

Lecture VI

VI 1a

General rules for making molecular orbitals (MO's)
(We will show where these general rules come from later)

① # AO's = # MO's [completeness theorem]

② When two orbitals (AO's) combine they make the lowest energy combination & the highest energy combination. [variational theorem]

③a Orbitals (eg. AO's) which are close in energy initially interact stronger than orbitals which are initially far apart in energy [2nd order perturbation theory]

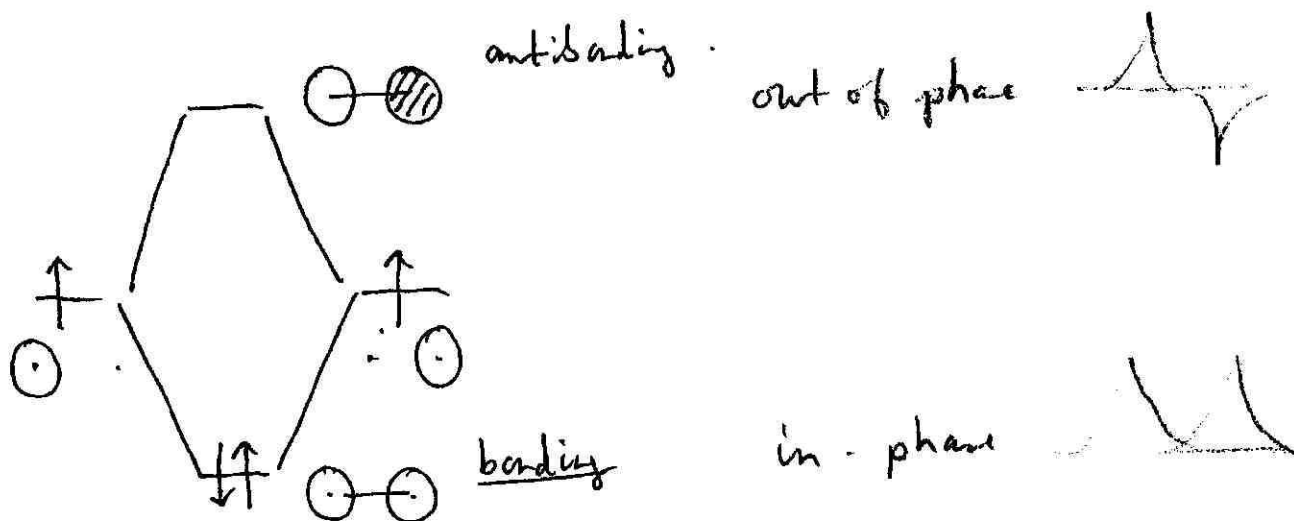
③b When orbitals of different initial energy interact, the low energy combination resembles more the initially lower energy orbital; the higher energy combination resembles the initially higher energy orbital. [“]

④ If the molecule has a C_2 rotation or a mirror plane (σ), which are all \parallel or \perp to each other, then MO's are either symmetric or antisymmetric with respect to the C_2 , σ and inversion center (i)
— [symmetry principles]

For now we will use rules ① & ②. In the next few lectures we'll add ③. For rule ④ we'll have to wait a few weeks to see what it means.

⑤ There is an implicit part of rule ③ that MO's are orthogonal. We'll explain the meaning of this point later.

Example 1

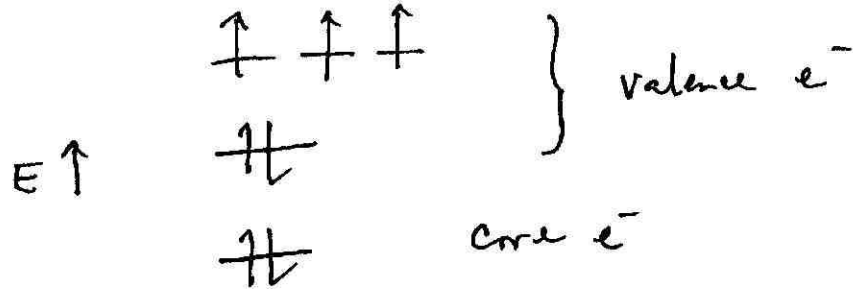
 H_2 

Note initially 2 AO's. \therefore 2 MO's (rule 1).
 The lowest energy combination is labelled bonding & the
 highest energy combination is labelled antibonding.
 The e^- follow the Aufbau principle: they occupy
 the lowest energy orbitals available.

Lecture VI N₂ Molecular Orbital diagram (M.O.)

