

See discussions, stats, and author profiles for this publication at:  
<https://www.researchgate.net/publication/244285762>

# Molecular electrostatic potential as reactivity index in hydrogen bond formation: An HF/6-31 + G(d) study of hydrogen-bonded (HCN)(n) clusters, n = 2, 3, 4, 5, 6, 7

ARTICLE *in* JOURNAL OF MOLECULAR STRUCTURE · SEPTEMBER 2000

Impact Factor: 1.6 · DOI: 10.1016/S0022-2860(00)00383-5

---

CITATIONS

22

---

READS

26

## 2 AUTHORS:



**Boris Galabov**

Sofia University "St. Kliment Ohridski"

117 PUBLICATIONS 1,344 CITATIONS

SEE PROFILE



**Petia Bobadova-Parvanova**

Rockhurst College

27 PUBLICATIONS 622 CITATIONS

SEE PROFILE

# Molecular electrostatic potential as reactivity index in hydrogen bond formation: an HF/6-31 + G(d) study of hydrogen-bonded (HCN)<sub>n</sub> clusters, $n = 2, 3, 4, 5, 6, 7$ <sup>☆, ☆☆</sup>

B. Galabov<sup>\*</sup>, P. Bobadova-Parvanova

*Department of Chemistry, University of Sofia, 1 James Bourchier Avenue, 1164 Sofia, Bulgaria*

Received 6 July 1999; accepted 13 September 1999

## Abstract

Ab initio molecular-orbital calculations of (HCN)<sub>n</sub> clusters for  $n = 2, 3, 4, 5, 6, 7$  were performed following the procedure of King and Weinhold [B.F. King, F. Weinhold, J. Chem. Phys. 103 (1995) 333]. Geometry optimisation and vibrational frequency calculations at the optimised geometry were carried out at HF/6-31 + G(d) level of theory. The calculations confirm the known linear relations between the energy of hydrogen bond formation ( $\Delta E^{(n)}$ ) and: (1) the hydrogen bond length ( $r_{\text{N} \cdots \text{H}}^{(n-1)}$ ); (2) the change of the neighbouring C–H bond length ( $\Delta r_{\text{C-H}}^{(n)}$ ); and (3) its characteristic vibrational frequency shift ( $\Delta \nu_{\text{C-H}}^{(n)}$ ). An excellent linear dependence is found between the energy of hydrogen bond formation ( $\Delta E^{(n)}$ ) and the molecular electrostatic potential at the end nitrogen atom ( $V_{\text{N}}^{(n-1)}$ ). A perfect linear relation also exists between  $\Delta E^{(n)}$  and the molecular electrostatic potential at the end hydrogen atom ( $V_{\text{H}}^{(n-1)}$ ). The results obtained confirm that the molecular electrostatic potential at atomic sites can be used as a reactivity index reflecting the ability of molecules to participate in hydrogen bonding. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** (HCN)<sub>n</sub> clusters; Molecular electrostatic potential; Hydrogen bond

## 1. Introduction

Hydrogen bond formation is an important phenomenon that determines essential properties of many chemical and biological systems. Numerous experimental and theoretical studies aim to describe the hydrogen bond in terms of structural and electronic properties of the electron donor and acceptor mole-

cules. In view of the known importance of the electrostatic interaction in hydrogen bonding [1–14], it is not surprising that the molecular electrostatic potential has been used as a tool in describing hydrogen bonding. The positions of the minima of the molecular electrostatic potential associated with the electron donating centre in isolated molecules have been successfully used to predict the sites and directionality of hydrogen bonds in a variety of systems [15–17]. A linear relation has been found between the calculated energies of hydrogen bond formation and the magnitude of the molecular electrostatic potential at a fixed distance from the proton accepting centre in a series of complexes between hydrogen fluoride and various acceptors [15]. In recent studies from this laboratory

<sup>☆</sup> Dedicated to Professor James R. Durig on the occasion of his 65th birthday.

<sup>☆☆</sup> Taken in part from the thesis of P. Bobadova-Parvanova which will be submitted in partial fulfillment of the PhD degree.

<sup>\*</sup> Corresponding author. Tel.: + 359-2-6256-421; fax: + 359-2-9625-438.

E-mail address: galabov@chem.uni-sofia.bg (B. Galabov).

[18,19] the applicability of the molecular electrostatic potential in predicting the energy of hydrogen bond formation has also been demonstrated. Hydrogen-bonded complexes between hydrogen fluoride and two series of nitrile and carbonyl derivatives have been investigated using ab initio molecular-orbital calculations at the HF/6-31 + G(d,p) level. It was found that an accurately defined quantity, the molecular electrostatic potential *at* the electron donating atom, rather than the potential *in the vicinity* of the nitrile or carbonyl group, correlates excellently with the energy of hydrogen bond formation for the respective series. A perfect linear dependence that unifies the two series of proton-acceptor molecules has been found. It has been demonstrated that the molecular electrostatic potential at atomic sites can be used as a reactivity index reflecting the ability of molecules from the series studied to participate in hydrogen bonding.

