# Sometimes it seems Atomic Orbitals alone do not work for molecules

- Bonding in a compound of divalent beryllium, such as beryllium hydride, BeH_2- Be has a configuration of $1s^2 2s^2$
- The only way that we can obtain two unpaired electrons for bonding in beryllium is to promote one of the $2s$ electrons to the $2p$ level- energy required
- It is observed that Be does form reasonably stable bonds with other atoms
- Moreover, the two bonds in BeH_2 and similar molecules are completely equivalent; this would not be the case if the electrons in the two bonds shared Be orbitals of different types, as in the "excited state" diagram above
- These facts suggest that it is incorrect to assume that the distribution of valence electrons that are shared with other atoms can be described by atomic-type *s, p*, and *d* orbitals at all.

2p

2s ↑↓

1s ↑↓
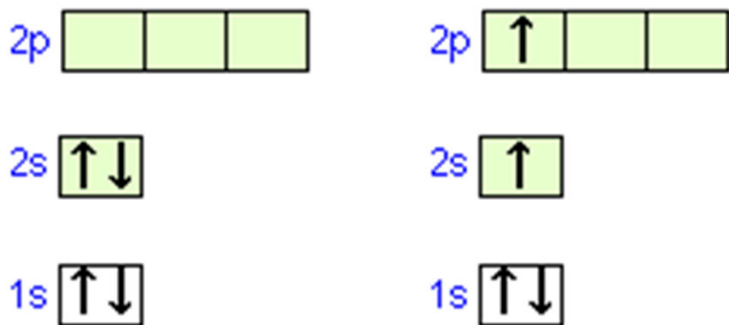
Be atom in ground state

2p ↑

2s ↑

1s ↑↓

Be atom in excited state

The case for Hybrid Orbitals

- For BeH_2, we know from experimental evidence that the molecule is linear and therefore the electron density surrounding the central atom is no longer spherical, but must be concentrated along two directions 180° apart, and we need to construct a function Ψ^2 having these geometrical properties

- There are any number of ways of doing this, but it is convenient is to use a particular set of functions ψ (which we call *hybrid orbitals*) that are constructed by combining the atomic *s,p,d,*and *f* functions that are already familiar to us.

- You should understand that *hybridization is not a physical phenomenon*; it is merely a *mathematical operation* that combines the atomic orbitals we are familiar with in such a way that the new (hybrid) orbitals possess the geometric and other properties that are reasonably consistent with what we observe in a wide range (but certainly not in all) molecules

- In other words, hybrid orbitals are abstractions that describe reality fairly well in certain classes of molecules (and fortunately, in much of the very large class of organic substances) and are therefore a useful means of organizing a large body of chemical knowledge... but they are far from infallible e.g. H_2O and H_2S
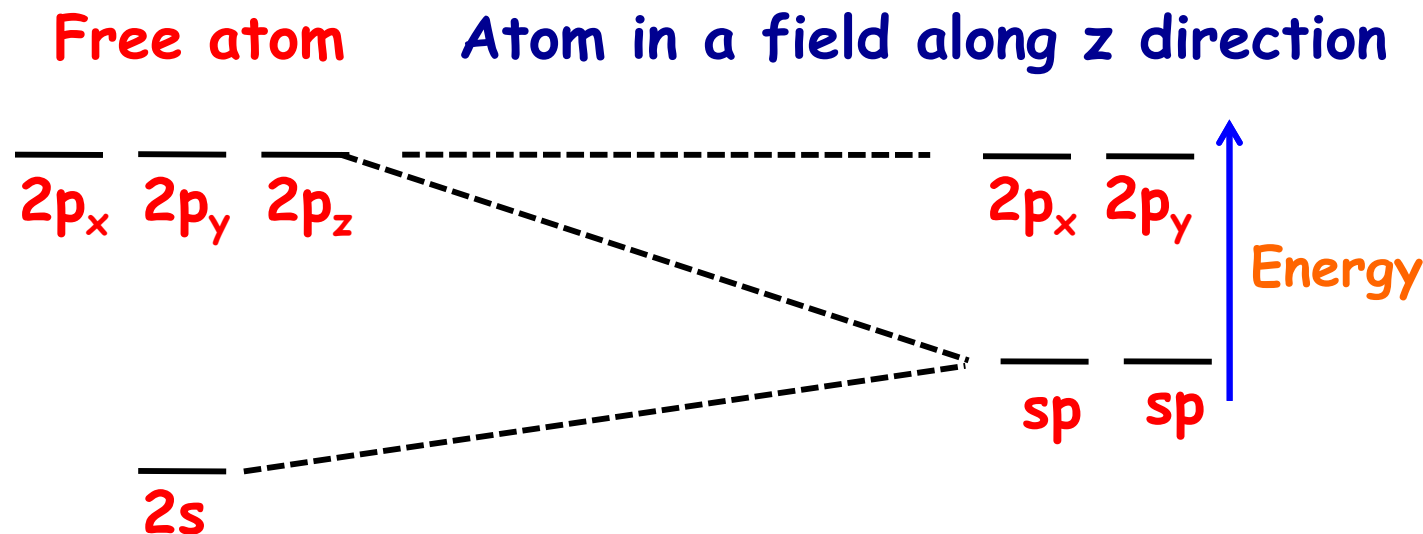
Hybrid AOs: Linear Combination of one S and one P → lowering of energy

Hybrid (1e) Orbitals

- Linear combination of atomic orbital's within an atom leading to more effective bonding situation

Linus Pauling, ~1930

Free atom   **Atom in a field along z direction**

2p$_x$ 2p$_y$ 2p$_z$ 2p$_x$ 2p$_y$

Energy

2s

sp   sp

- Hybridization is a VBT concept. Use of experimental information
- All hybrid orbitals equivalent and are orthonormal to each other

Linear Geometry: s&p mix: sp hybrid AOs

2 equivalent hybrid orbitals of the same energy and shape (<u>different directions</u>)

$$\varphi_{h1}^{sp} = c_1 \psi_s + c_2 \psi_p$$

$$\varphi_{h2}^{sp} = c_1 \psi_s - c_2 \psi_p$$

S and P orbital of the Same atom – Constructive and destructive interference!
Not same as S_{AB} (overlap)

