

\* did not finish  
in 1 lecture

- $e^-$  and proton combine to form Hydrogen
- total energy of companionship Negative

- favorable for  $e^- \ni p^+$  to bond, so they do!

$$\text{gain } \underline{\underline{-13.6 \text{ eV/pair}}} \text{ or } \underline{\underline{\approx -1300 \text{ kJ/mol}}}$$

(cf NaCl  $\sim -400 \text{ kJ/mol}$ , very stable!)

- larger # of  $p^+ \ni e^-$  combine to form larger atoms
- lower overall energy by combining

? Can we say the same about 2 hydrogen atoms?

! Yes, they can lower their energy by combining to form a hydrogen molecule  $H_2$

Combination of atoms = chemical bond  $\Rightarrow$  Chemistry

? This is not chemistry?!?

- need QM + EM to understand bonds
- behavior of solids comes from constituents + geom
- the rest is NOT stamp collecting... Complexity

- Once we "solve" atoms the game is not over, a "just" chemistry
  - even He requires numerical soln
  - by Fe ( $26e^-$ ) forget it.
  - solids?  $\sim 10^{23}$  atoms! complexity is staggering  $\hat{=}$  intractable
  - resort to approximate methods  $\hat{=}$  qualitative rules
  - chemistry takes over where phys leaves off; line is blurry

General Mechanical prop of bonds

- clearly, must have an attractive force
- obvious candidate is Coulomb - electrostatic

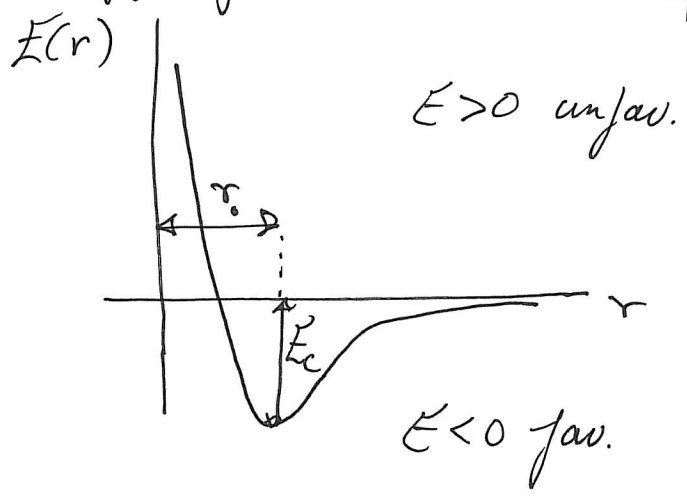
Example: Na easily gives up its outer  $e^-$  ( $\rightarrow$  Ne)  
 Cl desp. wants another  $e^-$  ( $\rightarrow$  Ar)

- "excess"  $e^-$  of Na can make Cl happy
- creates  $Na^+$  and  $Cl^-$ 
  - these two will attract each other
  - less obvious: leads to crystal lattice,  $\sim 0.28$  nm spacing

? why don't they get closer?

- electrostatic forces are not the only ones acting
  - when ions are very close together,  $e^-$  clouds are distorted
  - leads to short-range repulsive forces
    - try to restore undistorted ions
    - only when sep dist  $\sim$  atomic radius

energy of 2 atoms vs. sep



key points

- 1)  $E \rightarrow 0$  for large  $r$ 
  - attractive for  $r_0 < r < \infty$
  - favorable to bond
- 2) very small  $r < r_0$ 

repulsive
- 3) minimum at  $r = r_0$ 

attractive  $\therefore$  repulsive balance

- 
- On the HW: two "model" potentials for this
  - $r_0 =$  equil distance
  - what happens when we compress a crystal?



- this is the incr in energy due to work on moving 6 faces
- each face has moved by  $(\frac{a}{2r_0})\Delta r$  relative to opposite

since each side moves by  $(\frac{\Delta r}{r_0})a$   
 %chg side of cube

- as stress increases from 0  $\rightarrow$  T, the work done is on total

$$W = 6 \cdot \left(\frac{1}{2} T a^2\right) \cdot \left(\frac{a \Delta r}{2r_0}\right) = \frac{3}{2} T \frac{a^3 \Delta r}{r_0}$$

6 faces                  hydrostatic face                  distance

- comparing with  $\Delta E$ , gives

$$T = \frac{1}{3r_0} \left( \frac{\partial^2 E}{\partial r^2} \right) \bigg|_{r_0} \left( \frac{\Delta r}{r_0} \right)$$

