# Contribution of the Shape Factor $\sigma(\mathbf{r})$ to Atomic and Molecular Electronegativities

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The contribution of the shape factor $\sigma(\mathbf{r})$ to the electronegativity is established. This shape factor, measuring the shape of the electron density $\rho(\mathbf{r})$, is defined as $\sigma(\mathbf{r}) = \rho(\mathbf{r})/N$ and integrates to unity: $\int\sigma(\mathbf{r})\,\mathrm{d}\mathbf{r} = 1$. A new response function is thereby introduced, giving the change of the energy of an atomic or molecular system with respect to the shape factor $\sigma(\mathbf{r})$. Finally, a physical interpretation is given for this response function.

## 1. Introduction

In density-functional theory,[1] the electronic chemical potential $\mu$ of an atomic or molecular system is defined as the derivative of the energy $E$ with respect to the number of electrons $N$ at a constant external potential $v(\mathbf{r})$ (i.e., the potential due to the nuclei in the system):

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{\nu(\mathbf{r})} \tag{1}$$

Following Iczkowski and Margrave,[2] Parr and co-workers identified this chemical potential with the negative of the electronegativity $\chi$ (i.e., $\mu = -\chi$).[3] In practice, this derivative 1 is calculated using a finite difference approximation with $\Delta N = \pm 1$:[4]

$$\mu \approx \left(\frac{\Delta E}{\Delta N}\right)_{\nu(\mathbf{r})} \tag{2}$$

Using this approximation in combination with a quadratic relationship for the $E = E[N]$ curve, one finds the well-known Mulliken expression[5] for the electronegativity:

$$\chi = \frac{I + A}{2} \tag{3}$$

with $I$ and $A$ the ionization energy and electron affinity, respectively. It can thus be seen that an evaluation of $\chi$ requires the knowledge of the system's energy response to a change in number of electrons. Due to the Hohenberg and Kohn theorms,[6] the number of electrons $N$ exactly determines the electron density at constant external potential. This electron density $\rho(\mathbf{r})$ can be written as the product of this number of electrons $N$ and a shape factor $\sigma(\mathbf{r})$:[1,7]

$$\rho(\mathbf{r}) = N\sigma(\mathbf{r}) \tag{4}$$

From this expression, it can be seen that the number of electrons determines the size or extent of the electron density, whereas the shape is determined by $\sigma(\mathbf{r})$.

A detailed theoretical analysis of the influence of the variation of this shape factor on the electronegativity, which is given in the next section, was not yet established hitherto.

## 2. Contribution of the Shape Factor Variation to Electronegativity

We start from the two functional relationships

$$E = E[N,\nu] \tag{5}$$

(ref 1) and

$$E = E[N,\sigma] \tag{6}$$

That the latter relationship is meaningful is seen via equation 4: $\sigma$ and $N$ determine $\rho$ and therefore $N$, via the Hohenberg Kohn theorem,[6] $E$.

A change in energy from one ground state to another can thus be written in the following two ways:

$$\mathrm{d}E = \left(\frac{\partial E}{\partial N}\right)_{\nu} \mathrm{d}N + \int\left(\frac{\delta E}{\delta \nu(\mathbf{r})}\right)_{N} \delta\sigma(\mathbf{r})\,\mathrm{d}\mathbf{r} \tag{7}$$

or

$$\mathrm{d}E = \left(\frac{\partial E}{\partial N}\right)_{\sigma} \mathrm{d}N + \int\left(\frac{\delta E}{\delta \sigma(\mathbf{r})}\right)_{N} \delta\sigma(\mathbf{r})\,\mathrm{d}\mathbf{r} \tag{8}$$

Now $\sigma$ is a functional of $N$ and $v$,

$$\sigma = \sigma[N,\nu] \tag{9}$$

Since $N$ and $v$ determine $\rho$ and $N$ is known, $\sigma$ is also known. Expressing the variation of $\sigma$ in eq 8 via eq 9 and equating the coefficients of the independent variables in eqs 7 and 8, one obtains

$$\left(\frac{\partial E}{\partial N}\right)_{\nu} = \left(\frac{\partial E}{\partial N}\right)_{\sigma} + \int\left(\frac{\delta E}{\delta \sigma(\mathbf{r})}\right)_{N}\left(\frac{\partial \sigma(\mathbf{r})}{\partial N}\right)_{\nu} \mathrm{d}\mathbf{r} \tag{10}$$

