

On the exponential model for energy with respect to number of electrons

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Abstract Using an exponential model for the variation in energy with respect to the number of electrons it is shown that, within the model, the hardness, softness, electrophilicity and other global parameters connected to higher order derivatives follow an equalization principle after a molecule is formed from two separated species. Two generalizations of the model are also discussed, one of which presents discontinuity of the chemical potential at integer values of N .

Keywords Energy of atoms · Equalization rules · Derivative discontinuity

In the density functional chemical reactivity theory [1–6] the electronic chemical potential [7] has an important meaning, being identified, in some approximations, as the negative of the electronegativity as defined many years ago by Mulliken [8]. Higher order derivatives of the energy with respect to the number of electrons have also been subject to chemical interpretation [9–13]. The electronic chemical potential,

$$\mu = \left(\frac{\partial E}{\partial N} \right)_v, \quad (1)$$

like the macroscopic chemical potential of thermodynamics, has the property of equalization. This means that electrons flow from regions of high chemical potential to regions of low chemical potential until the chemical potential of the whole system equalizes. This very appealing similarity with the macroscopic chemical potential of thermodynamics has, however, a profound complexity because of the discontinuity of

the electronic chemical potential at integer number of electrons [14–23]. To advance in the chemical interpretation one has to resort to empirical models. Very recently, Chattaraj et al. [24] proposed a similar equalization principle for electrophilicity. One of the purposes of this work is to show that this result comes directly from using the exponential model. Hence, a simple model based on the geometric mean principle of chemical potential equalization will be discussed. It can be considered as an extension of the model presented years ago by Parr and Bartolotti [25], which has been discussed recently with numerical examples by Chattaraj et al. [24]. Later, some possible refinement of the model to include discontinuity of the chemical potential will be discussed.

When atoms A and B come together before charge transfer occurs, both of them are in a valence state [26] with chemical potential μ_A^0 and μ_B^0 , numbers of electrons N_A^0 , N_B^0 , and external potentials $v_A^0(r)$, $v_B^0(r)$ which do not necessarily correspond with the values for atoms A and B completely isolated in the universe. The model presented here addresses the question of what are the values of μ_A , μ_B , N_A , N_B after charge transfer occurs. Our model is based on the exponential dependence of the energy with respect to the number of electrons as proposed by Parr and Bartolotti [25],

$$E(N) = Ce^{-\alpha(N-Z)} + D \quad (2)$$

in such a way that,

$$\mu = \mu^0 e^{-\alpha(N-Z)} \quad (3)$$

where $\mu^0 = -\alpha C$, i.e., the chemical potential of the species before the charge transfer occurs. Although α is not a universal constant, it was found to fall within a “narrow” range ($\alpha = 2.15 \pm 0.59$).

Combining both equations

$$E(N) = E(N_0) - \frac{\mu^0}{\alpha} \left(e^{-\alpha(N-Z)} - 1 \right) \quad (4)$$

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where $E(N_0)$ is the energy of the neutral atom. Now, suppose the charge transfer is allowed to occur and some amount of charge ΔN flows from A to B or vice versa. The energy of the new composite quasimolecule will be

$$\begin{aligned} E_{AB}(\Delta N) &= E_A(N_A + \Delta N) + E_B(N_B - \Delta N) \\ &= E_A(N_0) + E_B(N_0) - \frac{\mu_A^0}{\alpha} (e^{-\alpha(\Delta N)} - 1) \\ &\quad - \frac{\mu_B^0}{\alpha} (e^{\alpha(\Delta N)} - 1) \end{aligned} \quad (5)$$

which attains a minimum with respect to electron transfer when the number of electrons transferred from B to A is

$$\Delta N^* = -\frac{1}{2\alpha} \ln\left(\frac{\mu_B^0}{\mu_A^0}\right) \quad (6)$$

Introducing Eq. (6) into Eq. (3) one finds that the chemical potential of atoms A and B after charge transfer are equalized to the geometric mean

$$\mu_A(\Delta N^*) = \mu_B(\Delta N^*) = -\sqrt{\mu_A^0 \mu_B^0} \quad (7)$$

This geometric mean equalization principle was postulated by Sanderson [27] decades ago.

