

Random Thoughts on Atomic-Site Electronegativity

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Given a molecular system with an external potential $v(\vec{r})$, Kohn-Sham density functional theory leads to a converged electron density, $\rho(\vec{r})$, and the corresponding energy, $E[\rho(\vec{r})]$.

Let us apply a small perturbation to the external potential,

$$v(\vec{r}) \longrightarrow v(\vec{r}) + \varepsilon \delta v(\vec{r}) \quad (1)$$

where ε is a parameter that we can use to tune the strength of the perturbation. This perturbation will cause a change in the electron density

$$\rho(\vec{r}) \longrightarrow \rho(\vec{r}) + \varepsilon \delta \rho(\vec{r}) \quad (2)$$

and in the atomic populations

$$N_A \longrightarrow N_A + \varepsilon \delta N_A \quad (3)$$

Due to the conservation of the number of electrons, we have

$$\sum_A \delta N_A = 0 \quad (4)$$

We can also compute the energy derivative with respect to ε ,

$$\frac{\partial E}{\partial \varepsilon} = \sum_A \left(\frac{\partial E}{\partial N_A} \right) \delta N_A \quad (5)$$

If we make the assumption that the atomic-site electronegativity value is the same for all atoms (A, B, C, ...),

$$\left(\frac{\partial E}{\partial N_A} \right) = \left(\frac{\partial E}{\partial N_B} \right) = \left(\frac{\partial E}{\partial N_C} \right) = \dots = \mu \quad (6)$$

the energy derivative in Eq. 5 becomes,

$$\frac{\partial E}{\partial \varepsilon} = \sum_A \left(\frac{\partial E}{\partial N_A} \right) \delta N_A = \mu \left[\sum_A \delta N_A \right] = 0 \quad (7)$$

which might correspond to Eq. 1.9 in Paul's note.

This is perplexing because this energy derivative seems to be non-vanishing in some cases. For example, when the external potential is changed by applying an electric field in the x-direction, the total energy might be linearly dependent on the value of ε with a slope proportional to the relaxed dipole moment of the molecule in the x-direction.