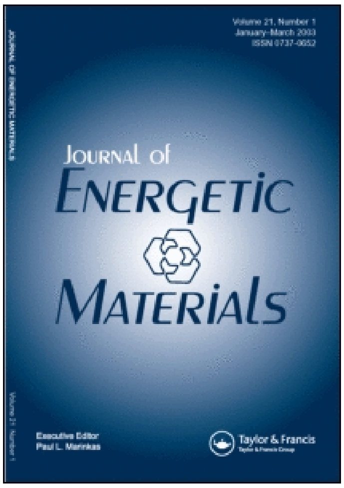

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Partial atomic charges calculation in nitrobenzenes

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PARTIAL ATOMIC CHARGES CALCULATION IN NITROBENZENES

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ABSTRCT

Reported in this communication is a simple procedure for calculating partial atomic charges, which is based on the electronegativity equallization principle. It has been used to study a total of 41 nitrobenzenes and the results obtained from it and ab initio method were copmpared. Very good correlations were found between them and the relevant parameters were given.

INTRODUCTION

Charge distribution of atoms in a molecule and electrostatic interaction among molecules are of great conceptual significance to chemists for understanding and prediction of many chemical problems [1]. The widely used method to describe the distribution is to assign partrial atomic charge to each of atoms in a molecule. These charges represent the simplest description of electron

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density function in molecule. Although theoretically it is possible to calculate them by quantum chemistry (QC) methods, it is computationally difficult for large molecules with ab initio methods and for very large molecules even with semiempirical QC methods. Therefore, much simpler and quicker methods , based on the electronegativity equalization (EE) pricinple, have been developed [2-5]. Recently, much attention has renewly been drawn to the calculation of partial atomic charges because various problems, including molecular mechnics calculations and molecular dynamics simulations in treatment of polar molecules, demand rapid calculation method with reasonable accuracy [6-7].

Most explosives consist of polar molecules in which the charge distribution in a molecule and electrostatic interactions among molecules must also affect their various properties, including their explosion property. As already shown by Mullay [8], the impact sensitivity of explosives are well correlated with the molecular electronegativity. Since the partial atomic charges are of fundamental importance and serious limitations exist for ab initio calculation, rapid empirical methods with chemical accuracy merit consideration. Along this line of thought, a modified EE method was developed during this study and successfully used to study a total of 41 nitrobenzenes. Reported in this paper is the background, procedure and results. Study on relationship among the atomic charge and properties are underway.

BACKGROUND

According to the original definition of Pauling, elecronegativity is the power of an atom in a molecule to attract electrons to itself [9], therefore it is understandable that charge transfer or redistribution must occur until electronegativities of all the atoms in a molecule become equal or the equalization of them is reached when different atoms are combined into the molecule. The currently accepted definition of it is based on electron density functional theory, and therefore, is conceptually clearer and more accurately manageable [10]. According to Parr et al [10], the charge redistribution when a heteronuclear molecule is formed are governed by two important atomic parameters, i.e. the electronegativity (χ) and chemical hardness (η) given by eqations 1 and 2 below,

$$\chi = -\mu = (\partial E / \partial n) \qquad (1)$$

$$\eta = 1/2(\partial^2 E / \partial n^2) \qquad (2)$$

where χ, μ, E and n respectively are the electronegativity, the chemical potential, energy and the total number of electrons in the system studied. The above definitions suggest that the quantities have important connection to the energy involved in charge transfer and hence govern the process accordingly.

Since the power of an atom in a molecule to attract electrons to itself shall increase when it is charged more positively, eqation 3 is assumed.

$$\chi_A = \chi_A^0 + 2\eta_A^0 Q_A \qquad (3)$$

where Q_A is the number of electrons transferred to the atom A and χ_A^0 and χ_A are effective electronegativities of the atom A in a molecule when not charged and charged (or before and after the charge transfer), respectively. Note the $\chi_A 0$ is not identical to the electronegativity of neutral atom A because the former is in a molecule and dependent on its valence state (say C sp^3 and Csp^2) and the latter is not (atom C).