In some studies [18,19] we have examined many hydrogen bonded complexes, but always formed by two molecules: electron-donating and electron-accepting molecules. It is of interest to investigate the applicability of the molecular electrostatic potential as reactivity parameter for longer hydrogen-bonded associates. The question is whether the molecular electrostatic potential can adequately describe the co-operative effects in hydrogen bonding. For this purpose in the present study a series of hydrogen-bonded (HCN)<sub>n</sub> clusters for  $n = 2, 3, 4, 5, 6, 7$  has been investigated. The HCN molecule is small enough to allow the use of relatively good basis sets for ab initio calculations. On the other hand, the (HCN)<sub>n</sub> clusters can be easily described because of their highly symmetrical geometry. It is known that the HCN molecules form linear hydrogen-bonded clusters in all phases [20,21]. In a recent study King and Weinhold [20] performed ab initio calculations of (HCN)<sub>n</sub> clusters for  $n = 2, 3, 4, 5, 6, 7$  and concluded that the co-operative effects are essentially non-linear and can be rationalised in terms of the fundamental  $n_N \rightarrow \sigma_{CH}^*$  “charge transfer” nature of hydrogen bonding. More recently Sokolov [14] demonstrated that the non-linear effects can be explained with a simple model including coulomb interaction of the effective atomic charges, inductive action of these charges on the neighbouring chemical bonds (which realise the co-operative effects) and the exchange repulsion of the atoms. As

was mentioned above in our previous studies [18,19] we have shown that the molecular electrostatic potential at atomic sites can rationalise the energy of hydrogen bond formation of different series of molecules. It is of great interest therefore to know whether such easily obtainable, accurately defined, and simple molecular quantity can adequately explain the non-linear co-operative effects of (HCN)<sub>n</sub> clusters and serve as a reactivity index in describing the formation of hydrogen bonded clusters.

## 2. Calculations

The properties of hydrogen-bonded (HCN)<sub>n</sub> clusters for  $n = 1, 2, 3, 4, 5, 6, 7$  were calculated at HF/6-31 + G(d) level of theory. The choice of this basis set allows full comparison with the results of King and Weinhold [20]. Harmonic vibrational frequencies (at the same level of theory) confirmed that the located structures correspond to minima having no imaginary frequencies. In determining the energy of hydrogen bond formation, the zero-point vibrational energy was taken into account. A scaling factor of 0.9135 was used [22]. The obtained interaction energies were also corrected for the basis set superposition error (BSSE) which is known to be appreciable in estimating the energy of hydrogen-bond formation [11]. The counterpoise method (CP) [23] was used. Its applicability in calculations of molecular complexes was recently reviewed [24]. Fragment relaxation energy terms were also taken into account to estimate BSSE [25]. All calculations were carried out with the GAUSSIAN 92W program package [26].

As a standard output of the program, the molecular electrostatic potential at the atoms of each (HCN)<sub>n</sub> cluster were also obtained. The molecular electrostatic potential at an atom Y can be defined as follows [27]:

$$V_Y \equiv V(R_Y) = \sum_{A \neq Y} \frac{Z_A}{|R_Y - R_A|} - \int \frac{\rho(r')}{|R_Y - r'|} dr' \quad (1)$$

where  $Z_A$  is the charge on nucleus A located at  $R_A$ ,  $\rho(r)$  is the electronic density function of the respective molecule as obtained from ab initio molecular-orbital calculations, and  $r'$  is a dummy integration variable. Eq. (1) is written in atomic units and contains a

Table 1

HF/6-31 + G(d) ab initio calculated non-corrected energy of hydrogen bond formation ( $\Delta E_n^{\text{SCF}}$ ), zero-point vibrational energy correction ( $\Delta E_n^{\text{ZPE}}$ ), counterpoise correction ( $\Delta E_n^{\text{CP}}$ ), relaxation correction ( $\Delta E_n^{\text{REL}}$ ), and totally corrected energy of hydrogen bond formation ( $\Delta E^{(n)}$ ) for the hydrogen-bonded (HCN) $_n$  clusters studied. All values are in kcal/mol

$n$	$\Delta E_n^{\text{SCF}}$	$\Delta E_n^{\text{ZPE}}$	$\Delta E_n^{\text{CP}}$	$\Delta E_n^{\text{REL}}$	$\Delta E^{(n)}$
2	−4.3424	0.7590	0.1468	0.0888	−3.3478
3	−5.4072	0.7939	0.1299	0.1184	−4.3650
4	−5.7687	0.8094	0.1255	0.1281	−4.7057
5	−5.9224	0.8140	0.1236	0.1310	−4.8538
6	−5.9960	0.8180	0.1456	0.1121	−4.9203
7	−6.0392	0.8209	0.1493	0.1217	−4.9473

summation over the atomic nuclei, treated as positive point charges, and an integration over the “continuous” negative charge distribution of the electrons.