} work to squish crystal

• IE:  $F = kx$

- perfectly general! does not depend so far on choice of  $E(r)$

define bulk modulus  $T = C \left( \frac{\Delta V_{ol}}{V_{ol}} \right) = C \frac{\Delta a^3}{a^3}$

$$\Rightarrow C \approx \frac{1}{9r_0} \left( \frac{\partial^2 E}{\partial r^2} \right) \bigg|_{r_0}$$



- then 8 Cl atoms at  $a\sqrt{3}$  ... sum over xtal
- converges

$$- \frac{ke^2}{a} \left( 6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} \dots \right)$$

crystal geom

- ends up as a constant
  - unique to each lattice
  - solve once...

general:

$$U_{\text{static}} = -M \left( \frac{ke^2}{a} \right)$$

electrostatic energy of crystal

fraction of pair + - energy  
"Madelung const"

- for NaCl,  $M \approx 1.748 \Rightarrow \underline{U_{\text{static}} \approx 8.94 \text{ eV}}$
- tend to be brittle, hard
- energy per ion gained by assembling!  
(HUGE)

Metallc more next time...

- like ionic, but  $\ominus$  charges are  $e^-$  and very mobile!
- lattice of  $\oplus$  with "sea" of shared electrons
- fluid-like sea  $\Rightarrow$  ductile, malleable

# Covalent Bond

- bonds so far based on unlike charges attracting
- what holds Si or C together? all neutral!
  - Si is partly conducting  $\Rightarrow$  some free  $e^-$
  - both have v. strong  $\hat{=}$  directional bonds like ionic
- Covalent bonding mech most important in chem
  - 'unexplainable w/o QM!
  - difficult... just a taste

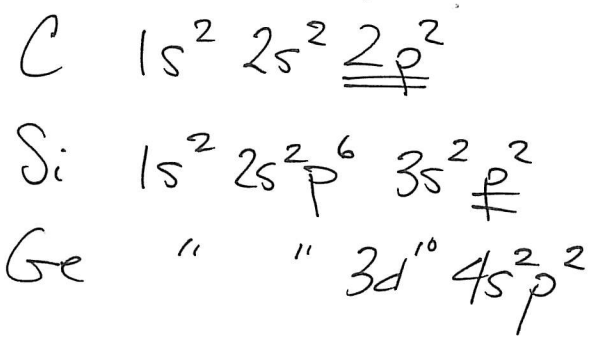
## Simplest example: $H_2$ $2p^1, 2e^-$

- $e^-$  orbit about both atoms
- can imagine diff arrangements...



-  $e^-$  can only partly screen  $p^+$   
 - some nuclear attraction until they're too close

• general: when  $e^-$  pairs can form in outer shell



• actually all tetravalent  
 • in solid, s and p  $e^-$  mix and bond

approx: 4 "dangling" bonds to share



(Covalent) all available (outer)  $e^-$  pair up, orbit around a pair of atoms

- none left to "wander"  $\therefore$  conduct electricity  
tend to be insulator / poor conductor

- thermal  $E$  can disrupt pairs  $\Rightarrow$  increased conductivity - "semicon"

## Variational Method for molecules

Schrodinger:  $-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = \left( \frac{\hbar^2}{2m} \nabla^2 + V \right) \psi = E\psi$

$-\frac{\hbar^2}{2m} \nabla^2 + V \equiv H$  "operator" like  $x$  or  $p = -\frac{\hbar}{i} \nabla$   
returns energy (Hamiltonian)

$\Rightarrow \boxed{H\psi = E\psi}$

• multiply both sides by  $\psi^*$  ( $\psi^*$  if complex),  $\int$  over volume

$$\int \psi^* H \psi dV = \int E |\psi|^2 dV = E \int \psi^2 dV$$

if  $\psi$  are solns,  $\boxed{E(\psi) = \frac{\int \psi^* H \psi dV}{\int \psi^2 dV}}$

problem: don't know  $\psi$ ! real choice minimizes  $E$ !

any other guess:  $E(\psi) \geq E_{\text{true}}$

$\Rightarrow$  choose reasonable  $\psi$  and minimize! (iterate)  
(parameterize  $\psi$  w/ constants)

e.g. H atom. Guess  $\psi = e^{-cr}$

here  $H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{ke^2}{r}$

plug in and minimize with respect to c ( $\frac{dE}{dc} = 0$ )

$$c = \frac{km e^2}{\hbar^2} = \frac{1}{a_0}$$

$$E_{min} = \frac{-me^4 k^2}{2\hbar^2} = -13.6 eV$$

in this case, we guessed exactly! lucky...

Say we guessed  $\psi = e^{-cr^2}$   $E_{min}$  only 15% off!

say  $\psi = e^{-c_1 r^2} + k e^{-c_2 r^2}$   $c_1, c_2, k$  variable parameters  
 $\Rightarrow E_{min} \sim 1.3\%$  off!

- more param  $\rightarrow$  more complex, but more accurate
- only need physically reasonable starting point
- problem in minimization  $\Rightarrow$  computers ...

How to guess? presume atomic states are good guesses  
i.e. weak coupling

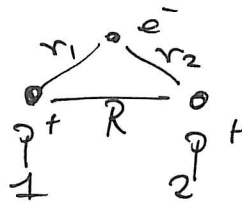
- linear combos of atomic orbitals (LCAO)  
"bonding/antibonding"

e.g. diatomic

$$\Psi = C_1 \phi_1 + C_2 \phi_2$$

$\phi_1, \phi_2 =$  atomic orbitals  
centered on atoms 1 & 2

e.g.  $H_2^+$  single  $e^-$ ,  $2p^+$



$p^+$  very heavy cf  $e^-$  ... presume  $R \approx$  fixed

relative energy changes only due to  $e^-$  now!

$$\underline{V = -ke^2 \left( \frac{1}{r_1} + \frac{1}{r_2} \right)} \quad \text{electrostatic; } e^- \text{ \& } 2p^+$$

try  $\phi_1, \phi_2$  as 1s states of H (normalized)

$$\phi_1 = \frac{1}{\sqrt{\pi a_0^3}} e^{-r_1/a_0} \quad \phi_2 = \frac{1}{\sqrt{\pi a_0^3}} e^{-r_2/a_0}$$

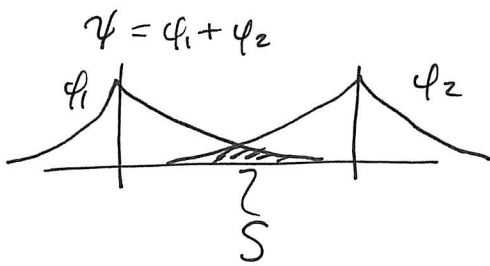
for  $H_2^+$ , try  $\Psi = C_1 \phi_1 + C_2 \phi_2$

$$\int \phi_1^2 dV = \int \phi_2^2 dV = 1 \quad (\text{normalized})$$

$$\Rightarrow \int \Psi^2 dV = C_1^2 + C_2^2 + 2C_1 C_2 \int \phi_1 \phi_2 dV$$

$S =$  "overlap integral" - "interference"

$S =$  "degree of interaction" - small unless BOTH  $\phi_1, \phi_2$  large  
i.e.  $\phi_1 \text{ \& } \phi_2$  overlap



$$S_{12} = \int \phi_1 \phi_2 dV$$

other term for  $E(\psi)$  has 3 integrals

$$\int \psi H \psi dV = C_1^2 \int \phi_1 H \phi_1 dV + C_2^2 \int \phi_2 H \phi_2 dV + 2C_1 C_2 \int \phi_1 H \phi_2 dV$$

energies  $\rightarrow$

	energy of 1 <sup>st</sup>	energy of e <sup>-</sup>	BOND!
	p <sup>+</sup> -e <sup>-</sup>	w/ 2 <sup>nd</sup> p <sup>+</sup>	Coupling
	pair		
	$H_{11}$	$H_{22}$	$H_{12}$

$H_{ij} = \int \phi_i H \phi_j dV$

if  $i=j$ , just energy of atomic state

$H_{11} = H_{22} = \text{hydrogen atom}$   
 $H_{12} = \text{Bond integral}$

} just energies

$$\Rightarrow E(\psi) = \frac{C_1^2 H_{11} + C_2^2 H_{22} + 2C_1 C_2 H_{12}}{C_1^2 + C_2^2 + 2C_1 C_2 S_{12}}$$

if  $R$  is large,  $\phi_1, \phi_2$  don't overlap  $\Rightarrow S_{12} \approx 0$

AND if  $V$  is short range,  $H_{12} \approx 0$

$$\text{then } E(\psi) = \frac{C_1^2 H_{11} + C_2^2 H_{22}}{C_1^2 + C_2^2} = 2 \text{ bare protons} + 1e^-$$

-or- one H and one proton!

