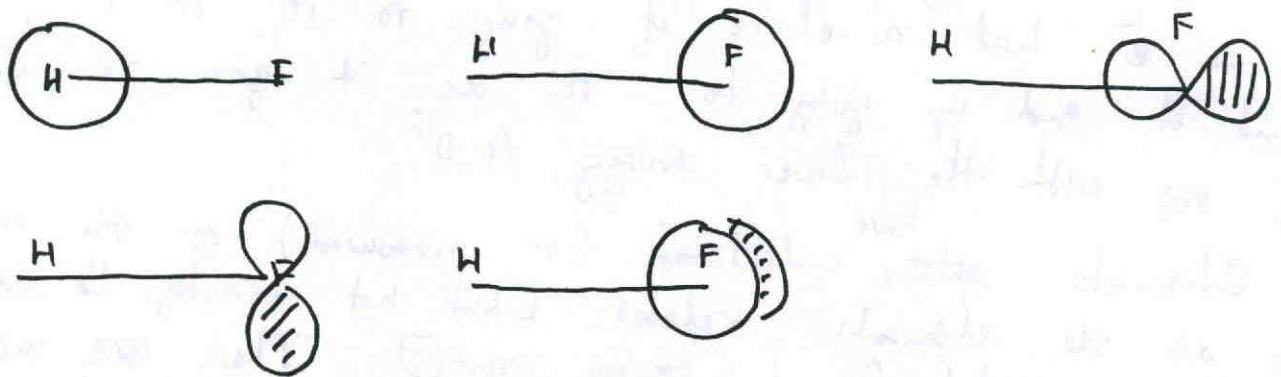


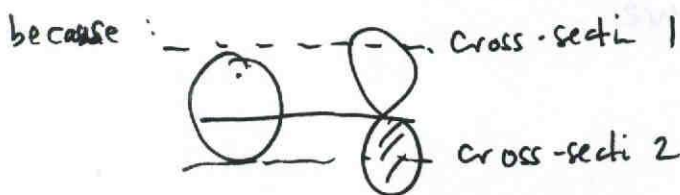
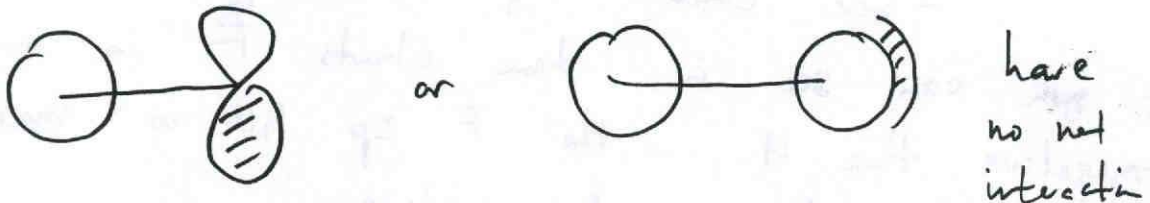
MO diagram for HF

① So far we have seen the MO diagrams for H_2 , N_2 and O_2 . We have some idea about how to make MO diagrams for molecules with 2 atoms and where the 2 atoms are the same element. What do we do when we have 2 atoms which are not the same element, say HF?

② Let's take a look at HF. By now we probably have the idea that MO's are based on AOs (and by AOs we mean AOs involving valence orbitals). For H the AO is 1s; for F the valence orbitals are 2s and 2p.

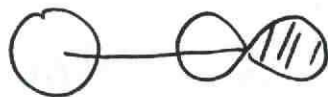


③ We can see by the same arguments we applied for N_2 and O_2 that



Cross-section 1 \nearrow ~~increases~~ increases; but \searrow for cross-section 2 λ decreases. No net change in energy.

So for the MO diagram we only need to consider the interaction between $\text{H} \text{---} \text{F}$ or $\text{H} \text{---} \text{F} \text{---} \text{---}$. This problem is hard enough that we'll just have to simplify it. Let's consider the interaction between



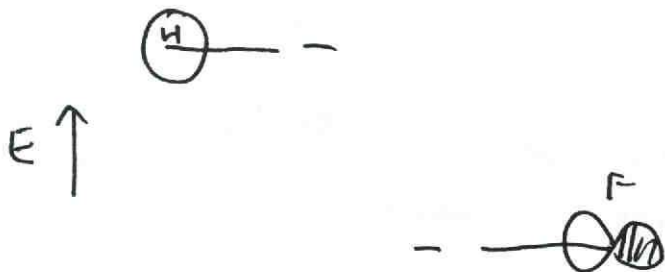
[As you'll see, we would get a very related answer had we just considered $\text{H} \text{---} \text{F}$.]

