

# ***N*-dependence of electronic energies in atoms and molecules: Mulliken and exponential interpolations**

Roman F. Nalewajski

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**Abstract** The unphysical artifact of the Mulliken (parabolic) interpolation of the dependence of the electronic energy of atoms and molecules on the system average number of electrons  $N$  is identified. To remedy this shortcoming a smooth exponential interpolation between the energies of the neutral system, its cation and anion is suggested. The trends exhibited by the associated electronegativity and chemical hardness scales are examined.

**Keywords** Chemical hardness · Chemical potential · Electronegativity · Electronic energy · Exponential interpolation of  $N$ -dependence · Mulliken interpolation ·  $N$ -discontinuity · Reactivity theory

## **1 Mulliken interpolation**

The grand-ensemble is capable of exhibiting the continuously varying average number of electrons  $N$  assuming both the fractional and integral values. As demonstrated by Perdew et al. [1–3] in the limit of vanishing absolute temperature  $T \rightarrow 0$  the ensemble-average electronic energy for the equilibrium state of a molecular/atomic system exhibits a piecewise linear behavior shown in Fig. 1a, between the neighboring integer values  $\{N_i^0\}$  of  $N$ . For the free neutral atom/molecule X containing the integer number  $N = N_0$  of electrons the relevant ground states  $\{\Psi_i^0 = \Psi(N_i)\}$  mixing with  $\Psi(N_0)$  are two *singly*-ionic states  $\Psi(N_0 + 1)$  and  $\Psi(N_0 - 1)$  of the corresponding anion  $X^-$  and cation  $X^+$ , respectively (see Fig. 1). Therefore, the “left” and “right” slopes of the ensemble-average energy function  $E(N)$  (Fig. 1), measuring the *biased*

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R. F. Nalewajski (✉)

Department of Theoretical Chemistry, Jagiellonian University, R. Ingardena 3, 30-060 Cracow, Poland  
e-mail: nalewajs@chemia.uj.edu.pl

estimates of the chemical potential  $\mu_X$  of the neutral system, the negative of the system electronegativity  $\chi_X$  [3–5],

$$\mu_X = \partial E(N)/\partial N|_{N_0} = \mu(N)|_{N_0} \equiv -\chi_X, \quad (1)$$

when it is known to act as the electron *donor* (Lewis basis) or *acceptor* (Lewis acid), respectively, read:

$$\begin{aligned} \mu_X^{(+)} &= (E_{X^+} - E_X)/(-1) \equiv -I_X = \varepsilon_{\text{HOMO}} \quad \text{and} \\ \mu_X^{(-)} &= (E_{X^-} - E_X)/1 \equiv -A_X = \varepsilon_{\text{LUMO}}. \end{aligned} \quad (2)$$

Here  $I_X$  and  $A_X$  stand for the system ionization potential and electron affinity, and we have used the Janak theorem [6,7] to identify these estimates as the “frontier” Kohn-Sham [8] eigenvalues corresponding to the Highest Occupied (HO) and Lowest Unoccupied (LU) Molecular Orbitals (MO), respectively (see Fig. 1b). This electronegativity discontinuity at the zero absolute temperature, called the  $N$ -discontinuity, has profound implications for the donor-acceptor systems [1–3]. Among others, it enforces the integer number of electrons in products of the chemical-bond dissociation.

This surprising grand-ensemble result is different from the *unbiased* finite-difference estimate  $\eta_M$  of Mulliken [4] (see Fig. 1b) of the chemical potential derivative, which amounts to the arithmetic average of the biased chemical potentials of Eq. (2):

$$\mu_M = \frac{\mu_X^{(-)} + \mu_X^{(+)}}{2} = -\frac{(I_X + A_X)}{2} = \left. \frac{\partial E^{(2)}(N)}{\partial N} \right|_{N_0} = \mu_M(N)|_{N_0}. \quad (3)$$

