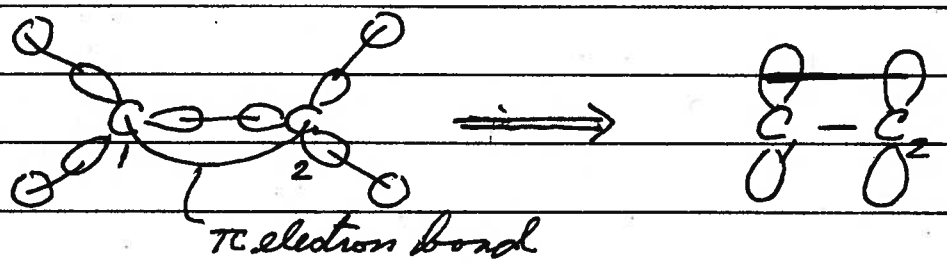
Hückel Theory - (Pi electron approximation)

Premise: σ electrons & π electrons may be treated separately

Consider the σ electron framework fixed. Solve for the molecular orbitals hosting the pi electrons

Ethene: $CH_2 = CH_2$



Determine π MO using variation principle

$$\varphi_\pi = \varphi = c_1 p_1 + c_2 p_2$$

p_1 & p_2 are π atomic orbitals on centers 1 & 2

c_1 & c_2 are to be determined

Use variation principle

$$\mathcal{E}(c_1, c_2) = \frac{\int \varphi^* \hat{H} \varphi \, d\tau}{\int \varphi^* \varphi \, d\tau}$$

Then $\frac{\partial \mathcal{E}}{\partial c_1} = \frac{\partial \mathcal{E}}{\partial c_2} = 0$

These equations result in

$$(H_{11} - \varepsilon S_{11}) C_1 + (H_{12} - \varepsilon S_{12}) C_2 = 0$$

$$(H_{12} - \varepsilon S_{12}) C_1 + (H_{22} - \varepsilon S_{22}) C_2 = 0$$

Where $H_{ij} = \int p_i^* \hat{H} p_j \, dv$

$$S_{ij} = \int p_i^* p_j \, dv$$

Since p_i are normalized p orbitals

$$S_{11} = S_{22} = 1$$

The Hückel approximation is

$H_{ii} = \alpha$ (an empirical parameter)
$H_{ij} = \beta$ $(i \neq j)$ (empirical)
$S_{ij} = 0$ if $i \neq j$

We then have

$$(\alpha - \varepsilon) C_1 + \beta C_2 = 0$$

$$\beta C_1 + (\alpha - \varepsilon) C_2 = 0$$

This results in the Secular equation

or $\frac{(\alpha - \varepsilon)}{\beta} C_1 + C_2 = 0$

$$- C_1 + \left(\frac{\alpha - \varepsilon}{\beta}\right) C_2 = 0$$

define $\frac{\alpha - \varepsilon}{\beta} = x$

Then $$x C_1 + C_2 = 0$$

$$C_1 + x C_2 = 0$$

for a non trivial solution we obtain the secular equation

$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0$$

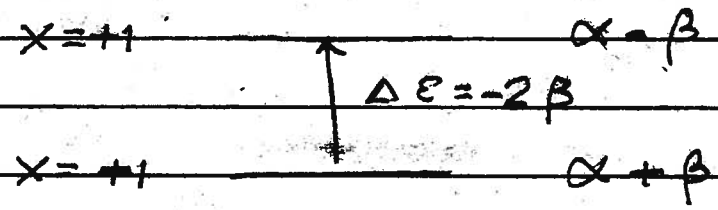
or $$x^2 - 1 = 0$$

$$\therefore \quad x = \pm 1$$

So $\varepsilon = \alpha \pm \beta$ are the allowed energies

(α & β are both negative. $\beta \cong -75$ kcals/mol)

