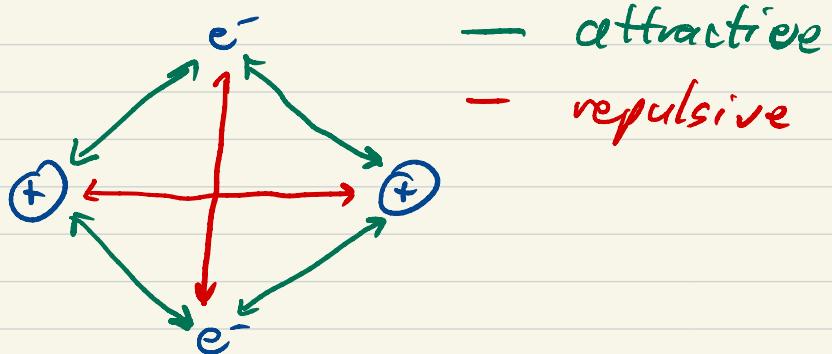


Lecture L1 - Molecular Structure

H_2 quantitatively



- attractive
- repulsive

In principle, can write down a Schrödinger eq for all four particles:

$$\hat{\Phi}(\vec{r}_1, \vec{r}_2, \vec{R}_\alpha, \vec{R}_\beta)$$

But in practice, because nuclei are so much heavier than electrons, can approximately separate

$$\hat{\Phi} \approx \Omega(\vec{R}_\alpha, \vec{R}_\beta) \Psi(\vec{r}_1, \vec{r}_2; \vec{R}_\alpha, \vec{R}_\beta)$$

parametric dependence

Called Born-Oppenheimer approximation

Following same logic as with atoms,
will write

$$\tilde{\Psi}(\tilde{r}_1, \tilde{r}_2) \approx \Psi_1(\tilde{r}_1) \Psi_2(\tilde{r}_2)$$

and solve

$$\left\{ -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{|\tilde{r}-\tilde{R}_{\alpha}|} + \frac{1}{|\tilde{r}-\tilde{R}_{\beta}|} \right) + \epsilon_{\text{ee}} \right\} \Psi = E$$

Ψ become "molecular orbitals"
 ϵ "molecular orbital energies"

algorithm

- choose positions of atoms
- choose vee model

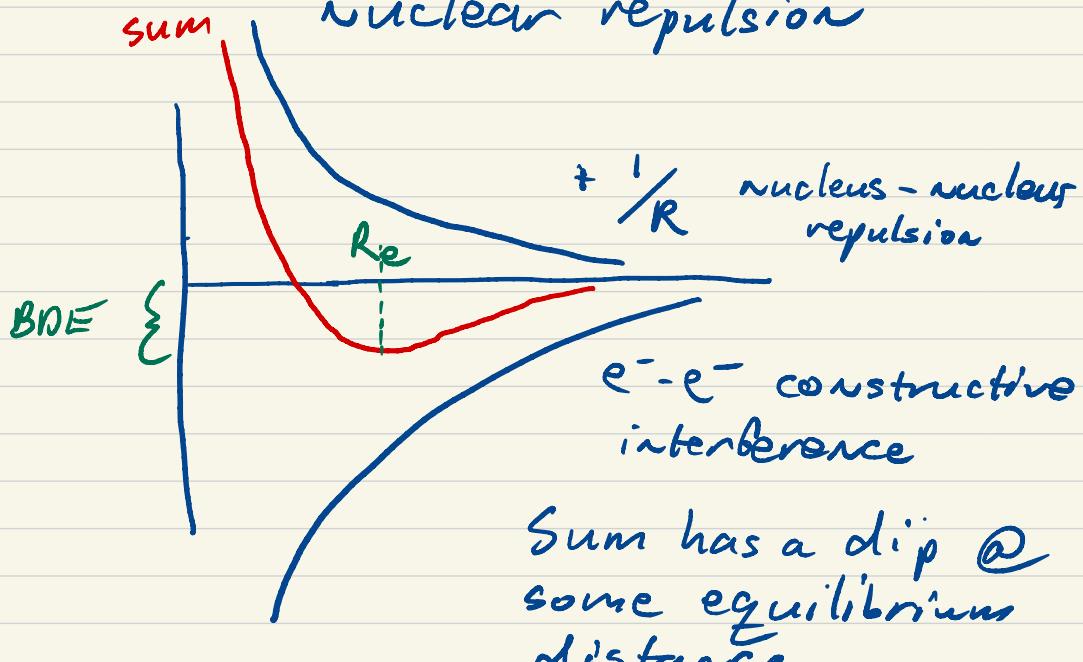
v_{Coulomb}

v_{exchange}

v_{correlation}

- guess and check Ψ ;
"SCF" algorithm

Will E ↓ monotonically as R ↓? no!



