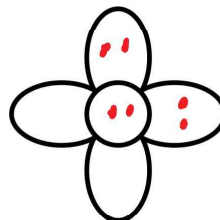# 1ˢᵗ Row Hydrides
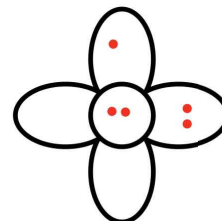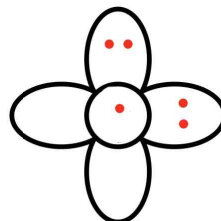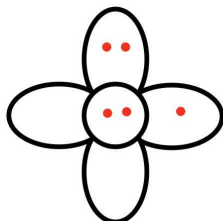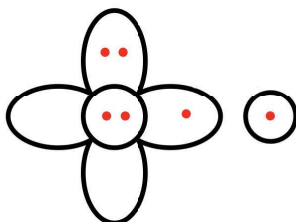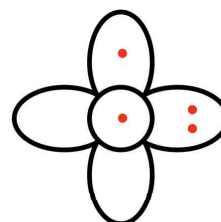
- Draw only outer electrons
- Points represent e- in orbitals

Ne

How about F?
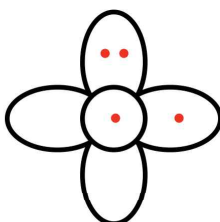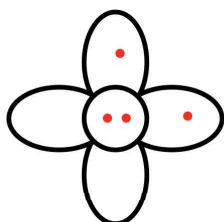
Three possible states

Bonding?

Oxygen (He+2s²2p⁴)

Consider a hydrogen atom approaching
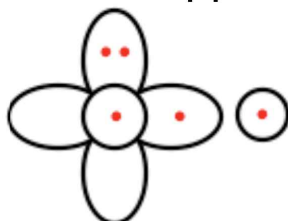
Now consider a second hydrogen atom approaching
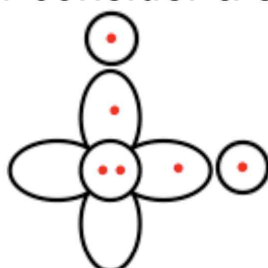
We expect a bond angle of:

The real angle in H_2O is:

Bond angle in H$_2$O

Why is the angle 104.5°?
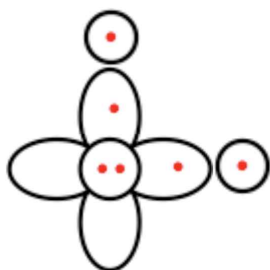
From wikipedia

What would happen to H$_2$S, H$_2$Se, H$_2$Te?

	H2O	H2S	H2Se	H2Te
Bond distance	0.96 Å	1.3 Å	1.5 Å	1.7 Å
Bond angle	104.5°	92.2 °	91 °	90.2 °

Nitrogen
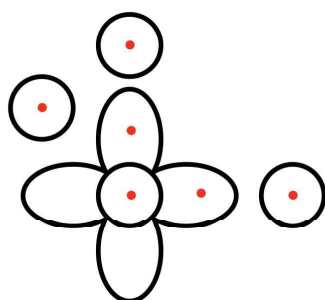
NH2	PH2	AsH2	SbH2
103.3°	91.7°	90.2°	90.3°
NH3	PH3	AsH3	SbH3
106.7°	93.3°	92.1°	91.6°

Carbon
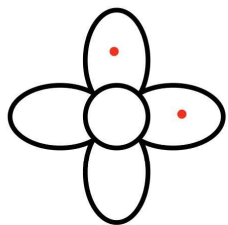
We expect CH_2 angle to be: $\sim 103°$

Experimentally it is:

- SiH_2 angle is 92°
- GeH_2 angle is 91°

- We failed to take something into account in carbon
- CH_4 is very stable
- We assumed $2s^2$ was part of the core

Carbon and hybrid orbitals

To make four bonds I need to promote one electron:
From configuration:

$$1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^0$$

To electronic configuration:

$$1s^2\ 2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1$$

I would expect CH_4 to make three bonds like NH_3 plus a weaker one with the $2s^1$ electron