$\therefore$ Energy levels are



Coefficients are given by

$$X C_1 + C_2 = 0$$

$$\frac{C_2}{C_1} = -X$$

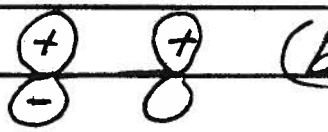
(Recall $\mathcal{E} = \alpha - \beta X$) so negative X corresponds to lower energy

$X = +1$ ——— $\alpha - \beta \Rightarrow \frac{p_1 - p_2}{\sqrt{2}}$

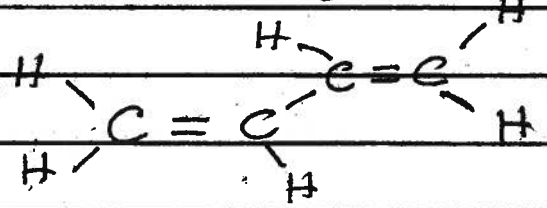
$X = -1$ ——— $\alpha + \beta \Rightarrow \frac{p_1 + p_2}{\sqrt{2}}$

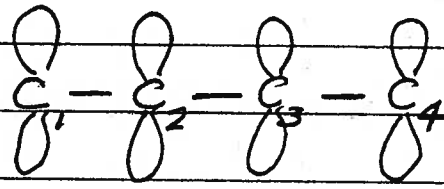
Consider the total π electron energy. With 2 electrons in the $\frac{p_1 + p_2}{\sqrt{2}}$ orbital the energy is

$$E_\pi = 2(\alpha + \beta)$$

Note $\frac{p_1 + p_2}{\sqrt{2}} \Rightarrow$  (bonding)

Consider butadiene





four pi electrons

π Molecular orbitals have the form

$$\varphi = \sum_{i=1}^{4} p_i c_i$$

Going through the usual variation procedure results in (using the Hückel approximation)

$$\begin{aligned} X c_1 + c_2 + 0 c_3 + 0 c_4 &= 0 \\ c_1 + X c_2 + c_3 + 0 c_4 &= 0 \\ 0 c_1 + c_2 + X c_3 + c_4 &= 0 \\ 0 c_1 + 0 c_2 + c_3 + X c_4 &= 0 \end{aligned}$$

where we have invoked an additional Hückel approximation.

$H_{ij} = 0$ whenever the atoms i & j are not directly bonded (~~not~~ nearest neighbors)

This results in the secular equation

$$\begin{vmatrix} X & 1 & 0 & 0 \\ 1 & X & 1 & 0 \\ 0 & 1 & X & 1 \\ 0 & 0 & 1 & X \end{vmatrix} = 0$$

So $x^4 - 3x^2 + 1 = 0$; $x^2 = \frac{3 \pm \sqrt{5}}{2}$

or $x = \pm 1.618$ & ∓ 0.618

$x = +1.618$ ——— $\alpha - 1.618\beta$

~~$x = +0.618$ ——— $\alpha - 0.618\beta$~~

$x = -0.618$ —⇅— $\alpha + 0.618\beta$

$x = -1.618$ —⇅— $\alpha + 1.618\beta$

Total π electron energy

$E_\pi = 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta)$

$E_\pi = 4\alpha + 4.472\beta$

Note that the E_π of two seperate ethenes is

$2E_\pi(CH_2CH_2) = 2(2\alpha + 2\beta) = 4\alpha + 4\beta$

The π electron energy of butadiene is lower by

0.472β & this is called the delocalization energy.

Lets see what the π MO's look like by solving for the c_i. Note that each root (value of x) has its own set of c_i's. We may solve for them in general as follows.

