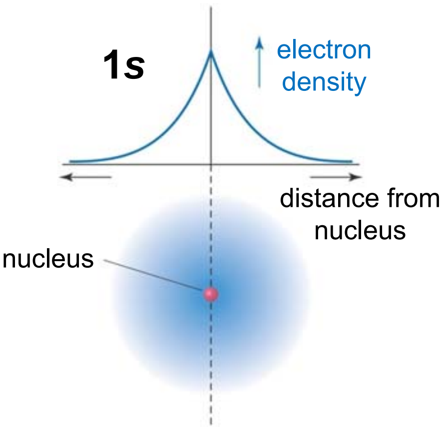
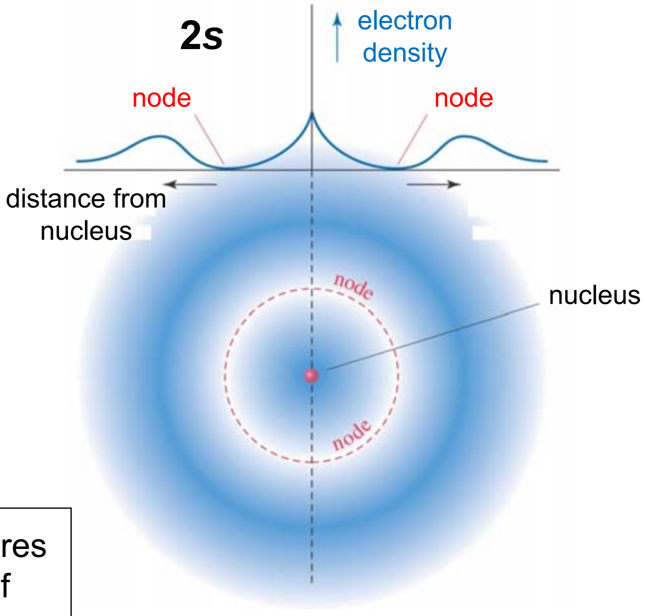
Electrons and Bonds in Space

- Lewis dot and dash structures are great for *accounting*, but don’t say much about three-dimensional arrangement of atoms and bonds
- For that, need *molecular orbitals*, built from atomic orbitals.

1*s*, 2*s* Atomic Orbitals



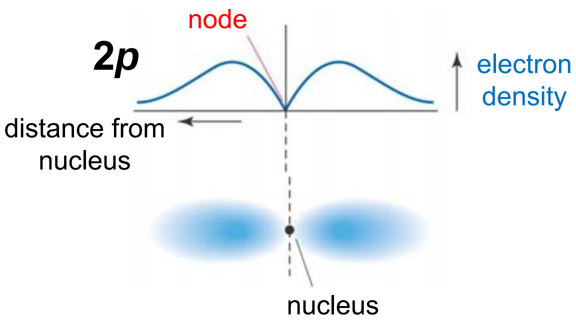


We will draw all s orbitals as spheres (circles) enclosing a percentage of electron density.

H[1*s*]: 

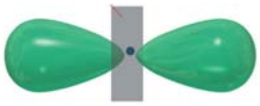
Reminder: n – l = # of nodes

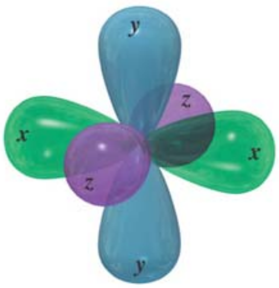
$2p$ Atomic Orbitals



Again, draw as solid lobes enclosing a percentage of electron density.

C[$2p_x$]:





$2p_x$, $2p_y$, *and* $2p_z$ *orbitals*

Molecular Orbitals

- Bonds, electrons between atoms in molecules are described by molecular orbitals.
- These are built from atomic orbitals via *orbital mixing*.

