

**CHARGE, BOND ORDER, AND FREE VALENCE FROM MOLECULAR ORBITALS**  
*(primarily applied to pi-electron systems)*

0. The zero differential overlap (ZDO) approximation states that the integral  $\langle \chi_k | \chi_\ell \rangle \approx 0$  when  $\chi_k$  and  $\chi_\ell$  are atomic orbitals on different atoms  $k$  and  $\ell$ . Since the a.o.'s are normalized,  $\langle \chi_k | \chi_k \rangle = 1$ .

Thus in the ZDO approximation  $\langle \chi_k | \chi_\ell \rangle = \delta_{k\ell}$  for a.o.'s on atoms  $k$  and  $\ell$ .

1. For the molecular orbital  $\phi_i = \sum_{k=1}^{\text{a.o.'s}} c_{ki} \chi_k$ , **an electron** in that orbital would have the electron density distribution

$$\phi_i^2 = c_{1i} c_{1i}^* \chi_1 \chi_1^* + c_{1i} c_{2i}^* \chi_1 \chi_2^* + c_{2i} c_{1i}^* \chi_2 \chi_1^* + c_{2i} c_{2i}^* \chi_2 \chi_2^* + \dots = \sum_k \sum_\ell c_{ki} c_{\ell i}^* \chi_k \chi_\ell^*$$

2. **TOTAL CHARGE ON ATOM:** Since  $\langle \phi_i | \phi_i \rangle = 1$  (i.e. normalization, the total probability of finding the electron somewhere is 1) one has, using the ZDO:

$$\begin{aligned} \langle \phi_i | \phi_i \rangle = 1 &= c_{1i} c_{1i}^* \langle \chi_1 | \chi_1 \rangle + c_{1i} c_{2i}^* \langle \chi_1 | \chi_2 \rangle + c_{2i} c_{1i}^* \langle \chi_2 | \chi_1 \rangle + c_{2i} c_{2i}^* \langle \chi_2 | \chi_2 \rangle + \dots = \sum_k \sum_\ell c_{ki} c_{\ell i}^* \langle \chi_k | \chi_\ell \rangle \\ &\quad \Downarrow \qquad \qquad \qquad \Downarrow \qquad \qquad \qquad \Downarrow \qquad \qquad \qquad \Downarrow \qquad \qquad \qquad \Downarrow \\ &= c_{1i} c_{1i}^* 1 \qquad + \qquad 0 \qquad + \qquad 0 \qquad + \qquad c_{2i} c_{2i}^* 1 \qquad + \dots = \sum_k \sum_\ell c_{ki} c_{\ell i}^* \delta_{k\ell} = \sum_{k=1}^{\text{a.o.'s}} |c_{ki}|^2 \end{aligned}$$

Separating this probability into contributions from different atoms,  $q_{ki}$ , the probability of finding an (single) electron in m.o.  $i$ , on atom  $k$  is:  $q_{ki} = |c_{ki}|^2$

If molecular orbital  $i$  is filled with  $n_i$  electrons ( $n_i = 0, 1, 2$ , the orbital occupancy), the **total electron density at atom  $k$  is:**  $q_k = \sum_i n_i |c_{ki}|^2$

In a pi-electron molecule, each atom will contribute 1 or two electrons to the pi-systems leaving a "core charge" of +1 or +2 on the atom. The **net total charge** on an atom,  $\zeta_k$ , becomes:

$$\zeta_k = (\text{core})_k - q_k = (\text{core}) - \sum_i n_i |c_{ki}|^2$$

- 3. BOND ORDER (AMOUNT OF BONDING):** A measure related to the degree of constructive or destructive interference (i.e. bonding or antibonding) between a.o.'s on atoms  $k$  and  $\ell$  in m.o.  $i$  is the cross term in the electron density  $c_{ki}c_{\ell i}\chi_k\chi_\ell^*$ .

Although there are fancier measures used when orbital overlap is explicitly considered, most ZDO calculations give the bond order between atoms  $k$  and  $\ell$  in m.o.  $i$  as  $p_{k\ell}^i = c_{ki}c_{\ell i}^*$ ,  $k \neq \ell$ . A net measure of bonding is the total bond order between atoms  $k$  and  $\ell$ :

$$p_{k\ell} = \sum_i^{\text{mos}} n_i p_{k\ell}^i = \sum_i^{\text{mos}} n_i c_{ki} c_{\ell i}^*$$

Note that this formula gives a bond order of 1 (single pi-bond) for the two electrons in the lowest energy pi-orbital of ethylene.

- 4. FREE VALENCE (RADICAL CHARACTER):** (see Lowe pp 253-254) This measure attempts to give the relative degree to which an electron is available as a "free" on an atom as opposed to participating in bonding:

Free valence on atom  $k$ :

$$F_k = N_{\text{max}} - N_k$$

where  $N_k$  is the sum of bond orders for all atoms bonded to atom  $k$  and  $N_{\text{max}}$  is the maximum bond order sum for any  $sp^2$  carbon atom: the central carbon atom in trimethylene methane  $(\text{CH}_2)_3\text{C}$ . As we will calculate  $N_{\text{max}} = \sqrt{3} = 1.732$

- 5. ATOM POLARIZABILITY (DEGREE TO WHICH AN ATOM IS SUSCEPTIBLE TO HAVING AN OPPOSITE CHARGE INDUCED BY INCOMING ELECTROPHILE OR NUCLEOPHILE)** (see Lowe pp. 252-253)

$$\pi_{kk} \equiv 4 \sum_i^{\text{occ mos}} \sum_j^{\text{unocc mos}} \frac{c_{ki}^2 c_{kj}^2}{E_i - E_j}$$

- 6. APPROXIMATE BOND ORDER-BOND LENGTH RELATIONSHIP**

for pi-bond orders in unsaturated hydrocarbons (see Lowe, pp 228-229)

$$R_{k\ell} = s - \frac{s - d}{1 + k \frac{(1 - p_{k\ell})}{p_{k\ell}}}$$

$p_{k\ell}$  = pi-bond order between atoms  $k$  and  $\ell$

$s$  = 1.54 Å (single bond length)

$d$  = 1.337 Å (double bond length)

$k$  = 0.765 ('adjustable' parameter;

this is value used by the Huckel Program)