Experimentally all four bonds are the same

Hybrid orbitals: 2s and 2p orbitals combine to make new hybrid orbitals

Carbon: sp hybridization
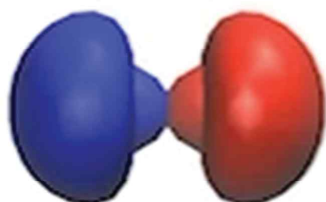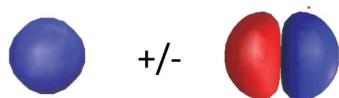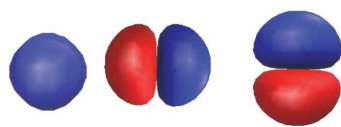
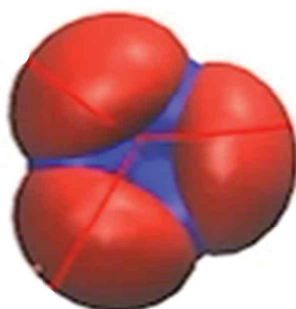| sp^1	sp^2	sp^3
2s orbital & 1 2p orbital	2s orbital & two 2p orbitals	2s orbital & three 2p orbitals

120°
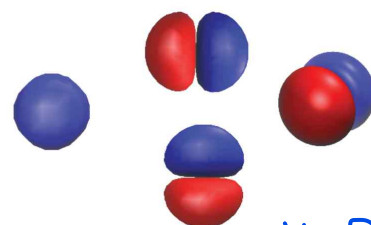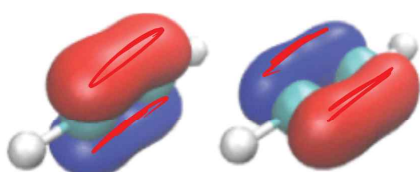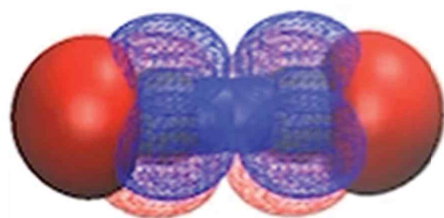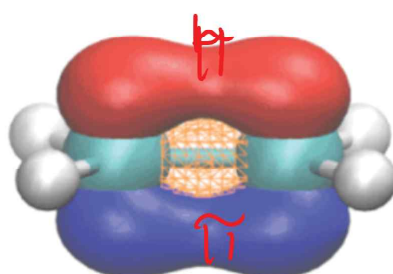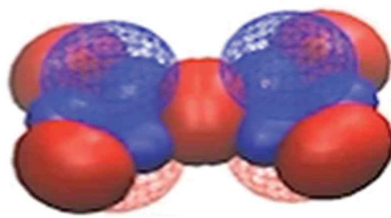
109°
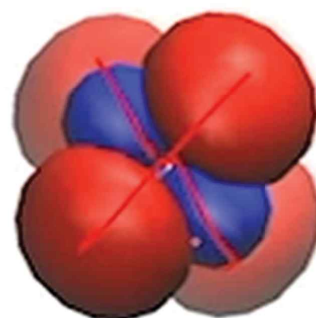
Carbon: bonds with sp orbitals

Ethyne (acetylene)	Ethylene	Ethane
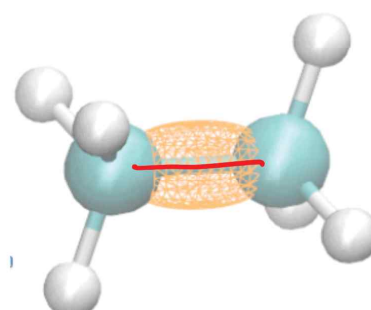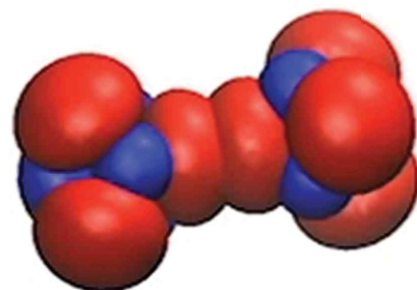
Molecular geometries: summary

