

## Lecture 22 Molecular Orbital Theory and Quantum Mechanics.

① We stated four general rules for the making of MO diagrams.

1. Number of molecular orbitals = number of atomic orbitals.
2. The most bonding, i.e., lowest energy ~~state~~ MO is the lowest possible <sup>energy</sup> orbital one can make. Also the highest energy MO is the highest possible energy orbital one can make.
3. When two orbitals mix, the amount the orbitals mix is inversely proportional to the initial difference in energy of the orbitals. Therefore orbitals which are initially close in energy mix (i.e., interact) more. When they do mix, the low energy combination resembles more the initial low energy orbital. The higher energy combination resembles more the initial high energy orbital.
4. If there are a set <sup>of</sup> ~~of~~ <sup>can be written</sup> mirror planes and  $C_2$  axes, then the MO's <sup>are</sup> symmetric or antisymmetric with respect to these axes.)

- ② For now we will not discuss rule 4. But let's review how what we now know about MO's help us understand rule 1-3. (You may want to look at page 19.1 as this page briefly reviews quantum (matrix) mechanics.)
- ③ We now know that MO's are eigenvectors of the Hamiltonian matrix. Rule 1 tells us that the number of M.O.'s = # A.O.'s i.e., that there are the same number of M.O.'s (in an M.O. diagram) the same number of eigenvectors as A.O.s. We can check for the three systems,  $H_2$ ,  $N_2$  &  $HF$  that this statement is correct.

	A.O.s	# A.O.'s	# eigenvectors (M.O.'s)
$H_2$	$\phi_{1sa}, \phi_{1sb}$	2	2
$N_2$	$\phi_{1sa}, \phi_{1sb}$ $\phi_{2sa}, \phi_{2sb}, \phi_{2sa}, \phi_{2sb}$ $\phi_{2sa}, \phi_{2sb}, \phi_{2sa}, \phi_{2sb}$	8	8
$HF$	$\phi_{Hs}, \phi_{Fp_z}$	2	2

It is important that the number of M.O.'s = # A.O.'s. Recall that one of the ideas underlying our quantum (matrix) mechanics is

that "any state,  $\vec{w}$ , can be expressed as a linear combination of the eigenvectors of any measurement matrix."

④ In particular the M.O.'s are the eigenvectors of the Hamiltonian matrix. Any state  $\vec{w}$  can be written as

$$\vec{w} = \alpha_1 \vec{\psi}_1 + \alpha_2 \vec{\psi}_2 + \dots + \alpha_N \vec{\psi}_N \quad (1)$$

where  $\vec{\psi}_i$  are the M.O.'s

$\alpha_i$  " " prob. amplitudes,  $\alpha_i = \vec{\psi}_i^\dagger \vec{w}$

$\vec{w}$  can be any of the different A.O.'s. Perhaps you can see with your common sense that in order for (1) to be correct there has to be as many M.O.'s as all the different A.O.'s. (Mathematicians say both the A.O.'s & the M.O.'s completely span the vector space.)

⑤ The same equation. All states  $\vec{w}$  can be written as

$$\vec{w} = \alpha_1 \vec{\psi}_1 + \alpha_2 \vec{\psi}_2 + \dots + \alpha_N \vec{\psi}_N \quad (1)$$

$\alpha_i$  are the probability amplitudes and  $\alpha_i^* \alpha_i$  are the probabilities.

Thus there is  $\alpha_1^* \alpha_1$  chance that ~~the~~ the measured energy of  $\vec{w}$  is  $E_1$ ,  $\alpha_2^* \alpha_2$  chance the measured energy is  $E_2$ , etc... (where  $E_1, E_2, \dots, E_N$  are the eigenvalue of  $\vec{\psi}_1, \vec{\psi}_2, \dots, \vec{\psi}_N$ )

⑥ The average measured energy of  $\vec{w}$  is just an <sup>weighted</sup> average of  $E_1, E_2, \dots, E_N$ .