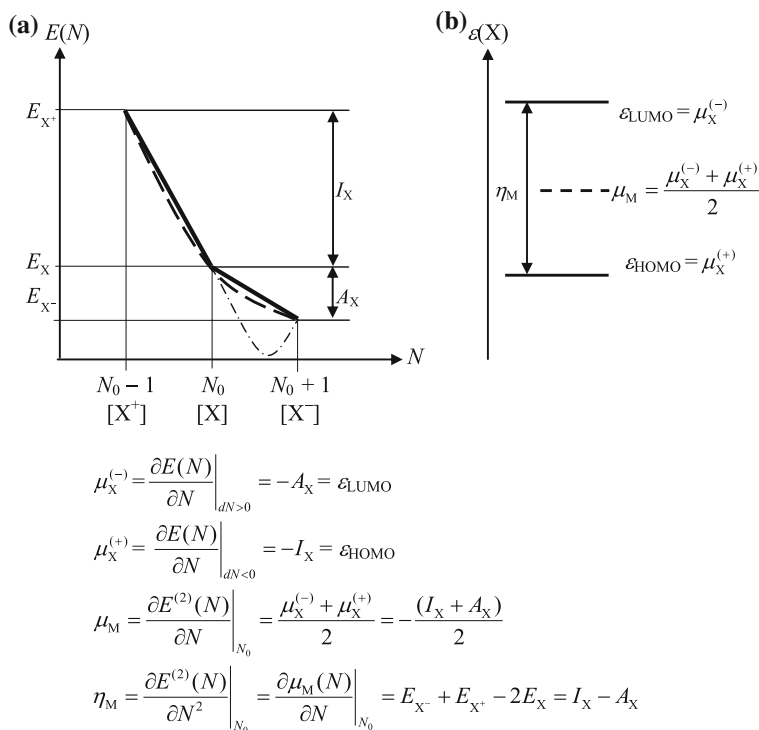
As indicated in the preceding equation (see also Fig. 1) this average value indeed represents the  $N_0$ -value of the derivative of the quadratic energy function  $E^{(2)}(N)$  passing through the points  $(E_X, E_{X^+}, E_{X^-})$ . This Mulliken’s (“radical”) estimate  $\mu_X \approx \mu_M$  should be applied as the unbiased measure, when we have no advance information about the donor/acceptor character of the system under consideration relative to its molecular environment.

Following the familiar ideas of Pearson and Parr [3,9,10] the second derivative of the energy function  $E(N)$ , i.e., its curvature,

$$\eta_X = \partial^2 E(N)/\partial N^2 \Big|_{N_0} = \eta_M(N)|_{N_0} = 1/S_X, \quad (4)$$

is used to measure the chemical hardness  $\eta_X$ , the inverse of chemical softness  $S_X$  of the electron distribution in X. Such concept is used in several intuitive rules of chemistry, e.g., the *Hard/Soft Acids and Bases* (HSAB) principle of Pearson [10] and related rules in theory of chemical reactivity.

This hardness derivative of the neutral system X can be estimated by finite differences as the derivative of the Mulliken estimate of the neutral system chemical