Our condition is minimizing  $E$  to get close to ground state

$$\Rightarrow \frac{\partial E}{\partial c_1} = \frac{\partial E}{\partial c_2} = 0$$

$$\Rightarrow \begin{cases} c_1 (H_{11} - E) + c_2 (H_{12} - ES_{12}) = 0 \\ c_1 (H_{12} - ES_{12}) + c_2 (H_{22} - E) = 0 \end{cases}$$

• general problem: solve for  $c_1/c_2$  ratios  
then you have  $\psi \Rightarrow E$

• start with  $n$  orbitals,  $\Rightarrow n$  equations

Since  $H^+$  is symmetric ( $p^+$  are identical)

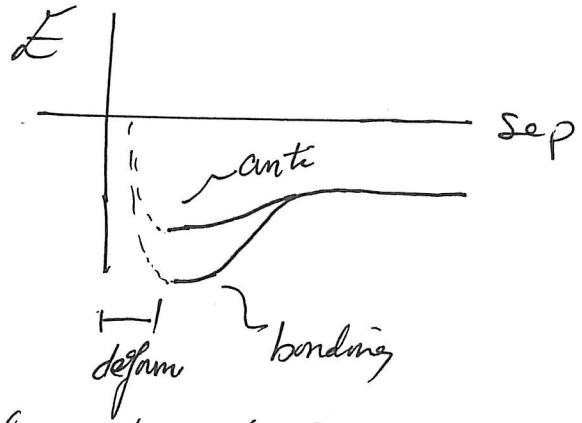
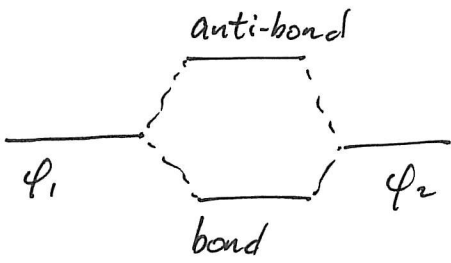
$$H_{12} = H_{22} \equiv H \quad \Rightarrow (H - E)^2 = (H_{12} - ES_{12})^2$$

$$2 \text{ solns: } \left[ E = \frac{H \pm H_{12}}{1 \pm S_{12}} = H \pm \frac{H_{12} - HS_{12}}{1 \pm S_{12}} \right]$$

got where

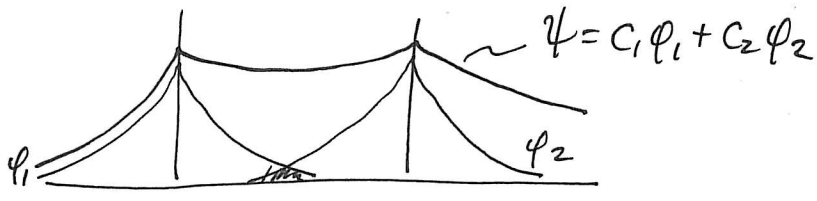
• large  $R$ :  $S_{12} = H_{12} = 0$  (no coupling/bonding)  
 $\Rightarrow \underline{E = H}$  bare particles  
(one  $H$  atom, one  $p^+$ )

• as  $R \downarrow$  bring together: overlap  $\rightarrow$  coupling ( $S_{12}, H_{12}$ ) incr  
 $\Rightarrow 2$  levels instead of one!