$s + p$
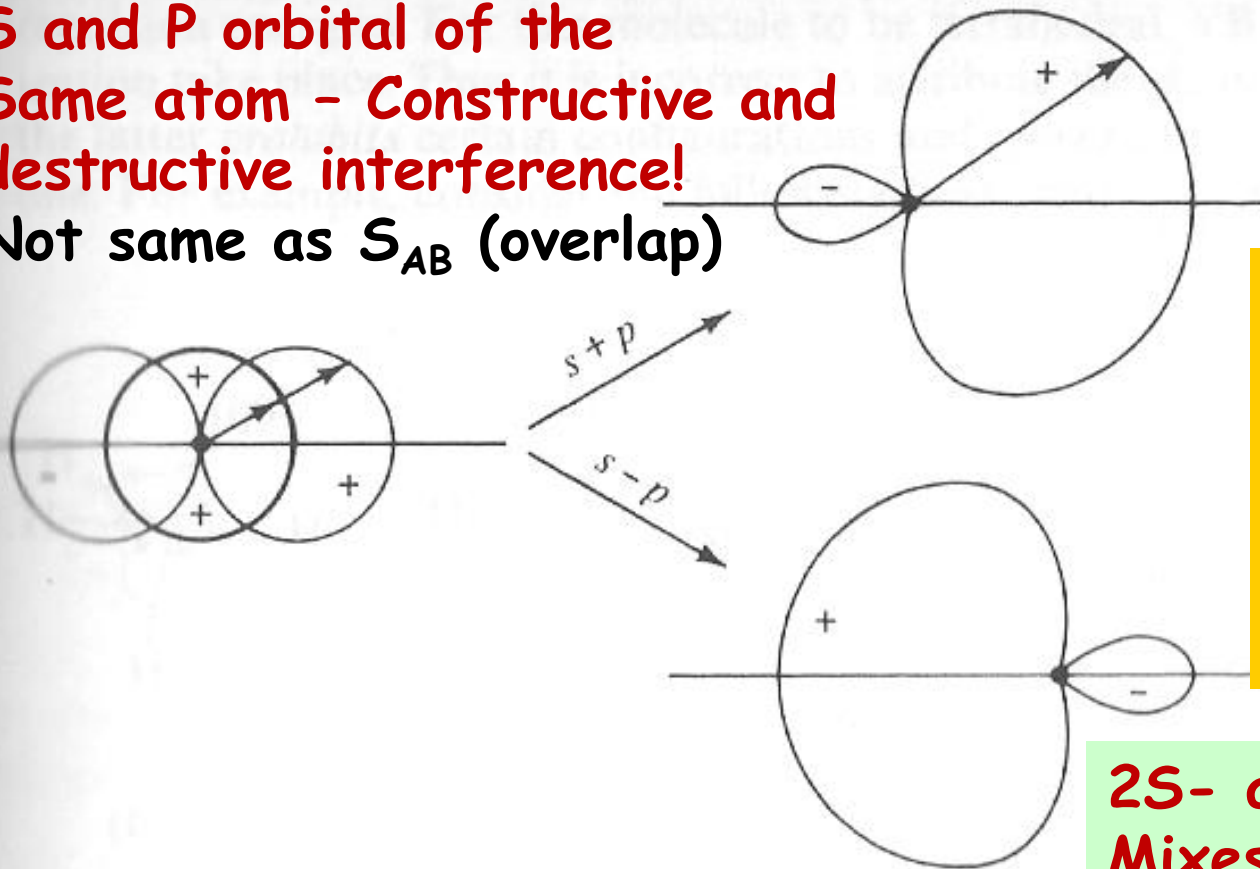
$s - p$

$$\varphi_{h1}^{sp} = \frac{1}{\sqrt{2}} \psi_s + \frac{1}{\sqrt{2}} \psi_p$$

$$\varphi_{h2}^{sp} = \frac{1}{\sqrt{2}} \psi_s - \frac{1}{\sqrt{2}} \psi_p$$

2S- and 2P- (similar energy) Mixes to form hybrid orbital which forms a MO with H (1S)

Contribution from s=0.5; contribution from p=0.5
Have to normalize each hybridized orbital
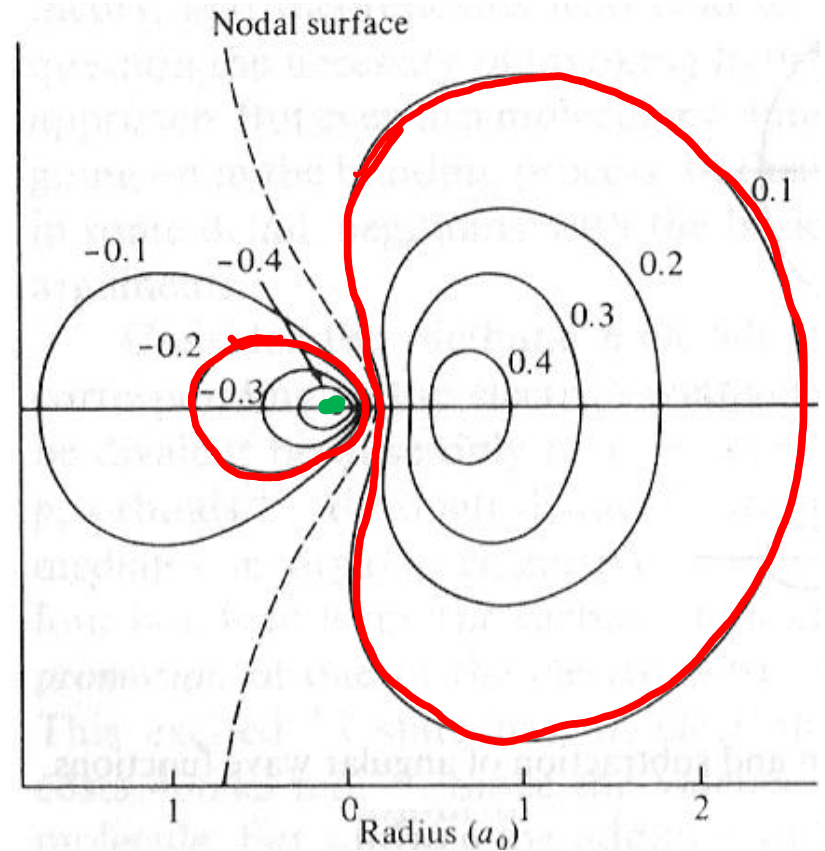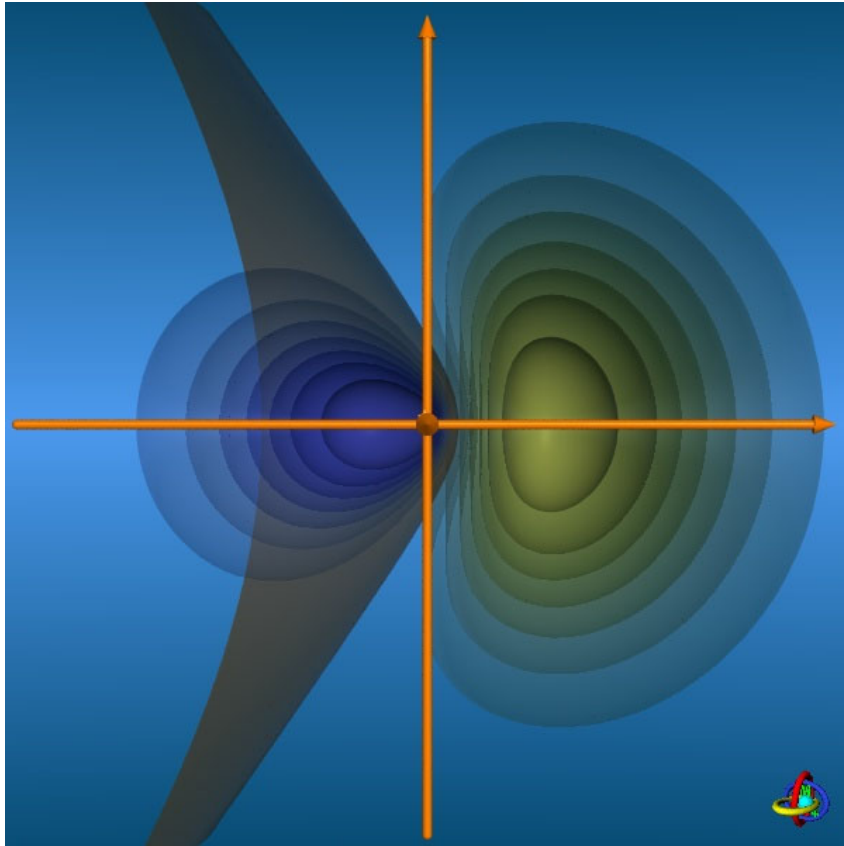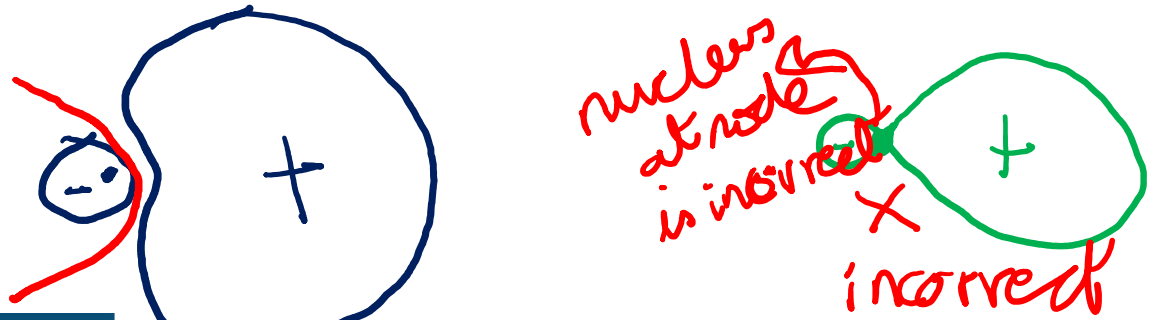
Recap: 2D/3D plots of 2s and 2pz WFs

