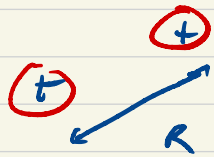
Qualitative bonding

What changes from atoms to molecules?

More nuclei!!



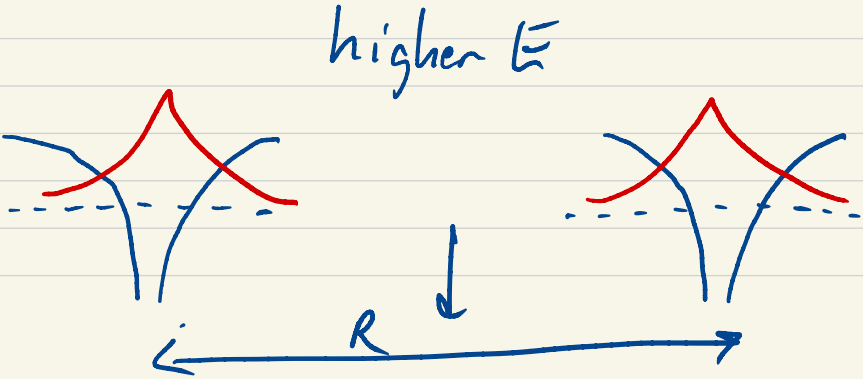
Very natural to think of nuclear motion to be seperable from electrons.

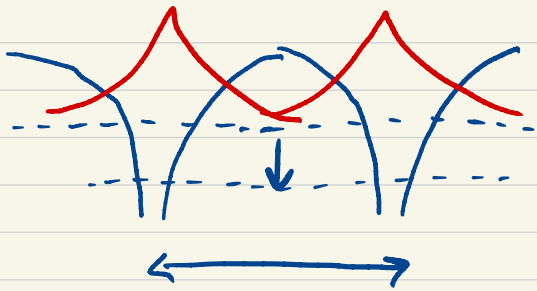
Basis of Born-Oppenheimer approximation.

$$E(R)$$

motivate by whether phase matters

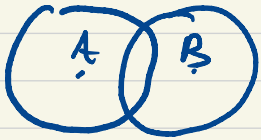
Now what might that look like?





energy lowers as wave overlap

Called a <u>bond</u>. Often drawn



A little more carefully for H_2

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

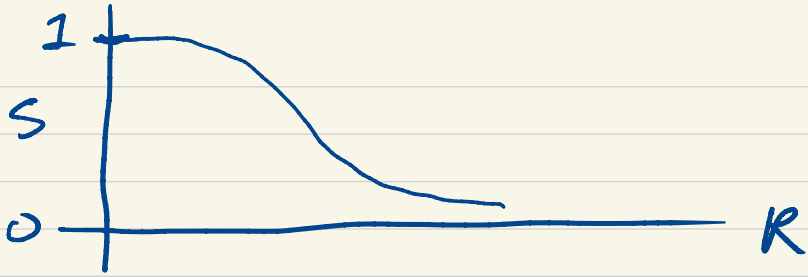
Normalize

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

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

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

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



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

What's it's energy? The Hamiltonian is going to be like that for an atom, except for having 2 nuclei

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

$$\langle \tilde{\sigma}_g | \hat{f} | \tilde{\sigma}_g \rangle =$$

F_{AA}, α
$\sim \varepsilon_{1s}$

$$\frac{1}{2(1+S)}\left\{ \langle 1s_A|\hat{h}|1s_A\rangle + \langle 1s_B|\hat{h}|1s_B\rangle + 2\langle 1s_A|\hat{h}|1s_B\rangle \right\}$$

"resonance"