⑤ ~~What~~ The first thing we need to decide are the ~~electron~~ energies of the H 1s and the F 2p orbitals. One way of answering this question is to ask if an e^- had a choice of going to H^+ or F^+ , which would it end up going to: the one it goes to, will be the one with the lower energy A.O.?

⑥ Chemists ~~often~~ ^{have} calculated (or measured) the values for all the elements related [but not exactly the same] as the one asked for in ~~section~~ part ⑤. There are measured values for all the elements: they are called the electronegativity values for all the elements.

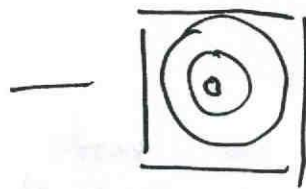
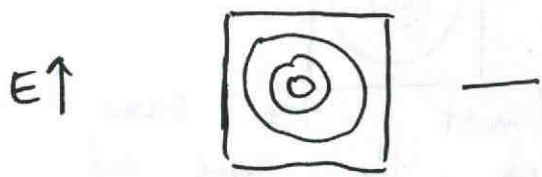
- see charts of electronegativity -

⑦ As you can see in these charts F is much more electronegative than H: the F 2p A.O. is much lower in energy than the H 1s. A.O. picture:

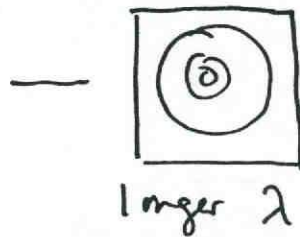
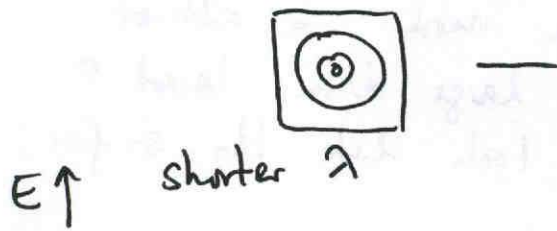


⑥ ~~How~~ How do we interact two AO's which start with a different energy? It would be great if we had an equation which told us how to interact the two AO's but for now [but not in 3-4 weeks] we don't. All we know is that electron waves are a lot like drum waves.

⑦ Let's try to imagine the case of 2 drum waves which are of unequal energy. Let's try drums with different size:



SAME SIZE DRUMS



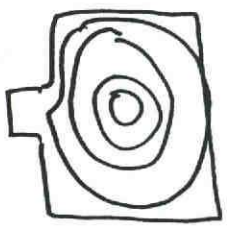
DIFFERENT SIZE DRUMS

⑧ Let's consider the case of a tiny drum and a big drum [problem 5 of Problem Set 3]

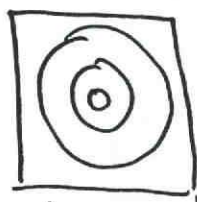
⑧ continued.