Called a potential energy surface (PES)

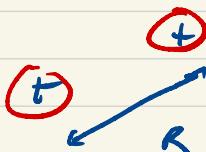
Note equilibrium distance

+ bond dissociation energy

Qualitative bonding

What changes from atoms to molecules?

More nuclei!!

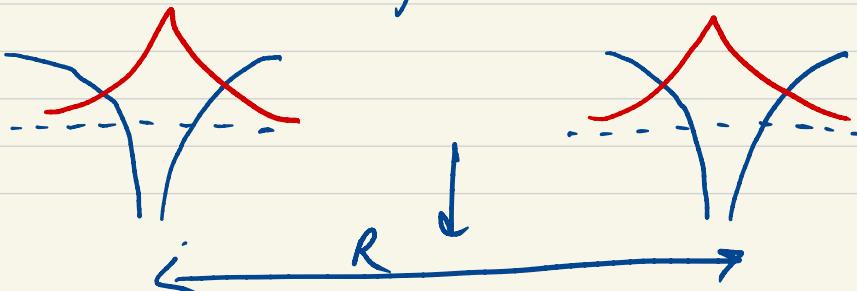


Very natural to think of nuclear motion to be separable from electrons.
Basis of Born-Oppenheimer approximation.

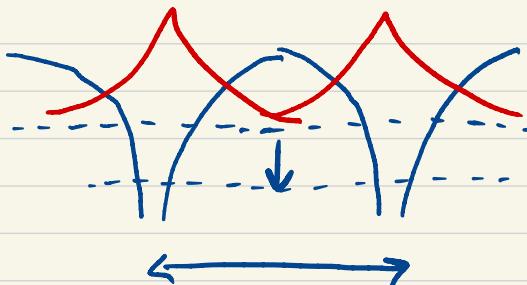
$$E(R)$$

Motivate by whether phase matters
Now what might that look like?

higher E



constructive
interference



energy lowers
as wave
overlap

Called a bond. Often drawn



A little more carefully for He_2

$$\sigma_g \approx 1s_A + 1s_B$$

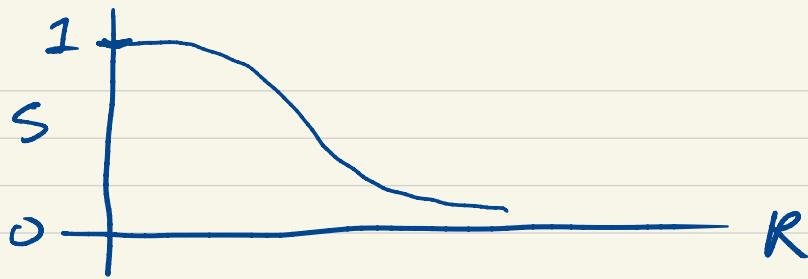
Normalize

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

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

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

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

$$F_{AB}, \beta \propto -s \quad 0 > \beta > \alpha$$

$$\begin{aligned} \langle E \rangle_{\sigma_3} &= \langle \tilde{\sigma}_3 | \hat{f} | \tilde{\sigma}_3 \rangle = \frac{2\alpha + 2\beta}{2(1+s)} \\ &= \frac{\alpha + \beta}{1+s} \\ &\approx \underline{\alpha + \beta(1-s)} \end{aligned}$$

(From Taylor expansion)

