



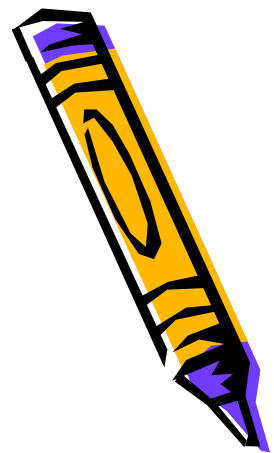
# Mulliken Population Analysis



1966 Nobel Prize motivation: "for Mulliken fundamental work concerning chemical bonds and the electronic structure of molecules by the molecular orbital method"



# The basics of quantum chemistry



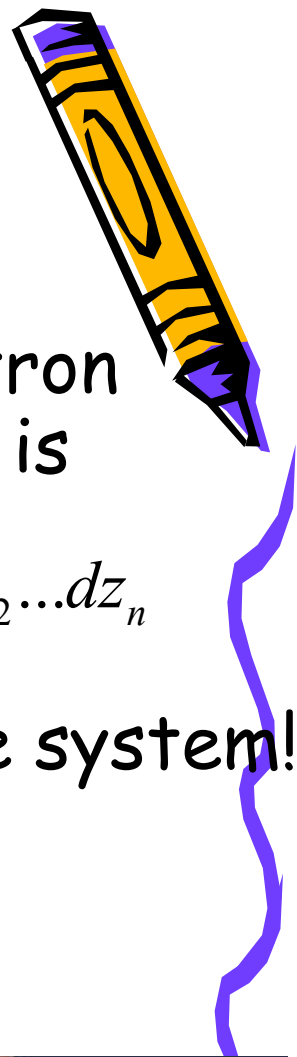
- The n-electronic wave function  $\psi$

$$|\psi(x_1, \dots, z_n, m_{s1}, \dots, m_{sn})|^2 dx_1 dy_1 dz_1 \dots dx_n dy_n dz_n$$

- probability of simultaneously finding  
 $\bar{e}$  1 with spin  $m_{s1}$  in the volume  $dx_1 dy_1 dz_1$  at  $(x_1, y_1, z_1)$   
 $\bar{e}$  2 with spin  $m_{s2}$  in the volume  $dx_2 dy_2 dz_2$  at  $(x_2, y_2, z_2)$   
and so on.



# One-electronic density



- The probability density  $\rho$  of finding an electron (**ANY!!!**) in the neighborhood of point  $(x,y,z)$  is

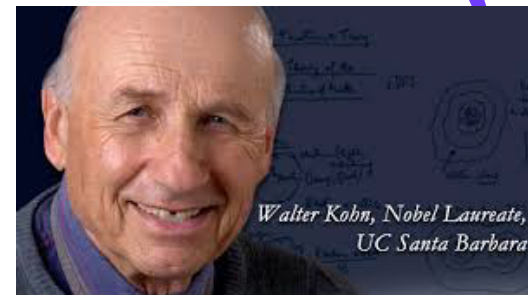
$$\rho(x, y, z) = n \sum_{\text{all } m_s} \int \dots \int |\psi(x, y, z, x_2, \dots, z_n, m_{s_1}, \dots, m_{s_n})|^2 dx_2 \dots dz_n$$

- In most cases - knowing the  $\rho$  is knowing the system!

$$\langle \hat{A} \rangle = \iiint A(x, y, z) \rho(x, y, z) dx dy dz$$

$$Z = \sum_{m_s} \iiint e \rho(x, y, z) dx dy dz = en$$

A **1.000.000\$** question –  
How does  $\rho$  look like?



# The Hartree-Fock case



- The n-electronic wave function  $\psi$  in the case of Hartree-Fock (HF) approximation:

$$\psi_{HF}(1, 2, \dots, n) = \det \begin{pmatrix} \phi_1(1) & \phi_2(1) \dots & \phi_n(1) \\ \phi_1(2) & \phi_2(2) \dots & \phi_n(2) \\ \dots & \dots & \dots \\ \phi_1(n) & \phi_2(n) \dots & \phi_n(n) \end{pmatrix}$$

- Home work (3 points bonus!). Prove:

$$\rho_{HF}(x, y, z) = \sum_j n_j |\phi_j|^2$$

$n_j$  is the "occupation number" ( $n_j = 0, 1, 2$ )



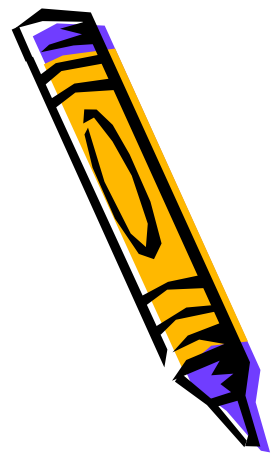
# The energy functional $\equiv$ density functional (W. Kohn)



- Exact WF: 
$$\rho(x, y, z) = \sum_j n_j |\phi_j|^2$$
- $n_j$  is the “generalized occupation number” ( $n_j \cong 0$  or  $1$ );  $\phi_j$  - natural orbitals  $j=1, \dots, \infty$
- Kohn - Sham :  $E = E[\Psi] = \int \Psi^* \hat{H} \Psi dV = E[\rho] = ?$
- HF:  $E^{HF}[\rho] = T[\rho] + V_{ne}[\rho] + (V_c[\rho] + V_{ex}[\rho])$
- DFT:  $E[\rho] = T[\rho] + V_{ne}[\rho] + (V_c[\rho] + V_{ex}[\rho] + V_{cor}[\rho])$   
single-electron theory including correlation!