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

F_{AB}, β $\propto$ $-S$

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

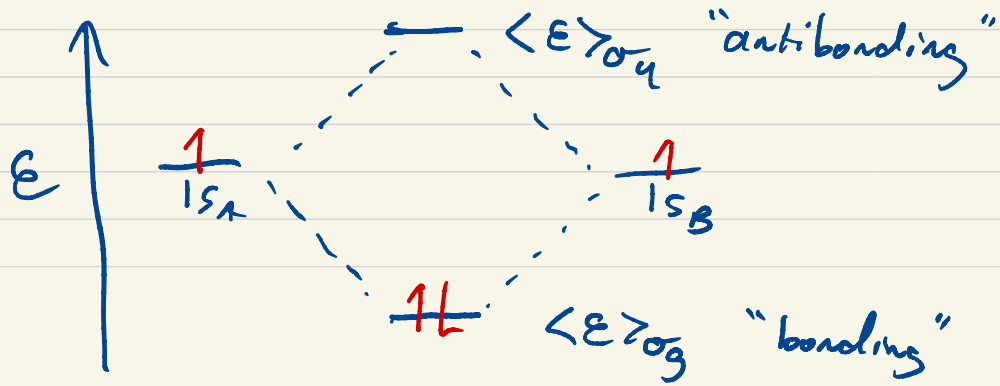
$$= \frac{\alpha + \beta}{1+S}$$

$$0 > \beta > \alpha$$

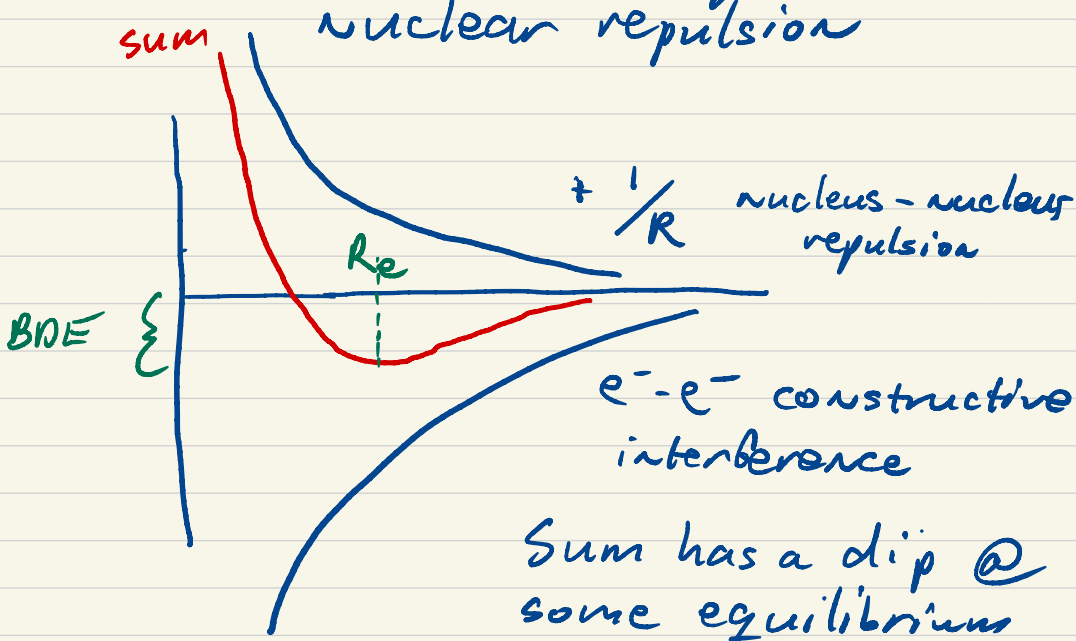
Could do the same for the other linear combination

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

$$\langle \varepsilon \rangle_{\sigma_u} = \frac{\alpha - \beta}{1-S}$$



Will E ↓ monotonically as R ↓? no!



Sum has a dip @ some equilibrium distance.

Called a potential energy surface (PES)

Note equilibrium distance + bond dissociation energy

What about # e^-?

<u>bond order</u> $= \frac{1}{2}(N_{bond} - N_{antibound})$

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

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

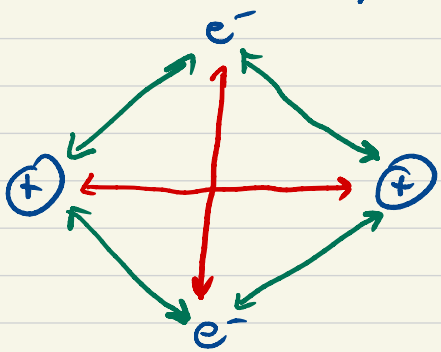
$H_2^- = \frac{2-1}{2} = \frac{1}{2}$ doublet

...