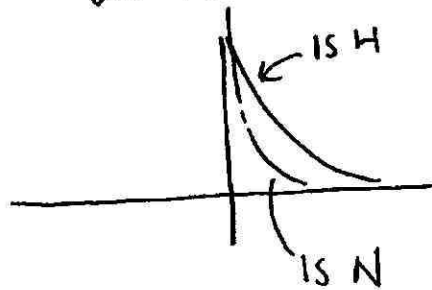
① Nitrogen atom's atomic orbitals (A.O.).

Aufbau principle tells us $(1s)^2 (2s)^2 (2p)^3$;
 $2 e^-$ in $1s$; $2 e^-$ in $2s$; $3 e^-$ in $2p$.



Core e^- are the noble gas shells which are completely filled (in this case He, but not Ne)

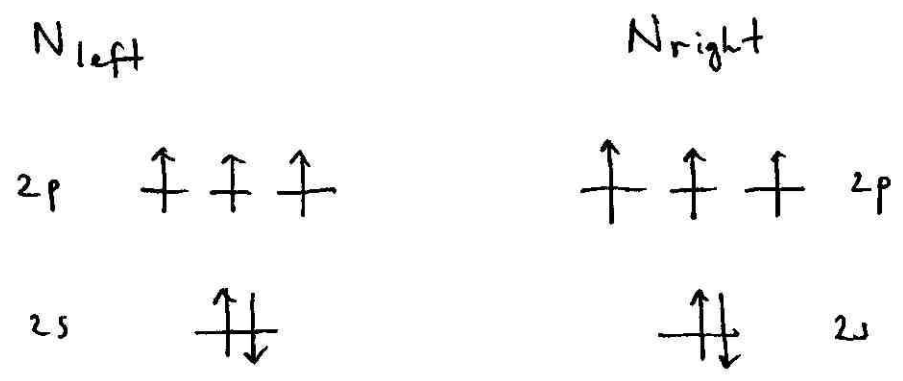
② Core e^- are located much closer to the nucleus than valence e^- . N has many more protons (which attract e^-) than H.



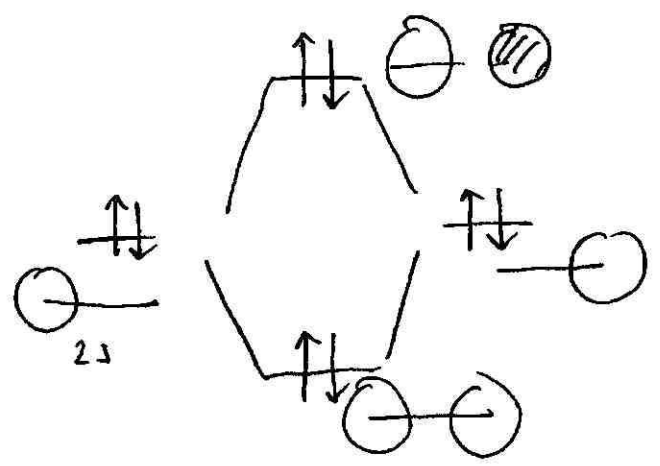
The core e^- are all close to the nucleus & they don't get to overlap much. So the bonding properties come from the valence e^- . \therefore Typical MO diagrams look mainly at the valence e^- . Core orbitals typically are not even drawn.

③ N_2

$N_{left} \cdots \cdots N_{right}$

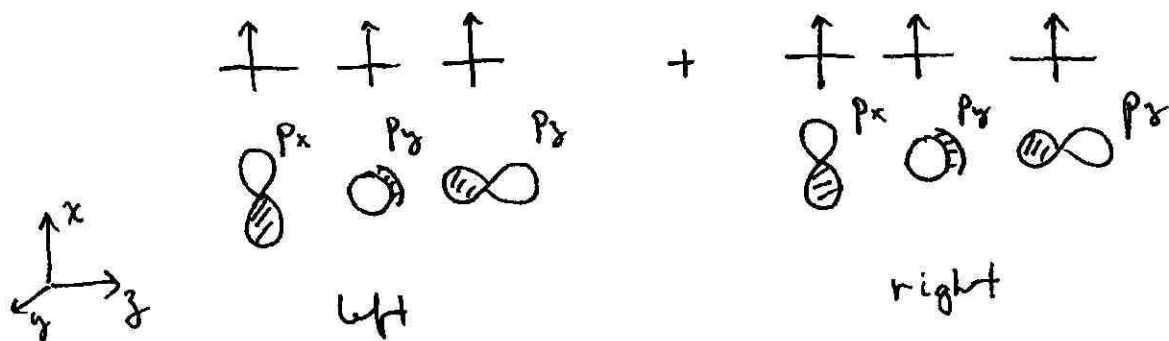


"Zeroth" order approximation. 2p orbitals interact w/ 2p orbitals; 2s interact with 2s.
 [Reason: According to rule ③ orbitals close in energy interact best. 2s of N_{left} is close in energy w/ 2s of N_{right} } 2p N_{left} are close in energy to 2p N_{right}