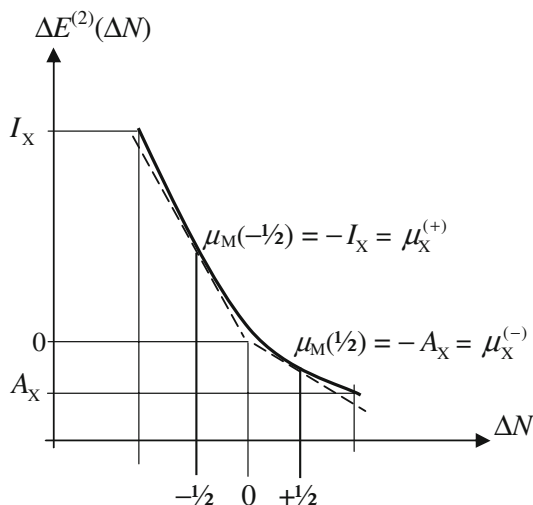


**Fig. 1** The average electronic energy  $E(N)$  of the equilibrium (ground) state of the *open* molecular system  $X$  at the absolute-zero temperature,  $T = 0$  K, as function of the (grand-canonical) ensemble-average number of electrons  $N$  (**bold solid line** in Panel **a**) and the chemical potential ( $\mu$ ) and chemical hardness ( $\eta$ ) estimates it implies. In Panel **b** the associated Kohn-Sham (KS) orbital interpretations are given. The Mulliken estimate of the chemical potential,  $\mu_M = \partial E^{(2)}(N)/\partial N$ , measures the derivative of the quadratic function  $E^{(2)}(N)$  obtained by parabolic interpolation of the ground-states of the neutral system  $X$ , its anion  $X^{-1}$  and cation  $X^{+1}$ , shown as the pointed-broken line in the diagram **a**. Its second derivative (curvature)  $\eta_M = \partial^2 E^{(2)}(N)/\partial N^2$  measures the system chemical hardness. This quadratic function generally exhibits the minimum for the fractionally charged anion,  $N_0 < N < N_0 + 1$ . The smooth exponential interpolation (**bold broken line**) does not produce this qualitatively incorrect behavior. The “left” and “right” derivatives  $\mu_X^{(+)}$  and  $\mu_X^{(-)}$  of  $E(N)$ , for  $dN \equiv N - N_0 < 0$  and  $dN > 0$ , respectively, are not equal at  $T = 0$  K, thus giving rise to the  $N$ -discontinuity of the system chemical potential  $\mu(N) = \partial E(N)/\partial N$  at the integer  $N = N_0$ , which identifies the neutral system  $X$ . As indicated in Panel **b** of the figure these chemical potential derivatives for the system acting as the Lewis acid or base, respectively, can be identified with the corresponding *frontier* KS orbitals by using Janak’s theorem, while the system chemical hardness measures the energy gap between them

potential [Eq. (3)], resulting from the parabolic interpolation between  $(E_{X^+}, E_X,$  and  $E_{X^-})$  (see Fig. 1a),

$$\eta_M = \left. \frac{\partial E^{(2)}(N)}{\partial N^2} \right|_{N_0} = \left. \frac{\partial \mu_M(N)}{\partial N} \right|_{N_0} = E_{X^-} + E_{X^+} - 2E_X = I_X - A_X. \quad (5)$$

It should be observed that this energy difference measures the energy of the *disproportionation* reaction, of the simultaneous reduction and oxidation of  $X$ :  $2X \rightarrow X^+ + X^-$ .



**Fig. 2** The parabolic interpolation of Mulliken reproduces the biased chemical potentials  $\mu_M(\Delta N) = \frac{\partial \Delta E^{(2)}(\Delta N)}{\partial \Delta N} = \mu_M + \eta_M \Delta N$  at the ionic transition states corresponding to  $\Delta N = \Delta N_M^{TS} = \pm 1/2$

The Mulliken parabolic interpolation of the energy displacements relative to  $E_X$ ,

$$\Delta E^{(2)}(\Delta N) = \mu_M \Delta N + \frac{1}{2} \eta_M (\Delta N)^2, \quad \Delta N = N - N_0 \tag{6}$$

around the ground-state energy  $\Delta E^{(2)}(0) = 0$  of the neutral atom/molecule X, fits the energy displacements corresponding to the system cation,  $\Delta E^{(2)}(-1) = I_X$ , and anion,  $\Delta E^{(2)}(1) = -A_X$ . As shown in Fig. 2 this smooth energy function exactly reproduces the biased chemical potentials of Eq. (2) at the ionic transition states (TS), corresponding to  $\Delta N_M^{TS} = \pm 1/2$ .

This energy function exhibits the minimum value (see Fig. 1a)

$$\Delta E^{(2)}(\Delta N_{\min.}) \equiv \Delta E_{\min.}^{(2)} = -\frac{\mu_M^2}{2\eta_M} = -\frac{(I_X + A_X)^2}{2(I_X - A_X)} < 0, \tag{7}$$

at the optimum amount of an external charge transfer (CT),

$$\Delta N_{\min.} = -\frac{\mu_M}{\eta_M} = \frac{I_X + A_X}{2(I_X - A_X)} > 0, \tag{8}$$

determined from the equilibrium condition:

$$\frac{d \Delta E^{(2)}(\Delta N)}{d \Delta N} = \mu_M + \eta_M \Delta N \equiv \mu^{(2)}(\Delta N) = 0. \tag{9}$$

Therefore, when  $3A_X < I_X$  this formula gives unphysical result of  $0 < \Delta N_{\min.} < 1$ , thus predicting positive chemical potential of the stable anion,

$$\mu^{(2)}(1) = \frac{1}{2} (I_X - 3A_X) = \mu_{X^-}^{(2)} > 0, \quad (10)$$

which is diagnosed as being unstable relative to the optimum CT-intermediate of Eq. (8).