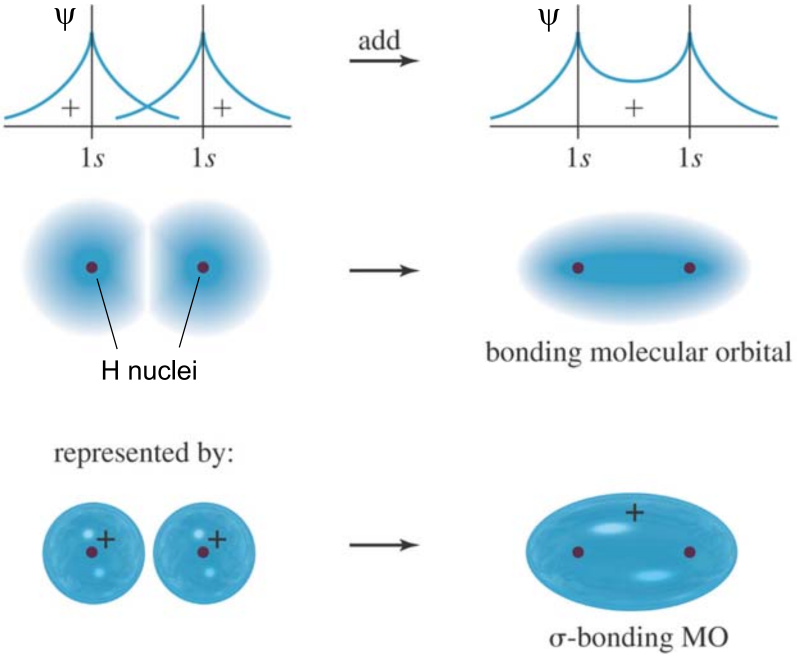
Rules of orbital mixing:

- Product (mixed) orbitals look like constructive and destructive combinations of starting orbitals, with some distortions.
- You end with the same number of orbitals you started with.
- Degree of mixing depends on orbital overlap, match between orbital energies.

The Single Bond in H_2

Constructive mixing yields a "bonding" orbital.

ψ = (e^- density) •
phase (+/-)



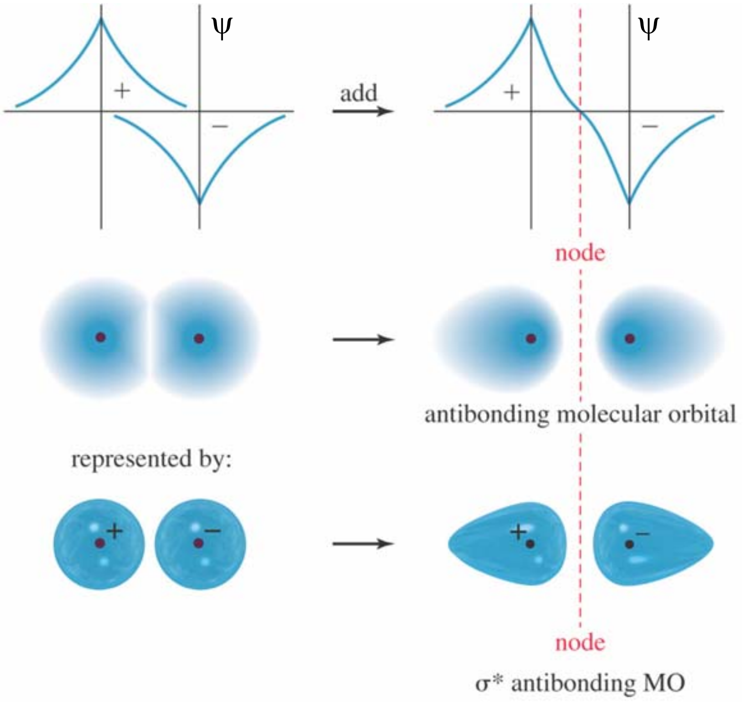
Start with linear combination of atomic orbitals (LCAO)