Using eq 4, the derivative $(\partial\sigma(\mathbf{r})/\partial N)_{\nu}$ can be written as

$$\left(\frac{\partial \sigma(\mathbf{r})}{\partial N}\right)_{\nu} = \frac{\partial}{\partial N}\left(\frac{\rho(\mathbf{r})}{N}\right)_{\nu} = \frac{1}{N}\left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)_{\nu} - \frac{1}{N^2}\rho(\mathbf{r}) = \frac{1}{N}\left(f(\mathbf{r}) - \frac{\rho(\mathbf{r})}{N}\right) \tag{11}$$

where we introduced the Fukui function $f(\mathbf{r})$.[1]

The term between brackets then represents the deviation of the Fukui function from the average electron density per electron, a combination intergrating to zero upon multiplication by the hardness kernel as pointed out by Ghosh.[8] Combining eqs 10 and 11, we obtain

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$$\left(\frac{\partial E}{\partial N}\right)_{\nu} = \left(\frac{\partial E}{\partial N}\right)_{\sigma} + \frac{1}{N}\int\left(\frac{\delta E}{\delta\sigma(\mathbf{r})}\right)_{N}\left(f(\mathbf{r}) - \frac{\rho(\mathbf{r})}{N}\right)\mathrm{d}\mathbf{r} \qquad (12)$$

or in terms of the electronegativity

$$\chi_{\nu} = \chi_{\sigma} - \frac{1}{N}\int\left(\frac{\delta E}{\delta\sigma(\mathbf{r})}\right)_{N}\left(f(\mathbf{r}) - \frac{\rho(\mathbf{r})}{N}\right)\mathrm{d}\mathbf{r} \qquad (13)$$

The electronegativity thus consists of two terms: an energy variation at constant shape factor and a contribution due to the variation of the shape factor at constant number of electrons modulated by a fluctuation term, involving the deviation of the Fukui function from the average electron density per electron. It is interesting to note that very recently Baekelandt, Cedillo, and Parr obtained a similar expression for the second derivative of $E$ with respect to $N$, the hardness.[9] In the next paragraph, the new response function, $(\partial E/\delta\sigma(\mathbf{r}))_N$ to be placed on equal footing with the well-known first-order response functions $(\partial E/\partial N)_{\nu}$ $(= -\chi_{\nu})$ and $(\delta E/\delta\nu(\mathbf{r}))_N$ $(=\rho(\mathbf{r}))$,[10] will be studied in more detail.

## 3. Interpretation of the new Response Function $(\delta E/\delta\sigma(\mathbf{r}))_N$

An exact expression of the new response function can be derived from perturbation theory. The change in external potential due to a change in number of electrons and shape factor is expressed via the first-order expression as[9]

$$\Delta\nu(\mathbf{r}) = \left(\frac{\partial\nu(\mathbf{r})}{\partial N}\right)_{\sigma}\Delta N + \int\left[\frac{\delta\nu(\mathbf{r})}{\delta\sigma(\mathbf{r}')}\right]_{N}\Delta\sigma(\mathbf{r}')\,\mathrm{d}\mathbf{r}' \qquad (14)$$

For a state $\Psi_k$, the first-order contribution to the energy due to this perturbation is[1]

$$E_k^{(1)} = \int\Psi_k^{*}\Delta\nu(\mathbf{r})\Psi_k\,\mathrm{d}x^N = \int\rho_k(\mathbf{r})\Delta\nu(\mathbf{r})\,\mathrm{d}\mathbf{r} \qquad (15)$$

Insertion of eq 14 in eq 15 yields

$$E_k^{(1)} = \int\left(\frac{\partial\nu(\mathbf{r})}{\partial N}\right)_{\sigma}\rho_k(\mathbf{r})\,\mathrm{d}\mathbf{r}\,\Delta N + \int\int\left[\frac{\delta\nu(\mathbf{r})}{\delta\sigma(\mathbf{r}')}\right]_{N}\rho_k(\mathbf{r})\Delta\sigma(\mathbf{r}')\,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}' \qquad (6)$$

Identification with eq 8 yields

$$\left[\frac{\delta E}{\delta\sigma(\mathbf{r})}\right]_{N} = \int\rho(\mathbf{r}')\left[\frac{\delta\nu(\mathbf{r}')}{\delta\sigma(\mathbf{r})}\right]_{N}\mathrm{d}\mathbf{r}' \qquad (17)$$

which, unfortunately, does not provide any additional physical insight into the new response function.