<u>covalent</u>, <u>non-polar</u> <u>bond</u>

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

More quantitatively



— attractive

— repulsive

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

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

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

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

Called Born-Oppenheimer approximation

Following same logic as with atoms, will write

$$\Psi(\vec{r}_1, \vec{r}_2) \simeq \psi_1(\vec{r}_1)\,\psi_2(\vec{r}_2)$$

and solve

$$\left\{ -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{|\vec{r}-\vec{R}_\alpha|} + \frac{1}{|\vec{r}-\vec{R}_\beta|}\right) + v_{ee} \right\}\psi = \epsilon\psi$$

ψ become "molecular orbitals"

ϵ " molecular orbital energies

algorithm

- choose positions of atoms
- choose v_{ee} model

  $v_{coulomb}$

  $v_{exchange}$

  $v_{correlation}$

- guess and check ψ_i

  "SCF" algorithm

H_2 B3LYP example 6-31G(d)

H – H 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?

$$E_{total} = \sum \varepsilon_i - V_{ee} + V_{N-N}$$

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?

$$H-H \rightarrow 2\ H\cdot$$

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

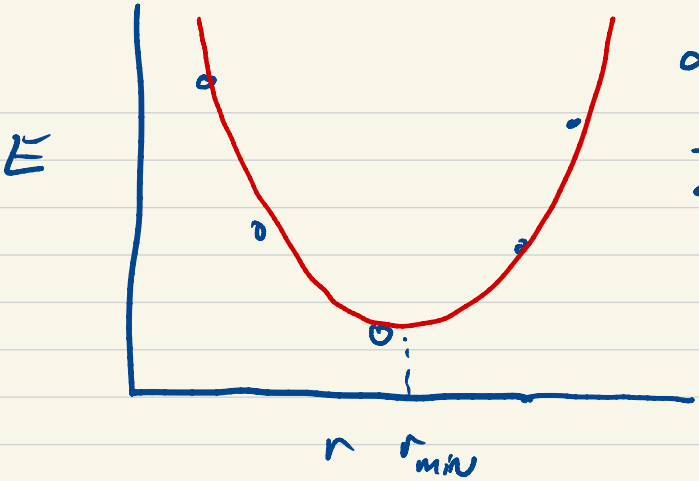
$E_{H\cdot} = -13.61$ eV exactly

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

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

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

BUT, atoms are not stationary



$\propto$ quadratic

$\Rightarrow$ harmonic oscillator!

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

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

$$\frac{1}{\mu} = \frac{1}{M_H} + \frac{1}{M_H}$$

$$= 2/M_H$$

$$\mu = M_H/2$$

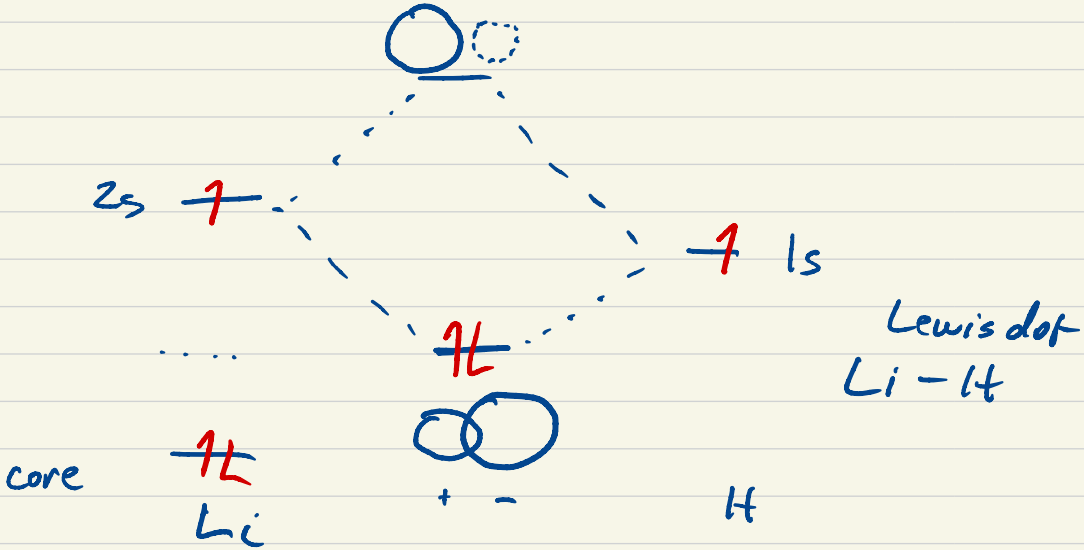
Other diatomics

rules

1. orbitals must overlap
2. orbitals must have energy match

$$\beta \propto \frac{S}{\Delta E}$$

What if atoms aren't the same?



Core is too compact to do anything

2s + 1s can constructively overlap

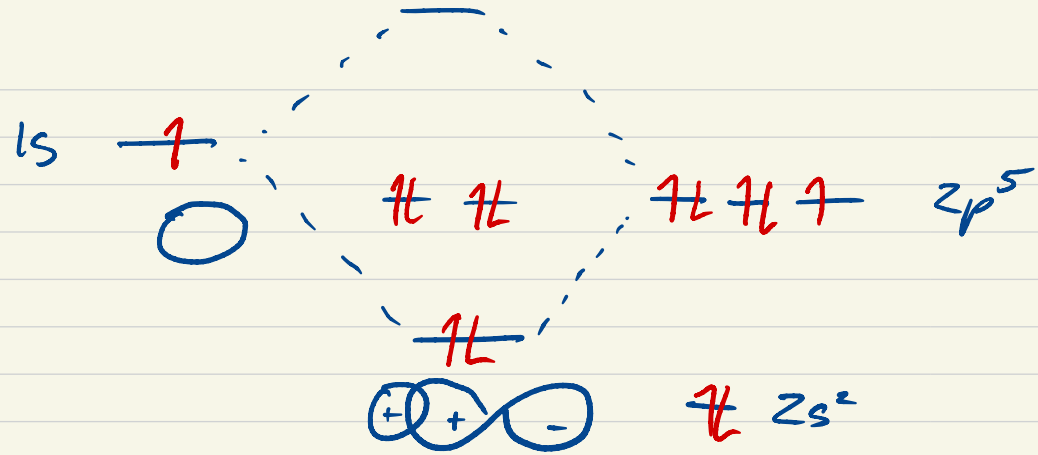
$$\varepsilon_{H1s} < \varepsilon_{Li\,2s}$$

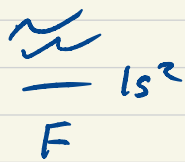
polar covalent bond

more H contribution than Li

$$Li^{\delta+} \cdots H^{\delta-}$$

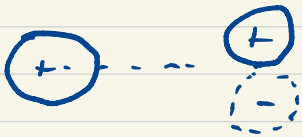
bond length vs H_2?



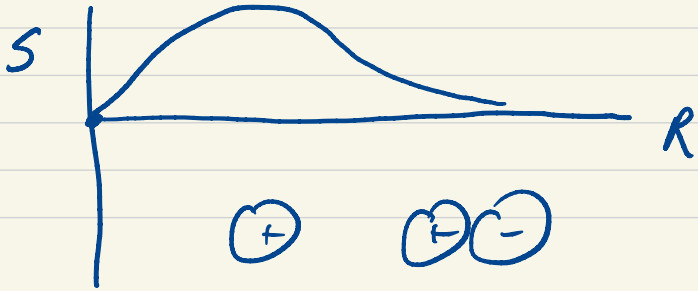


H

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



$S = 0$



Hs – F2p bond

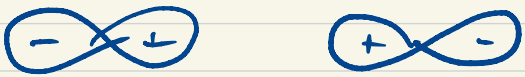
bond order $\underline{\underline{1}}$

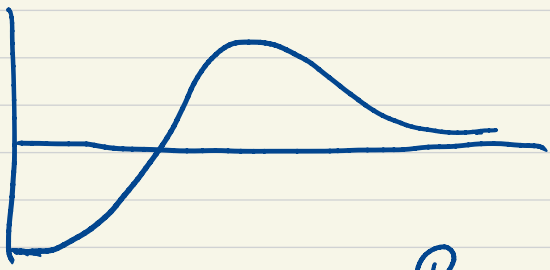
$H^{\delta+} - F^{\delta-}$

polar covalent

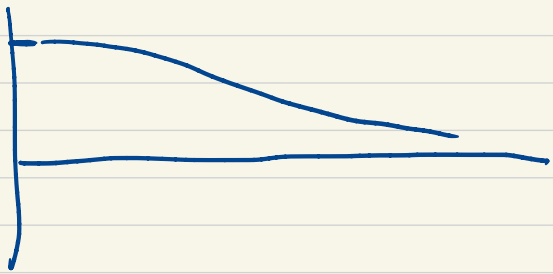
Can get more complicated.

N — N

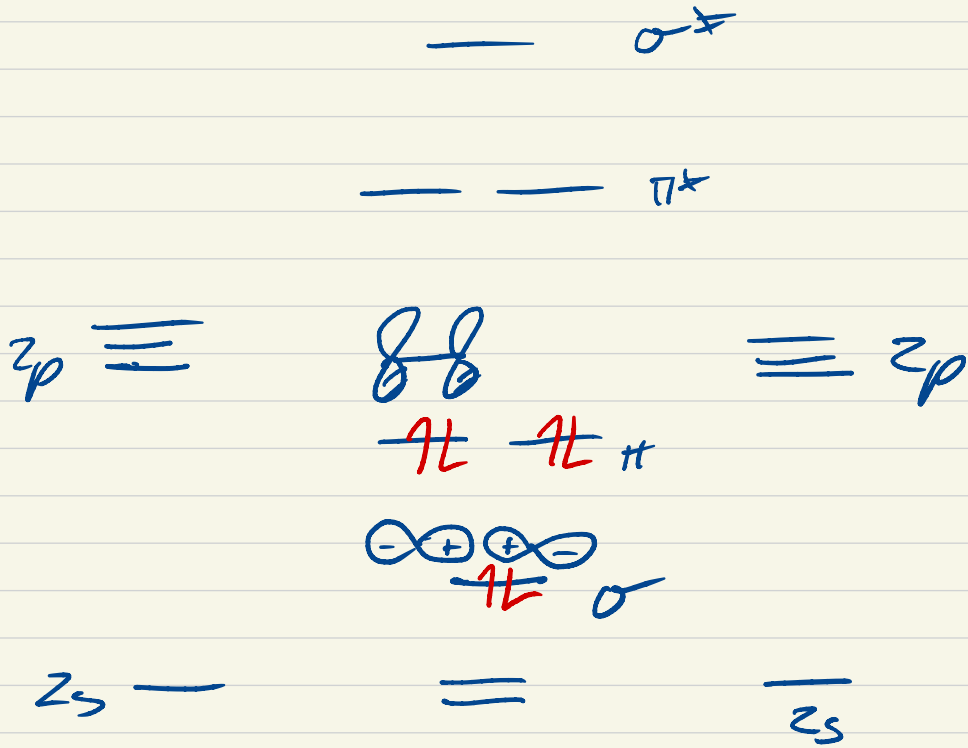




large, varying



smaller, monotonic



:N ≡ N:

1s — core — 1s

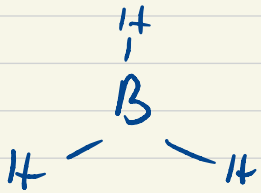
non-polar, covalent

triple bond order

expect short, strong ...

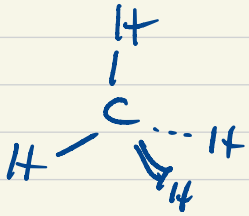
Chemical bonding both rich & complicated.

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



B 2s + 2 2p → sp^2

trigonal planar



C 2s + 3 2p → sp^3

tetrahedral

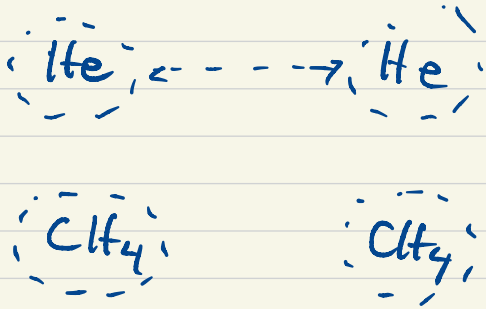
VSEPR model works shockingly well

Human "machine learning"

Quantitative molecular structure

ex H_2O , CH_4

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



"dispersion" interaction

dipole, ionic, ...