Higher derivatives of the energy with respect to the number of electrons are readily found. For instance, the hardness [28–30] is given by

$$\eta = \frac{\partial^2 E}{\partial N^2} = -\alpha \mu^0 e^{-\alpha(N-Z)}, \quad (8)$$

which, after charge transfer, and using the ΔN of Eq. (6) obtained at first order, also becomes equalized

$$\eta_A(\Delta N^*) = \eta_B(\Delta N^*) = \sqrt{\eta_A^0 \eta_B^0}. \quad (9)$$

In general, the k -th derivative

$$\frac{\partial^k E}{\partial N^k} = (-1)^{k+1} \alpha^{k-1} \mu^0 e^{-\alpha(N-Z)} \quad (10)$$

is equalized after charge transfer.

Interesting, the electrophilicity as introduced by Parr et al. [31] is

$$\omega = \frac{\mu^2}{\eta}, \quad (11)$$

which is, in this model, equal to the negative of the chemical potential divided by the constant α , $\omega = -\frac{\mu}{\alpha}$ and, after charge transfer, it becomes also equalized in a geometric mean:

$$\omega_A(\Delta N^*) = \omega_B(\Delta N^*) = \sqrt{\omega_A^0 \omega_B^0} \quad (12)$$

This latter equation was proposed by Chattaraj et al. [24] assuming the validity of the equalization of the chemical potential and the hardness. They found reasonable numerical evidence to justify this equalization principle.

Note also that the equalization is easily generalized to a polyatomic system,

$$(\mu_{ABC\dots P})^P = \prod_{i=A}^P \mu_i^0, \quad (13)$$

provided that the energy of all the participating atoms presents the same fall-off. To assume, however, that the exponential factor α is the same for all atoms has some unsuitable consequences. The higher derivatives of the energy with respect to the number of electrons converge only if $0 < \alpha < 1$, which seems to contradict the value found by Parr and Bartolotti ($\alpha = 2.15 \pm 0.59$) [25]. This might suggest that (1) the model is suitable only for low order derivatives, or (2) the parameter cannot be considered universal and a different parameter must be assigned for each species. The last possibility will be now discussed.

In the more general case, each atom has a characteristic decaying parameter, α , and the chemical potential as a function of the number of electrons will be given by

$$\begin{aligned} \mu_A &= \mu_A^0 e^{-\alpha_A(N_A - Z_A)} \\ \mu_B &= \mu_B^0 e^{-\alpha_B(N_B - Z_B)} \end{aligned} \quad (14)$$

Then, the energy of the quasimolecule AB after charge transfer will be

$$\begin{aligned} E_{AB}(\Delta N) &= E_A(N_A + \Delta N) + E_B(N_B - \Delta N) \\ &= E_A(N_0) + E_B(N_0) - \frac{\mu_A^0}{\alpha_A} (e^{-\alpha_A(\Delta N)} + 1) \\ &\quad - \frac{\mu_B^0}{\alpha_B} (e^{\alpha_B(\Delta N)} + 1), \end{aligned} \quad (15)$$

which attains a minimum with respect to the electron transfer when the number of electrons transferred is

$$\Delta N^* = -\frac{\ln\left(\frac{\mu_B^0}{\mu_A^0}\right)}{\alpha_A + \alpha_B} \quad (16)$$

In the equilibrium, the chemical potential of A, B and AB equalize. In contrast to the previous case, the chemical potential of the composed system does not become exactly the geometric mean of the chemical potentials of the isolated species,

$$\mu_A(\Delta N^*) = \mu_B(\Delta N^*) = \sqrt{\mu_A^0 \mu_B^0} \left(\frac{\mu_B^0}{\mu_A^0}\right)^{\frac{1}{2\alpha_A + \alpha_B}}. \quad (17)$$

Similar relations can be obtained for hardness and electrophilicity.

Summarizing, it has been demonstrated that the exponential model for the dependence of the energy of an atom or molecule as a function of the number of electrons allows a general geometric mean equalization principle to be derived for most of the global reactivity parameters commonly used in the density functional theory of chemical reactivity [3, 32, 33]. The equalization of chemical potential after charge

transfer is a well-known matter [25, 34–39]. The equalization of hardness has some troubles because of poor definition of local hardness [11, 39–46]. Depending on the definition, the local hardness could be a constant [39]. The equalization of electrophilicity should mean that there is no chemical meaning in local electrophilicity. As pointed out by Chattaraj et al. [24], as an electrophile interacts with a nucleophile its electrophilicity is reduced because of charge transfer, and the opposite happens to the nucleophile. Hence, it seems reasonable to expect a final equalization [47].