The oxygen column
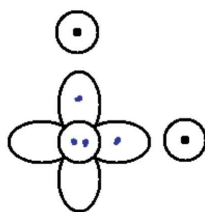
	H2O	H2S	H2Se	H2Te
Bond distance	0.96 Å	1.3 Å	1.5 Å	1.7 Å
Bond angle	104.5 °	92.2 °	91 °	90.2 °

The nitrogen column
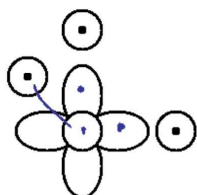
NH2	PH2	AsH2	SbH2
103.3	91.7	90.2	(90.3)*
NH3	PH3	AsH3	SbH3
106.7	93.3	92.1	91.6

The carbon column
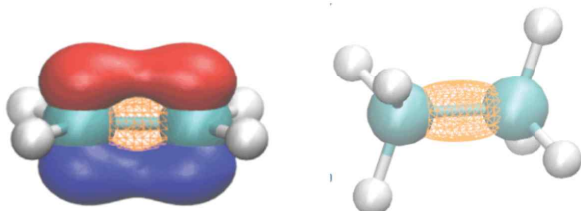
	CH2	SiH2	GeH2
Bond angle	132°	92°	91°

sp^1

$$\chi_{sp}^{(1)} = \frac{1}{\sqrt{2}}\left(\psi_{2s} + \psi_{2pz}\right)$$

$$\chi_{sp}^{(2)} = \frac{1}{\sqrt{2}}\left(\psi_{2s} - \psi_{2pz}\right)$$

sp^2

$$\chi_{sp2}^{(1)} = \frac{1}{\sqrt{3}}\psi_{2s} + \sqrt{\frac{2}{3}}\psi_{2pz}$$

$$\chi_{sp2}^{(2)} = \frac{1}{\sqrt{3}}\psi_{2s} - \frac{1}{\sqrt{6}}\psi_{2px} + \frac{1}{\sqrt{2}}\psi_{2py}$$

$$\chi_{sp2}^{(2)} = \frac{1}{\sqrt{3}}\psi_{2s} - \frac{1}{\sqrt{6}}\psi_{2px} - \frac{1}{\sqrt{2}}\psi_{2py}$$

sp^3

$$\chi_{sp3}^{(1)} = \frac{1}{\sqrt{4}}\left(\psi_{2s} + \psi_{2px} + \psi_{2py} + \psi_{2pz}\right)$$

$$\chi_{sp3}^{(2)} = \frac{1}{\sqrt{4}}\left(\psi_{2s} - \psi_{2px} - \psi_{2py} + \psi_{2pz}\right)$$

$$\chi_{sp3}^{(3)} = \frac{1}{\sqrt{4}}\left(\psi_{2s} + \psi_{2px} - \psi_{2py} - \psi_{2pz}\right)$$

$$\chi_{sp3}^{(4)} = \frac{1}{\sqrt{4}}\left(\psi_{2s} - \psi_{2px} + \psi_{2py} - \psi_{2pz}\right)$$

Bonding: a more quantitative view

- Consider a collection of atoms far away from each other
  - Electronic states is the collection of atomic states
- Bring atoms together so wavefunctions overlap
  - The wavefunctions will change
  - The energy of the states will change

- Consider a di-atomic molecule with like atoms (homopolar bond)
  - Approximate molecular orbital: a linear combination of atomic orbitals:

$$\psi(\vec{r}) = a_L \psi_L(\vec{r}) + a_R \psi_R(\vec{r})$$

Bonding: a more quantitative view at LCAO

$$H\psi(\vec{r}) = E\psi(\vec{r}) \qquad \text{with} \qquad \psi(\vec{r}) = a_L \psi_L(\vec{r}) + a_R \psi_R(\vec{r})$$

