Short Communication

Correlation of the Position of the Bond Functions in H–X with Electronegativity

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S type Gaussian bond functions are optimized for HF, H_2O, NH_3, and CH_4. The optimization is carried out with respect to the exponent and position in the H–X bond. The position is found to correlate well with the electronegativity of Pauling and Allred-Rochow.

Key words: Bond functions, optimized $\sim$, for HF, H_2O, NH_3, CH_4

In some recent articles [1, 2] we have compared the performance of optimized bond functions with $3d$ type polarization functions for SCF calculations. It was generally observed that bond functions were more efficient. Some time ago, we also suggested [3] that it might be possible to correlate parameters which characterize optimized basis functions with electronegativity. In this communication, we would like to report that we have observed a linear relationship between the position of the optimized bond function expressed as a fraction of the X–H bond length and the electronegativity of the X atom, X = C, N, O, and F.

Our calculations were conducted using the POLYATOM [4] system of Gaussian SCF programs kindly supplied by Professor Moskowitz. CH_4, NH_3, OH_2, and FH were considered in their experimental equilibrium geometries. Huzinaga's [5] $(9s, 5p)$ basis set was contracted to a $(4s, 3p)$ according to Dunning's rules [6] for the X atom. For the hydrogen atom, four basis functions were employed [5], contracted to two with an effective exponent of 1.2 for NH_3 and HF. A value of 1.275 [7] was used for H_2O and 1.225 [8] was used for CH_4. A $1s$ type Gaussian function was placed along the X–H bond and both the position along the bond and the exponent

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were varied until a minimum in the energy was reached. This minimum was obtained by passing a second-degree polynomial including a cross term through points in the vicinity of the suspected minimum and then finding the minimum for the polynomial analytically. The results are summarized in Table 1.

Table 1. Optimized bond-function parameters for X–H

Molecule	Position[a]	Exponent	Energy (a.u.)
CH_4	0.35	1.10	-40.20336
NH_3	0.40	1.13	-56.19658
OH_2	0.44	1.13	-76.02954
FH	0.49	1.23	-100.03596

[a] Expressed as a fraction of the bond length measured from the hydrogen atom

In Fig. 1 we have plotted the electronegativities of both Pauling [9] (E_P) and Allred-Rochow [10] (E_{AR}) vs our calculated position of the bond function (d) expressed as a fraction of the bond length of X–H measured from the H atom. A least square fit of the data results in

$$d = 0.0878\, E_{AR} + 0.131, \tag{1a}$$

$$d = 0.1056\, E_P + 0.0754, \tag{1b}$$

for E_{AR} and E_P respectively. The standard deviation for Eq. (1a) is 0.001 and for Eq. (1b) is 0.003. However, the electronegativities of Mulliken [11] do not seem to correlate well with our data.
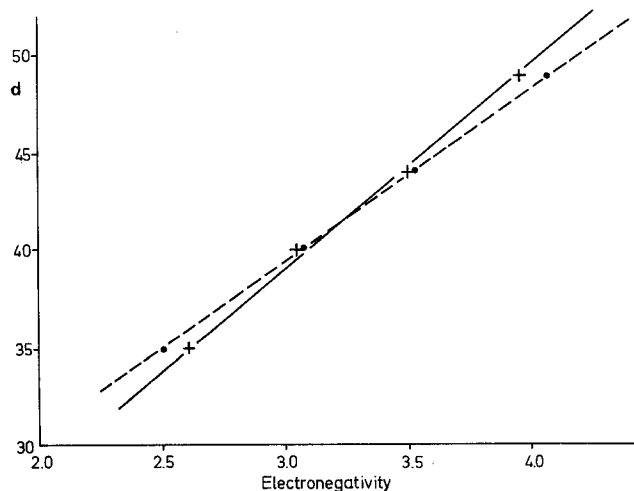

Fig. 1. Plot of electronegativity versus d measured as a fraction of the bond length from the hydrogen atom. The solid line and + are for the electronegativity of Pauling. The dashed line and · are for the electronegativity of Allred-Rochow

For a correlation to exist, we feel that it is important that the same type of polarization process be involved. Thus, we would not expect the value for LiH to be accurately expressed by Eq. (1). For X–H we are observing a tendency to form X^-H^+ and a shift of charge from H to X. In LiH we should expect the partial formation of Li^+ and a very diffuse H^-, as well as a shift of charge from Li to H. Consequently, the wavefunctions necessary to describe these two situations place different requirements on the basis sets.

We feel that bond functions are capable of describing a physical effect, i.e. the transfer of charge inside a chemical bond. By placing a $1s$ Gaussian function in the bond and varying its position and size, we are in a certain sense measuring "... the power of an atom in a molecule to attract electrons to itself" [12]. We also hope that correlations of this type will help establish optimum bond functions for many different types of chemical bonds thus facilitating good calculations on large molecules.

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