# MO-LCAO approximation



- In the formula:  $\rho_{HF}(x, y, z) = \sum_j n_j |\phi_j(x, y, z)|^2$

$\rho$  is found as the sum the probability-density functions of all MOs  $\phi_j$

- The MOLCAO approximation:

$$\phi_j = \sum_{s=1}^b c_{sj} \chi_s = c_{1j} \chi_1 + c_{2j} \chi_2 + \dots + c_{bj} \chi_b$$

$$\text{Thus } \rho = \sum_{j=1}^m n_j \phi_j^* \phi_j = \sum_{r=1}^b \sum_{s=1}^b \sum_{j=1}^m n_j c_{rj}^* c_{sj} \chi_r^* \chi_s = \sum_{r=1}^b \sum_{s=1}^b D_{rs} \chi_r^* \chi_s$$

where  $m$  is the number of MOs;  
and  $b$  – is the number of AOs



# Density Matrix



$$D_{rs} = \sum_{j=1}^m n_j c_{rj}^* c_{sj}$$

- $c_{rj}$  – the contribution of  $r$ -AO to  $j$ -MO
- The probability density associated with one electron in  $\phi_j$  is  $|\phi_j|^2$

Normalization condition:

$$\int |\phi_j|^2 dV_j = 1 = c_{1j}^2 + c_{2j}^2 + \dots + c_{bj}^2 + \sum_{r < s} 2c_{rj} c_{sj} S_{rs}$$

where the  $S$ 's are overlap integrals:

$$S_{rs} = \int \int \chi_r \chi_s dv_r dv_s$$



# Mulliken population analysis

$$\int |\phi_j|^2 dV_j = 1 = c_{1j}^2 + c_{2j}^2 + \dots + c_{bj}^2 + \sum_{r < s} 2c_{rj}c_{sj}S_{rs}$$

- An electron in the MO  $\phi_j$  contributes :
  - ♦  $n_{rj} = n_j c_{rj}^2$  to the net population in AO  $\chi_r$ ,
  - ♦  $n_{r-s,j} = 2n_j c_{rj}c_{sj}S_{rs}$  to the overlap population of  $\chi_r$  and  $\chi_s$ .
- *Mulliken* proposed a method that apportions the electrons of an  $n$ -electron molecule into :
  1. Net populations  $n_r$  in the AOs;
  2. Overlap populations  $n_{r-s}$  for all pairs of AOs.

$$n_r = \sum_j n_{r,j} \quad \text{and} \quad n_{r-s} = \sum_j n_{r-s,j}$$





# Mulliken characteristics



- The sum of all the net and overlap populations equals the total number of electrons in the molecule:

$$\sum_r n_r + \sum_{r>s} \sum_s n_{r-s} = n = \int \rho dV = \sum_j n_j \int |\phi_j|^2 dV$$

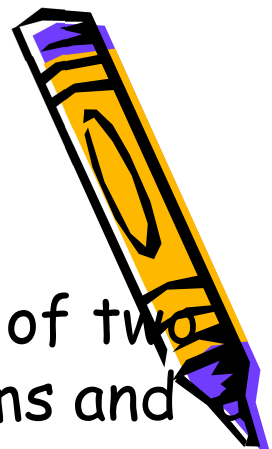
- Gross atomic (A) population :  $n_A = \sum_{r \in A} n_r + \frac{1}{2} \sum_{(r>s) \in A} \sum_{s \in A} n_{r-s}$
- Mulliken charge of atom A :  $Z_A = en_A$
- Mulliken's matrix ( $M_{rr} = n_r$  and  $M_{rs} = n_{r-s}$ ) could be divided according to atomic indexes A, B, ...

Then number of blocks in the A-B part of the matrix M defines bond order between atoms A and B

NOTE:  $M_{rs} = D_{rs} * S_{rs}$



# Bonding Mulliken population analysis example: $C_2H_2$



- $C\equiv C$  bonding. There are two  $\pi$  orbitals composed of two  $2p_x$  and two  $2p_y$  atomic orbitals of the two C atoms and  $\sigma$  bond composed of the  $1s$ ,  $2s$  and  $2p_z$  orbitals.
- The Gaussian output. Density matrix  $D_{rs}$  (C1-C2 part)

| C2\C1           | 1S       | 2S       | 2P <sub>Z</sub> | 2P <sub>X</sub> | 2P <sub>Y</sub> |
|-----------------|----------|----------|-----------------|-----------------|-----------------|
| 1S              | 0.04570  | -0.12510 | 0.14378         | 0.00000         | 0.00000         |
| 2S              | -0.12510 | 0.24810  | -0.28900        | 0.00000         | 0.00000         |
| 2P <sub>Z</sub> | -0.14378 | 0.28900  | -0.30554        | 0.00000         | 0.00000         |
| 2P <sub>X</sub> | 0.00000  | 0.00000  | 0.00000         | 0.75822         | 0.00000         |
| 2P <sub>Y</sub> | 0.00000  | 0.00000  | 0.00000         | 0.00000         | 0.75822         |

