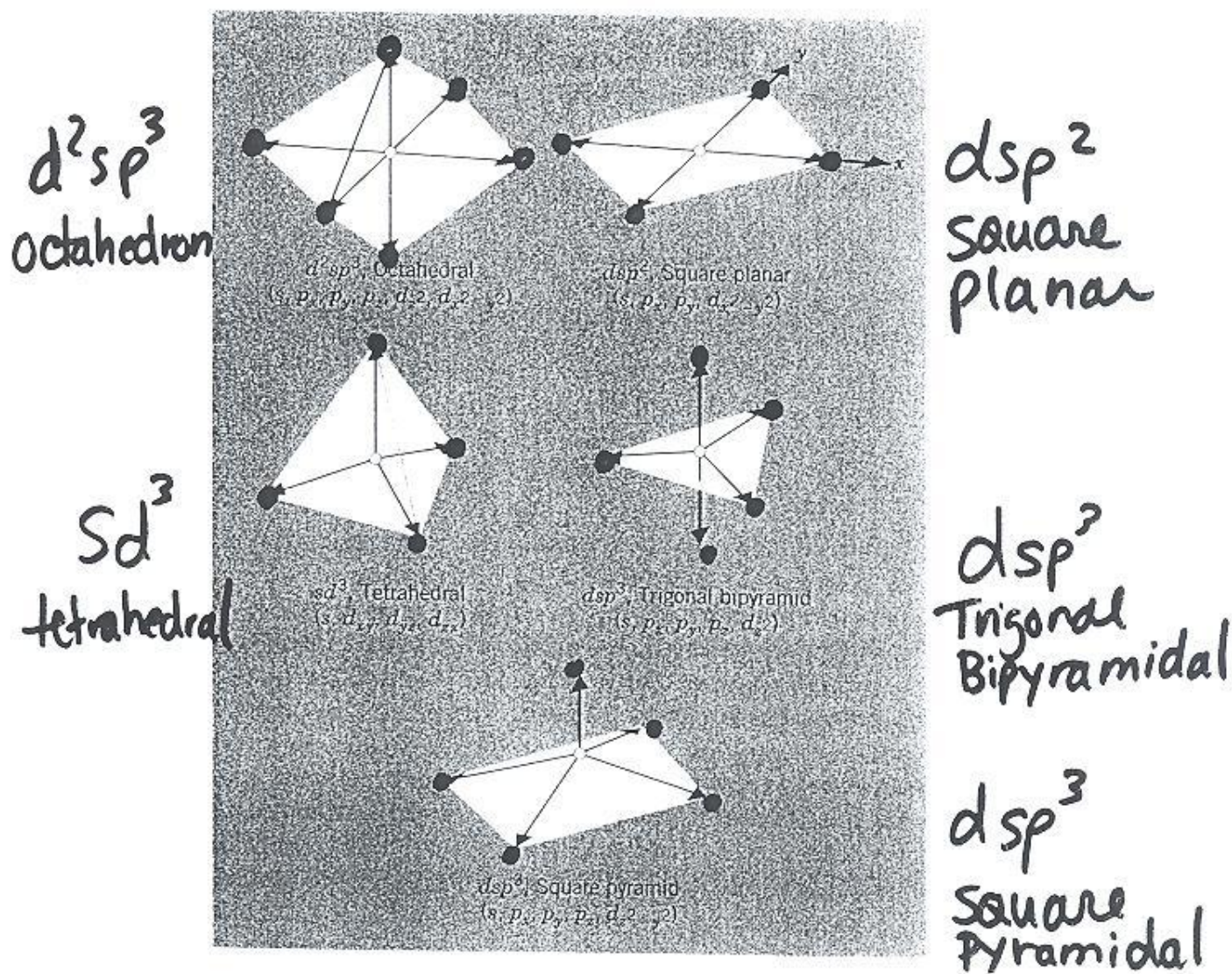
family sp^3 hybrids





Hybridization with s,p,d orbitals:

d orbitals become available after the second row



Five Main Types

Geometries are:

Six coordinate (octahedron)

Five coordinate (trigonal bipyramidal tbp and square pyramid)

Four coordinate (tetrahedral, square planar)

(Note that the dx^2-y^2 and dz^2 are chosen in particular cases because of standard coordinate labels – we assign the x and y axis to coincide with the ligands)

1. d^2sp^3 octahedral hybridization
 $dx^2-y^2, dz^2, p_x, p_y, p_z$
2. dsp^2 square planar hybridization
 dx^2-y^2, s, p_x, p_y
3. sd^3 tetrahedral hybridization
 dxy, dxz, dyz, s
4. dsp^3 trigonal bipyramidal hybridization
 dz^2, s, p_x, p_y, p_z
5. dsp^3 square pyramidal hybridization
 $dx^2-y^2, s, p_x, p_y, p_z$

These hybridization schemes help to explain bonding and to correlate structures, albeit in a qualitative sense. (molecular orbital theory is used more commonly now, as it is possible to be quantitative)