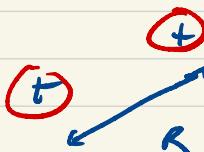


# Qualitative bonding

What changes from atoms to molecules?

More nuclei!!

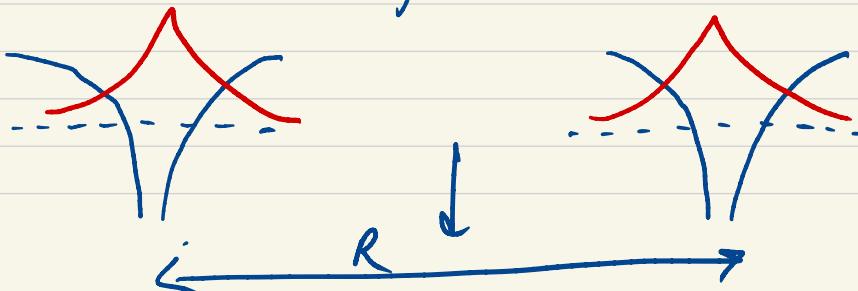


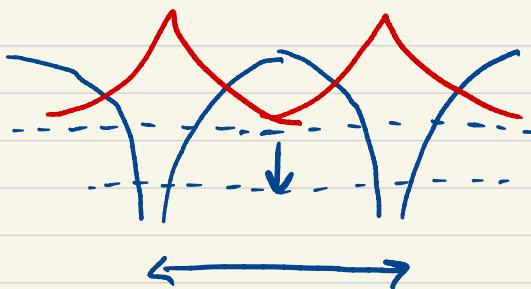
Very natural to think of nuclear motion to be separable from electrons.  
Basis of Born-Oppenheimer approximation.

$$E(R)$$

Now what might that look like?

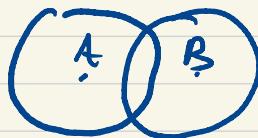
higher  $E$





energy lowers  
as wave  
overlap

Called a bond. Often drawn



A little more carefully for  $\text{H}_2$

$$\sigma_g = 1s_A + 1s_B$$

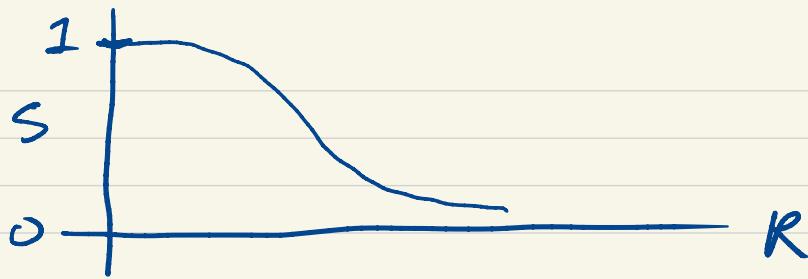
Normalize

$$\tilde{\sigma}_g = \sigma_g / \langle \sigma_g | \sigma_g \rangle^{1/2}$$

$$\langle \sigma_g | \sigma_g \rangle = \langle 1s_A + 1s_B | 1s_A + 1s_B \rangle$$

$$= \cancel{\langle 1s_A | 1s_A \rangle}^1 + \cancel{\langle 1s_B | 1s_B \rangle}^1 + 2\cancel{\langle 1s_A | 1s_B \rangle}^S$$

$S$ : "overlap" of the  $1s$  on  
each atom



$$\tilde{\sigma}_g = \frac{|s_A + s_B|}{\sqrt{2(1+s)}} \quad \text{varies w/ } R$$

What's it's energy? The Hamiltonian is going to be like that for an atom, except for having  $Z$  nuclei:

$$\hat{f} = -\frac{\hbar^2}{2m_e} \nabla^2 + \sum_{\text{nuclei}} \frac{Ze^2}{4\pi\epsilon_0} \cdot \frac{1}{|r-R_n|} + V_{ee}$$

$$\langle \tilde{\sigma}_g | \hat{f} | \tilde{\sigma}_g \rangle = \frac{1}{Z(1+s)} \left\{ \langle |s_A| \hat{h} | s_A \rangle + \langle |s_B| \hat{h} | s_B \rangle + 2 \langle |s_A| \hat{h} | s_B \rangle \right\}$$