A reference to Table 1 shows that this is more a rule rather than an exception (see Table 1), so that this shortcoming often affects predictions of electronegativity and hardness descriptors of electronic gas in atomic and molecular species. In the fixed-curvature (parabolic) scheme of Mulliken this gives rise to severely overestimated values of both these parameters. It is the main purpose of this work to explore the alternative, exponential interpolation scheme, which guarantees the negative values of chemical potential for stable anions, and exhibits the intuitively expected variations of chemical hardness with the system oxidation state.

## 2 Exponential interpolation

An alternative continuous interpolation of the  $N$ -dependence of the system energy is provided by the exponential function

$$\Delta E^{(e)}(\Delta N) = \alpha + \beta \exp(\gamma \Delta N), \quad (11)$$

where the condition  $\Delta E^{(e)}(0) = 0$  implies:  $\alpha = -\beta$ . Fitting the remaining two parameters on the remaining conditions  $\Delta E^{(e)}(-1) = I_X$  and  $\Delta E^{(e)}(1) = -A_X$  finally gives:

$$\Delta E^{(e)}(\Delta N) = \frac{I_X A_X}{A_X - I_X} \left[ 1 - \left( \frac{A_X}{I_X} \right)^{\Delta N} \right]. \quad (12)$$

This formula predicts the following chemical potential and hardness functions:

$$\mu^{(e)}(\Delta N) = -\frac{I_X A_X}{I_X - A_X} \ln \left( \frac{I_X}{A_X} \right) \left( \frac{A_X}{I_X} \right)^{\Delta N} < 0, \quad (13)$$

$$\eta^{(e)}(\Delta N) = \frac{I_X A_X}{I_X - A_X} \left[ \ln \left( \frac{I_X}{A_X} \right) \right]^2 \left( \frac{A_X}{I_X} \right)^{\Delta N} > 0. \quad (14)$$

The negative character of  $\mu^{(e)}(\Delta N)$  follows from the convex nature of the energy [3]:  $I_X > A_X$ .

Therefore, this continuous interpolation always generates the physical, negative values of the chemical potential, for both the stable neutral and ionic species. It implies that atomic/molecular systems become more electronegative with increasing net charge

**Table 1** Interpolation data for representative atoms and molecules

X	$I_X$ (eV)	$A_X$ (eV)	$\frac{I_X}{A_X}$	$\Delta N_{\text{min.}}$ (a.u.)	$-\Delta E_{\text{min.}}^{(2)}$ (eV)	$-\mu_M$ (eV)	$-\mu_X^{(e)}$ (eV)	$\mu_M$ (eV)	$\eta_X^{(e)}$ (eV)	$\frac{\mu_X^+}{\mu_X}$	$\frac{\eta_X^+}{\eta_X}$
H	13.6	0.75	18.5	0.56	2.00	7.18	2.30	12.86	6.66		
Li	5.40	0.62	8.7	0.63	0.95	3.01	1.52	4.78	3.28	13.5	14.7
B	8.30	0.28	29.6	0.53	1.15	4.29	0.98	8.02	3.33		
C	11.3	1.27	8.9	0.63	1.97	6.27	3.14	10.00	6.86		
O	13.6	1.46	9.3	0.62	2.34	7.54	3.64	12.16	8.13		
F	17.4	3.40	5.1	0.74	3.86	10.41	6.89	14.02	11.25		
Na	5.15	0.55	9.4	0.62	0.88	2.85	1.38	4.60	3.08	9.2	9.2
Al	6.00	0.46	13.0	0.58	0.94	3.23	1.28	5.54	3.29		
Si	8.15	1.39	5.9	0.71	1.68	4.77	2.96	6.76	5.24		
P	10.5	0.74	14.2	0.58	1.62	5.62	2.11	9.76	5.60		
S	10.4	2.08	5.0	0.75	2.34	6.22	4.20	8.28	6.77		
Cl	13.0	3.60	3.6	0.89	3.68	8.30	6.42	9.36	8.24	2.2	1.2
K	4.34	0.50	8.7	0.63	0.76	2.42	1.22	3.84	2.64	7.4	7.1
Ga	6.1	0.3	20.3	0.55	0.88	3.2	0.95	5.8	2.86		
Ge	8.0	1.2	6.7	0.68	1.56	4.6	2.68	6.8	5.08		
As	9.8	0.8	12.3	0.59	1.56	5.3	3.41	9.0	8.54		
Se	9.76	2.02	4.8	0.76	2.24	5.89	4.01	7.74	6.32		
Br	11.8	3.37	3.5	0.90	3.41	7.59	5.90	8.44	7.40	2.2	1.2
Rb	4.19	0.49	8.6	0.63	0.74	2.34	1.19	3.70	2.56	6.7	6.2