⑨ We can guess that the lowest drum mode is

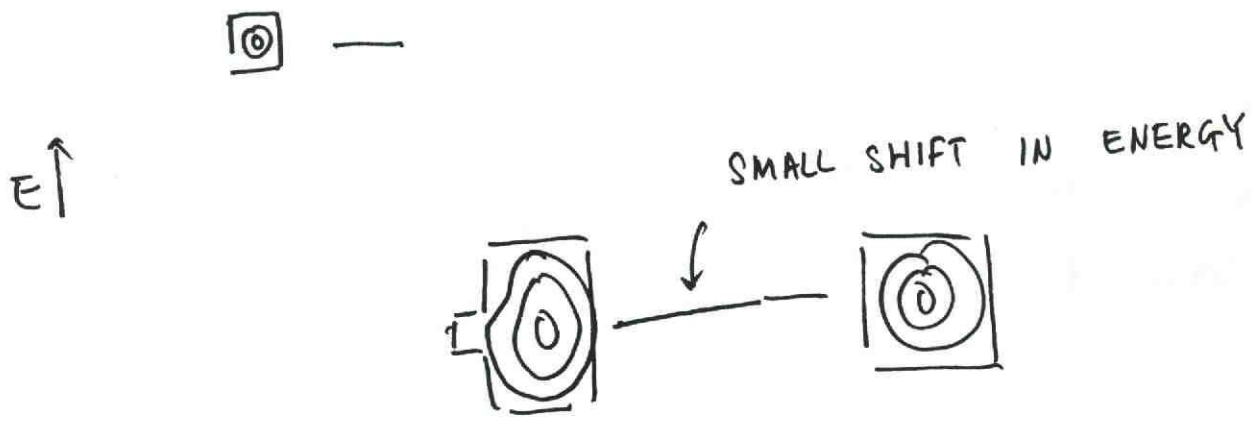





It looks almost the same as the original




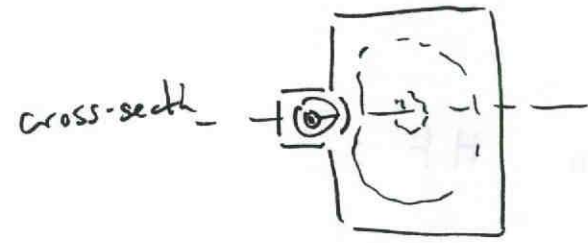
If the ~~two~~ mode looks almost the same this means the wave length is almost the same and therefore the energy is almost the same.

⑩ Conclusion : The n combined drum mode is almost the same energy as the original large drum lowest E drum mode. The overall picture looks like this so far:

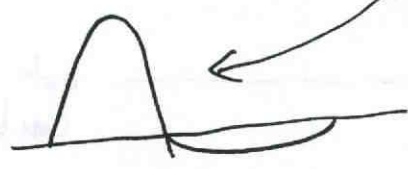


11) Now what about the drum mode which comes from ? We might suspect from our previous MO diagram that it has to do with the out-of-phase combination of  &  & 


So the  drum mode will split into the out of phase part



cross-section

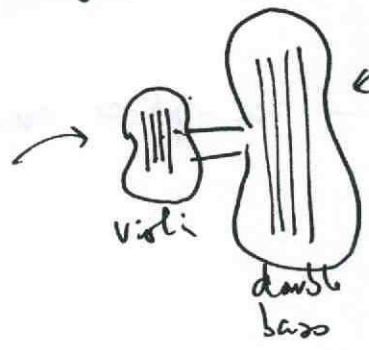


most of the wave spends its time on the small drum mode.

12) The wavelength is very much like the original  since that is where the ~~drum~~ wave spends most of its time. ~~length~~ [If this helps imagine an musical instrument like this :

like this :

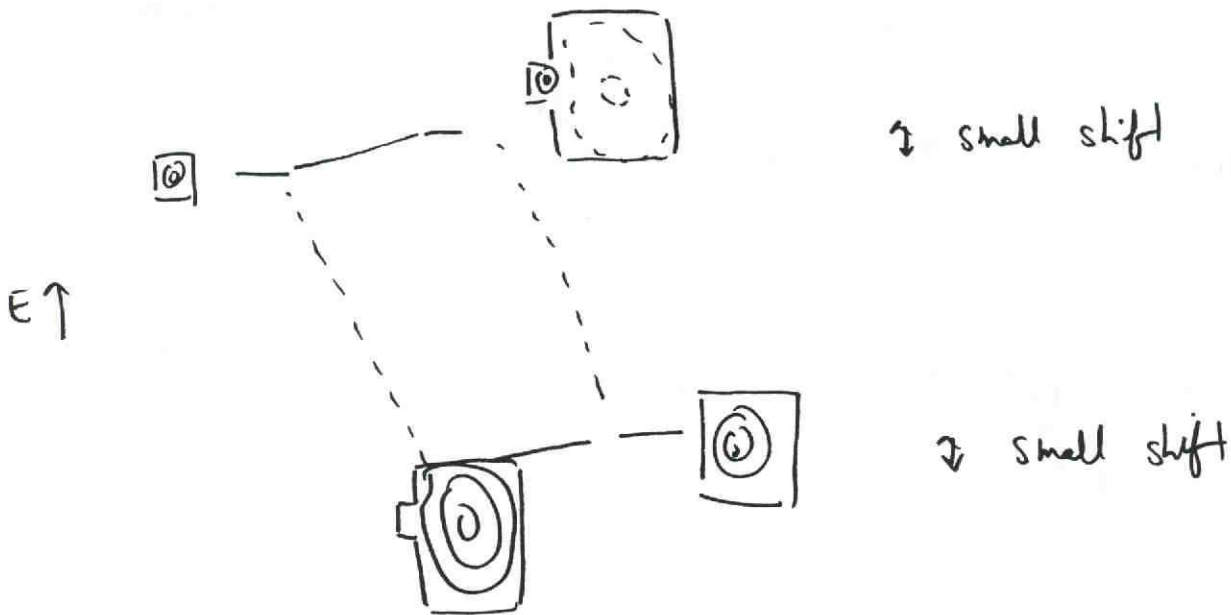
strings here sounds a lot like a violin.