Multiply by Y_L from left and integrate over all space:

$$H(a_L \psi_L + a_R \psi_R) = E(a_L \psi_L + a_R \psi_R)$$

$$a_L \int \psi_L H \psi_L d^3r + a_R \int \psi_L H \psi_R d^3r = E\left[\int \psi_L^2 d^3r + \int \psi_L \psi_R d^3r\right]$$

$$a_L H_{LL} + a_R H_{LR} = E\left[1 + S_{LR}\right] \; a_L$$

Multiply by Y_R from left and integrate over all space:

$$a_L H_{RL} + a_R H_{RR} = E\left[1 + S_{RL}\right] \; a_R$$

$$H_{LL} = H_{RR} = h_0 \qquad\qquad \text{Neglect Overlap}$$

$$H_{RL} = H_{LR} = -V_2 \qquad\qquad S_{RL} = S_{LR} = 0$$

Bonding in homopolar diatomic molecule

In matrix form:

$$a_L h_0 - a_R V_2 = E a_L$$
$$-a_L V_2 + a_R h_0 = E a_R$$

$$\begin{bmatrix} h_0 & -V_2 \\ -V_2 & h_0 \end{bmatrix} \begin{bmatrix} a_L \\ a_R \end{bmatrix} = E \begin{bmatrix} a_L \\ a_R \end{bmatrix}$$

Eigenvalue Problem

$$\begin{vmatrix} h_0 - E & -V_2 \\ -V_2 & h_0 - E \end{vmatrix} = 0 = \left(h_0 - E \right)^2 - V_2^2$$

Eigenvalues (energies) $\qquad$ Eigenvectors (wavefunction)

$$E_1 = h_0 - V_2 \qquad \longrightarrow \qquad a_L = a_R$$
$$E_2 = h_0 + V_2 \qquad \longrightarrow \qquad a_L = -a_R$$