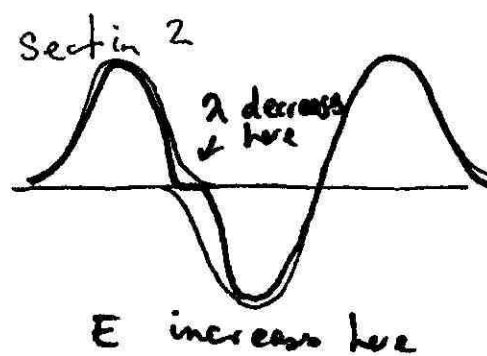
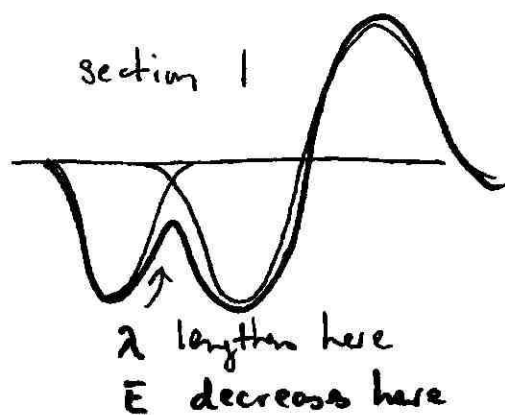
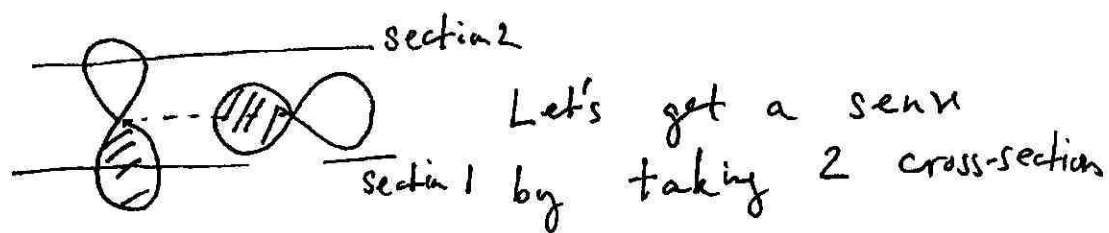


None of the N_2 bonding seems to come from 2s orbitals (once the 2s interacts w/ 2p this is no longer true.)

④ Turn to 2p orbitals.



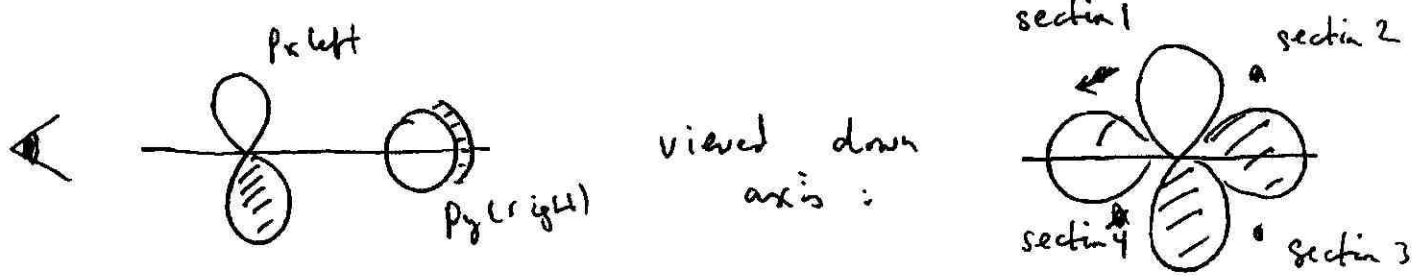
⑤ How do these orbitals interact?
 Consider P_x (left) with P_z (right).



In section 1 $E \uparrow$ goes up but in section 2 E goes down.
 \therefore no net change. As energy does not change there is no net change in $P_x + P_z$ combination \therefore P_x and P_z do not interact.