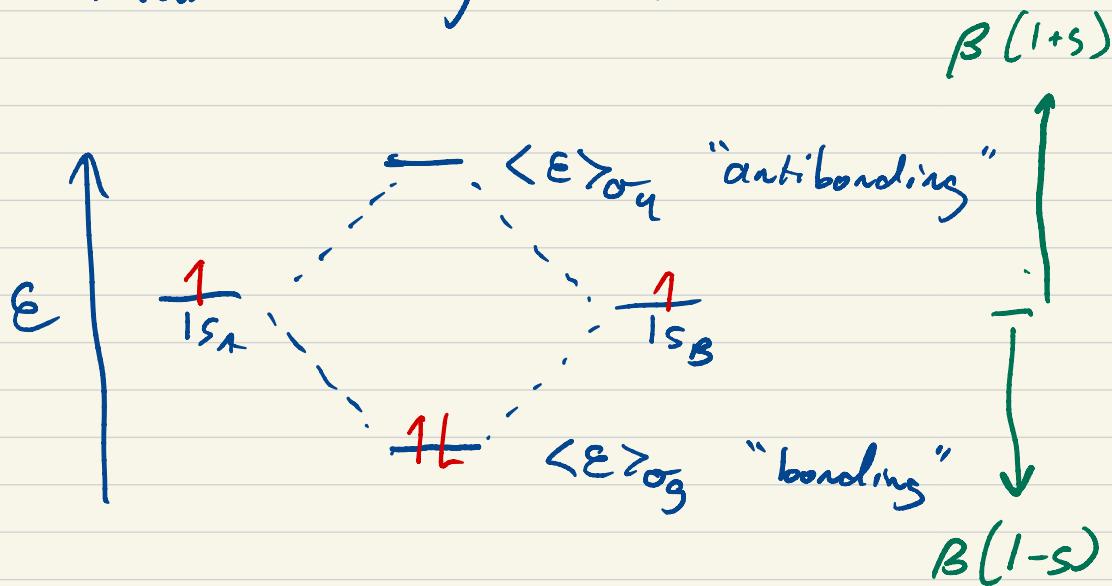
Could do the same for the
other linear combination

$$\sigma_u = (ls_A - ls_B) / \sqrt{2(1-s)}$$

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

$$\approx \underline{\alpha - \beta / (1-s)}$$

Anti-bonding more disturbed
than bonding favored



What about # e⁻?

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

$$H_2 = \frac{2-0}{2} = 1 \quad \text{singlet}$$

$$H_2^+ = \frac{1-0}{2} = \frac{1}{2} \quad \text{doublet}$$

$$H_2^- = \frac{2-1}{2} = \frac{1}{2} \quad \text{doublet}$$

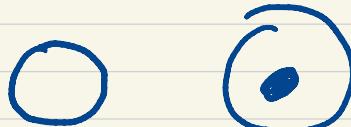
...

covalent, non-polar bond

What if atoms aren't the same?

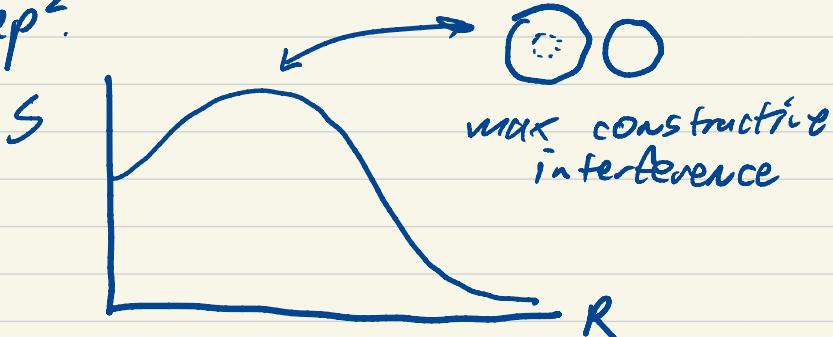


Li: Core is too compact to participate



$$\epsilon_{H1s} < \epsilon_{Li2s}$$

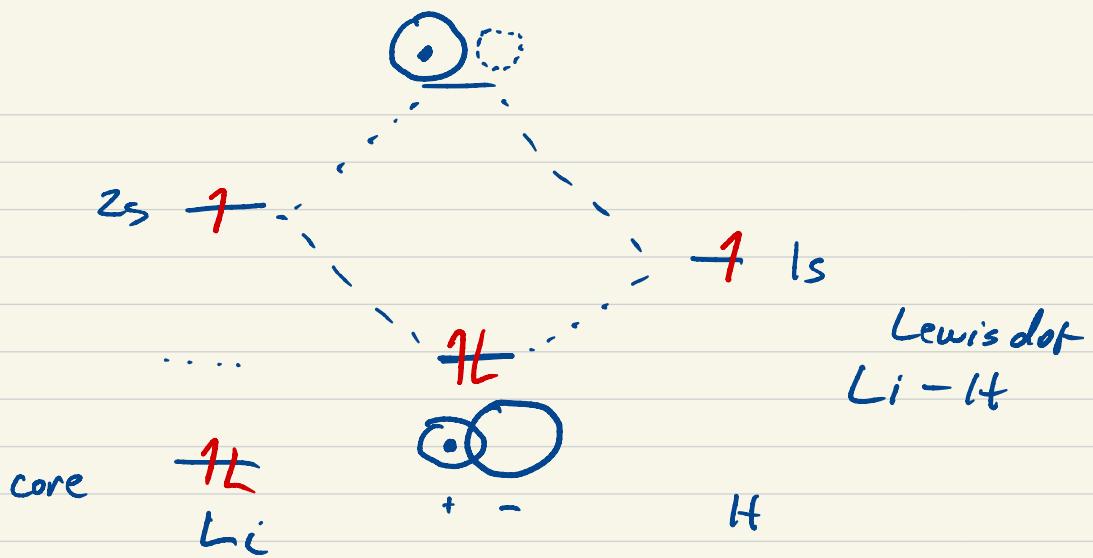
Overlap?