…but we need to make another one…

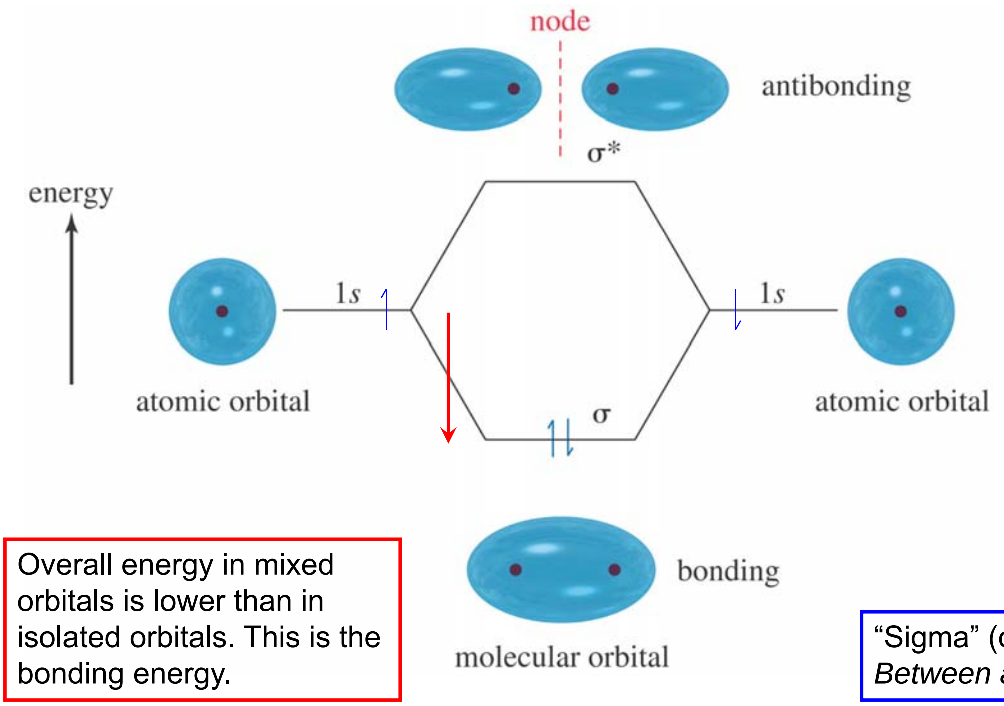
The Single Bond in H_2

Destructive mixing yields an "anti-bonding" orbital.

ψ = (e^- density) •
phase (+/-)



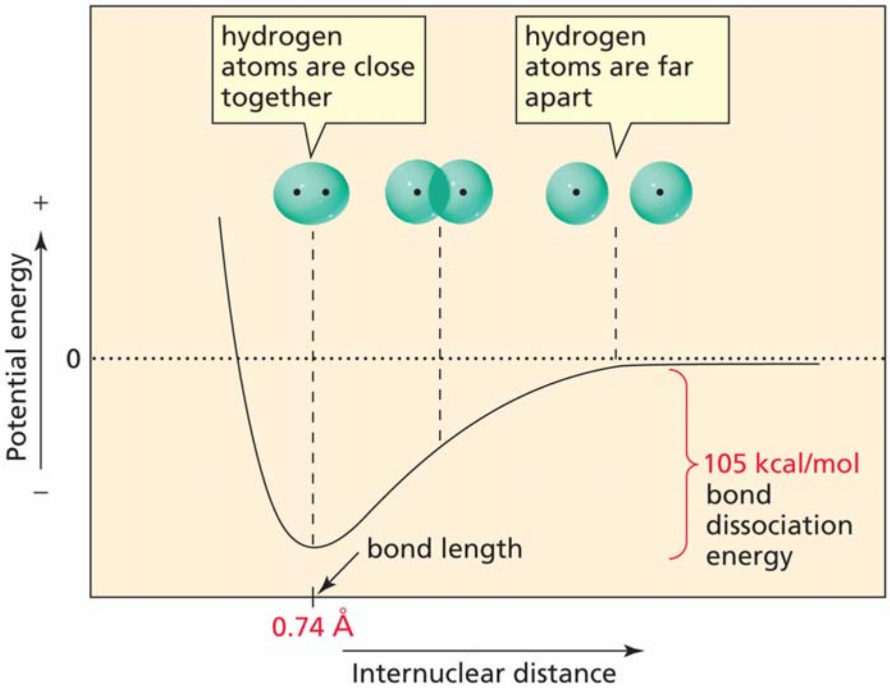
Mixing *s* Orbitals



Overall energy in mixed orbitals is lower than in isolated orbitals. This is the bonding energy.

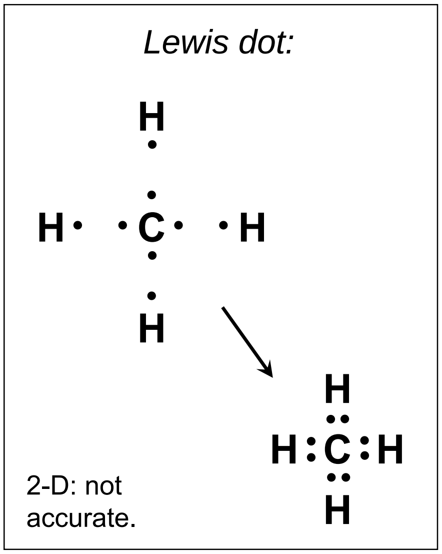
“Sigma” (σ) bond: *Between atoms.*

Orbital Mixing is Responsible for Bond Strength



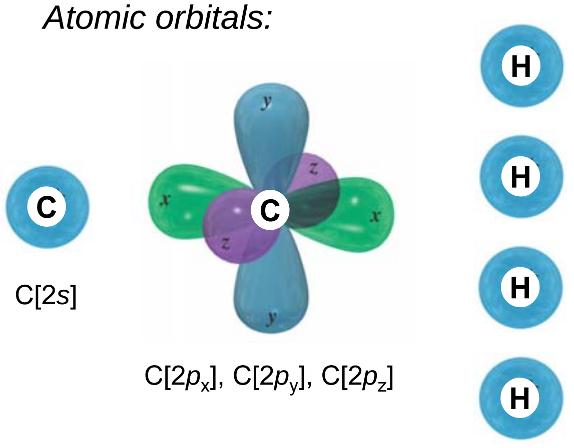
How Do We Use Orbital Mixing to Describe Molecular Structures?