Since $C_1 x + C_2 = 0 \Rightarrow \frac{C_2}{C_1} = -x$

Since $C_1 + x C_2 + C_3 = 0$

$$1 + \frac{C_2}{C_1} x + \frac{C_3}{C_1} = 0 \Rightarrow \frac{C_3}{C_1} = -1 + x^2$$

Since $C_2 + x C_3 + C_4 = 0$

$$\frac{C_2}{C_1} + x \frac{C_3}{C_1} + \frac{C_4}{C_1} = 0$$

$$\frac{C_4}{C_1} = x - x(-1 + x^2) = 2x - x^3$$

$\therefore \psi = C_1 p_1 + C_2 p_2 + C_3 p_3 + C_4 p_4$

$$= C_1 \left(p_1 + \frac{C_2}{C_1} p_2 + \frac{C_3}{C_1} p_3 + \frac{C_4}{C_1} p_4 \right)$$

$$= C_1 \left\{ p_1 - x p_2 + (x^2 - 1) p_3 + (2x - x^3) p_4 \right\}$$

$\therefore$ we have a different set of coefficients for each x

& we fix C_1 by requiring

$$\int \psi \psi \, dv = 1 = C_1^2 \int \{ \quad \} \, dv$$

or $C_1^2 = \dfrac{1}{1 + x^2 + (x^2 - 1)^2 + (2x - x^3)^2}$

This results in $\psi_j = \sum_{i=1}^{4} p_i C_{ij}$; $j = 1,4$

$\psi_1 = 0.3717 p_1 + 0.6015 p_2 + 0.6015 p_3 + 0.3717 p_4$

$\psi_2 = 0.6015 p_1 + 0.3717 p_2 - 0.3717 p_3 - 0.6015 p_4$

$\psi_3 = 0.6015 p_1 - 0.3717 p_2 - 0.3717 p_3 + 0.6015 p_4$

$\psi_4 = 0.3717 p_1 - 0.6015 p_2 + 0.6015 p_3 - 0.3717 p_4$

When we have an electron in ψ_j it has the density

$$\psi_j^2 = \sum_{i=1}^{4} \sum_{k=1}^{4} p_i p_k C_{ij} C_{jk}$$

Integrating this gives 1 (the single electron in ψ_j)

$$\int \psi_j^2 dv = 1 = \sum_{i=1}^{4} \sum_{k=1}^{4} \delta_{ik} C_{ij} C_{jk} = \sum_{i=1}^{4} (C_{ij})^2$$

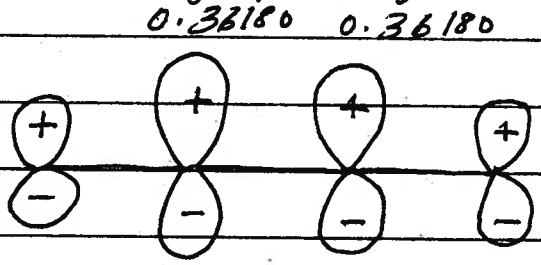
This suggests that the single electron is distributed over the four atoms as $(C_{ij})^2$. So for one electron in ψ_1 the fraction of it on atom 1 is $C_{11}^2 = 0.13816$
the fraction on atom 2 is $(0.6015)^2 = C_{12}^2 = 0.36180$
by symmetry the fraction on atom 3 is also 0.36180
& the fraction on atom 4 is 0.13816

Summing these gives 1.000 as required. Likewise if we had one electron in ψ_2 it would be distributed (among the 4 atoms) as

0.36180, 0.13816, 0.13816 & 0.36180.

We represent this graphically as

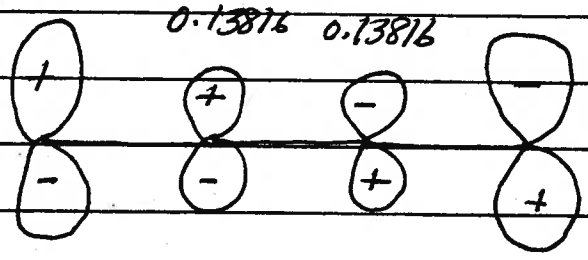
$\psi_1 =$



where the algebraic signs come from the signs in ψ_1

Likewise

$\psi_2 =$



Another useful index is the π bond order which is defined as

$$P_{rs}^{\pi} = \sum_{i=1}^{1} n_i C_{ri} C_{si}$$

$$p_{12}^{\pi} = 2\left\{(0.3717)(0.6015) + (0.6015)(0.3717)\right\}$$

$$= 0.8943 = p_{34}^{\pi}$$

$$p_{23}^{\pi} = 2\left\{(0.6015)^2 - (0.3717)^2\right\} = 0.4473$$

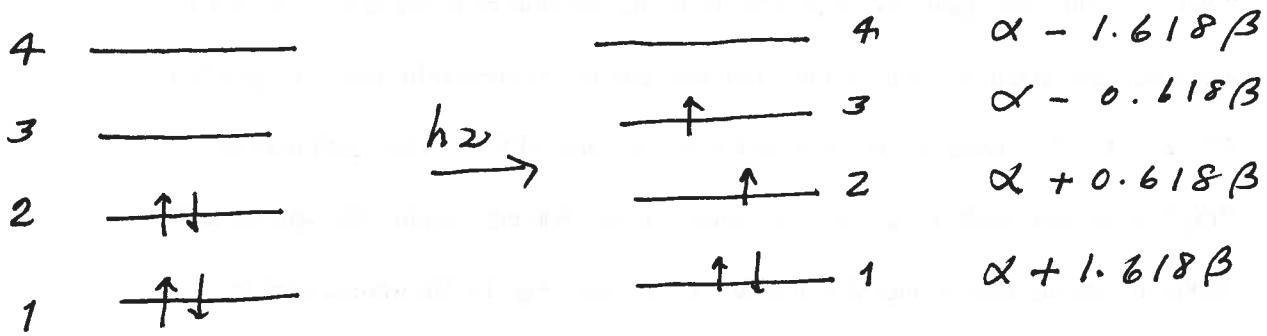
What is π "charge" on each atom?

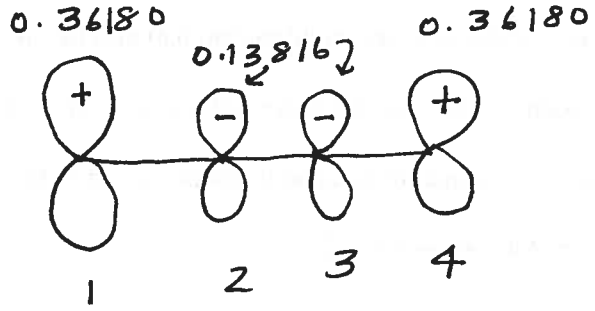
on atom $1.2\left((0.13816)^2 + (0.36180)^2\right)$

~~If~~ $N_1^{\pi} = 1.0$;

indeed $N_r^{\pi} = 1.0$; $r = 1, 2, 3$ & 4.

Suppose we excite from ψ_2 to ψ_3

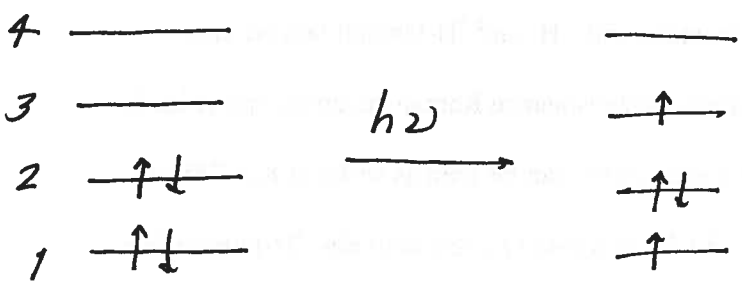




Charge on atom 1. $2(0.13816) + (0.3618) + (0.3618) = 1$

no change.

What if we excite from $\psi_1 \rightarrow \psi_3$

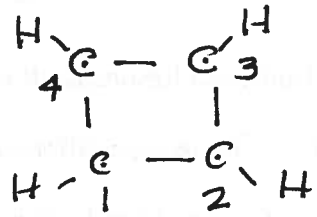


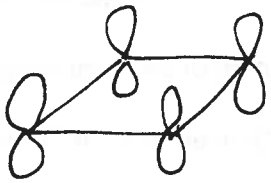
Charge on 1: $(0.13816) + 2(0.36180) + (0.36180)$

$= 1.22356$ ∴ terminal atoms become negative

$$(CH_2CHCHCH_2) \xrightarrow{h\nu} \overset{\delta-}{(}CH_2\overset{\delta+}{C}H\overset{\delta+}{C}H\overset{\delta-}{C}H_2)$$

Cyclobutadiene

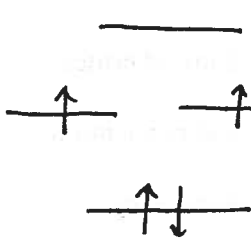




$$\begin{vmatrix} x & 1 & 0 & 1 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 1 & 0 & 1 & x \end{vmatrix} = 0 = x^2(x^2-4)$$

roots $x = 0, 0 ; x = \pm 2$

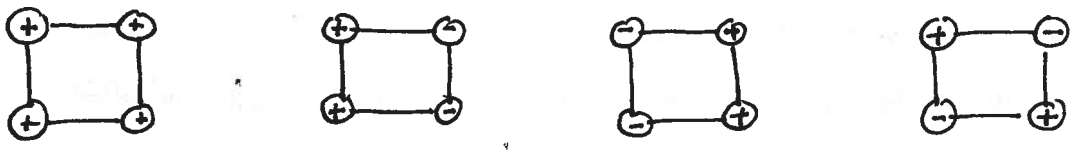
$$x = \frac{\alpha - E}{\beta} ; \quad E = \alpha - x\beta$$



$E_\pi = 2\alpha + 4\beta$

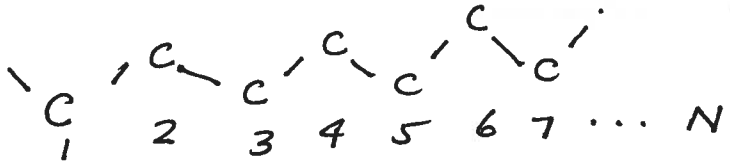
note: this is the same as two isolated CH_2CH_2 molecules

cyclobutadiene is very reactive (a di radical) & has only been isolated at low temp ~ 4K. It is not a square & has two short & two long bonds.



Linear Polyene:

Consider a "linear" molecule with N carbons



Set up the secular equation ☹ solve it ☺

$$E_j = \alpha + 2\beta \cos\left(\frac{j\pi}{N+1}\right) \qquad j = 1, 2, \ldots N$$

& if $\psi_j = \sum p_k C_{jk}$

$$C_{jk} = \sqrt{\frac{2}{N+1}} \sin\left(\frac{jk\pi}{N+1}\right) \; ; \; k = 1, 2, 3, \ldots N$$

Note: $N = 4$ (butadiene)

$$E_j = \alpha + 2\beta \cos\left(\frac{j\pi}{5}\right)$$

$$E_1 = \alpha + 2\beta \cos\frac{\pi}{5} = \alpha + 2\beta(0.8090) = \alpha + 1.6180\beta$$

$$E_2 = \alpha + 2\beta \cos\frac{2\pi}{5} = \alpha + 2\beta(0.3090) = \alpha + 0.6180\beta$$

$$E_3 = \alpha + 2\beta \cos\frac{3\pi}{5} = \alpha + 2\beta(-0.3090) = \alpha - 0.6180\beta$$

$$E_4 = \alpha + 2\beta \cos\frac{4\pi}{5} = \alpha + 2\beta(-0.8090) = \alpha - 1.6180\beta$$