$$\sigma = c_1 1s_H + c_2 2s_{Li}$$

atoms are no longer the same
so $c_1 \neq c_2$! math... (secular eq)

$$\Rightarrow \sigma_g \quad c_1 > c_2 \quad \sigma_u \quad c_2 > c_1$$



energy? <0 >0 <0

$$\epsilon_0 \approx \epsilon_{1s}^H - \beta S - \beta^2 \cdot \frac{1}{|\epsilon_{1s}^H - \epsilon_{2s}^{Li}|}$$

must have overlap

must have decent energy match

contributing orbitals must be close in ϵ

$$\epsilon_{0+} \approx \epsilon_{2s}^{Li} - \beta S + \beta^2 \cdot \frac{1}{|\epsilon_{1s}^H - \epsilon_{2s}^{Li}|} >0$$

always unfavorable

polar covalent bond
more H contribution than Li

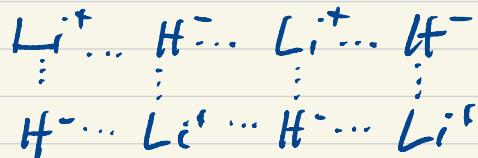


bond length vs H_2 ?

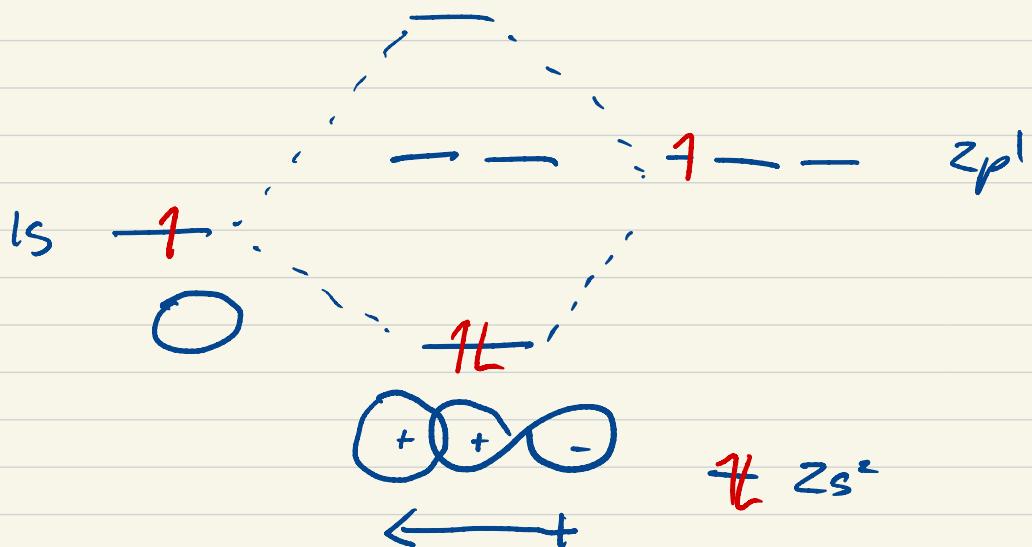
charge x'fer \rightarrow ionic compound

So how does LiH exist in nature?