F.A., &  
 $\sim E_{IS}$   
 "resonance"

resonance - energy advantage from  $e^-$  getting to wander across both nuclei

$$F_{AB}, \beta \propto -s$$

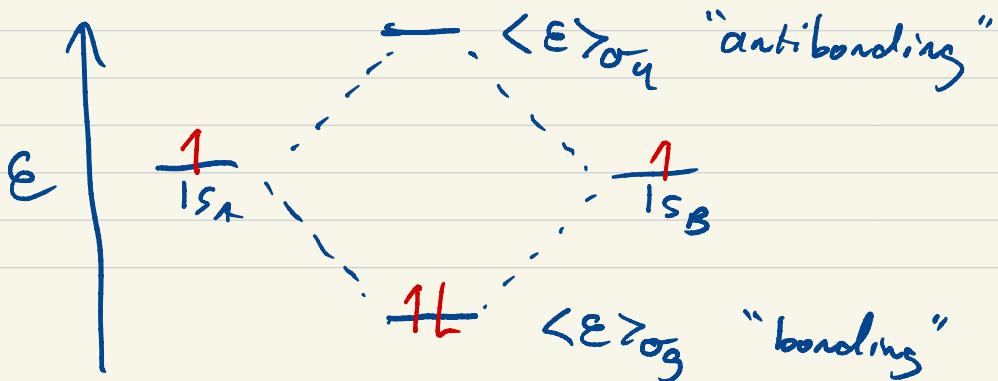
$$\langle \epsilon \rangle_{\sigma_g} = \langle \tilde{\sigma}_g | \hat{f} | \tilde{\sigma}_g \rangle = \frac{2\alpha + 2\beta}{2(1+s)} \\ = \frac{\alpha + \beta}{1+s}$$

$$0 > \beta > \alpha$$

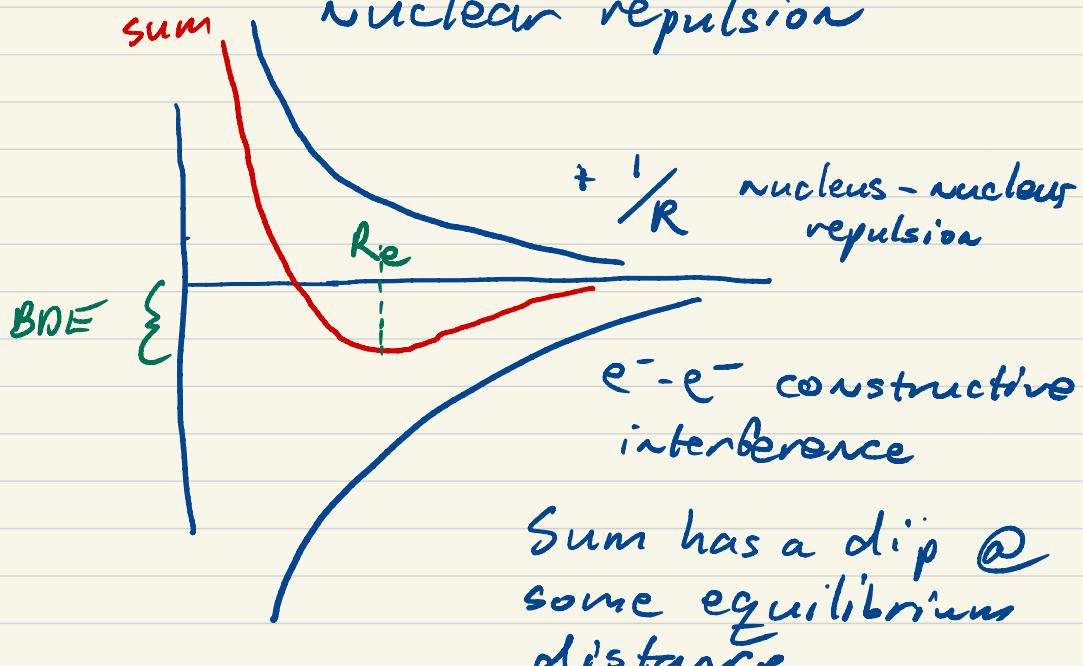
Could do the same for the other linear combination

$$\sigma_u = (1s_A - 1s_B) / \sqrt{2(1-s)}$$

$$\langle \epsilon \rangle_{\sigma_u} = \frac{\alpha - \beta}{1-s}$$



Will  $E$  ↓ monotonically as  $R$  ↓? no!