For an atom in a molecule, its electronegativity is also affected by charges on all the other atoms and the Madelung potential term [11] is neccesary to account for the effect.

$$\chi_A = \chi_A^0 + 2\eta_A^0 Q_A + \Sigma Q_B / R_{AB} \qquad (4)$$

where R_{AB} is internuclear distance between atoms A and B and the sum runs over all atoms except the atom A itself.

The total charge in a molecule is kept constant during the transfer (usually zero for neutral molecule).

$$\Sigma Q_A = \text{const.} \qquad (5)$$

where the sum runs over all atoms in a molecule. Because the electronegativities of all the atoms in a molecule become equal, the molecular electronegativity χ_m is defined as follows.

$$\chi_m = \chi_A = \chi_B = \chi_C = \cdots \qquad (6)$$

For a molecule consisting of a total of n atoms, there are n equations of form 4 for the n atoms. Together with the condition for charge conservation (eq. 5), the n+1 simultaneous equations could be used to solve the n variables Q and the molecular electronegativity χ_m if the parametes χ_A^0 and η_A^0 in eq.4 and the molecular geometry are known.

PROCEDURE

Throughout this work, charges obtained from ab initio STO-3G calculation were taken as observations and the experimental molecular geometries were taken from data of crystal structures with the hydrogen atoms being placed according to standard stereochemical rules [12,13]. The ab initio STO-3G calculations were performed by using the Gaussian-82 program [14]. The method used in this study was based on the EE principle, with a factor F

Table 1. Refcodes of compounds studied in this work

No.	Refcode	Substituents					
		1	2	3	4	5	6
1	DNBENZ10	NO_2		NO_2			
2	DNITBZ11	NO_2			NO_2		
3	ZZZFYW01	NO_2	NO_2				
4	BAGFIY	NH_2	NH_2				
5	ZZZWOU01	NH_2	NH_2	NH_2	NH_2	NH_2	NH_2
6	CATCOL12	OH	OH				
7	PHGLOL	OH		OH		OH	
8	BENZDC01	COOH		COOH			
9	PHTHAC01	COOH	COOH				
10	TEPHTH12	COOH			COOH		
11	DCLBEN03	Cl			Cl		
12	HCLBNZ11	Cl	Cl	Cl	Cl	Cl	Cl
13*	OFNAPH01						
14#	BENZEN						
15§	HEXANE						
16	NITRBE	NO_2					
17	TNBENZ10	NO_2		NO_2		NO_2	
18	ZZZMUC01	NO_2		NO_2		NO_2	CH_3
19	NITOLU	NO_2			CH_3		
20	MNIANL01	NO_2		NH_2			
21	NANILI	NO_2			NH_2		
22	QQQFNG02	NO_2			NH_2	NO_2	
23	CUZDEG	NO_2				NO_2	NH_2
24	TNIOAN	NO_2		NO_2	NH_2	NO_2	
25	ONITAN	NO_2	NH_2				
26	DNPHOL	NO_2				NO_2	OH
27	MNPHOL10	NO_2		OH			
28	DNOPHL01	NO_2		NO_2			OH
29	ONITPH	NO_2	OH				
30	PICRAC	NO_2		NO_2		NO_2	OH
31	BENCLN02	NO_2		NO_2			Cl
32	DOXWIW	NO_2				Cl	Cl
33	CAGPUV	NO_2		Cl	Cl		
34	CLNIBZ01	NO_2				Cl	
35	CDNPOL	NO_2		NO_2	OH	Cl	
36	NTCPOL01	NO_2	OH			Cl	
37	KAYSUY	NO_2			CHO		
38	NACPON10	NO_2			$COCH_3$		
39	NIBZAL	NO_2	CHO				
40	NIPHAZ	NO_2				N_3	
41	NO_2					CN	

*; Octafluoronaphthalene. #; Benzene. §; Hexane C_6H_{14}

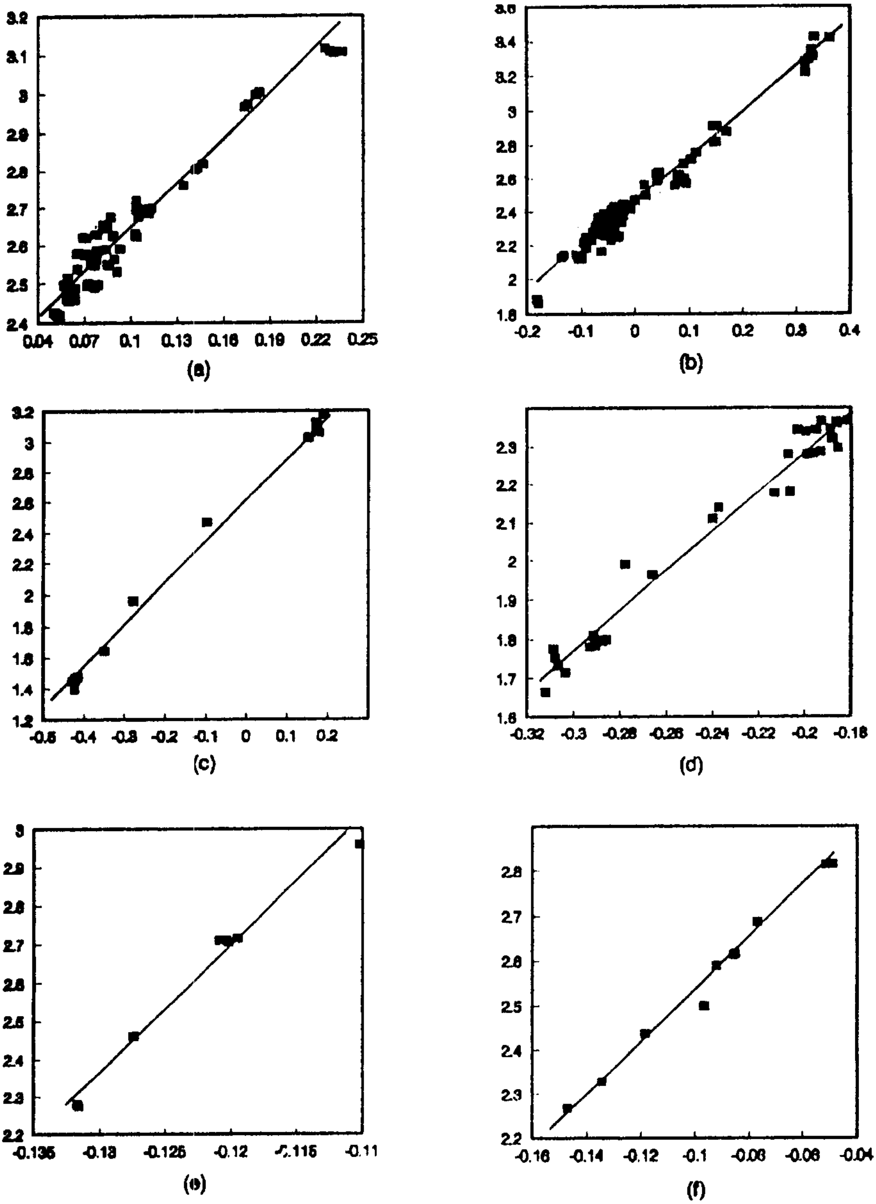

Fig.1 $\chi_A - \Sigma Q_B / R_{AB}$ (1/F) versus Q_A in eq. (7)' from standard set for atoms: (a) H (b) C (c) N (d) O (e) F (f) Cl

$\chi_A = \chi_B = \cdots = \chi_m = (\Sigma 1/ \chi_A^0)^{-1}$, taken as harmony mean introduced.

$$\chi_A = \chi_A^0 + 2\eta_A^0 Q_A + \Sigma Q_B / R_{AB} (1/F) \qquad (7)$$

$$\chi_A - \Sigma Q_B / R_{AB} (1/F) = \chi_A^0 + 2\eta_A^0 Q_A \qquad (7)'$$

where the factor F bears a meaning similiar to effective diaelectric constant used in many Molecular Mechanics Programs such as MM3 [15]. Its incorpration into eq. 6 dramatically improves the accuracy. The value of F used was 6.25.

The values of χ and η for neutral atoms are availabe in literature [4, 10], but the χ_A^0 and η_A^0 have different meaning from them as stated above, and therefore, they were treated as empirical parameters in this work and were derived from the observations.

The basic steps of the procedure are as follows.

1. The STO-3G calculation was performed on selected model molecules containing various functional groups , which are called as standard set and listed in the table 1(Nos. 1-15)

2. By solving eqs. (7)' and (5) for the standard set using the charges obtained in step 1., derive parameters χ^0 and η^0 for all types of atoms which were listed in table 2. The regression lines for atoms H, C, N, O, F and Cl were respectively displayed in (a) ,(b), (c), (d), (e), and (f) of figure 1.

3. By using the derived parameters obtained from step 2 and eqs. (7)' and (5) , calculation were performed on each molecule in test set, which consists of the remaining part of table 1. The comparison between this and ab intio methods were displayed in fig.2, where (a) for structures Nos.16-19, (b) for 20-25, (c) for 26-30, (d) for 31-36 and (e) for 37-41, respectively.

The program used in this study was written by the present authors in

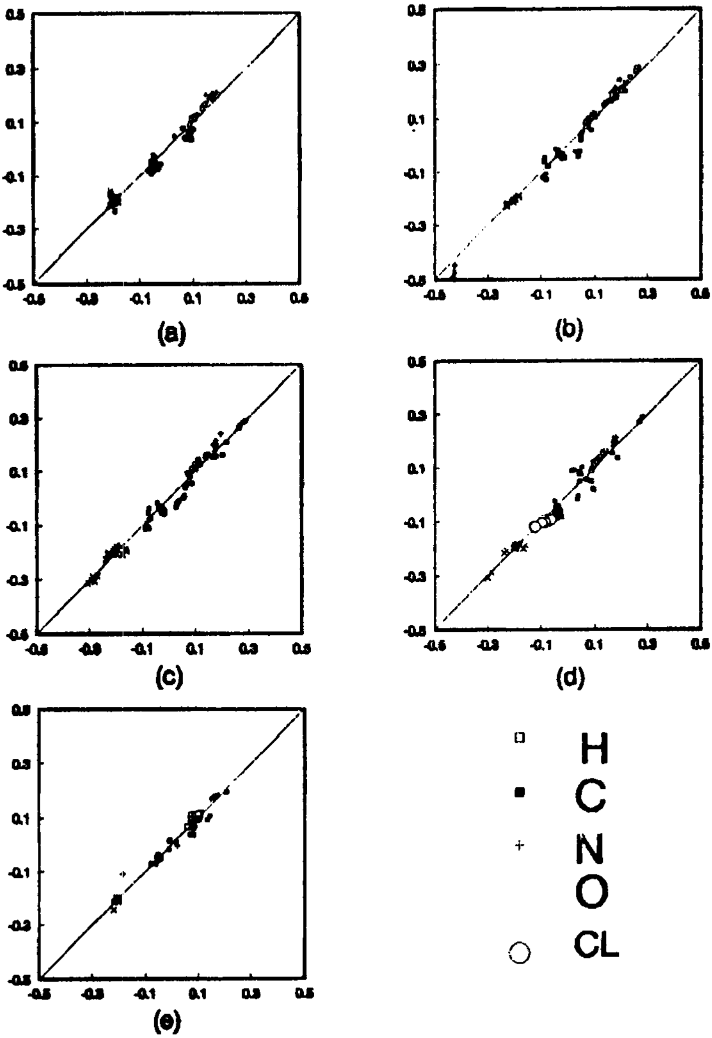

Fig.2 STO-3G charges versus EEM charges for structures Nos.
(a) 16-19 (b) 20-25 (c) 26-30 (d) 31-36 (e) 37-41

FORTRAN 77 for an IBM 486 machine. The required computing time is approximately proportional to squared number of atoms in a molecule and less than one thousandth of the time for corresponding STO-3G calculation on average.

Table 2. Electronegativity and Hardness for Atoms H,C,N,O,F,Cl in molecule

	H	C	N	O	F	Cl
χ^*	2.20	2.55	3.06	3.44	3.98	3.16
$\chi_A{}^0$	2.263	2.462	2.623	3.197	4.134	3.102
$\eta_A{}^0$	1.934	1.405	1.388	2.313	4.570	2.988
R	.968	.964	.999	.939	.996	.986

* for neutral atom

DISCUSSION

As shown by the fig. 1 and table 2, a very good correlation exists between quantities in both sides of the eq. (7)'. There is no need to subclassify atom type for each type of the atoms (say Csp ^{2} and Csp ^{3}). In fact, no improvement could be made if subclassifying was made, whose results were not reported here. Since the method is based on empirical ground, no clear physical explanation could be made, but the overall trend is chemically intuitive, as shown by the values in table 2.

As shown by the fig.2, almost identical charges could be obtained by this method compared with the results from ab initio method. Since almost same level of accuracy as the STO-3G method could be reached and only neglible computing time is required compared with the STO-3G method, the Electronegativity Equalization Method (EEM) is capable of handling very large molecules which the ab initio method is not.

More importantly, this method does not depend on what kind of ab initio charge being used as observation, according to the discussion in section PROCEDURE above. It is believed that this method could in principle reach the same level of accuracy when more accurate results form more rigorous quantum chemistry method or from other sources are used as observations. There seems no need to modify the procedure or to increase computing time or to require more advanced computer for such a treatment.

IMPACT SENSITIVITY AND ATOMIC PARTIAL CHARGE

Murray et al. have found that the charges at both C and N atoms of a $C - NO_2$ linkage in nitroaromatics are invariably positive[16]. The same sign of charges in adjacent atoms must cause a certain degree of instability. They found a relation between the impact sensitivity and $V_{mid,max}$. The $V_{mid,max}$ is the largest V_{mid}, the potential at the mid point of a $C - NO_2$ linkage. The V_{mid} was represented by :

$$V_{mid} = (Q_C + Q_N) / 0.5R$$

where R, Q_C, Q_N respectively are the bond length, atomic partial charges at the C and N atoms. The charges they used were calculated at STO-5G level

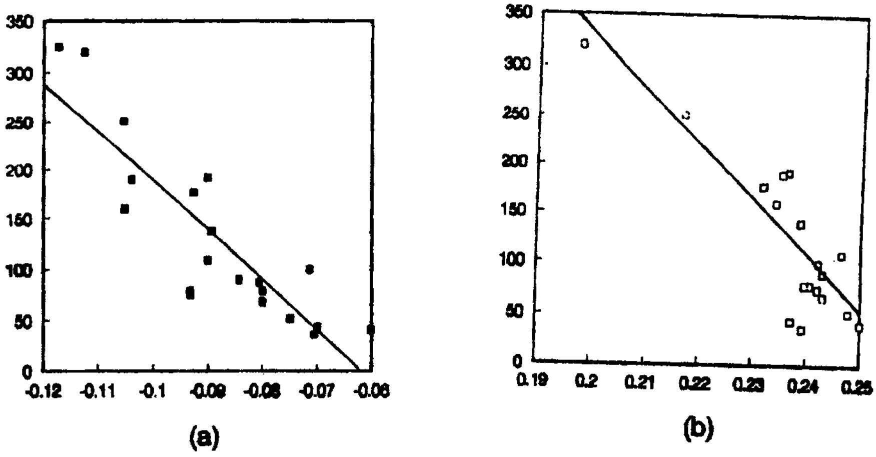

Fig.3 Impact Sensitivity and Atomic Partial Charge

(a) h_{50} versus $V_{mid,\,max}$ (b) h_{50} versus S using crystallographic geometries. Fig. 3(a) illustrated the relation for a total of 20 compounds they studied, but using the charges calculated by the EEM in this work. The correlation coefficient is 0.85, very close to their result of 0.86, showning the charges by the EEM in this work could serve for the same purpose with almost same accuracy, at least for the compounds studied.

Fig. 3(b) is a plot of h_{50} versus S, S being the total charge for the NO_2 group, calculated by the EEM in this work. The line seems equally good as the plot in Fig. 3(a). The coefficient is 0.86. The total charge in NO_2 group represents the charge transferred from other atoms in the molecule through the conjugation system. Since the charge transfer should stabilize the molecule, therefore, the more charge is transferred into the region, the smaller the potential and the more stable the molecule should be.

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