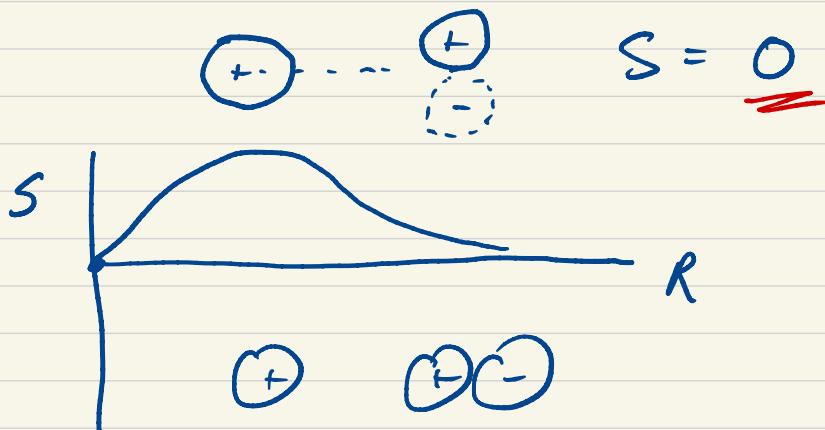
As salt!



Across table, B-H



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



Longer bond

Why not BH_2 ? or BH_3 ?

H

B - H

H

B - H

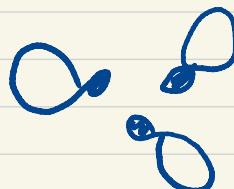
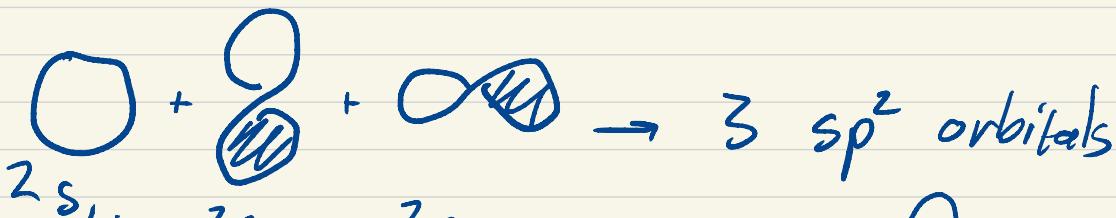
H

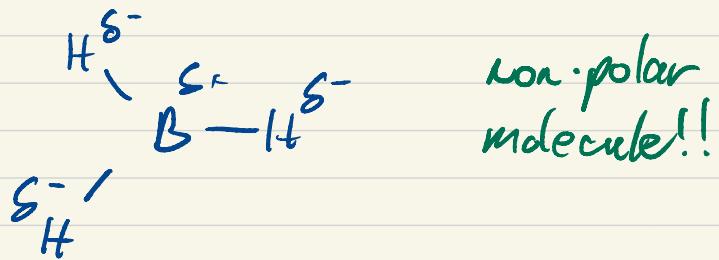
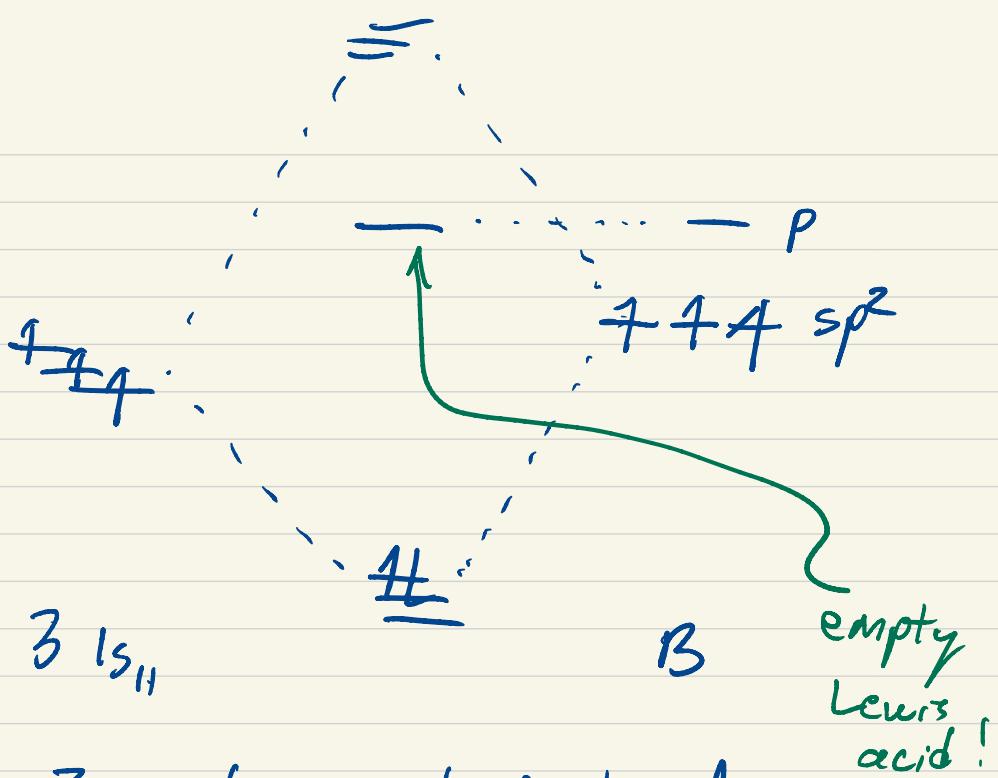
So far have limited ourselves to combinations of 2 orbitals, but we could do more

Eg $1s_{\text{H}}$ $2p_{\text{Li}}$ $2s_{\text{Li}}$ " $1s_{\text{H}} + sp_{\text{Li}}$

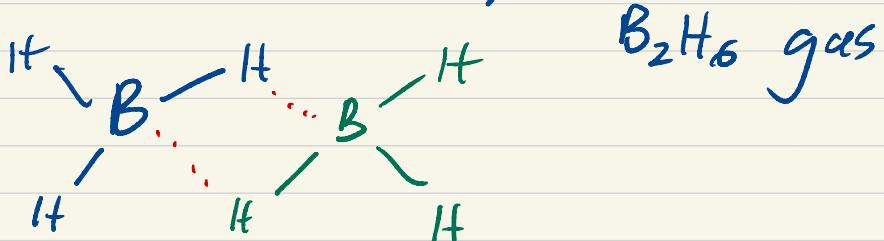


Origin of concept of "hybridization"





How does it exist, really?



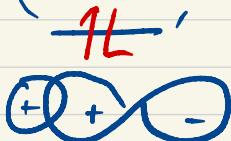
Same ideas lead to tetrahedral CH_4 ...

H-F

1s - 1



1L 1L



1L 1L 1L

2p⁵

1L 2s²

H

H-F:

\approx
1s²

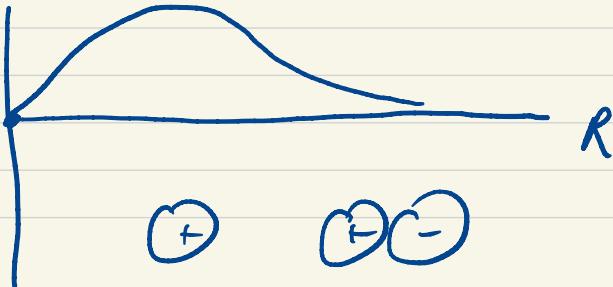
F

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



$$S = \underline{\underline{0}}$$

S



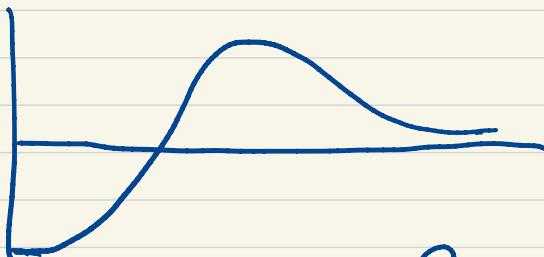
Hs - F_{2p} bond

bond order 1



polar covalent

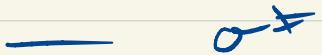
Can get more complicated.



large, varying



smaller,
monotonic



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



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

:N≡N:



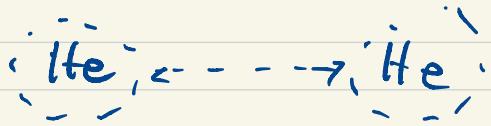
non-polar, covalent

triple bond order

expect short, strong ...

O_2 & role of antibonding orbitals

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



"dispersion"



interaction

dipole, ionic, ...