The molecular orbitals are simply found

$$\psi_1 = c_{11}p_1 + c_{12}p_2 + c_{13}p_3 + c_{14}p_4$$

$$c_{11} = \sqrt{\frac{2}{3}} \sin$$

so $$c_{1k} = \sqrt{\frac{2}{5}} \sin\left(\frac{k\pi}{5}\right)$$

$$c_{11} = \sqrt{\frac{2}{5}} \sin\frac{\pi}{5} = \sqrt{\frac{2}{5}}(0.587785) = 0.3717$$

$$c_{12} = \sqrt{\frac{2}{5}} \sin\frac{2\pi}{5} = \sqrt{\frac{2}{5}}(0.9510565) = 0.6015$$

etc.

For cyclic chains with N even, the energies are given by

$$E_j = \alpha + 2\beta \cos\frac{2\pi j}{N} \quad ; \quad \cancel{N = 0, \pm 1}$$

$$j = 0, \pm 1, \pm 2, \cdots \pm\left(\frac{N}{2} - 1\right); \frac{N}{2}$$

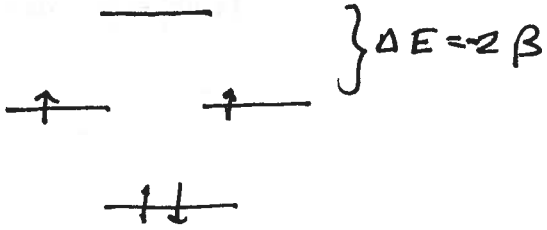
So for cyclic butadiene $N = 4$

$$j = 0, \pm 1, 2$$

$$E_0 = \alpha + 2\beta$$

$$E_{\pm 1} = \alpha + 2\beta \cos\frac{2\pi}{4} = \alpha$$

$$E_2 = \alpha + 2\beta \cos\pi = \alpha - 2\beta$$



These are the same eigenvalues as we derived before

\# for Benzene, $N = 6$

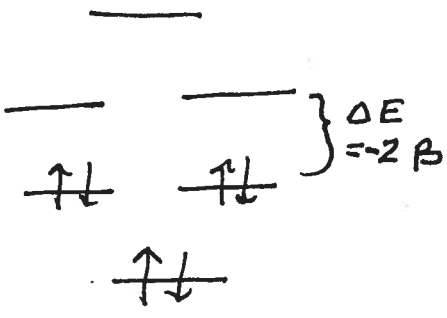
$$E_j = \alpha + 2\beta \cos\frac{\pi j}{3} \quad ; \quad j = 0, \pm 1, \pm 2, 3$$

$$E_0 = \alpha + 2\beta$$

$$E_{\pm 1} = \alpha + 2\beta \cos\frac{\pi}{3} = \alpha + \beta$$

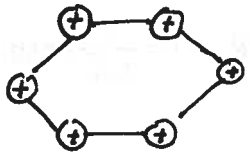
$$E_{\pm 2} = \alpha + 2\beta \cos\frac{2\pi}{3} = \alpha - \beta$$