Energy as an exponential decaying function of the number of electrons is a very reasonable assumption and, in many respects, more reasonable than the quadratic model [29, 48]. It is a monotonically decaying convex function that can also, in a limited manner, explain the electron saturation of the atomic or molecular species. It is known that an atom cannot be stable with more than one negative charge [48]. However, the quadratic model has been the model most used because it accounts for the negative of the chemical potential, the Mulliken’s definition of electronegativity, and gives very simple formulas for hardness and other local parameters, which is not the case for the exponential model where the value of the parameter α remains as a free variable that is very probably different for each atomic or molecular species. However, both models and the variant presented here suffer from not including the discontinuity of the chemical potential at integer number of electrons. Here, we propose a new modification of the exponential model that presents a discontinuity in the chemical potential.

Define the energy as a function of the number of electrons as

$$E(N) = ce^{-\alpha(N)(N-Z)} + d \tag{17}$$

with $\alpha(N)$ defined as

$$\alpha(x) = \sum_{i=0}^M \alpha_i \chi_{A_i}(x); \quad M \geq N, \alpha_i \in \mathbb{R} \tag{18}$$

A_i are open intervals between $(i, i+1)$ with i an integer, and

$$\chi_A(x) = \begin{cases} 1 & \text{if } x \in A \\ h \neq 1 & \text{otherwise} \end{cases} \tag{19}$$

with h a constant. In general, the constant is undefined and it is not necessary to know its value. For example, consider the energy of a neutral atom and its first two cations

$$\begin{aligned} E(N = Z) &= c + d \\ E(N = Z - 1) &= ce^{-\beta_Z} + d \\ E(N = Z - 2) &= ce^{-\beta_{Z-1}} + d \end{aligned} \tag{20}$$

with $\beta_z = h\alpha_z$. Hence, the constants to be found are the β_N with N an integer. Now, the chemical potential will be given by

$$\begin{aligned} \mu(N) = \frac{\partial E(N)}{\partial N} &= -c\alpha(N)e^{-\alpha(N)(N-Z)} \\ &\quad - c(N-Z)\alpha'(N-Z)e^{-\alpha(N)(N-Z)} \end{aligned} \tag{21}$$

where $\alpha'(N)$ is the derivative of the function α , and is given by

$$\alpha'(N) = \begin{cases} 0 & \text{if } N \in A \\ \text{undefined} & \text{otherwise} \end{cases} \tag{22}$$

Hence, the chemical potential is

$$\mu(N) = \begin{cases} -c\alpha_N e^{-\alpha_N(N-Z)} & \text{if } N \in A \\ \text{undefined} & \text{otherwise} \end{cases} \tag{23}$$

and it is discontinuous at integer values of N . Further studies of the model are necessary to find the best way to fit the parameters and to evaluate the consequences regarding chemical interpretations. Figure 1 shows the piecewise exponential model of Eq. (17) for the oxygen atom.

To conclude, it is important to note the comments made by von Szentpaly last year [49] in respect to Chattaraj’s work [24]. His main arguments against calling the “principle of X equalization” (X = electronegativity, hardness or electrophilicity) is the lack of universality. It is unfair to place the uncertainty principle of Heisenberg and electrophilicity equalization at the same level. In fact, we have shown here that they are valid only under the very simple exponential model in its simpler form. In this work, we called them “principles” just because it is the generalized language, but in a more rigorous way they should be called “rules”.

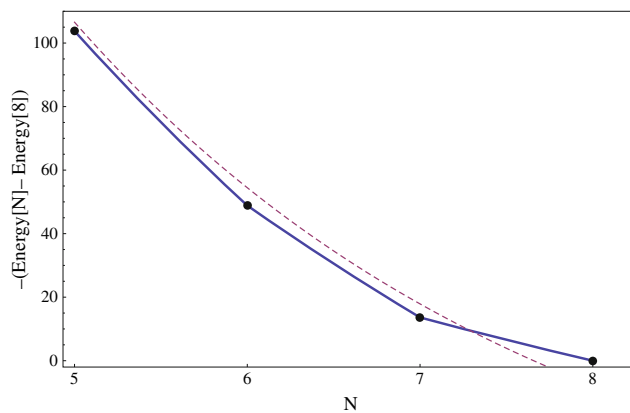


Fig. 1 Absolute value of the energy of oxygen as a function of the number of electrons, N . Dots Experimental values, continuous line piecewise exponential model of Eq. (17), dashed line best fit of single exponential model of Eq. (2) ($\alpha=0.35$). The values of energy are relative to the energy of the neutral atom

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