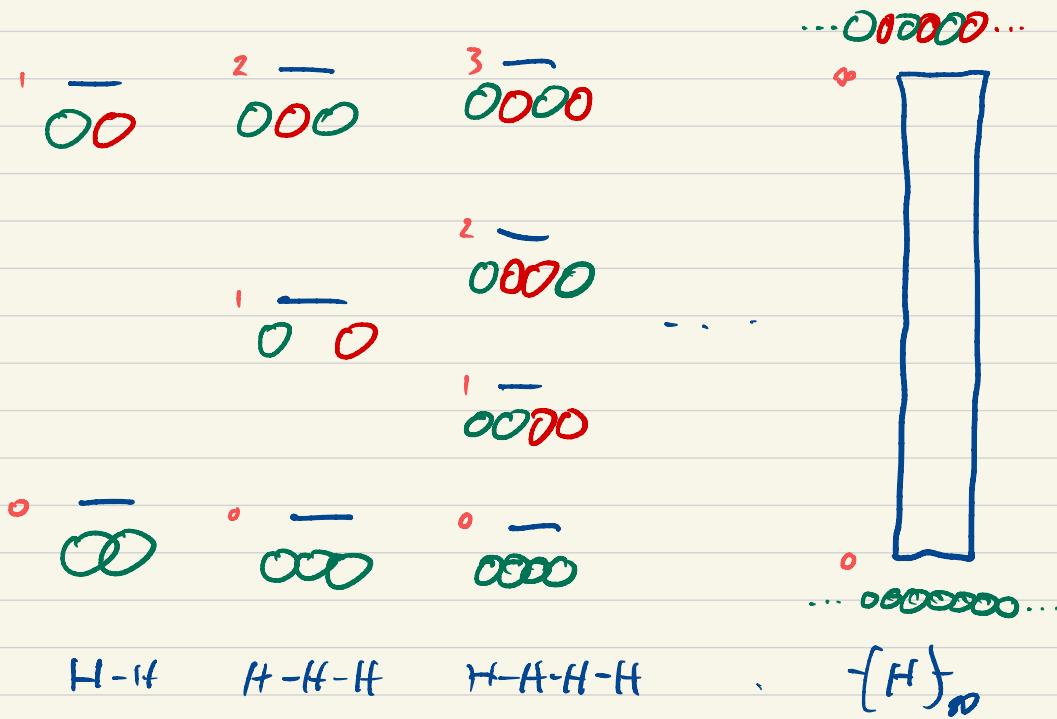
Example of class of "ion-bonded" interactions that dictate physical properties.

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

CH_4 , C_2H_6 , ...

Band structure

Chain of H atoms example



As length of chain increases, number of states ↑, with increasing # of nodes.

For very large n, becomes an energy band

Ideas translate to metals

p

d

s

M (atom)



p



d



s

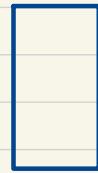
M(s)

Fermi
level

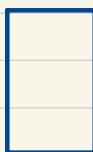
characteristic
of a conductor



metal
(Fe)



semi
conductor
(Si)



Fermi
level

insulator
(SiO₂)

H₂ B3LYP example 6-31G(d)

1H - 1H 0.743 exp't

Webmo example

see SCF

see molecular orbitals

What if we didn't know bond length?

Compute energy vs distance.

Which energy?

$$E_{\text{total}} = \sum \epsilon_i - V_{ee} + V_{n-n}$$

overcounting

R	E (eV)	B3LYP/ 6-31G*
0.6	-31.281	
0.65	-31.608	
0.7	-31.767	
0.75	-31.803	
0.80	-31.751	
0.85	-31.636	
0.90	-31.474	

Minimum around 0.75.

Could keep trying points or use a fit

Fit gives 0.742 Å

What if we want the bond energy?

What do we mean by bond energy?