The question now arises as to how a change in shape factor can be accomplished at a constant number of electrons $N$. Within an orbital formalism (closed shell case), the shape factor $\sigma(\mathbf{r})$ can be written as

$$\sigma(\mathbf{r}) = \frac{1}{N}\sum_{i=1}^{N}|\psi_i(\mathbf{r})|^2 \qquad (18)$$

One possible way to model the change in shape factor, leaving the number of electrons constant, is substitution of one particular orbital $\psi_i$ in this expression by a different one, $\psi_j$. The shape factor then becomes

$$\sigma(\mathbf{r}) = \frac{1}{N}[|\psi_1|^2 + |\psi_2|^2 + ... + |\psi_{i-1}|^2 + |\psi_{i+1}|^2 + ... + |\psi_N|^2 + |\psi_j|^2] \qquad (19)$$

The contribution to the electronegativity due to the change in shape factor, governed by the new response function $(\delta E/\delta\sigma(\mathbf{r}))_N$, can now be evaluated in a finite difference approximation

$$\left(\frac{\delta E}{\delta\sigma(\mathbf{r})}\right)_{N} \approx \left(\frac{\Delta E}{\Delta\sigma(\mathbf{r})}\right)_{N} \qquad (20)$$

Using a Koopmans type approximation, the finite difference expression of the response function then becomes

$$\left(\frac{\Delta E}{\Delta\sigma(\mathbf{r})}\right)_{N} \approx \frac{\epsilon_j - \epsilon_i}{|\psi_j(\mathbf{r})|^2 - \psi_i(\mathbf{r})|^2}N \qquad (21)$$

It can immediately be seen that in this approximation, the response function will be zero when the orbitals $i$ and $j$ have the same energy (i.e., when they belong to a degenerate set of orbitals).

Finally, consider the special case where $\psi_i$ and $\psi_j$ are the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the atomic or molecular system. The response function becomes

$$\left(\frac{\Delta E}{\Delta\sigma(\mathbf{r})}\right)_{N} \approx \frac{\epsilon_{\mathrm{LUMO}} - \epsilon_{\mathrm{HOMO}}}{|\psi_{\mathrm{LUMO}}(\mathbf{r})|^2 - |\psi_{\mathrm{HOMO}}(\mathbf{r})|^2}N \approx N\frac{\eta}{|\psi_{\mathrm{LUMO}}(\mathbf{r})|^2 - |\psi_{\mathrm{HOMO}}(\mathbf{r})|^2} \qquad (22)$$

with $\eta$ the hardness.[11] Due to the proportionality of the hardness and the inverse of the polarizability $\alpha$,[12] eq 22 can be rewritten as

$$\left(\frac{\Delta E}{\Delta\sigma(\mathbf{r})}\right)_{N} \propto \frac{N}{\alpha}\frac{1}{(|\psi_{\mathrm{LUMO}}(\mathbf{r})|^2 - |\psi_{\mathrm{HOMO}}(\mathbf{r})|^2)} \qquad (23)$$

As could be intuitivily expected, the polarizability shows up in the expression for the new response function. The results indicates that the more polarizable a system, the smaller the energy change associated with a change in shape factor, in agreement with chemical intuition. A polarizable system will thus show the tendency to change its shape factor more easily under the application of an external perturbation than a less polarizable system. The HOMO−LUMO density difference transforms the polarizability (a global property) in a local property. It has to be remarked finally that eq 23 only provides a very crude approximation to the real response function in this case, only serving to provide physical insight in the problem. A change in shape factor at constant number of electrons can only be calculated exactly by infinitesimally changing each Kohn−Sham orbital, thereby preserving orthonormality of each orbital couple.

## 4. Conclusion

The contribution of the shape factor to the electronegativity was established. This gave rise to a new response function representing the change of the system's energy with respect to this shape factor, which shows an inverse proportionality with the polarizability.

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