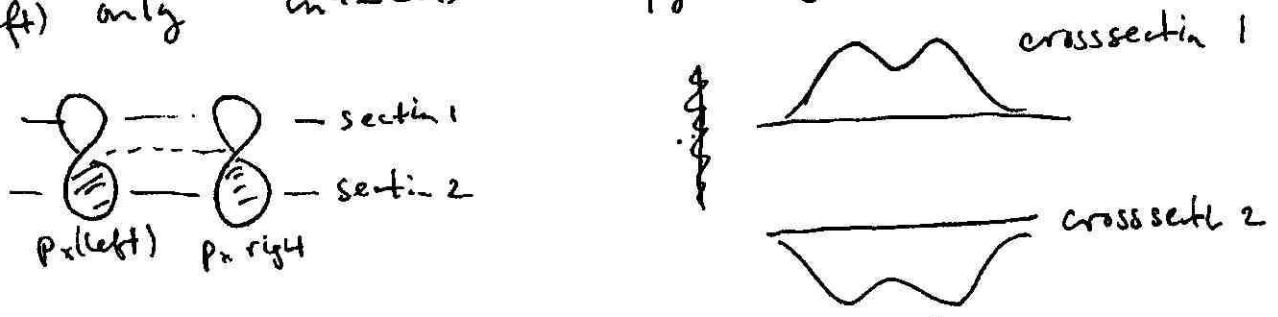
In exactly the same manner we find P_z & P_y do not interact.

Exercise II.2 Consider P_x (left) and P_y (right).



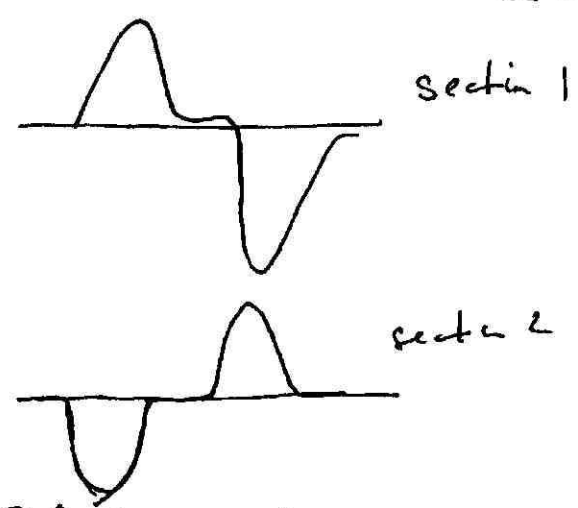
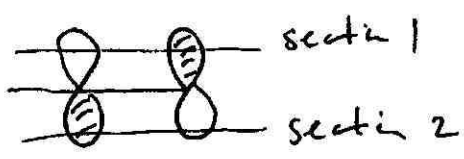
Consider the 4-sections (all coming in & out of the paper) Show for these four sections the net interaction between P_x (left) & P_y (right) is zero. For any uniform full distribution of crosssection do you think the net interaction will always be zero? [In math getting a uniform full distribution of samplings is called integration.]

⑥ From the previous section we conclude P_x (left) interacts only with the p orbital which is P_x (right). Similarly P_y (left) only interacts with P_y (right) and P_z (left) only interacts with P_z (right).



in both cases λ is larger, $E \downarrow$ (good down)

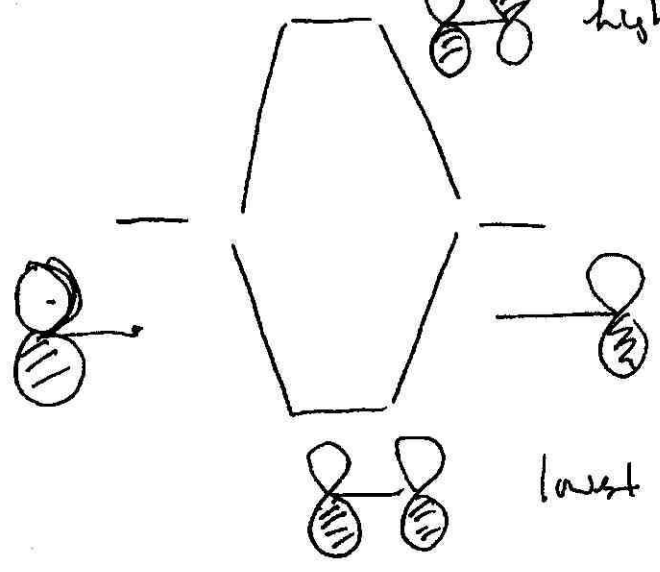
or



in both cases λ shorter, $E \uparrow$ (goes up)