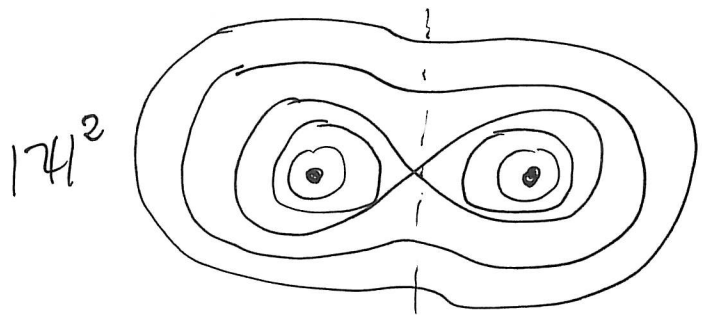


as  $p^+$  come together, single level splits into 2

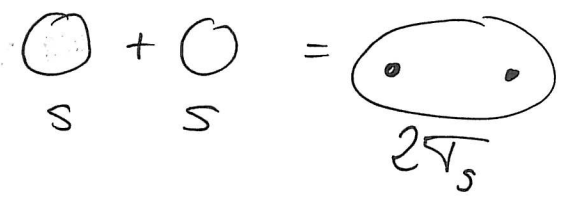
**Lower level**: Bonding orbital, adds  $\phi_1 + \phi_2$ ,  $C_1 = C_2$



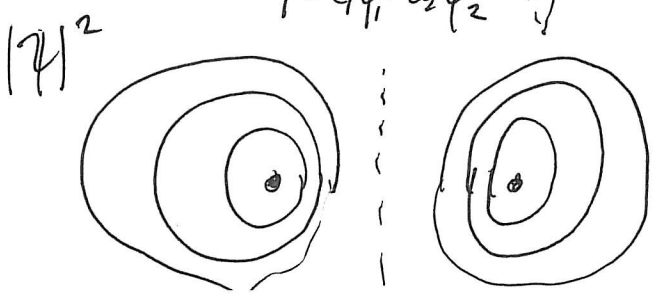
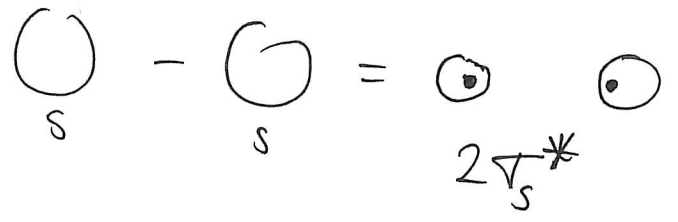
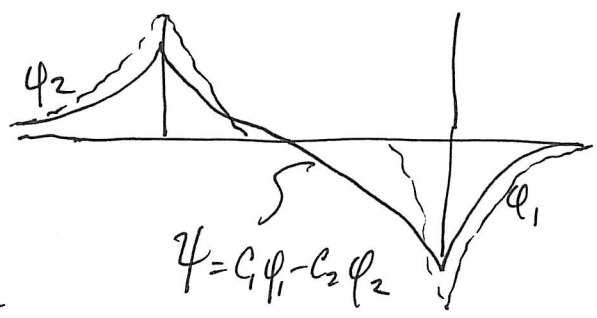
Symmetric



Combined s orbitals



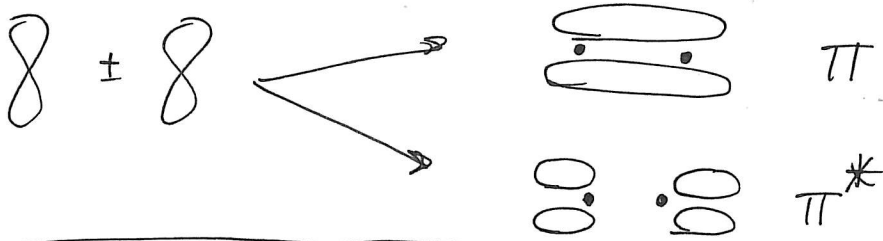
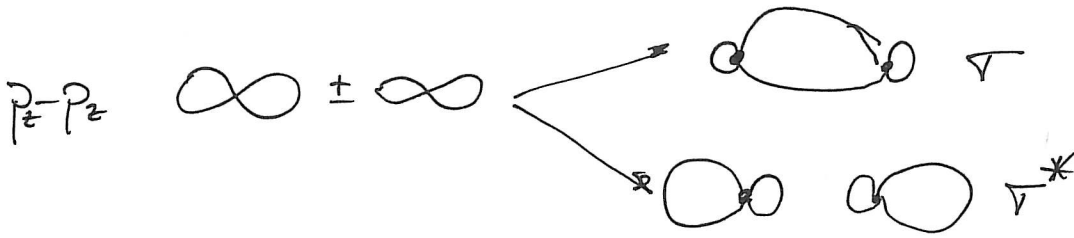
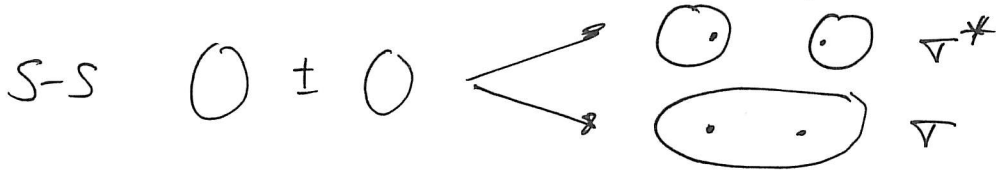
**Upper level**: Anti bonding; subtract  $\phi_1 - \phi_2$