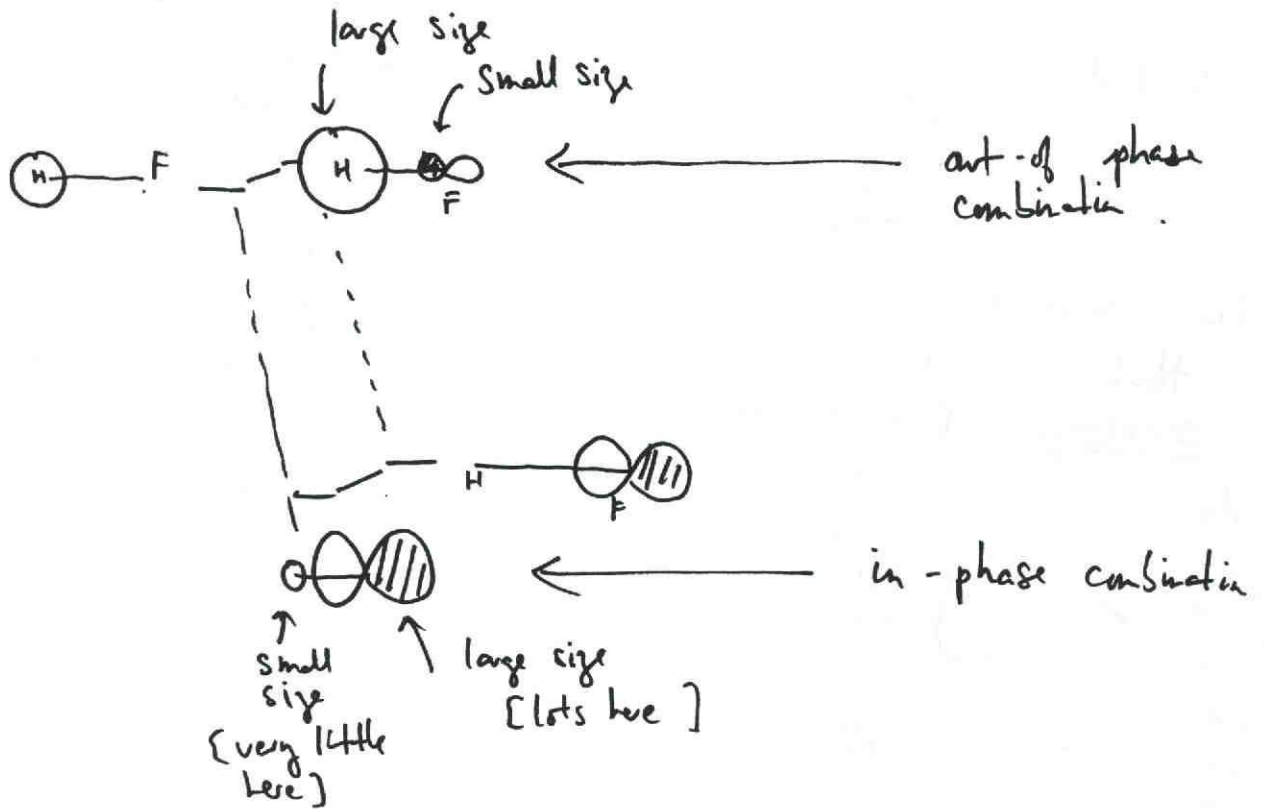
strings ~~are~~ a string here sounds a lot like a double bass]

13) But since we are interested in the out-of-phase combination, ~~it~~ the combined drum mode will be slightly higher in energy.