What does methane (CH_4) *look like?*



2-D: not accurate.

Atomic orbitals:



C[2*s*]

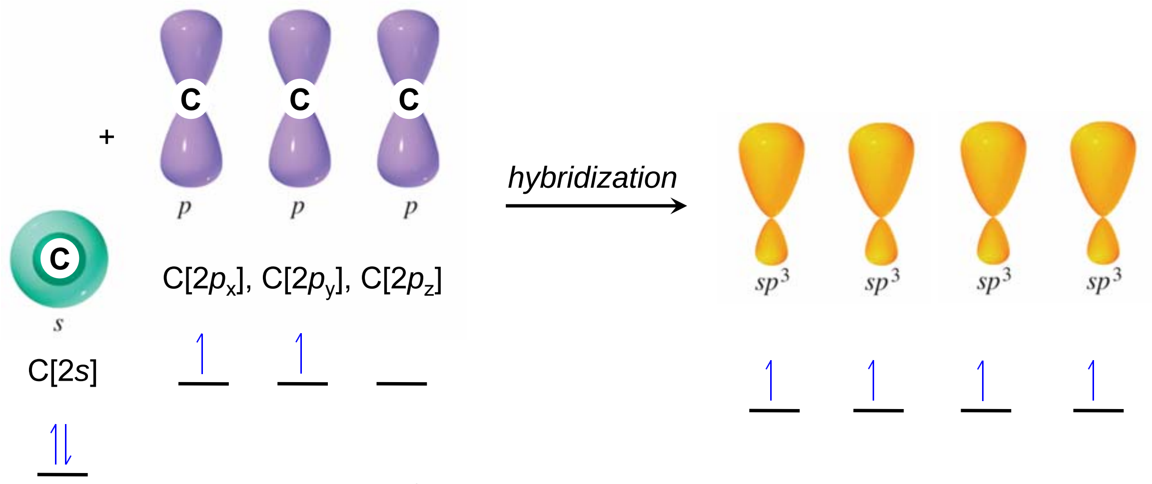
C[2p_x], C[2p_y], C[2p_z]

How do we put all these together?

4 x H[1*s*]

Hybrid Atomic Orbitals

First: "Hybrid orbitals" are formed from *s* and *p* orbitals (on one atom) to create all σ bonds and lone pairs.



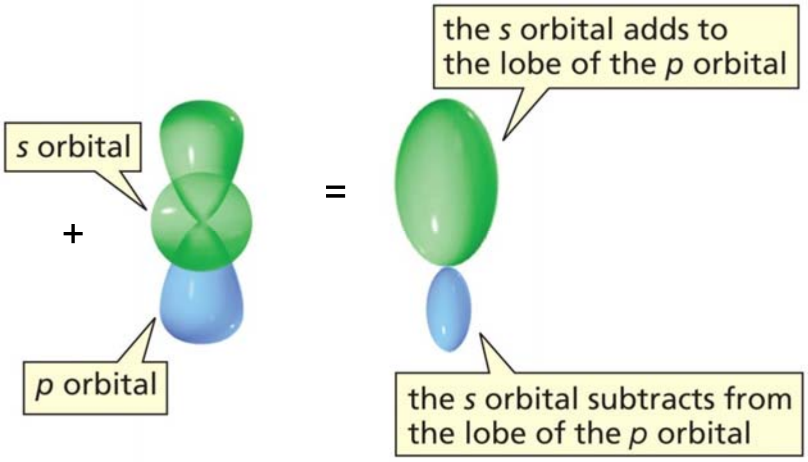
C[2*s*]

C[2p_x], C[2p_y], C[2p_z]

- Called "sp^3" because they come from one *s* and three *p*'s;
- Four of them, because we started with four atomic orbitals to make them.