Anti-symmetric

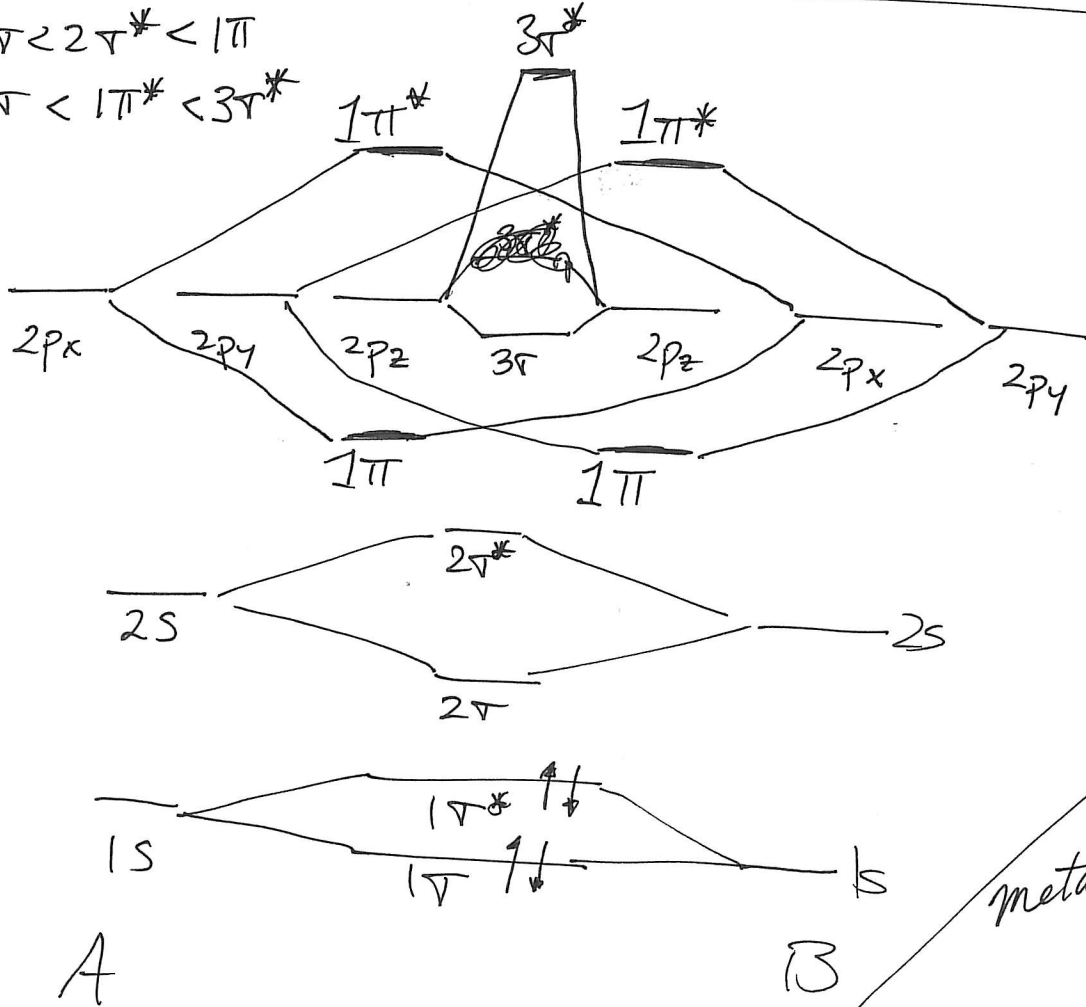


more complex LCAO:



$1\sigma < 1\sigma^* < 2\sigma < 2\sigma^* < 1\pi$   
 $< 3\sigma < 1\pi^* < 3\sigma^*$

~~2s~~  
~~2p~~  
~~1s~~



next:  
 metals: solids