Mulliken Population Analysis

electron density function $\rho(r)$

probability of finding an electron in a small volume element: $\int \rho(r)dr = n$

normalization: n is total number of electrons

$\rho(r)$ expressed by a set of A basis functions: $\rho(r) = \sum_{\mu,\nu}^{A} P_{\mu\nu} f_\mu^B f_\nu^B$

with the elements of the density matrix: $P_{\lambda\sigma} = 2\sum_{i=1}^{occ} c_{\lambda i}^* c_{\sigma i}$

integration : $\int \rho(r)dr = \sum_{\mu}^{A}\sum_{\nu}^{A} P_{\mu\nu} S_{\mu\nu} = n$

with normalized basis function ($S_{\mu\mu} = 1$):

$P_{\mu\mu}$ represents a number of electrons associated with a particular basis function f_μ^B, *net population* of f_μ^B

The sum of the off-diagonal elements: $Q_{\mu\nu} = 2P_{\mu\nu}S_{\mu\nu} \quad (\mu \neq \nu)$

is referred to as an *overlap population* (f_μ and f_ν maybe on the same atom or on 2 different atoms)

total electronic charge is now apportioned into two parts: $\sum_{\mu}^{A} P_{\mu\mu} + \sum_{\mu}^{A}\sum_{<\nu}^{A} Q_{\mu\nu} = n$

Gross population for f_μ: $q_\mu = P_{\mu\mu} + \sum_{\mu\neq\nu} P_{\mu\nu}S_{\mu\nu}$

This particular portioning scheme is NOT unique. Nor is any other!

Gross atomic population on atom X (f_μ centred on X): $q_X = \sum_{\mu}^{X} q_\mu$

total charge (Z_X = atomic number of X): $Z_X - q_X$