Table 1 continued

X	$I_X$ (eV)	$A_X$ (eV)	$\frac{I_X}{A_X}$	$\Delta N_{\min.}$ (a.u.)	$-\Delta E_{\min.}^{(2)}$ (eV)	$-\mu_M$ (eV)	$-\mu_X^{(e)}$ (eV)	$\mu_M$ (eV)	$\eta_X^{(e)}$ (eV)	$\frac{\mu_X^+}{\mu_X}$	$\frac{\eta_X^+}{\eta_X}$
In	5.9	0.3	19.7	0.55	0.86	3.1	0.94	5.6	2.80		
Sn	7.35	1.25	5.9	0.70	1.52	4.3	2.67	6.1	4.73		
Sb	8.65	1.05	8.2	0.64	1.55	4.85	2.52	7.6	5.31		
Te	9.01	1.97	4.6	0.78	2.14	5.49	3.83	7.04	5.83		
Cs	3.89	0.47	8.3	0.64	0.69	2.18	1.13	3.42	2.39	6.7	6.2
Bi	8.43	0.95	8.9	0.63	1.47	4.69	2.34	7.48	5.10		
OH	13.2	1.83	7.2	0.66	2.48	10.41	3.40	14.02	6.73		
SH	10.5	2.3	4.6	0.78	2.50	6.4	4.47	8.2	6.79		
SeH	8.8	3.2	2.7	1.07	3.21	6.0	5.09	5.6	5.15		
NH <sub>2</sub>	11.4	0.74	15.4	0.57	1.73	6.07	2.16	10.66	5.92		
PH <sub>2</sub>	9.83	1.25	7.9	0.65	1.79	5.54	2.95	8.58	6.09		
SF <sub>6</sub>	15.4	0.6	25.7	0.54	2.16	8.0	2.03	14.8	6.57		
SO <sub>3</sub>	12.7	1.7	7.5	0.65	2.36	7.2	3.95	11.0	7.94		
Cl <sub>2</sub>	11.6	2.4	4.8	0.76	2.66	7.0	4.77	9.2	7.51		
Br <sub>2</sub>	10.6	2.6	4.4	0.82	2.72	6.6	4.84	8.0	6.80		
I <sub>2</sub>	9.4	2.6	3.6	0.88	2.65	12.0	4.62	6.8	5.94		

From the electronegativities and hardnesses reported in Ref. [3]

$$q = -\Delta N:$$

$$\begin{aligned}\mu^{(e)}(-1) &= \frac{I_X^2}{I_X - A_R} \ln\left(\frac{A_X}{I_X}\right) = \mu_{X^+}^{(e)} \\ < \mu^{(e)}(0) &= \frac{I_X A_X}{I_X - A_X} \ln\left(\frac{A_X}{I_X}\right) = \mu_X^{(e)} \\ < \mu^{(e)}(1) &= \frac{A_X^2}{I_X - A_X} \ln\left(\frac{A_X}{I_X}\right) = \mu_{X^-}^{(e)}.\end{aligned}\quad (15)$$