2s

2p$_z$

x or y
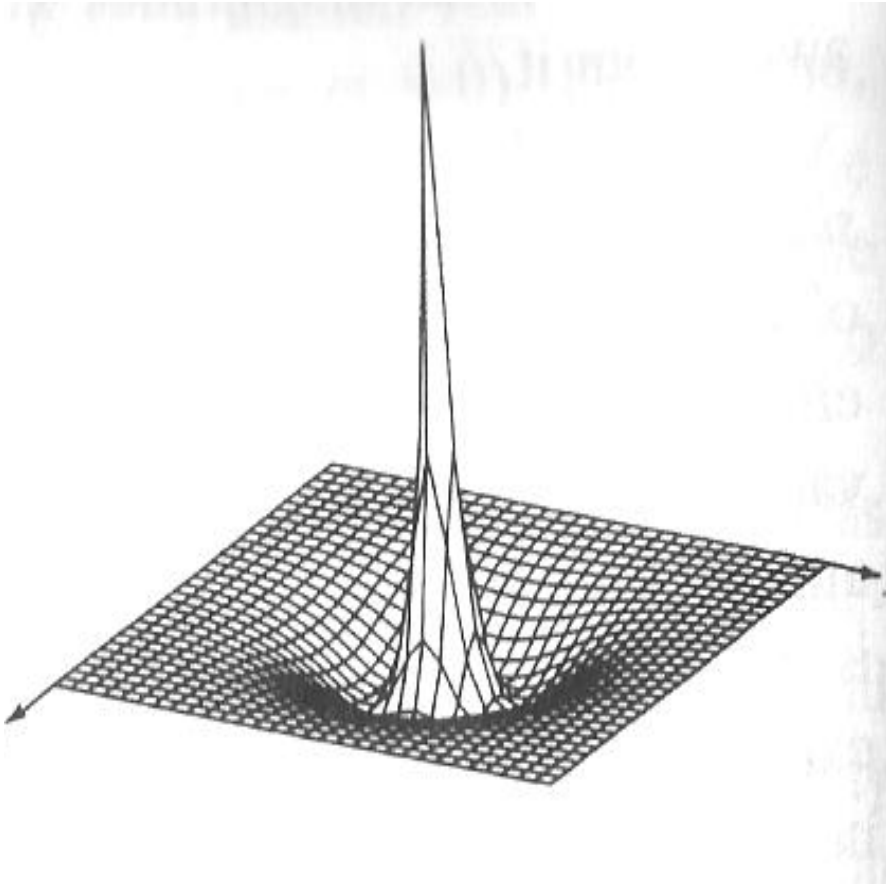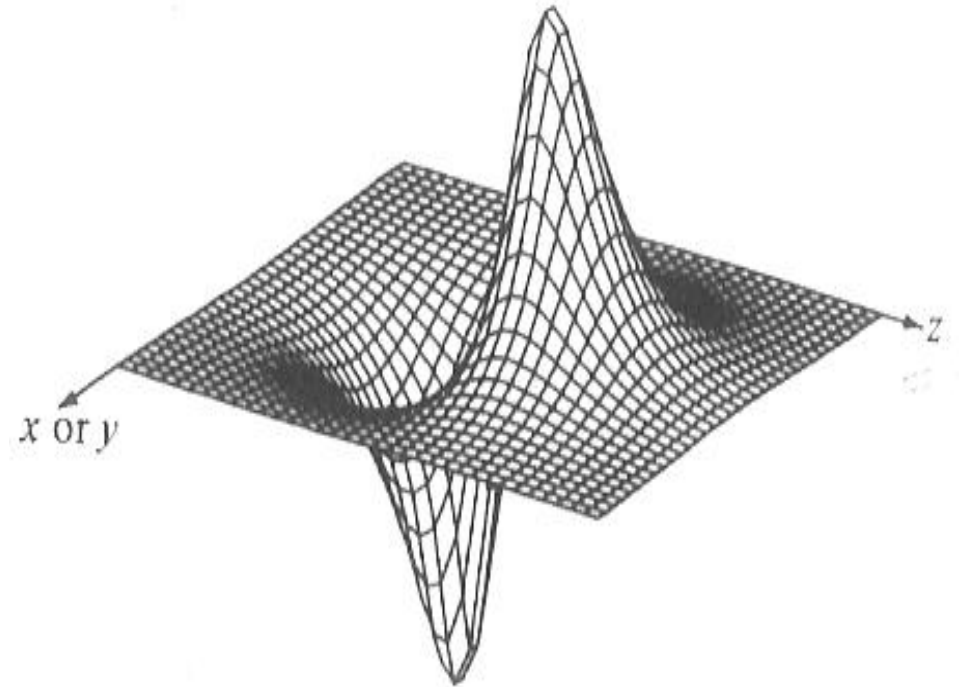
z