Bonding in homopolar diatomic molecule

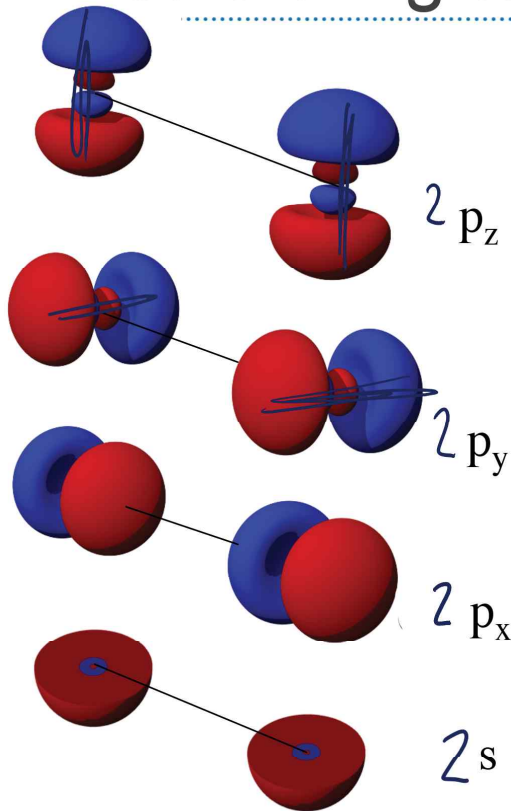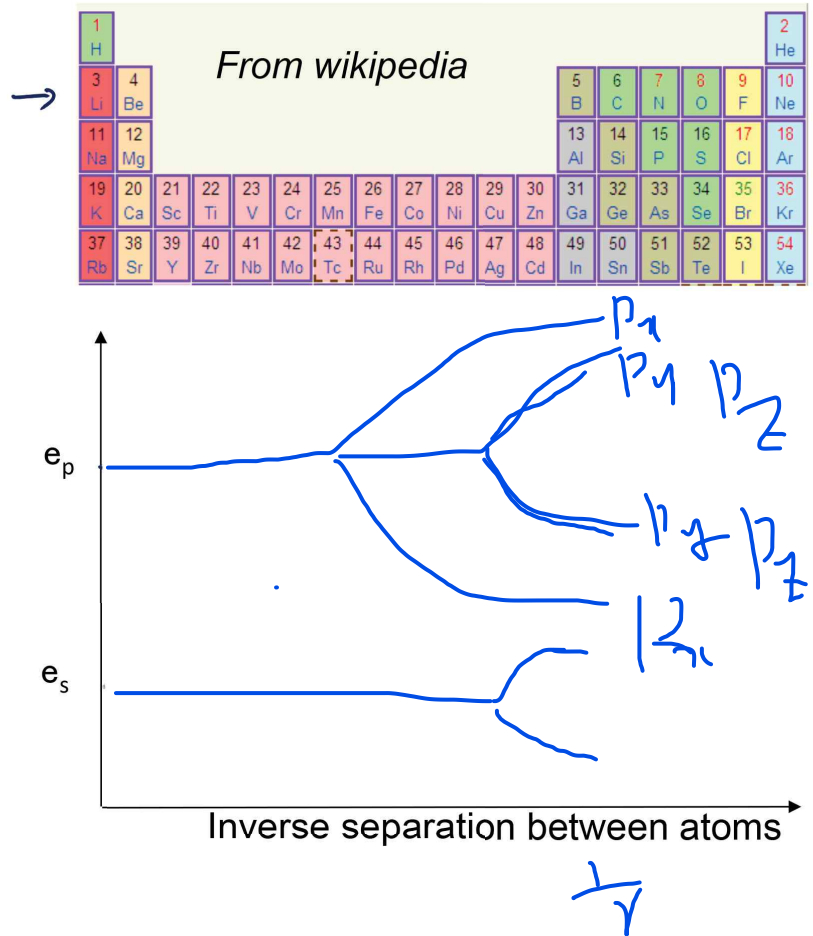We can use the H_2^+ solution to obtain a qualitative picture of diatomic H and He
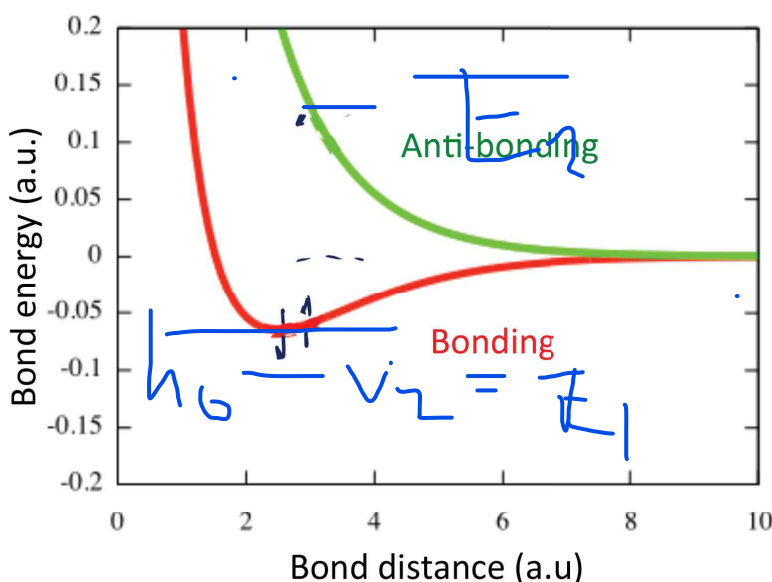
H_2 molecule: strong bond (~4.5eV)

He_2 molecule: very weak bond

Let's bring to Li-row atoms together

$2 p_z$

$2 p_y$

$2 p_x$

$2 s$

From wikipedia

e_p

e_s

Inverse separation between atoms

Adapted from: W. Harrison, "Electronic structure and the properties of solids"
Images from Wikipedia

Heteropolar diatomic molecule

$$\begin{bmatrix} h_0^{(1)} & -V_2 \\ -V_2 & h_0^{(2)} \end{bmatrix} \begin{bmatrix} a_L \\ a_R \end{bmatrix} = E \begin{bmatrix} a_L \\ a_R \end{bmatrix}$$

Polar energy: $\quad V_3 = \dfrac{h_0^1 - h_0^2}{2}$

Average energy of cation and anion: $\quad \overline{h} = \dfrac{h_0^1 + h_0^2}{2}$

Energies: $\quad E_b = \overline{h} - \sqrt{V_2^2 + V_3^2}$

$\quad\quad\quad\quad E_a = \overline{h} + \sqrt{V_2^2 + V_3^2}$