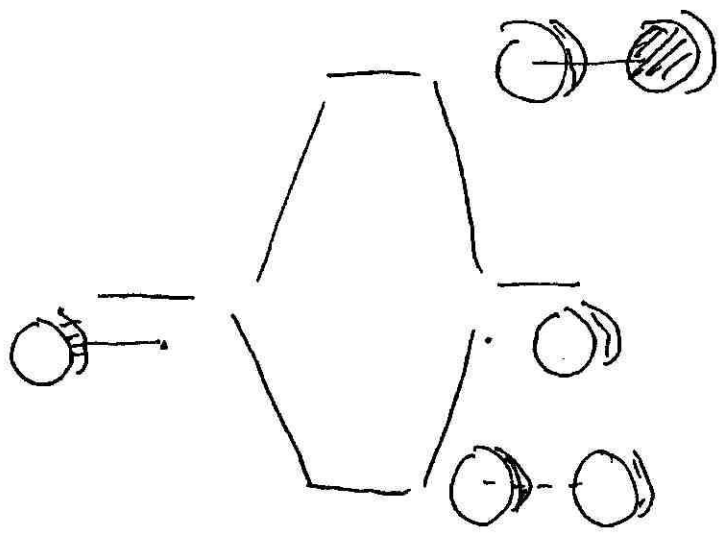
Applying rule (2) (rule 1)
highest energy combination

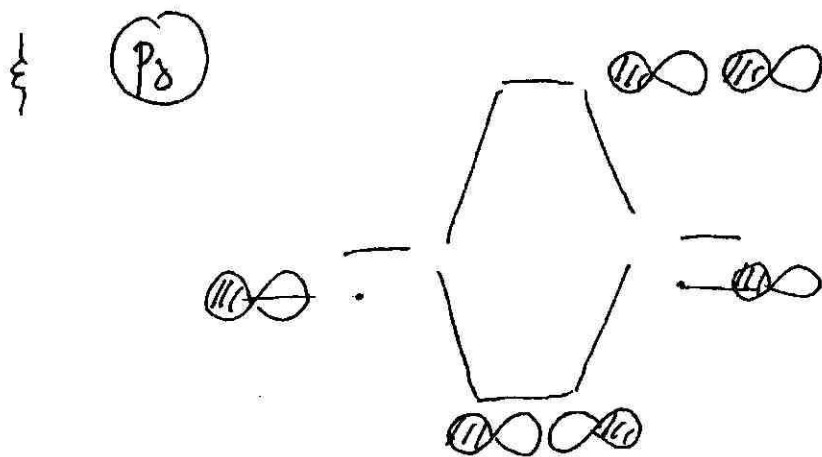
2 A.O.s \rightarrow 2 M.O.s



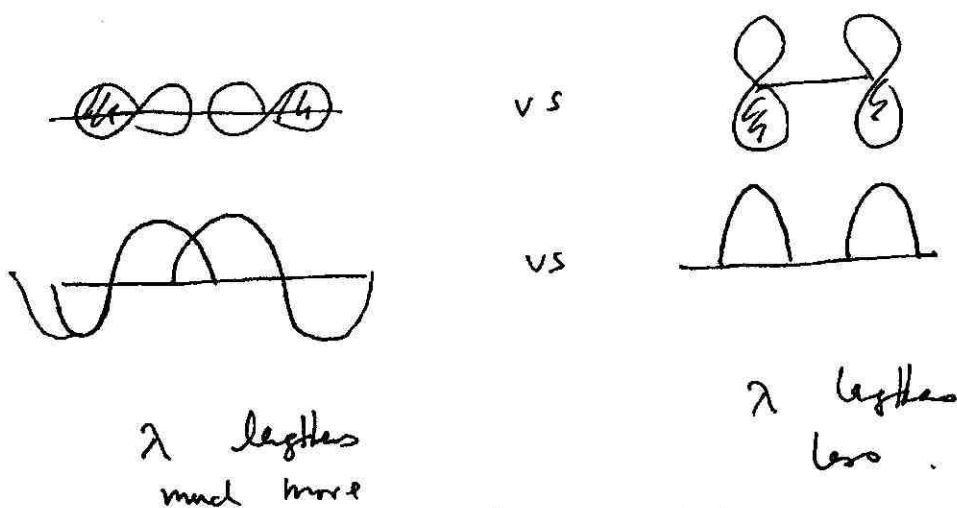
Similarly

P_y





Note λ length is greater for p_z than p_x (or p_y) as lobes are directly pointed at each other.



Putting together s, p_x, p_y, p_z picture:

