

분자의 전기음성도에 관한 이론적 고찰

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On the Electronegativity of Molecule

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요 약. Density functional theory에서의 전기음성도의 정의에 의해 전기음성도를 가전자 (valence electron)만을 고려하여 구하였다. 전기음성도는 Hartree-Fock의 궤도 에너지 (orbital energy)로 표시되는데 이로부터 구한 분자의 전기음성도 값은 다른 값들과 좋은 상관관계 (correlation)를 보여준다. 또한 분자를 형성할 때 Sanderson의 법칙 (electronegativity equalization principle)이 만족됨을 보였다.

ABSTRACT. Molecular electronegativity (EN) values are calculated employing the density functional definition of EN: the negative of the chemical potential in the density functional theory. Calculations are limited to the use of valence electrons (valence electron approximation). Our formula for the EN is given in terms of Hartree-Fock (HF) orbital energies. Resulting EN values for molecules as well as atoms exhibit a remarkable correlation with other existing scales. For molecules, we have achieved electronegativity equalization principle (Sanderson's principle).

1. INTRODUCTION

The concept of electronegativity is one of the most frequently used concepts in chemistry which has had a considerable success in understanding the large amount of chemical phenomena. None the less it has never been satisfactorily defined. The most widely accepted definitions of EN are due to Pauling¹ and Mulliken². Both these and other definitions implicitly assumed the EN to be an intrinsic property of an element independent of whether an atom is isolated or bonded in a molecule.

Recently, in a very important treatment for

the EN, Parr and his collaborators³ identified it with the negative of the chemical potential in the density functional theory⁴, $\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)$. They proposed that the EN should be a property of total electrons in an atom, not just that of valence electrons as was conventionally considered⁵. Since then much progress has been made towards the determination of the EN values⁶⁻¹² employing the density functional theory (DFT).

In the previous paper¹³, we treated the problem with the aid of Hartree-Fock method, and provided some formula for the atomic case by approximating the DFT. In this paper, we

extend the idea to the diatomic molecules, and for heteronuclear diatomics we have achieved electronegativity equalization principle (Sanderson's principle).

2. THEORY¹³

The value of the electronegativity (χ) of N electron system is given by the formula³

$$\mu = (\partial E_u / \partial N) \quad (1)$$

where E_u denotes the ground state energy with the external potential u . And the Hohenberg-Kohn theorem can be extended^{3,8,9} to an energy functional of the first-order reduced density matrix $\gamma(l', l)$ corresponding to density ρ , then one may expand γ in terms of a basis $\{\phi\}$. The density may be represented by

$$\rho(\mathbf{1}) = \gamma(\mathbf{1}, \mathbf{1}) = \sum_{kl} \phi_k^*(\mathbf{1}) \gamma_{lk} \phi_l(\mathbf{1}) \quad (2)$$

In principle, one should use the total electrons in Eq. (1). However, electrons that interact appreciably with bond formation are essentially those in the valence shell (N_v in number), and ignoring core electrons may be a good approximation which simplifies the problem substantially. Eq. (1) then reduces to

$$\mu = \partial E_u / \partial N_v \text{ or } \mu = \partial E_u / \partial \rho_v \quad (3)$$

For the density given by Eq. (2), One has the following identities

$$\begin{aligned} \sum_l \gamma_{lm} (\partial \rho / \partial \gamma_{lk})_{\phi} &= \sum_l \phi_k^* \gamma_{lm} \phi_l \\ &= \phi_k^* (\partial \rho / \partial \phi_m^*)_{\tau} \end{aligned} \quad (4)$$

and

$$\begin{aligned} \sum_{kl} \gamma_{lk} (\partial \rho / \partial \gamma_{lk})_{\phi} &= \rho \\ &= \sum_k \phi_k^* (\partial \rho / \partial \phi_k^*)_{\tau} \end{aligned} \quad (5)$$

Thus for a functional A of the form

$$A[\rho] = \int a(\rho) d\tau \quad (6)$$

where $a(\rho)$ is a function of the density given by Eq. (2), one obtains

$$\sum_l \gamma_{lm} (\partial A / \partial \gamma_{lk})_{\phi} = \int \phi_k^* (\partial A / \partial \phi_m^*)_{\tau} d\tau \quad (7)$$

and

$$\begin{aligned} \sum_{kl} \gamma_{lk} (\partial A / \partial \gamma_{lk})_{\phi} &= \sum_k \int \phi_k^* (\partial A / \partial \phi_k^*)_{\tau} d\tau \\ &= \int \rho (\partial A / \partial \rho) d\tau \end{aligned} \quad (8)$$

With the Hartree-Fock density

$$\rho^{\text{HF}} = \sum_k n_k \phi_k^* \phi_k \quad (n_k = 0, 1 \text{ or } 2) \quad (9)$$

where $\{\phi\}$ is a set of HF orbitals, the Eq. (8) becomes

$$\sum_k n_k (\partial A / \partial n_k)_{\phi} = \int \rho^{\text{HF}} (\partial A / \partial \rho^{\text{HF}}) d\tau \quad (10)$$

The exact form of $E_u[\rho]$ is not known except for one electron systems. This is true even in the case of HF energy functional²¹. But, the HF kinetic energy may be well approximated²² by Thomas-Fermi method²³ and its systematic gradient expansions, and the exchange energy part by χ_s -type functional²⁴. The kinetic energy is mainly due to the electrons in the inner shell, with the electron density there being high and significantly oscillating. Hence ignoring the gradient terms in the energy functional (or the kinetic energy functional) would result in large error. But, the error might be small for valence electrons, because density is relatively low and slowly varying for them. Therefore, for valence electrons with HF energy and HF density, the following identity may hold to a good approximation.

$$\sum_k n_k (\partial E / \partial n_k) = \int \rho_v^{\text{HF}} (\partial E_u[\rho^{\text{HF}}] / \partial \rho_v^{\text{HF}}) d\tau \quad (11)$$

where the summation is over orbitals in the valence shell.

The chemical potential determined by the variational minimization should be a constant. If determined otherwise, it has a variation in \vec{r}

$$(\partial E_u / \partial \rho) = \mu(\vec{r}) \quad (12)$$

In this case one may define the chemical potential as⁷

$$\mu = \int \mu(\vec{r}) \rho(\vec{r}) d\vec{r} / \int \rho(\vec{r}) d\vec{r} \quad (13)$$

For valence electrons, one obtains

$$\mu = \int \rho_v (\delta E_v / \delta \rho_v) d\tau / \int \rho_v d\tau \quad (14)$$

Substituting the relation^{8,14}

$$\frac{\partial E}{\partial n_k} = \epsilon_k \quad (\epsilon_k : \text{HF orbital energy}) \quad (15)$$

into Eq. (11) and using Eq. (14) with HF density, one obtains

$$\sum_k n_k \epsilon_k = \sum_k n_k \left(\frac{\partial E}{\partial n_k} \right) \approx \mu \int \rho_v^{\text{HF}} d\tau = \mu N_v \quad (16)$$

Therefore, there results a formula for the EN (χ) in terms of HF orbital energies

$$\chi = -\mu = -\frac{\sum_k n_k \epsilon_k}{N_v} \quad (17)$$

which is the average valence electron binding energy (in Koopman's sense).

Values computed with Eq. (17) are compiled in Table 1 of Ref. 13. For all the atoms in the first through fourth row main group good

agreement with other estimates is found.

3. MOLECULAR ELECTRONEGATIVITIES

For atoms electronegativities were determined by considering only valence electrons. Extension of this idea to molecule is straightforward. For molecules this corresponds to considering EN as a property of electrons forming a chemical bond, that is, electrons in occupied bonding or antibonding MO's. Hereafter we will identify 'valence orbitals' with these MO's.

Analogous to Eq. (3), for molecular electronegativity, we also have

$$\mu = \frac{\partial E}{\partial N_v} = \frac{\delta E}{\delta \rho_v} \quad (18)$$

where N_v and ρ_v denote the number and density of 'valence electrons', or bonding electrons, respectively. In an MO approximation

$$\chi = -\frac{\sum_i n_i E_i}{N_v} \quad (E_i : \text{MO energy}) \quad (19)$$

where the summation is over 'valence MO's.

For homonuclear diatomics the net number of bonding electrons is related to bond order through $N = 2 \times (\text{bond order})$. Heteronuclear diatomics are not classified by bonding or antibonding character. We take N_v as the number of electrons that are engaged in a bond as usual. For example, we average over 1π and 5σ orbitals for CO molecule.

Table 1 represents EN values for some homonuclear diatomics calculated by Eq. (19). together with other estimates normalized to our scale. we used the Nethercot's¹⁵ relation $\chi_M = 2.6\chi_p$, in which χ_p is Pauling's EN values and χ_M is Mulliken's EN value in eV. Furthermore, $\chi(\text{present}) = 0.201\chi_p$, so that we have $\chi(\text{present}) = 0.0070\chi_M$. The results are in reasonable agreement.

For heteronuclear diatomics, we take N_v as

Table 1. EN values of homonuclear diatomics

Molecules	Ref.	Eq. (19)	Other Estimates in our scale	
			χ_M	SBC Model ^a
H ₂	b	0.5310	0.500	0.502
Li ₂	c	0.1813	0.210	0.200
B ₂	d	0.3412	—	—
C ₂	e	0.4203	0.508	—
N ₂	e	0.5680	0.562	0.685
	f	0.622	—	—
O ₂	g	0.634	0.673	0.667
F ₂	c	0.4744	0.728	0.614
Be ₂	f	0.3232	—	—

(Values in atomic units.)

a. Ref. 16; * Orbital energies are from; b. W. Colos and C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 219 (1960); c. B. J. Ransil, *Rev. Mod. Phys.*, **32**:239, 245 (1960); d. A. A. Padgett and V. Griffing, *J. Chem. Phys.*, **30**, 1286 (1959); e. Minimal basis set calculation: C. W. Sherr, *J. Chem. Phys.*, **23**, 569 (1955); f. Extended basis set calculation: P. E. Cade, K. D. Sales and A. C. Wahl, *J. Chem. Phys.*, **44**, 1973 (1966); g. M. Kotani, Y. Mizuno, K. Kayama and E. Ishiguro, *J. Phys. Soc. Japan.*, **12**, 707 (1957)

the number of electrons that are engaged in a bond as in the case of homonuclear diatomics. Table 2 includes EN values for some heteronuclear diatomics computed from the formula. And results are compared with those from the geometric mean¹⁶,

$$\chi_{AB} = (\chi_A \chi_B)^{1/2} \quad (20)$$

We also list EN values calculated by SBC model¹⁶ adjusted to our scale for comparison. We find good agreement again.

At this point, by agreement we mean rather than a good correlation exists between them,

Table 2. EN values of heteronuclear diatomics

Molecule	Ref.	Present	Geometric mean ^a	SBC model ^b our scale	
				Eq. (22)	Eq. (8)
LiH	<i>c</i>	0.3055	0.3178	0.2919	0.2919
NaH	<i>d</i>	0.2752	0.3073	0.2849	0.2604
HF	<i>e</i>	0.6363	0.6414	0.6153	0.7714
LiF	<i>f</i>	0.3484	0.4077	—	—
NaF	<i>g</i>	0.4262	0.3942	—	—
KF	<i>h</i>	0.4011	0.3563	0.2954	0.3353
HCl	<i>d</i>	0.4762	0.5398	0.5516	0.5978
LiCl	<i>g</i>	0.3760	0.3431	—	—
NaCl	<i>i</i>	0.3474	0.3317	0.3297	0.3738
CO	<i>j</i>	0.5954	0.5859	—	—
	<i>f</i>	0.5773	—	—	—
	<i>k</i>	0.6111	—	—	—
NH	<i>d</i>	0.5377	0.5185	—	—
OH	<i>d</i>	0.5734	0.5934	—	—

(Values in atomic units.)

a. Atomic values are from Ref. 13; *b.* Eq. (22) and Eq. (8) in the text of Ref. 16; * Orbital energies are from; *c.* A. M. Karo, *J. Chem. Phys.*, **30**, 1241 (1959); *d.* P. E. Cade and W. M. Huo, *J. Chem. Phys.*, **47**: 614, 647(1967); *e.* A. M. Caro and L. C. Allen, *J. Chem. Phys.*, **31**, 968(1959); *f.* Ref. *c* of Table 1; *g.* R. L. Matcha, *J. Chem. Phys.*, **47**: 4595, 5295 (1967); *h.* R. L. Matcha, *J. Chem. Phys.*, **49**, 1264(1968); *i.* R. L. Matcha, *J. Chem. Phys.*, **48**, 335 (1968); *j.* W. M. Huo, *J. Chem. Phys.*, **43**, 624 (1965); *k.* A. D. McLean and M. Yoshimine, *Int. J. Quantum Chem.*, **18** 313 (1967).

than an exact numerical agreement. EN is not a measurable quantity and there is still no definite definition for it. And it would be meaningless to mention their numerical exactness.

4. ELECTRONEGATIVITY EQUALIZATION

There is no doubt that if two species of different electronegativities come together to form a third, a unique common electronegativity results (Sanderson's principle)^{3,17}. Our EN values satisfy this principle.

We can express a MO as a linear combination of atomic orbitals. For example, $1\sigma_g$ of N_2 molecule has the form

$$1\sigma_g = c_1(1s_A) + c_2(1s_B) + c_3(2s_A) + c_4(2s_B) + \dots$$

Let n_i be the occupation number of i -th MO in the 'valence orbitals'. The contribution of k -th AO to i -th MO is the square of the expansion coefficient $|c_{ik}|^2$, so that we may consider Eq. (19) as

$$\chi = \frac{\sum_{i,k} n_i |c_{ik}|^2 E_i}{\sum_{i,k} n_i |c_{ik}|^2} \quad (21)$$

Two 'valence orbitals' of N_2 molecule are $3\sigma_g$ and $1\pi_u$. Minimal basis set calculation of N_2 EN value by Eq. (21) gives 0.565; which is in close agreement with the minimal basis set value 0.568 in Table 1. Extended basis set calculation gives 0.625, which also agrees well with extended basis set result 0.622 in Table 1.

Now this modification will be applied to heteronuclear diatomics to illustrate the electronegativity equalization principle.

For a singly bonded molecule, LiH for example, EN is equal to the highest occupied MO energy. Let χ_{Li} and χ_H are EN values of Li and H atom in LiH molecule respectively, then

$$\chi_{\text{Li}} = - \sum_k |C_{k,2\sigma}|^2 n_{2\sigma} E_{2\sigma} / \sum_k |C_{k,2\sigma}|^2 n_{2\sigma} \\ = - E_{2\sigma} \quad (22)$$

$$\chi_{\text{H}} = - \sum_l |C_{l,2\sigma}|^2 n_{2\sigma} E_{2\sigma} / \sum_l |C_{l,2\sigma}|^2 n_{2\sigma} \\ = - E_{2\sigma} \quad (23)$$

$$\chi_{\text{LiH}} = - \sum_m |C_{m,2\sigma}|^2 n_{2\sigma} E_{2\sigma} / \sum_m |C_{m,2\sigma}|^2 n_{2\sigma} \\ = - E_{2\sigma} \quad (24)$$

Here the sums over the contributions from the AO's those belong to Li and H respectively in Eq. (22) and Eq. (23), in Eq. (24) over the all contributions from the AO's those belong to LiH. Hence we have

$$\chi_{\text{Li}} = \chi_{\text{H}} = \chi_{\text{LiH}} = - E_{2\sigma} = 0.3055 \quad (\text{Table 2})$$

For systems having multiple bonds, we have to average over 'valence orbital' energies. The result for CO is compiled in Table 3.

χ_{C} and χ_{O} are clearly equalized by forming a bond, when compared to atomic value: $\chi_{\text{C}}=0.487$, $\chi_{\text{O}}=0.704$. Furthermore, they are nearly the same as molecular EN values. Therefore we have achieved Sanderson's principle.

5. DISCUSSION AND CONCLUSIONS

Our electronegativity values should be smaller than their true values. The error is mainly due to the fact that the Hartree-Fock theory neglects the correlation effect, thence gives smaller EN values. For H_2 molecule, for example, Eq. (19) predicts $\chi=0.5310$, while more rigorous study¹⁰ gives 0.65068. For atomic case, correlation term contributes to the EN about a few eV¹², and its contribution to molecules, of course, is likely to be even larger. If orbital

energies were obtained by solving self-consistent equations including this correlation properly¹⁸, the result might have turned to be quite satisfactory notwithstanding the 'valence electron' approximation. This is the greatest merit of our formula: the more accurate our orbital energies are, the better the result.

A comparison of our formula to the original one considering total electrons may be appropriate. EN has been assumed to be a property of valence electrons. Furthermore, according to the recent study, the chemical potential is equal to the negative of the Koopman's ionization potential¹⁹, and the ground-state energy (and the first-order density matrix) is determined completely by the properties of the highest occupied MO in the HF theory²⁰. These results tacitly support our formula.

EN is not a measurable molecular constant and therefore a characteristic value cannot be given to it. So, extension of our idea for atoms to molecules is somewhat controversial, and another attempt must be made to support the validity of our results. Extension of the idea to polyatomic molecules is also straightforward. But we pause to look around. Since EN is not a measurable quantity it is still difficult to give precise meaning to EN values of polyatomic molecules. Therefore the theory that explains the chemical phenomena (or reactions) in terms of EN values of polyatomic molecules must precede the extension.

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Table 3. Equalization of EN in CO

	χ_{O}	χ_{C}	χ_{CO}	
			Eq. (21)	other*
Minimal	0.514	0.568	0.542	0.577
Extended	0.572	0.629	0.599	0.595

* From Table 2.

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