

MO theory of  $\pi$ -electrons in conjugated and aromatic molecules: Hückel theory

Hückel model: uses hybridization and the localized VB model to describe the  $\sigma$ -bonded skeleton (the rigid framework which determines the shape of the molecule) and MO theory to describe the delocalized  $\pi$ -electrons.

For the  $\pi$ -electrons, Hückel theory makes the following simplifying assumptions:

- all C atoms are identical  $\rightarrow \alpha$  is the same for each AO
- all overlap integrals are zero,  $s = 0$
- all resonance integrals between neighboring carbons are equal, call this  $\beta$
- all other resonance integrals are zero

This gives a simple structure to the determinant:

- 1) all diagonal elements are  $\alpha - E$
- 2) all off-diagonal elements between neighboring atoms are  $\beta$
- 3) all other elements are 0

example: butadiene. We have 4  $\pi$ -electrons

(insert picture here, label carbons 1,2,3,4)

The Hückel energies are

$$\det \begin{bmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{bmatrix} = 0 \quad (1)$$

The solution is  $E = \alpha \pm 1.62\beta$  and  $E = \alpha \pm 0.62\beta$ . Since  $\beta < 0$  the  $\pi$ -electrons in butadiene have total energy  $E_\pi = 2(\alpha + 1.62\beta) + 2(\alpha + 0.62\beta) = 4\alpha + 4.48\beta$ . What should we compare this to? In ethene we have  $E_\pi = 2(\alpha + \beta)$  so that two individual  $\pi$ -bonds have energy  $4\alpha + 4\beta$ . Thus we can say the delocalization energy in butadiene is  $0.48\beta$ , which is approximately 110 kJ/mol. This is the *extra* stabilization energy due to conjugation.

example: cyclobutadiene.

(insert picture here, label carbons 1,2,3,4)

The Hückel energies are

$$\det \begin{bmatrix} \alpha - E & \beta & 0 & \beta \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ \beta & 0 & \beta & \alpha - E \end{bmatrix} = 0 \quad (2)$$

The solution is  $E = \alpha \pm 2\beta$  and  $E = \alpha$  (doubly degenerate). Hence  $E_\pi = 2(\alpha + 2\beta) + 2\alpha = 4\alpha + 4\beta$ . In this case there is *no* extra stabilizing energy!

#### Hückel model for monocyclic polyenes

The matrix method works but the  $\pi$ -electron MO energies can also be obtained using a graphical method. To use the graphical method, we must inscribe a regular polygon with the shape of the polyene in a circle of radius  $2\beta$  with one vertex pointing downwards. Each point for which the polygon touches the circle corresponds to an orbital. The orbital energies are obtained by assigning the center of the circle an energy of  $\alpha$ .

example: cyclobutadiene

(insert figure here)

example: benzene

(insert figure here)

With these tools we can predict that  $\text{C}_3\text{H}_3^+$  is more stable than  $\text{C}_3\text{H}_3$  or  $\text{C}_3\text{H}_3^-$ ; cyclobutadiene is a diradical and thus is very reactive;  $(\text{CH})_5^-$  is more stable than  $(\text{CH})_5$  or  $(\text{CH})_5^+$ . These predictions have been verified by experiment and demonstrate that the Hückel model has predictive power.

One weakness of the Hückel model is that it only treats the  $\pi$ -electrons. The  $\sigma$ -framework strain energy of cyclobutadiene (arising from  $90^\circ$  instead of  $120^\circ$  bond angles) is *not* taken into account. This is fixed in the extended Hückel method developed by Roald Hoffmann (Nobel Prize 1981).

#### Bonding in Solids – metals, conductors, semiconductors, insulators

We can explain the difference between conductors, semiconductors, and insulators from simple LCAO-MO considerations. Up until now, we have been building the MOs assuming a particular internuclear separation. The  $s \approx 0$  approximation gave us the bonding and antibonding energies of  $E = \alpha \pm \beta$  where  $\alpha$  is the energy of an electron in an atomic orbital *in the molecular environment*. Since  $\alpha = (E_{\text{bonding}} + E_{\text{antibonding}})/2$ , this is, for different

internuclear separations, the average of the bonding and antibonding energies. Why does it change value?

(figure here)

Now for solids:  $n$  AOs combine to give  $n$  MOs. Think about sodium with a single valence electron  $3s^1$ . As we bring more and more atoms together with a *fixed* lattice spacing, the MO energies only spread out a finite amount; hence we get a band. To think about this, consider the lattice spacing to be *very* large. Then the width (the difference between bonding and antibonding energies) is essentially zero even though there are many, many MOs. To a first approximation we can just “fill in” the region between the highest and lowest MO energies with a continuum of levels (called a band).

Na (sodium,  $3s^1$ ): the 3s band is only half filled. The empty orbitals permit the movement of electrons by promoting electrons to the open levels at almost no energy cost. Therefore we have conductivity.

Mg (magnesium,  $3s^2$ ): the 3s band is filled, so it would seem there is no conduction? However, the 3p band overlaps the 3s band.

(figures for Na and Mg here)