1 Löwdin and Mulliken population analysis

We have $|\phi_\mu\rangle$ atomic (or atomic-like) orbitals, not necessarily orthonormal, and we want to write KS orbitals for our system: $|\psi_\alpha\rangle$, as sums over said atomic orbitals:

$$|\psi_\alpha\rangle = \sum_\mu c_\mu^{(\alpha)} |\phi_\mu\rangle.$$

The generalized orthonormality relations for KS orbitals is written as:

$$\langle\psi_\alpha|\hat{S}|\psi_\beta\rangle = \delta_{\alpha\beta}.$$

where $\hat{S}$ is an operator defined in the US PP framework. The charge density $\rho(\mathbf{r})$ is given by

$$\rho(\mathbf{r}) = \sum_{\mu,\nu} P_{\mu\nu} \left(\phi_\nu^* \hat{S} \phi_\mu\right)(\mathbf{r})$$

where

$$P_{\mu\nu} = \sum_\alpha c_\mu^{(\alpha)} c_\nu^{(\alpha)*}$$

define an operator $\hat{P}$, and

$$\left(\phi_\nu^* \hat{S} \phi_\mu\right)(\mathbf{r}) = \phi_\nu^*(\mathbf{r})\phi_\mu(\mathbf{r}) + \sum_{lm} \langle\phi_\nu|\beta_l\rangle q_{lm}(\mathbf{r}) \langle\beta_m|\phi_\mu\rangle$$

where the β's and q's are components of the US PP.

1.1 Mulliken population analysis

We write the total number of electrons N as:

$$N = \int \rho(\mathbf{r}) d\mathbf{r} = \mathrm{Tr}\hat{P}\hat{S} = \sum_\mu (\sum_\nu P_{\mu\nu} S_{\nu\mu}) \equiv \sum_\mu q_\mu$$

where q_μ is the *Mulliken charge* associated to state μ :

$$q_\mu = \sum_\nu \sum_\alpha c_\mu^{(\alpha)} c_\nu^{(\alpha)*} S_{\nu\mu}$$

and

$$S_{\nu\mu} = \langle\phi_\nu|\hat{S}|\phi_\mu\rangle = \int \phi_\nu^*(\mathbf{r})\phi_\mu(\mathbf{r}) d\mathbf{r} + \sum_{lm} \langle\phi_\nu|\beta_l\rangle Q_{lm} \langle\beta_m|\phi_\mu\rangle$$

with

$$Q_{lm} = \int q_{lm}(\mathbf{r}) d\mathbf{r}.$$

In general, this matrix is not diagonal, even with NC PP. The coefficients $c_\mu^{(\alpha)}$ are obtained by inverting the linear system:

$$\langle\phi_\nu|\hat{S}|\psi_\alpha\rangle = \sum_\mu c_\mu^{(\alpha)} S_{\nu\mu}$$

that is

$$c_\mu^{(\alpha)} = (\hat{S}^{-1})_{\mu\nu}\langle\phi_\nu|\hat{S}|\psi_\alpha\rangle$$

and finally

$$q_\mu = \sum_{\alpha\nu}\langle\psi_\alpha|\hat{S}|\phi_\mu\rangle(\hat{S}^{-1})_{\mu\nu}\langle\phi_\nu|\hat{S}|\psi_\alpha\rangle.$$

1.2 Löwdin population analysis

The total number of electrons N can be alternatively written as

$$N = \mathrm{Tr}\left[\hat{S}^{1/2}\hat{P}\hat{S}^{1/2}\right] = \sum_\mu \tilde{q}_\mu.$$

where $\tilde{q}_\mu$ is called *Löwdin charge* associated to state μ. Let us introduce an auxiliary set of atomic orbitals $\tilde{\phi}$ via :

$$|\tilde{\phi}_\mu\rangle = \sum_\nu(\hat{S}^{-1/2})_{\nu\mu}|\phi_\nu\rangle, \qquad |\phi_\mu\rangle = \sum_\nu(\hat{S}^{1/2})_{\nu\mu}|\tilde{\phi}_\nu\rangle,$$

for which the generalized orthonormality relation

$$\langle\tilde{\phi}_\mu|\hat{S}|\tilde{\phi}_\nu\rangle = \delta_{\mu\nu}$$

holds. The KS orbitals for our systems can be rewritten as

$$|\psi_\alpha\rangle = \sum_\mu c_\mu^{(\alpha)}|\phi_\mu\rangle = \sum_\mu \tilde{c}_\mu^{(\alpha)}|\tilde{\phi}_\mu\rangle$$

where

$$\tilde{c}_\mu^{(\alpha)} = \sum_\nu(\hat{S}^{1/2})_{\nu\mu}c_\nu^{(\alpha)}.$$

By comparison with the above expression of $\tilde{q}_\mu$ we get

$$\tilde{q}_\mu = \sum_\alpha|\tilde{c}_\mu^{(\alpha)}|^2 = |\langle\tilde{\phi}_\mu|\hat{S}|\psi_\alpha\rangle|^2$$

Reference: *Modern Quantum Chemistry*, A. Szabo and N. Ostlund (Dover, NY 1996), p. 153