3D projection (plot) of <u>AOs (Total Wavefunction R(r) x Θ(θ))</u>

2s-2p hybrid AOs are quite complex
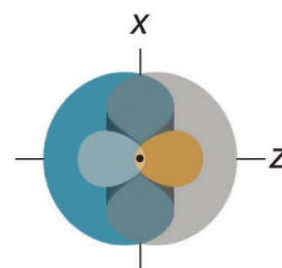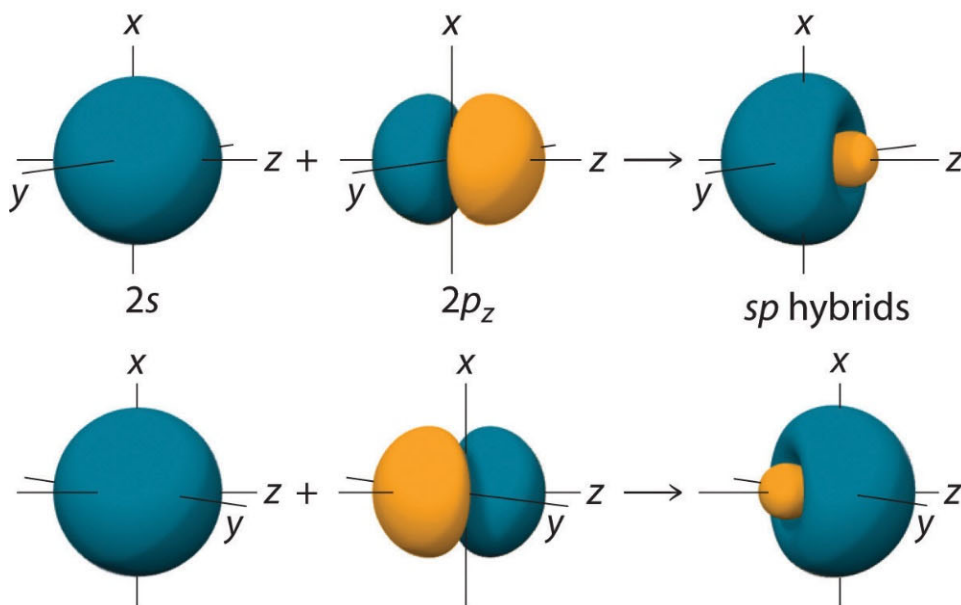

2s **2s**

2p_z

2s

+Z

2p_z
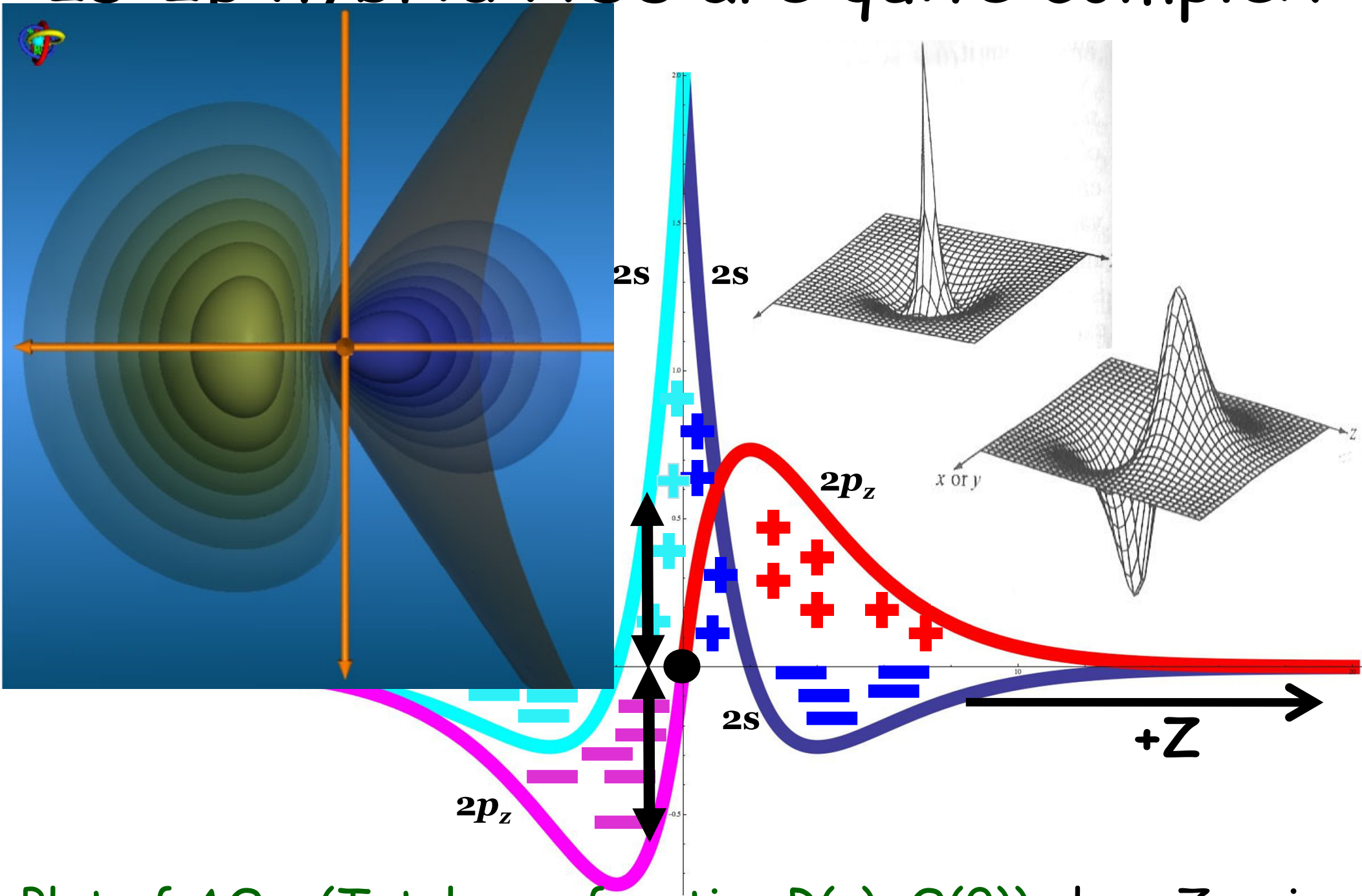
Plot of <u>AOs (Total wavefunction R(r)xΘ(θ))</u> along Z-axis

Contours & bonding of sp-hybridization
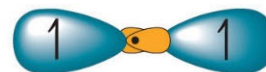
nucleus
at node
is incorrect

+

X
incorrect

Nodal surface

-0.1   -0.4

-0.2

-0.3

0.1

0.2

0.3

0.4

1   0   1   2
Radius (a_0)