$$\Delta E = 2E_{H\cdot} - E_{H_2}$$

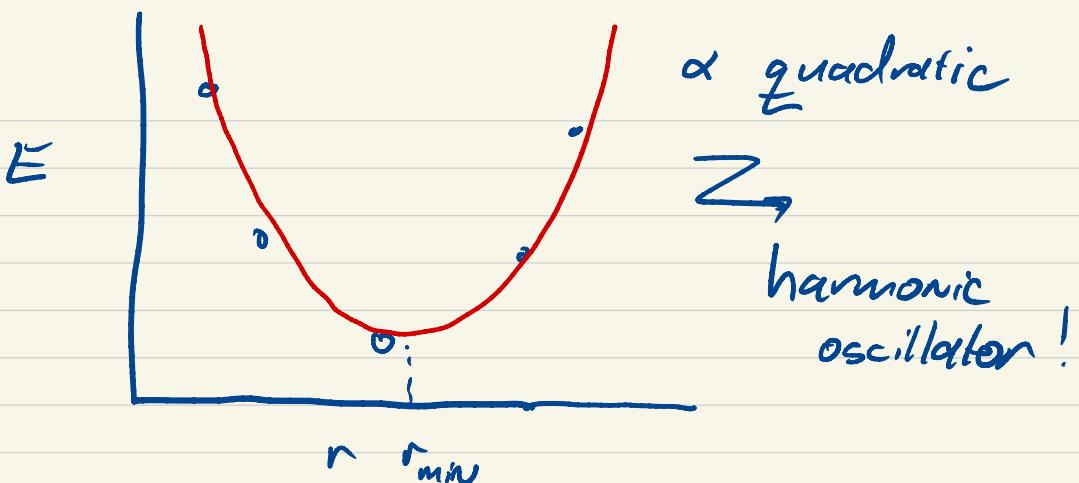
$$E_{H\cdot} = -13.61 \text{ eV} \quad \text{exactly}$$

$$E_{H\cdot}^{\text{B3LYP}} = -13.52 \text{ eV}$$

$$E_{H_2}^{\text{B3LYP}} = -31.80$$

$$\Delta E^{\text{B3LYP}} = 4.76 \text{ eV} = 459 \text{ kJ/mol}$$

BUT, atoms are not stationary



$$k = \frac{d^2 E}{dr^2} = \sim 42 \text{ eV}/\text{\AA}^2$$

$$\omega = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

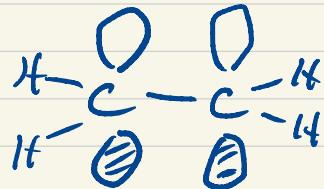
$$\begin{aligned} \frac{1}{\mu} &= \frac{1}{M_H} + \frac{1}{M_H} \\ &= 2/M_H \end{aligned}$$

$$\mu = M_H/2$$

Linear expansions + Hückel model

Typically applied to π systems of organics

e.g. ethylene



$$\psi = \sum_{\alpha} c_{\alpha} \phi_{\alpha} \quad \text{where } \phi_{\alpha} \text{ is p orbital on atom } \alpha$$

$$\hat{f} |\psi\rangle = \varepsilon |\psi\rangle$$

$$(\hat{f} - \varepsilon) |\psi\rangle = 0$$

$$\left(\sum_{\alpha} (\hat{f} - \varepsilon) c_{\alpha} \right) |\psi\rangle = 0$$

$$\sum_{\alpha} \left[\langle \phi_{\beta} | \hat{f} | \phi_{\alpha} \rangle - \varepsilon \langle \phi_{\beta} | \phi_{\alpha} \rangle \right] c_{\alpha} = 0$$

AB

$$\sum_{\alpha} [F_{\alpha\alpha} - \varepsilon S_{\alpha\alpha}] c_{\alpha} = 0$$

linear secular equations

ethylene

$$\begin{pmatrix} F_{11} - \epsilon S_{11} & F_{12} - \epsilon S_{12} \\ F_{21} - \epsilon S_{21} & F_{22} - \epsilon S_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

Will have two solutions

Hückel approximation for π systems

$$F_{ii} = \alpha \quad S_{ci} = 1$$

$$F_{ij} = \beta \quad \text{if adjacent} \quad S_{cj} = 0$$

$$\begin{pmatrix} \alpha - \epsilon & \beta \\ \beta & \alpha - \epsilon \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

eigenvalues & eigenvectors of
secular matrix

$$\begin{vmatrix} \alpha - \epsilon & \beta \\ \beta & \alpha - \epsilon \end{vmatrix} = 0$$

$$(\alpha - \epsilon)^2 - \beta^2 = 0$$

$$\alpha - \epsilon = \pm \beta$$

$$\epsilon = \alpha \pm \beta$$

$$\epsilon_1 = \alpha + \beta$$

back-substitute

$$\begin{pmatrix} -\beta & \beta \\ \beta & -\beta \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

$$\hookrightarrow c_1 = c_2$$

$$\epsilon_2 = \alpha - \beta$$

$$\begin{pmatrix} \beta & \beta \\ \beta & \beta \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

$$\hookrightarrow c_1 = -c_2$$

$$\alpha - \beta - \cancel{\text{88}} \pi^*$$

$$\alpha + \beta - \cancel{\text{88}} \pi$$