Equation (14) also correctly predicts that electron distributions in atoms and molecules become harder with increasing ionization:

$$\begin{aligned}\eta^{(e)}(-1) &= \frac{I_X^2}{I_X - A_X} \left[ \ln\left(\frac{A_X}{I_X}\right) \right]^2 = \eta_{X^+}^{(e)} \\ > \eta^{(e)}(0) &= \frac{I_X A_X}{I_X - A_X} \left[ \ln\left(\frac{A_X}{I_X}\right) \right]^2 = \eta_X^{(e)} \\ > \eta^{(e)}(1) &= \frac{A_X^2}{I_X - A_X} \left[ \ln\left(\frac{A_X}{I_X}\right) \right]^2 = \eta_{X^-}^{(e)}.\end{aligned}\quad (16)$$

These mutual relations can be summarized in terms of the following ratios:

$$\begin{aligned}\mu_{X^+}^{(e)}/\mu_X^{(e)} &= \mu_X^{(e)}/\mu_{X^-}^{(e)} = \eta_{X^+}^{(e)}/\eta_X^{(e)} = \eta_X^{(e)}/\eta_{X^-}^{(e)} = I_X/A_X \\ &= \mu_X^{(e)}(-1/2)/\mu_X^{(e)}(1/2) = \mu_M(-1/2)/\mu_M(1/2) > 1.\end{aligned}\quad (17)$$

Therefore, the exponential interpolation preserves the ratio of the Mulliken electronegativities for the cation and anion TS.

### 3 Results and discussion

In Table 1 we have compared representative results of the parabolic and exponential interpolations for selected atoms and molecules exhibiting stable anions, for which the Mulliken descriptors have been reported [3]. A few experimental values of the chemical potential and hardness ratios appearing in the preceding equation are also listed, to be compared with the  $I_X/A_X$  factor predicted by the exponential scheme. This analysis indicates that the latter is indeed of the same order as the relative increases in the electronegativity and hardness parameters due the system ionization, thus semi-quantitatively validating Eq. (17).

The  $\Delta N_{\min.}$  and  $\Delta E_{\min.}^{(2)}$  entries of the table confirm the negative electronegativity feature predicted for the anions by the parabolic interpolation, with only a single exception of SeH being detected, for which  $\Delta N_{\min.} > 1$ . In the remaining cases the energy minimum appears in the region of fractional negative charge,  $0 < \Delta N_{\min.} < 1$ . It is seen to lie below the  $(-A_X)$  level, as shown in Fig. 1a, thus confirming the negative electronegativity of the anion predicted by the parabolic fit.



A comparison between the corresponding electronegativity values for neutral species,  $\chi_X = -\mu_X$ , as predicted by the two interpolation schemes,  $\{-\mu_M, -\mu_X^{(e)}\}$ , reveals that the Mulliken slopes are indeed severely overestimated, compared to a more physical exponential predictions. In a given period of elements both electronegativity scales are seen to exhibit the highest values for halogens. However, while the Mulliken scheme predicts a steady increase in atomic electronegativity with increasing group number, the exponential scale exhibits the period minimum value at about Group 3. Both electronegativity scales correctly predict a diminishing trend in the given group, with increasing period (size) of the atom.

It is also of interest to examine the values of the exponential charges, for which the chemical potential function of Eq. (13) reproduces the biased chemical potentials of Eq. (2). The corresponding displacements read:

$$\Delta N^{(e)} = \pm \frac{I_X - A_X}{A_X} / \ln^2 \left( \frac{I_X}{A_X} \right). \quad (18)$$

Although the exponential interpolation preserves the ratio of the TS-electronegativities of Eq. (17) these displacements exceed the physical meaningful range  $\Delta N = \pm 1$ .

The inflated,  $N$ -independent curvature  $\eta_M$  of the parabolic interpolation, due to the unphysical energy minimum at a fractional negative charge, is also seen to strongly exceed a more physical  $N$ -flexible hardness  $\eta_X^{(e)}$  of the exponential scheme, with two schemes generally exhibiting a similar, monotonically increasing trend with increasing group number, within the given period of elements. As intuitively expected, for the fixed group number both hardness descriptors are monotonically decreasing with the increasing size of an atom.

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