Hybrid Atomic Orbitals

First: "<u>Hybrid orbitals</u>" are formed from *s* and *p* orbitals (on one atom) to create all σ bonds and lone pairs.



s orbital

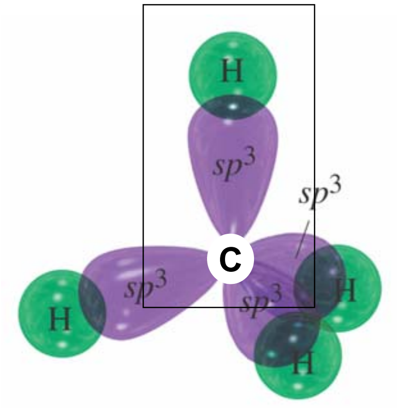
p orbital

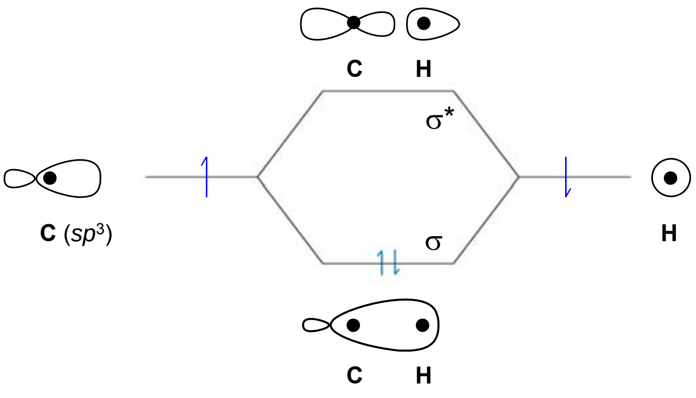
the *s* orbital adds to the lobe of the *p* orbital

the *s* orbital subtracts from the lobe of the *p* orbital

Bonds from Hybrid Molecular Orbitals

Second: Hybrid orbitals mix with partner orbitals.



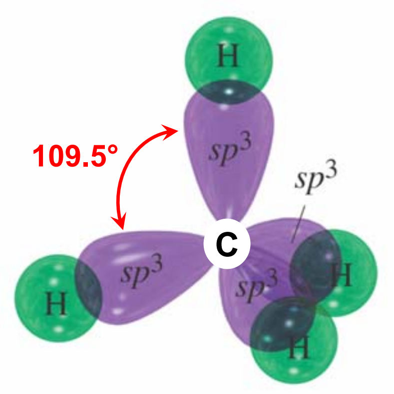


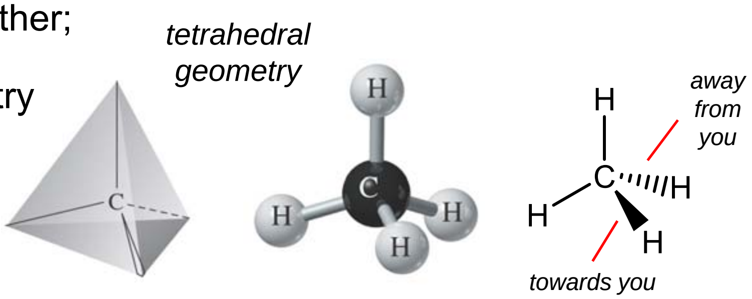
Each of four (C_{sp^3} + H) mixings yields a σ bonding and σ* antibonding orbital.

Valence-Shell Electron Pair Repulsion (VSEPR) Theory Determines Geometry

Methane (CH_4):

- Each σ bonding and non-bonding electron pair repels each other (by electron-electron repulsion);
- These electron pairs organize themselves to maximze distance from each other;
- For CH_4, that geometry is tetrahedral.

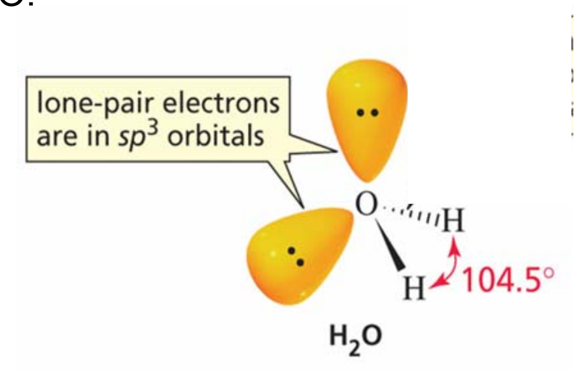


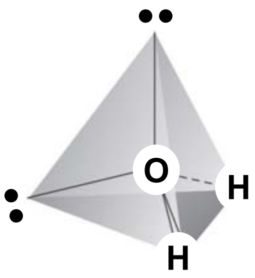


Valence-Shell Electron Pair Repulsion (VSEPR) Theory Determines Geometry

σ bonds (but not π bonds), electron pairs repel each other.

H_2O:





Actually, lone pairs repel *slightly* better than σ bonds.
So, H-O-H angle is < 109.5°.