review

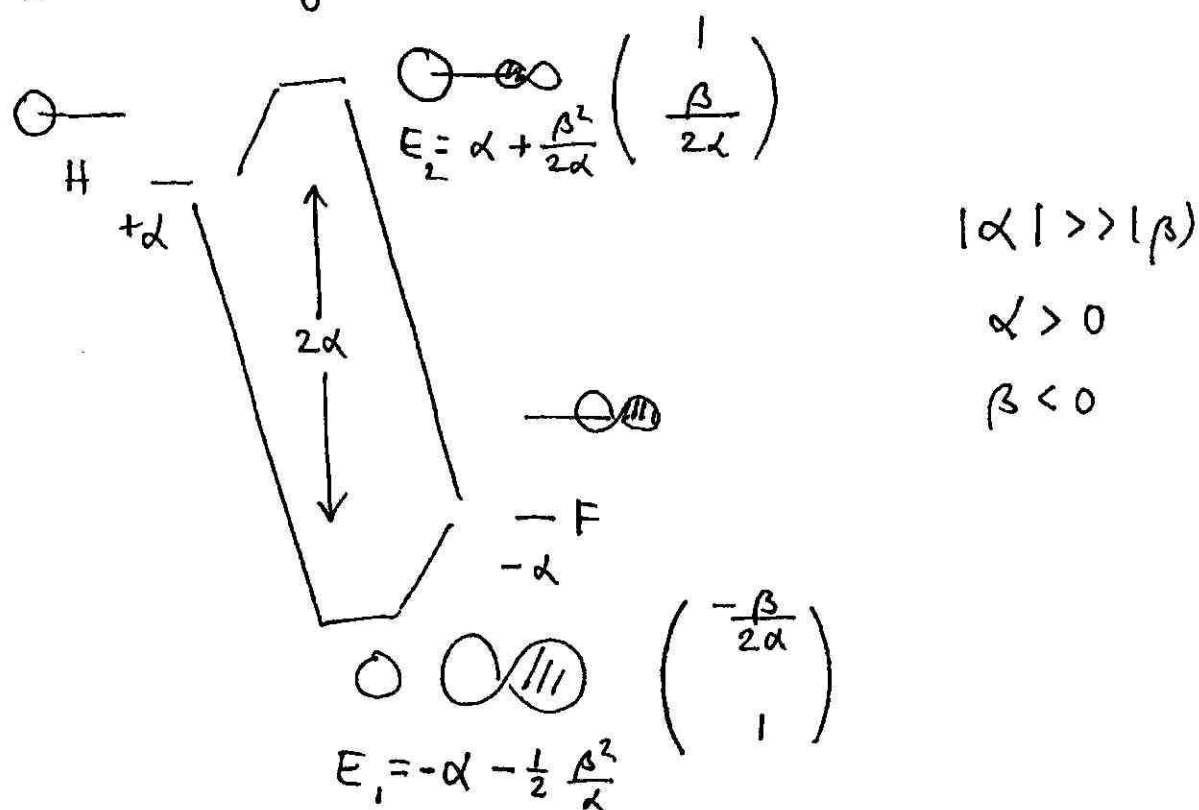
- example w/ dice -

$\therefore$  the lowest possible average, the lowest possible energy is just the lowest  $E_i$  value & the highest possible average is the highest  $E_i$  value.

This justifies rule 2.

⑦ This brings us to the final rule (for now) that when two orbitals mix, the interaction is inversely proportional to the <sup>initial</sup> energies of the orbitals. The low energy MO resembles more the initially low energy orbital. The high energy MO resembles more the initially high energy orbital.

⑧ To see that this rule is true, let's examine again the HF problem.



We note that  $\Delta E = \text{diff. of initial orbitals}$   
 $= 2\alpha$

The low energy M.O. has energy

$$E_1 = -\alpha - \frac{\beta^2}{\Delta E}$$

The orbital initially was at energy  $-\alpha$ .

$\frac{-\beta^2}{\Delta E}$  represents the stabilization energy of this orbital

The stabilization energy  $\epsilon$  is inversely proportional to  $\Delta E$ , as stated by rule 3. Furthermore the lower energy orbital is more like the F orbital, also a rule 3 state.

In the same way looking at the high energy orbital we can find the other statements in rule 3 are true.

This concludes our discussion of the source of the rules 1-3 for making M.O. diagrams.