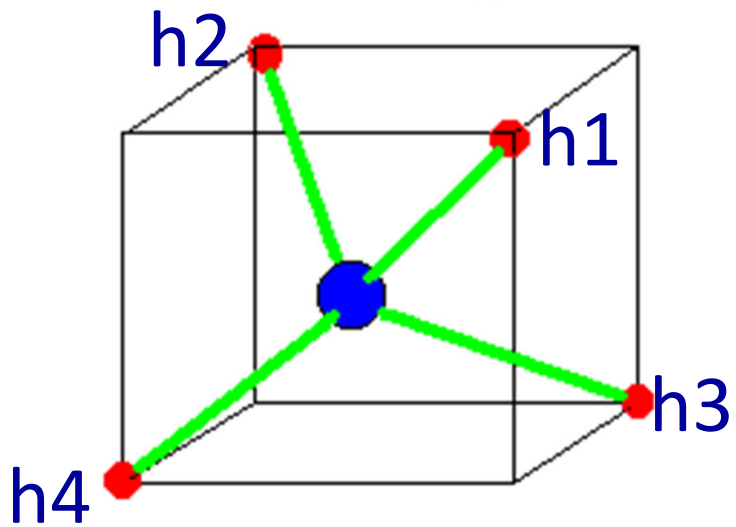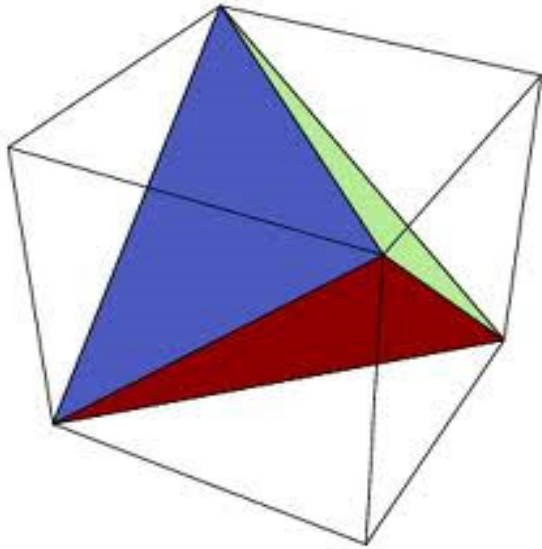# The case of BeH$_2$

Trigonal Geometry: Mixing s & 2-p

p_x and p_y can be combined with s to get three 3 equivalent hybrids at 120° to each other

sp^2 hybrids

Hybrids shown together

	2p	1 __ __		1 1 __		__ __	2p
E			Promotion →		Hybridization →	1 1 1	sp^2
	2s	1↓		1			
		B (ground state)		**B** (excited state)		**B** (sp^2 hybridized)	
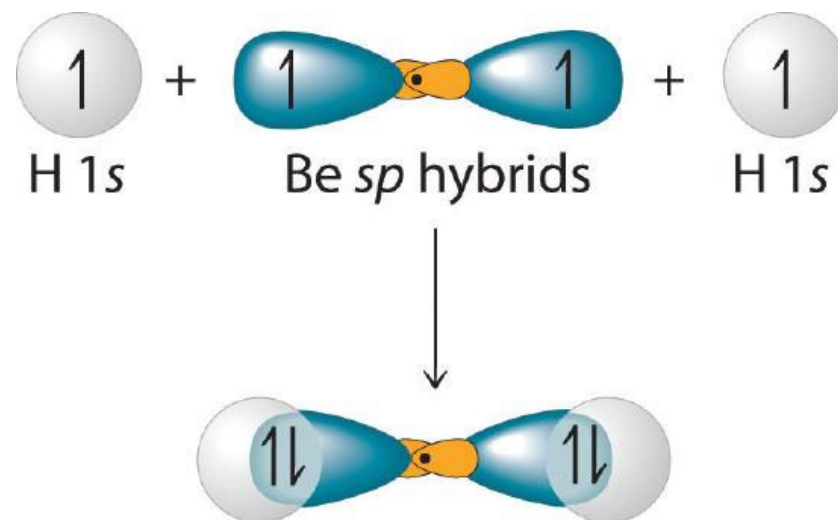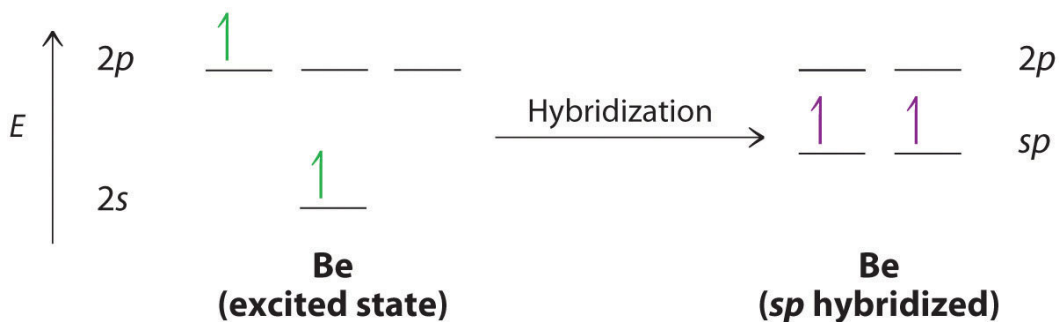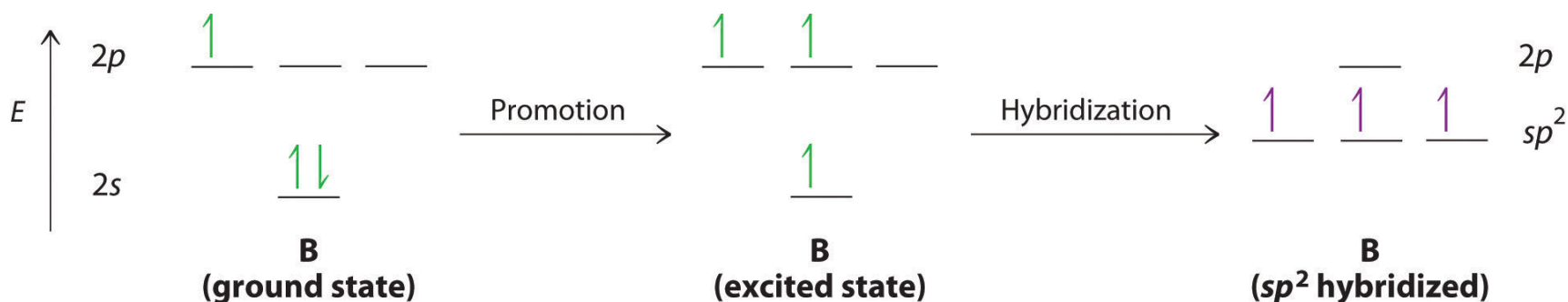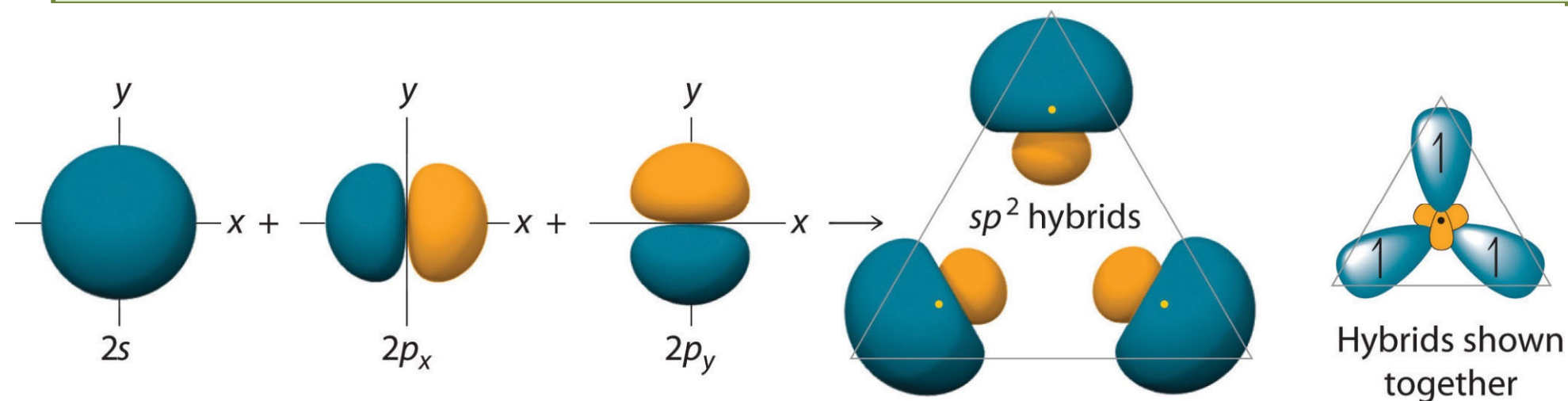
Hybridization of s & 3-p:sp³: Tetrahedral