Called a potential energy surface (PES)

Note equilibrium distance

+ bond dissociation energy

What about # e<sup>-</sup>?

$$\underline{\text{bond order}} = \frac{1}{2} (N_{\text{bond}} - N_{\text{antibond}})$$

$$\text{H}_2 = \frac{2-0}{2} = 1 \quad \text{singlet}$$

$$\text{H}_2^+ = \frac{1-0}{2} = \frac{1}{2} \quad \text{doublet}$$

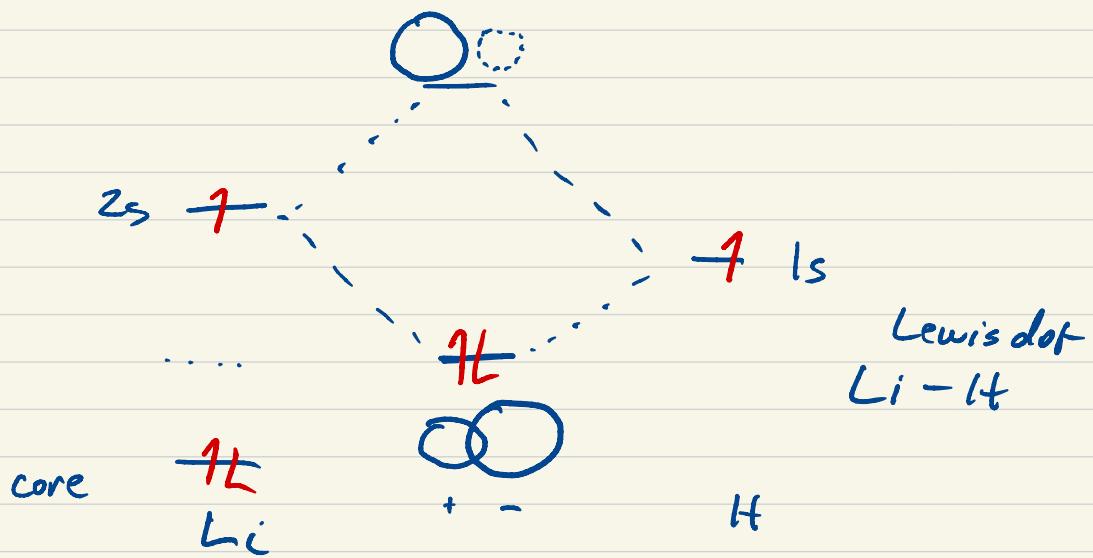
$$\text{H}_2^- = \frac{2-1}{2} = \frac{1}{2} \quad \text{doublet}$$

...

covalent, non-polar bond

The "splitting" (extent of bonding) is a function of overlap, distance, and energy match.

What if atoms aren't the same?



Core is too compact to do anything

$2s + 1s$  can constructively overlap

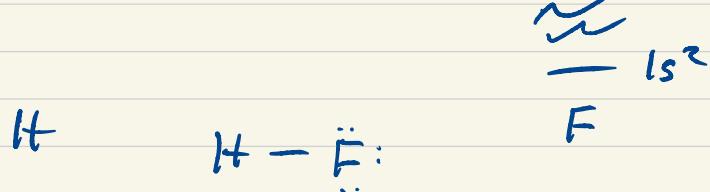
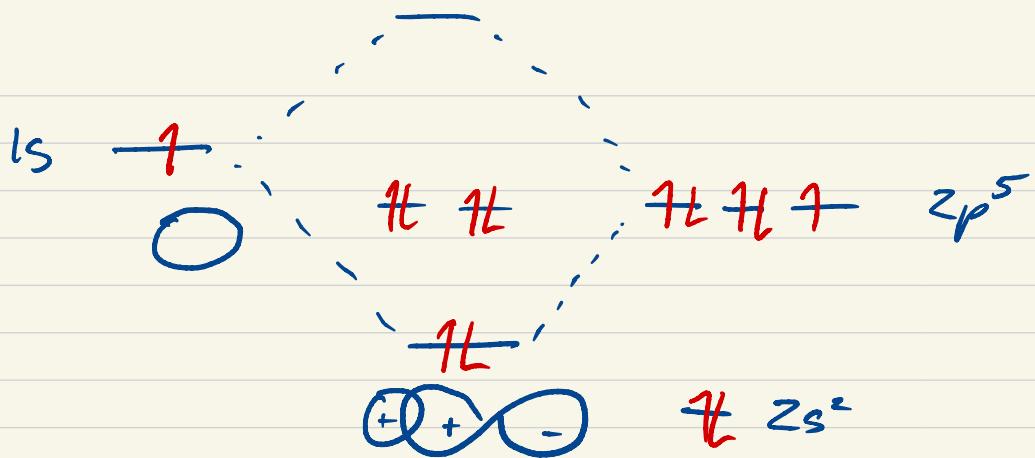
$$E_{H1s} < E_{Li2s}$$

