**M.Sc Second Semester CC7 Paper**
**Physical Chemistry**

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# Charge Density (Electron)

For a molecular orbital $\Psi_i = \sum_j Cij\ 2pj$ where $2p_j = 2p_z$ (j) where j refers to a specific carbon atom (or its electron). Since $2p_z$ orbitals are orthonormal, the normalization of $\Psi_i$ leads to

$$\int |\ \Psi i\ |^2\ dt = \sum_j Cij^2 \int |\ 2p_j\ |^2\ dt = 1$$

implies $\sum_j Cij^2 = 1$

This means $Cij^2$ is the fraction of the π–charge on the j-th carbon atom when there is an electron in i-th molecular orbital, $\Psi_i$. The sum of the π-electron charges of the j-the carbon atom on all the molecular orbitals gives the total π-electron charge on the j-th carbon atom and is given by

$$q_j = \sum_j n_i\ Cij^2$$

Where $n_i$ is the number of electrons (or carbon atoms) in the i-th molecular orbital.

For example in ethene,

$$E_1 = \alpha + \beta$$
$$E_2 = \alpha - \beta$$

$$q_1 = 2\ C_{11}^2 = 2 \text{ x } \left(\frac{1}{\sqrt{2}^2}\right) = 1$$

Similarly $q_2 = 1$

In case of butadienes,

$$q_1 = 2C_{11}^2 + 2C_{21}^2 + OC_{31}^2 + OC_{42}^2$$
$$= 2(0.3717)^2 + 2(0.6015)^2 = 1.000$$
$$q_2 = 2(0.6015)^2 + 2(0.3217)^2 = 1.00$$

Note that calculation should be carried out with bonding molecular orbitals only

# Bond Order

Between two adjacent carbon atoms, say r and s we have the corresponding coefficients $C_{ir}$, $C_{is}$ for the i-th molecular orbitals ($\Psi_i$).

We define π-bond order between two adjacent atoms (r,s) as

$$P_{rs} = \sum_i n_i \; C_{ir}.C_{is}$$

Where $n_i$ is the number of electrons in the i-th molecular orbital. Since there is also a σ-bond between the two carbon atoms, we define total bond order

$$P_{rs}^{total} = 1 + Prs = 1 + \sum_i n_i \; C_{ir}.C_{is}$$

In ethene:

$$P_{12} = 2C_{11}C_{12} = 2\frac{1}{\sqrt{2}}.\frac{1}{\sqrt{2}}$$

$$P_{12}^{total} = 1 + 1 = 2$$

In case of butadiene

$$P_{12} = 2C_{11}.C_{12} + 2C_{21}.C_{22}$$
$$= 2(0.3717 \text{ x } 0.6015) + 2(0.6015 \text{ x } 0.3717) = 0.894$$

$$P_{23} = 2C_{12}.C_{13} + 2C_{22}.C_{23}$$
$$=2(0.6015 \text{ x } 0.6015) + 2\ (0.3717 \text{ x } -0.3717) = 0.447$$

$$P_{34} = 2C_{13}.C_{14} + 2C_{23}.C_{24}$$
$$=2(0.6015 \text{ x } 0.3717) + 2(0.3717 \text{ x } 0.6015) =0.894$$

Therefore,

$$P_{12}^{total} = 1 + 0.894 = 1.894$$

$$P_{23}^{total} = 1 + 0.447 = 1.447$$