9) The overall picture looks like this:



15) Translating this picture to HF:



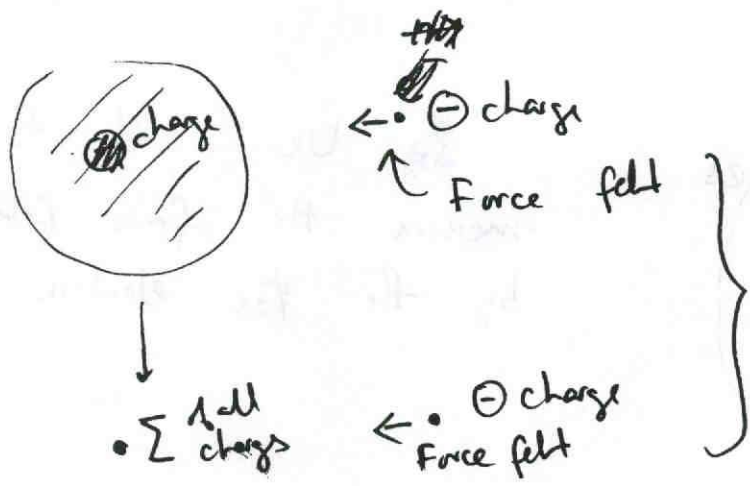
2) The HF diagram obeys our third rule for making MO diagrams

3a) Orbitals (eg. A.O.'s) which are close in energy, initially interact more strongly than orbitals which are initially far apart in energy.

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.

[consequence of 2nd order perturbation theory]

7) To end this lecture we need to understand why F is more electronegative than H. To understand this we need to know some physics [Gauss' Law] which states if we want to know the force on a spherical electric distribution applies to a charge we can collapse the electric distribution to its center & if the ~~charge~~ distribution is inside the charge in question i.e.,

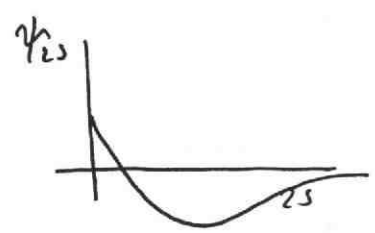
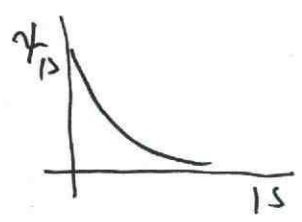


forces felt are exactly equal.

⑧ But if the ^{spherical} electric distribution is outside the charge in question, ~~the~~ the charge feels no force at all:

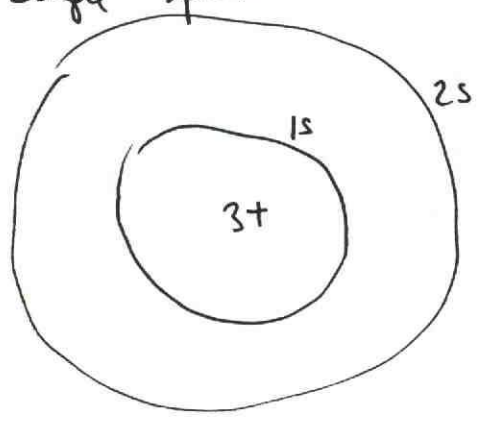


⑨ Let's apply ~~the~~ ~~case~~ Gauss' Law to the Li atom. Li has two types of AOs ~~orbitals~~: 1s & 2s which are filled.



ψ_{1s} is most of the time inside while ψ_{2s} is most of the time outside.

⑩ Simple picture :



~~By~~ We wish to measure the force felt by the ψ_{2s} electron.

(21) By Gauss' law



The 2s feels a net charge of around $1+$ charge.

(22) Let's move to Be which is $(1s)^2(2s)^2$. What charge does a 2s e^- feel. The two 1s e^- are inside but the other 2s e^- is $\frac{1}{2}$ time inside & $\frac{1}{2}$ time outside.

By Gauss law net charge felt for force is:

$$4(+)+2(-)+\frac{1}{2}(-)=\text{Net } 1\frac{1}{2}(+)$$

Be feels an effective net charge of $1\frac{1}{2}(+)$. Therefore Be 2s orbital feels more $(+)$ charge; it is lower in energy; Be is more electronegative than Li.

(23) This same approach can be applied to B which $\therefore (1s)^2(2s)^2(2p)^1$. 2s & 2p are around the same size

$$\therefore 5(+)+2(-)+\frac{1}{2}2(-)=\text{Net } 2(+)\text{ \& so forth.}$$

(24) We come up with the following table.

	Li	Be	B	C	N	O	F
approx. effective nuclear charge	1	$1\frac{1}{2}$	2	$2\frac{1}{2}$	3	$3\frac{1}{2}$	4
true effective nuclear charge	1.28	1.91	2.42	3.14	3.83	4.45	5.10
approx. Pauling electronegativity	1	$1\frac{1}{2}$	2	$2\frac{1}{2}$	3	$3\frac{1}{2}$	4
exact Pauling electronegativity	.98	1.57	2.04	2.55	3.04	3.44	3.98

~~H~~ Li (and H) are a lot more electronegative
than F.