$$\varphi_{h1}^{sp^3} = \frac{1}{2}\psi_s + \frac{1}{2}\psi_{p_x} + \frac{1}{2}\psi_{p_y} + \frac{1}{2}\psi_{p_z}$$
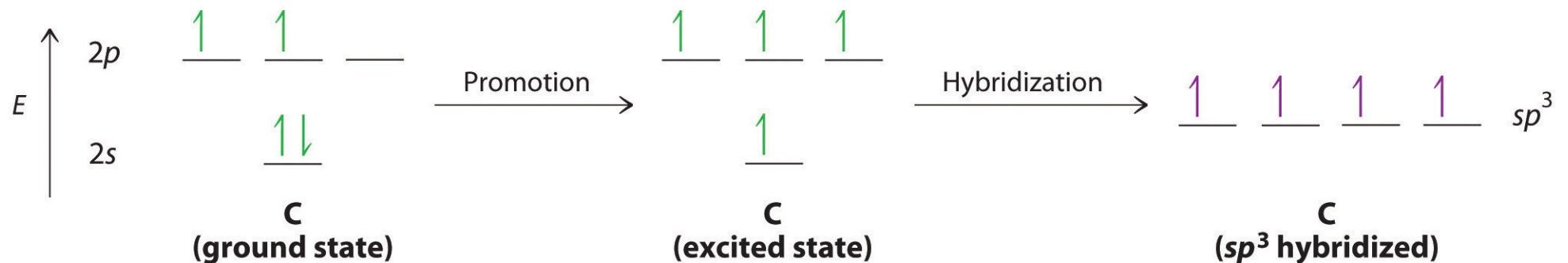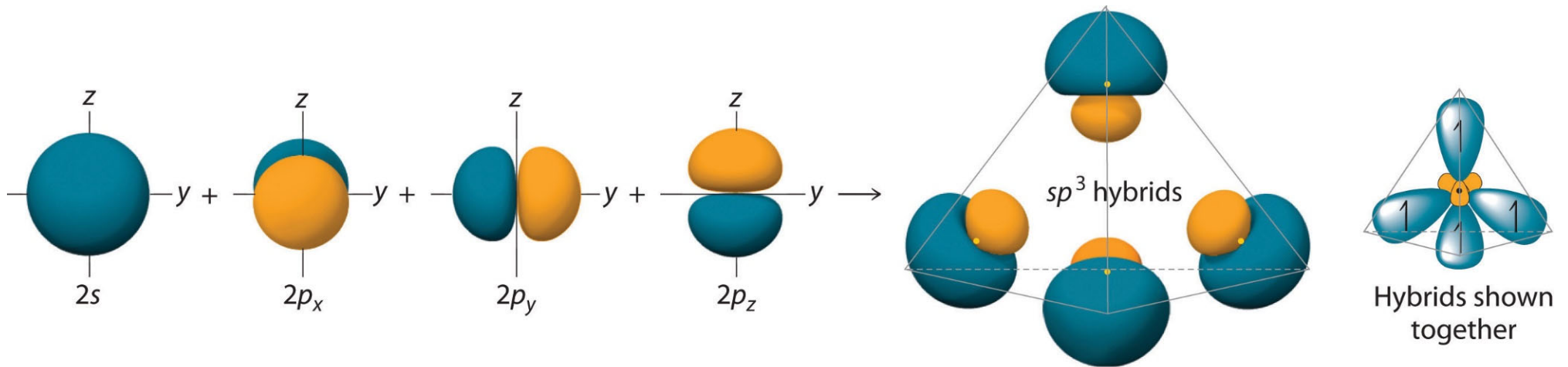
$$\varphi_{h2}^{sp^3} = \frac{1}{2}\psi_s - \frac{1}{2}\psi_{p_x} - \frac{1}{2}\psi_{p_y} + \frac{1}{2}\psi_{p_z}$$

$$\varphi_{h3}^{sp^3} = \frac{1}{2}\psi_s + \frac{1}{2}\psi_{p_x} - \frac{1}{2}\psi_{p_y} - \frac{1}{2}\psi_{p_z}$$

$$\varphi_{h4}^{sp^3} = \frac{1}{2}\psi_s - \frac{1}{2}\psi_{p_x} + \frac{1}{2}\psi_{p_y} - \frac{1}{2}\psi_{p_z}$$
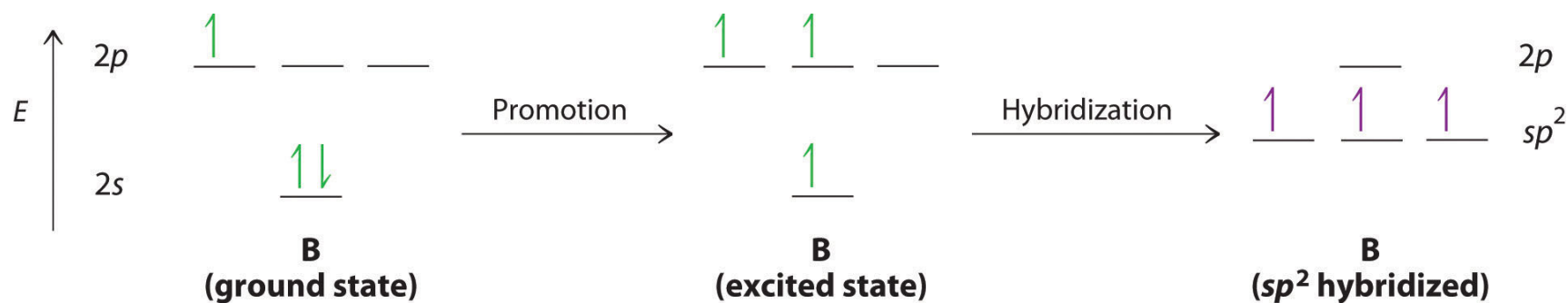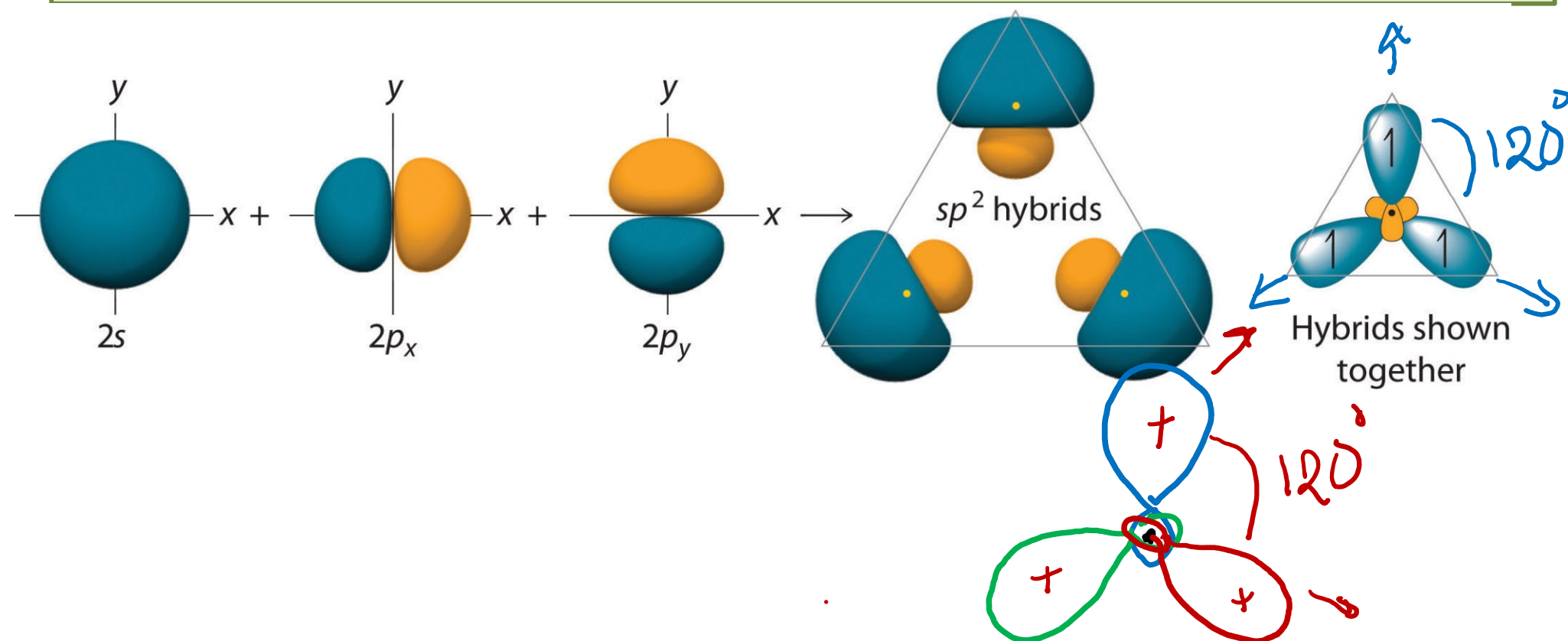
Contributions from s = 25%; p=75%

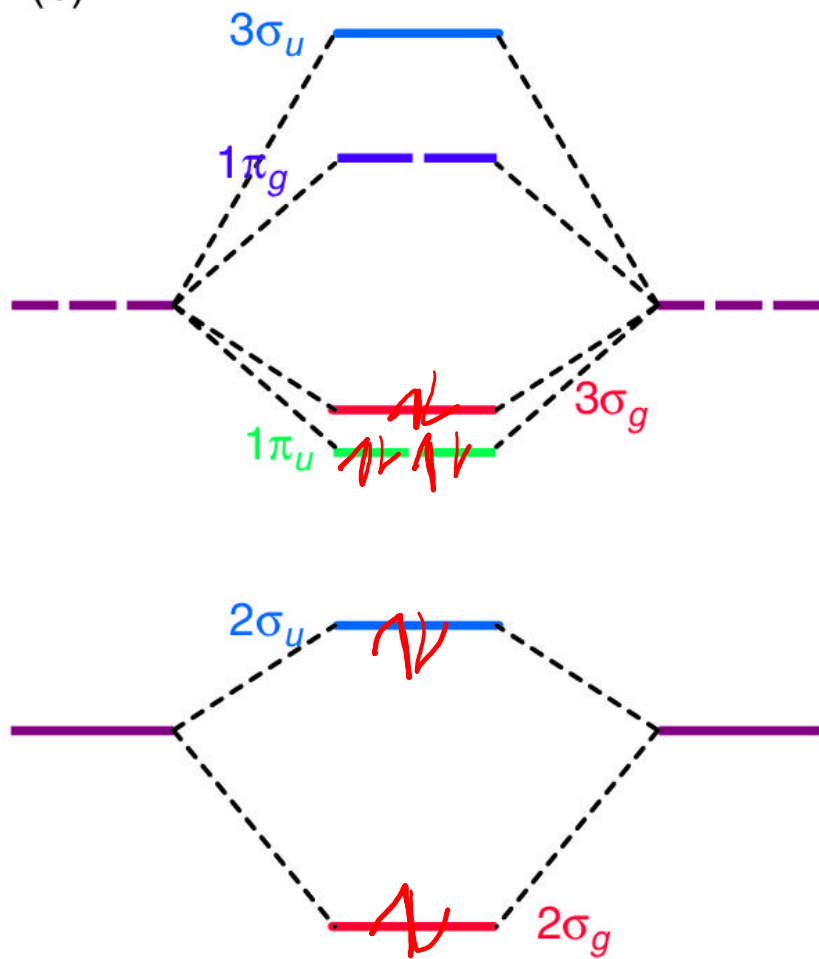# What if h1 is oriented along z-axis?

Trigonal Geometry: Mixing s & 2-p

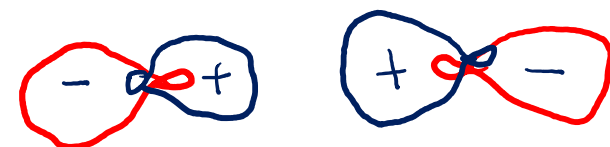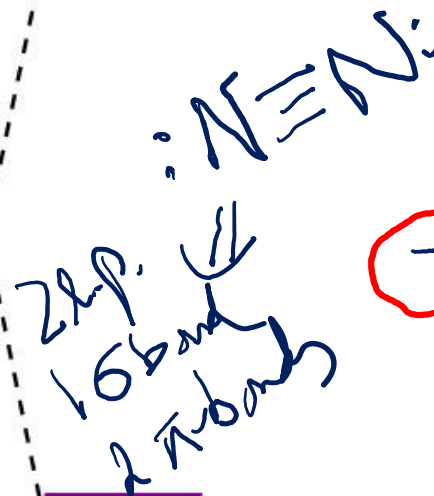p_x and p_y can be combined with s to get three 3 equivalent hybrids at 120° to each other

sp^2 hybrids

Hybrids shown together

	B (ground state)		B (excited state)		B (sp^2 hybridized)	

E

2p   1   __   __   1   1   __   __   __   2p

Promotion →   Hybridization →   1   1   1 sp^2

2s   1↓   1

B
(ground state)

B
(excited state)

B
(sp^2 hybridized)

(b)

$3\sigma_u$

$1\pi_g$

$1\pi_u$ $3\sigma_g$

$2\sigma_u$

$2\sigma_g$

$: N \equiv N :$

Hybrid MO for N₂

(a)

σ^*

π^*

$2p$

$2p_{x,y}$

sp_c sp_d

sp_a

sp_b

π

$2s$

AO   HAO   HAO   AO

σ

$2h.p.$
1σ bond
2π-bonds

$:N \equiv N:$
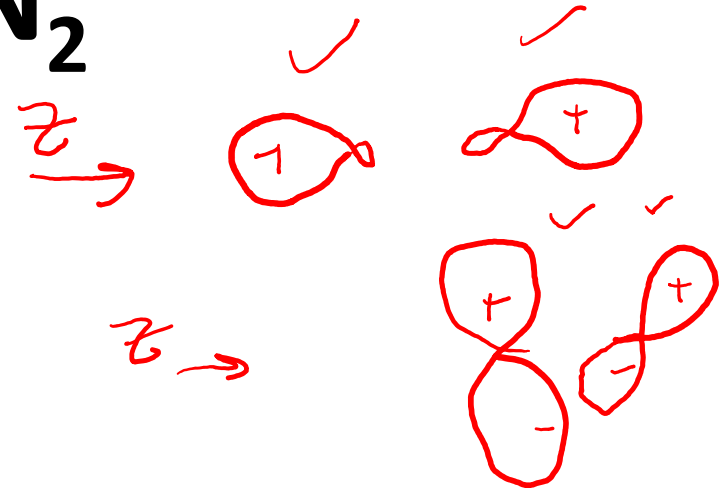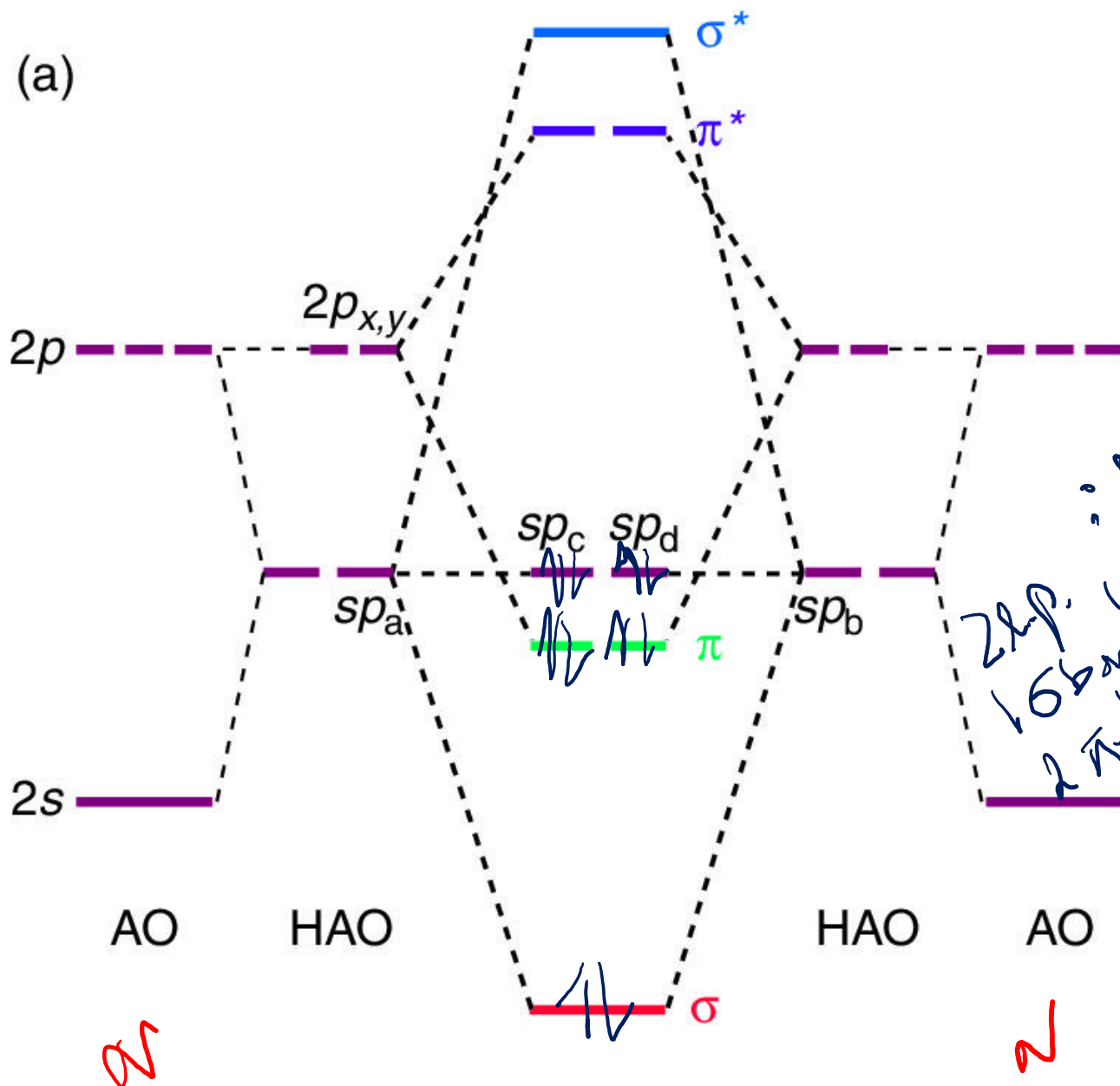
$\rightarrow R \leftarrow$

Blue will give S > 0

Red will be S = 0