polar covalent bond

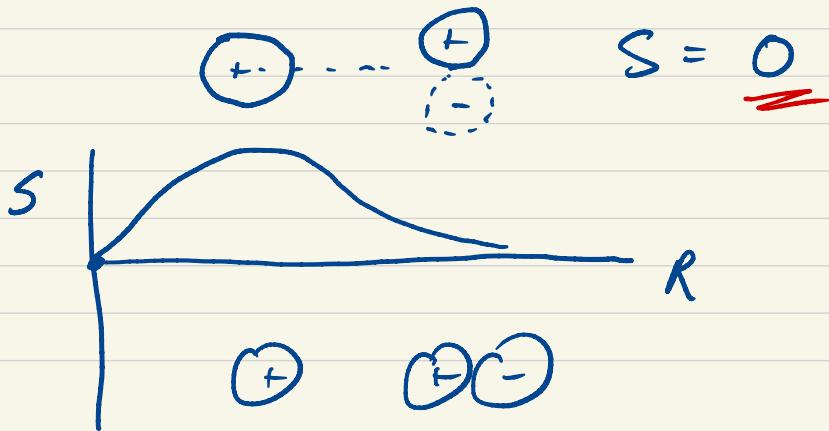
more H contribution than Li



bond length vs  $H_2$ ?



H 1s closest in energy match with F 2p. Can they overlap?



Hs - F<sub>2p</sub> bond

bond order 1



polar covalent

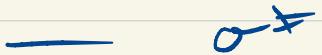
Can get more complicated.



large, varying



smaller,  
monotonic



$$z_p \equiv \begin{array}{c} 88 \\ \text{--- ---} \end{array} \equiv z_p$$

$\pi_L - \pi_L \pi$



$$z_s - = \overline{z_s}$$

:N≡N:

1s — core — 1s

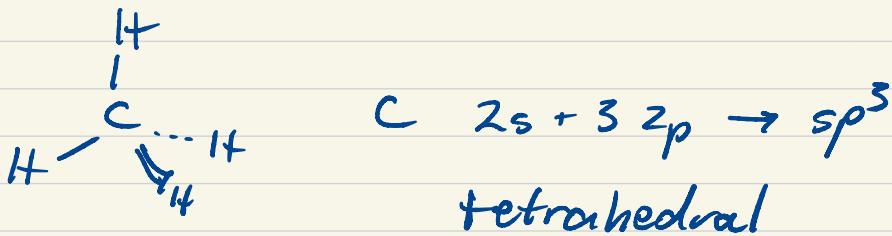
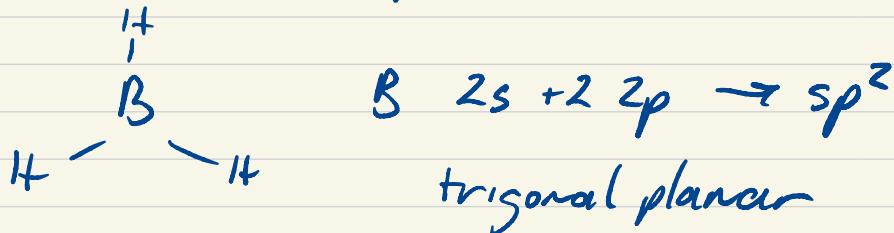
non-polar, covalent

triple bond order

expect short, strong ...

Chemical bonding both rich & complicated.

While not a particularly compelling theoretical basis, often rationalized in terms of "hybridization"



$\pi$  - bonding

$\pi^x$  — —

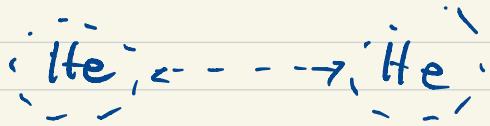
—

$\pi$  — —

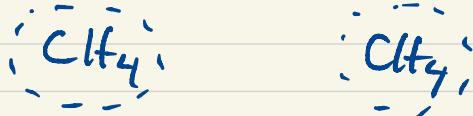
$C_2$      $C_3$

Band structure

While covalent bonds are strongest, for the same "itinerant" reasons, even things with 0 bond order will attract, weakly.



"dispersion"



interaction

dipole, ionic, ...

Example of class of "ion-bonded" interactions that dictate physical properties.

Eg BP order of He, Ne, Kr, Ar,

CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, ...