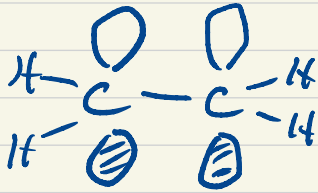
Example of class of "ion-bonded" interactions that dictate physical properties.

Eg BP order of He, Ne, Kr, Ar, CH_4, C_2H_6, ...

Linear expansions + Hückel model

Typically applied to π systems of organics

eg ethylene



$$\psi = \sum_\alpha c_\alpha \phi_\alpha$$ where ϕ_α is p orbital on atom α

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

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

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

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

$$\forall \beta$$

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

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

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

$F_{ij} = \beta$ <u>if</u> <u>adjacent</u> $\quad S_{ij} = 0$

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

eigenvalues & eigenvectors of secular matrix

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

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

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

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

$\varepsilon_1 = \alpha + \beta$

back-substitute

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

$$\hookrightarrow \quad c_1 = c_2$$

$\varepsilon_2 = \alpha - \beta$

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

$$\hookrightarrow \quad c_1 = -c_2$$

$\alpha - \beta$ —

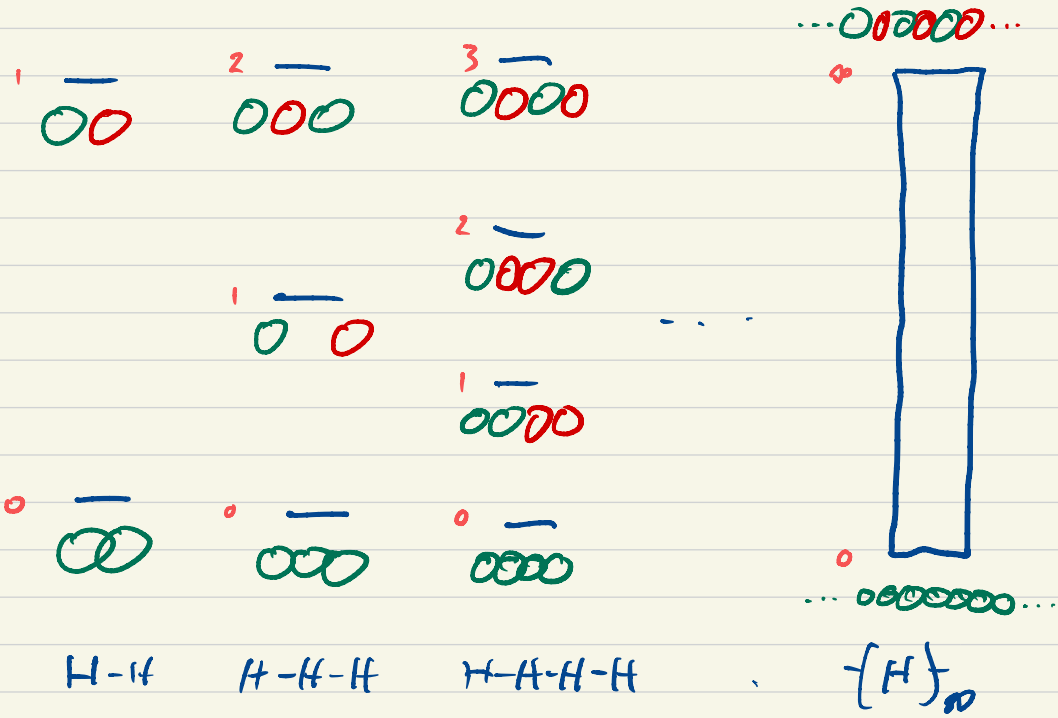
π^*

$\alpha + \beta$ —

π

Band structure

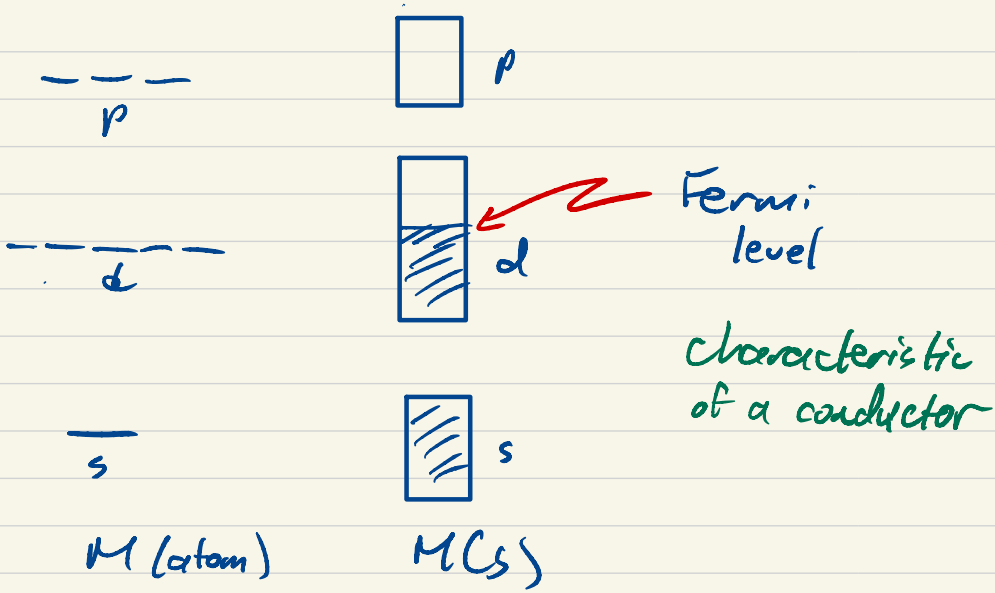
Chain of H atoms example

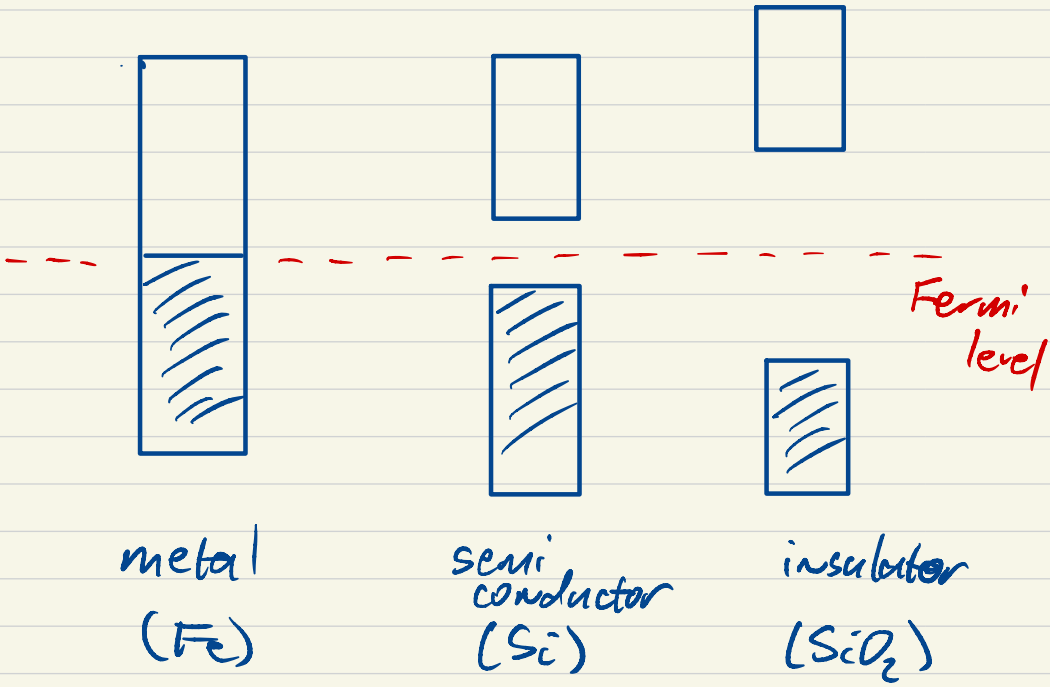


As length of chain increases, number of states ↑, with increasing # of nodes.

For very large n, becomes an energy band

Ideas translate to metals


p
d
s
p
d
s
Fermi level
characteristic of a conductor
M (atom)
M (s)


Fermi level
metal
(Fe)
semi conductor
(Si)
insulator
(SiO_2)