COMMENTS

Comment on “Contribution of the Shape Factor $\sigma(\vec{r})$ to Atomic and Molecular Electronegativities”

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In an interesting paper De Proft and Geerlings[1] studied the influence of the variation of the shape factor in the chemical potential of density functional theory, μ, which is associated with Mulliken’s definition of electronegativity,[2] χ_v. The shape factor, $\sigma(\vec{r})$, is defined through the relationship $\rho(\vec{r}) = N\sigma(\vec{r})$, where $\rho(\vec{r})$ is the electron density of the system with N electrons. From the study of the variations of the energy as function of N and functional of $\sigma(\vec{r})$, De Proft and Geerlings[1] arrived at the following equation for the electronegativity χ_v:

$$\chi_v = \chi_\sigma - \frac{1}{N}\int\left[\frac{\delta E}{\delta\sigma}\right]_N (f(\vec{r}) - \rho(\vec{r})/N)\,\mathrm{d}^3r \tag{1}$$

It consists of two contributions: the first one, χ_σ, is the variation of the electronegativity at constant shape factor, and the second one represents the variation in energy due to the variation of the shape factor at constant number of electrons modulated by a fluctuating term. $f(\vec{r})$ is the Fukui function.[3] An important quantity in this equation is the response function $[\delta E/\delta\sigma(\vec{r})]_N$. They found that

$$\left[\frac{\delta E}{\delta\sigma(\vec{r})}\right]_N = \int \rho(\vec{r}\,')\left[\frac{\delta v(\vec{r}\,')}{\delta\sigma(\vec{r})}\right]_N \mathrm{d}^3r' \tag{2}$$

Further, they analyzed it using an approximated perturbative model. In this Comment, we show that it is possible to elaborate further on this new response function and its implications for the electronegativity.

Recognizing that

$$\left[\frac{\delta v(\vec{r}\,')}{\delta\sigma(\vec{r})}\right]_N = N\frac{\delta v(\vec{r}\,')}{\delta\rho(\vec{r})} + N\frac{\delta\mu}{\delta\rho(\vec{r})} \tag{3}$$

where $\delta v(\vec{r})/\delta\rho(\vec{r}\,')$ is the inverse of the well-known density response function $\delta\rho(\vec{r})/\delta v(\vec{r}\,')$ and therefore obeys the important equation

$$\frac{\delta v(\vec{r}\,')}{\delta\rho(\vec{r})} = \frac{\delta v(\vec{r})}{\delta\rho(\vec{r}\,')} \tag{4}$$

The use of the fundamental equation of density functional theory

$$E[\rho(\vec{r})] = F[\rho(\vec{r})] + \int v(\vec{r})\,\rho(\vec{r})\,\mathrm{d}^3r \tag{5}$$

permits us to find that

$$\frac{\delta v(\vec{r}\,')}{\delta\rho(\vec{r})} = -\eta(\vec{r},\vec{r}\,') + \frac{\delta\mu}{\delta\rho(\vec{r}\,')} \tag{6}$$

where the definition of the hardness kernel has been used

$$\eta(\vec{r},\vec{r}\,') = \frac{\delta^2 F[\rho(\vec{r})]}{\delta\rho(\vec{r})\,\delta\rho(\vec{r}\,')} \tag{7}$$

The second term on the right-hand side of eqs 3 and 6 can be identified with the new function $h(\vec{r})$ introduced recently by Baekelandt et al.[4] Studying this new function they found that

$$\eta^\sigma = \int h(\vec{r})\,\sigma(\vec{r})\,\mathrm{d}^3r \tag{8}$$

where η^σ is the global hardness at constant σ.

Putting eq 6 into eq 3 one obtains

$$\left[\frac{\delta v(\vec{r}\,')}{\delta\sigma(\vec{r})}\right]_N = -N\eta(\vec{r},\vec{r}\,') + 2Nh(\vec{r}) \tag{9}$$

Equations 2−9 plus the definition of the local hardness, $\eta(\vec{r})$, yield the following exact equation for the response function in terms of more fundamental quantities as the number of electrons and local hardness function

$$\left[\frac{\delta E}{\delta\sigma(\vec{r})}\right]_N = -N^2\eta(\vec{r}) + 2N^2\eta^\sigma \tag{10}$$

The equation has a very simple physical interpretation. It says that the greater the hardness is, the more energy will be necessary to deformate the density in a specific point at a constant number of electrons. Because the hardness is inversely proportional to the polarizability, the equation is also in agreement with the finding of De Proft and Geerlings.[1] The energy cost to deformate the density will depend locally through the local hardness of the different regions of the molecule. This is an important property in considering the applications to molecules.

Putting eq 10 into eq 1, one finds

$$\chi_v = \chi_\sigma + N\eta - N\int\eta(\vec{r})\,(\rho(\vec{r})/N)\,\mathrm{d}^3r \tag{11}$$

This equation shows that the electronegativity is primordially determined by the flow of electrons. The variation of the density shape has a negligible contribution. This is so because the second and third term on the right-hand side of the last equation cancel out approximately. In the commonly used approximation of $f(\vec{r}) = \rho(\vec{r})/N$, they cancel out exactly. Moreover, Chattaraj et al.[5] have showed that in the gradient expansion for the Fukui function

$$f(\vec{r}) = (\rho(\vec{r})/N)(1 + \alpha\phi(\vec{r};\,\rho(\vec{r}),\,\nabla\rho(\vec{r}),\,...)) \tag{12}$$

the parameter α is very small in all the studied cases. Therefore, any contribution of the variation of σ at constant N to the

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electronegativity comes only from the gradient term of the Fukui function and will be small.

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References and Notes

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