$$E_3 = \alpha + 2\beta \cos\pi = \alpha - 2\beta$$

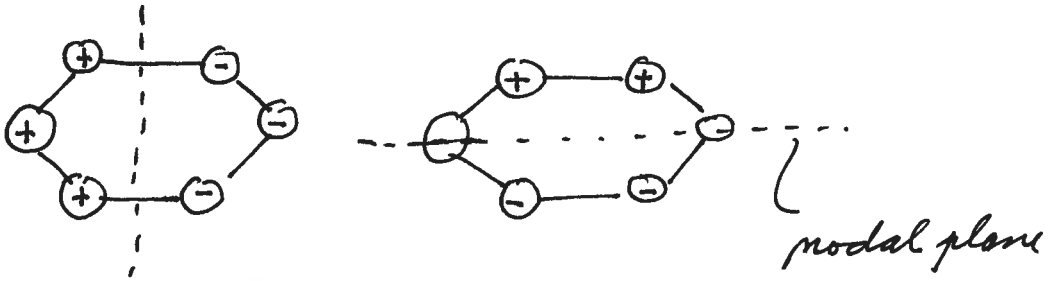


Benzene Orbitals

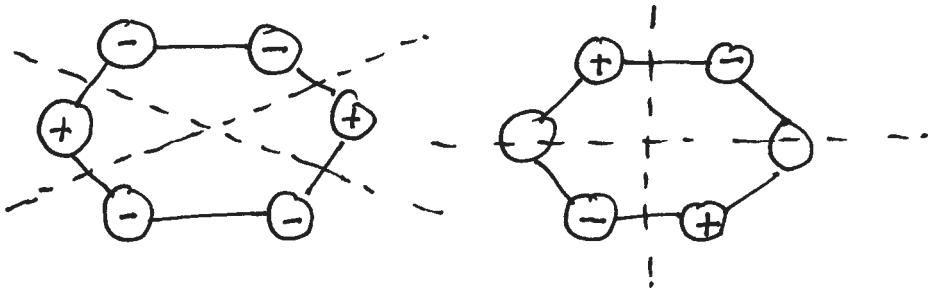
$E_0 \Rightarrow \psi_0 \Rightarrow$



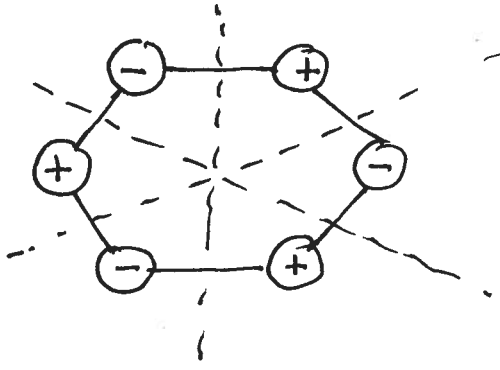
$\psi_{\pm 1} \Rightarrow$



$\psi_{\pm 2} \Rightarrow$

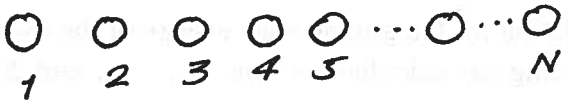


$\psi_3 \Rightarrow$



Model for one dimensional solid

"valence one electron atoms"



$$E_j = \alpha + 2\beta \cos\left(\frac{j\pi}{N+1}\right) \qquad j = 1, 2, \cdots N$$

Lowest energy $j = 1$.

$$E_1 = \alpha + 2\beta \cos\left(\frac{\pi}{N+1}\right)$$

Highest energy $j = N$

$$E_N = \alpha + 2\beta \cos\left(\frac{N\pi}{N+1}\right)$$

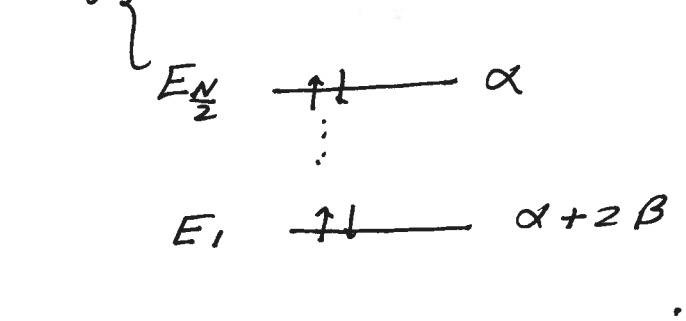
for large N

$$E_1 \cong \alpha + 2\beta \quad \& \quad E_N = \alpha - 2\beta$$

& for $\frac{N}{2}$

$$E_{\frac{N}{2}} = \alpha + 2\beta \cos\left[\frac{N\pi}{2(N+1)}\right]$$

$$\sim \alpha + 2\beta \cos\frac{\pi}{2} = \alpha$$



$\Rightarrow$ conductor