### 3. Results and discussion

#### 3.1. Interaction energy

The non-corrected energy of hydrogen bond formation calculated as a difference between the respective SCF energies ( $\Delta E_n^{\text{SCF}}$ ), the zero-point vibrational energy correction ( $\Delta E_n^{\text{ZPE}}$ ), the counterpoise correction ( $\Delta E_n^{\text{CP}}$ ), the relaxation correction ( $\Delta E_n^{\text{REL}}$ ), and totally corrected energy of hydrogen bond formation ( $\Delta E^{(n)}$ ) for the hydrogen-bonded (HCN) $_n$  clusters studied are presented in Table 1. It is worth mentioning that the values of  $\Delta E_n^{\text{CP}}$  and  $\Delta E_n^{\text{REL}}$  are of the same order of magnitude. This is a further evidence that the omission of the fragment relaxation energy terms in estimating the BSSE corrections can introduce significant errors [19,25].

As is discussed by King and Weinhold [20] the dependence of  $\Delta E^{(n)}$  versus  $n$  is non-linear. The values of interaction energy tend asymptotically to approximately −5 kcal/mol. This is a manifestation of the non-linear co-operative effects in (HCN) $_n$  clusters.

Table 2

HF/6-31 + G(d) ab initio calculated values of the last formed hydrogen bond length ( $r_{\text{N}\cdots\text{H}}^{(n-1)}$ ) and the change in the neighbouring C–H bond length ( $\Delta r_{\text{C-H}}^{(n)}$ ) and its infrared frequency shifts ( $\Delta \nu_{\text{C-H}}^{(n)}$ ) with respect to the corresponding values for isolated HCN molecule for the hydrogen-bonded (HCN) $_n$  clusters studied

$n$	$r_{\text{N}\cdots\text{H}}^{(n-1)}$ (Å)	$\Delta r_{\text{C-H}}^{(n)}$ (Å)	$\Delta \nu_{\text{C-H}}^{(n)}$ (cm <sup>−1</sup> )
2	2.3366	0.0042	−53
3	2.2926	0.0054	−64
4	2.2791	0.0057	−71
5	2.2758	0.0058	−73
6	2.2738	0.0059	−74
7	2.2728	0.0060	−75

As will be shown further in the text the non-linear dependence between  $\Delta E^{(n)}$  and  $n$  can be convincingly explained in terms of molecular electrostatic potential.

#### 3.2. Structural and infrared spectral parameters

The optimised structure of the hydrogen-bonded (HCN) $_n$  clusters studied is shown in Fig. 1. In accordance with experiment and with the previous ab initio calculations performed by King and Weinhold [20] all (HCN) $_n$  clusters are linear and possess  $C_{\infty v}$  symmetry. Detailed investigation of the structural and infrared parameters of all (HCN) $_n$  clusters that are object of the present study and the changes occurred due to formation of hydrogen bonds has been provided by King and Weinhold [20]. Comparison with the available experimental values is also discussed there [20]. That is why limited discussion on dependencies between these parameters and the energy of hydrogen bond formation will be given here.

The HF/6-31 + G(d) ab initio calculated values of the last formed hydrogen bond length ( $r_{\text{N}\cdots\text{H}}^{(n-1)}$ ) and the change in the neighbouring C–H bond length ( $\Delta r_{\text{C-H}}^{(n)}$ ) with respect to the corresponding value for isolated HCN molecule for the hydrogen-bonded (HCN) $_n$  clusters studied are given in Table 2. The geometry

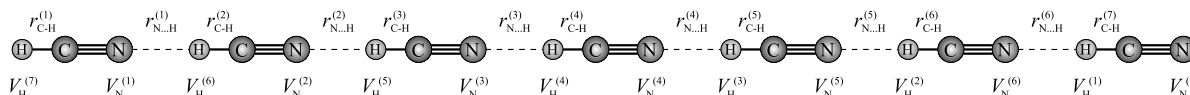


Fig. 1. Structure of hydrogen-bonded (HCN) $_n$  clusters studied and definition of geometrical parameters ( $r_{\text{N}\cdots\text{H}}^{(n-1)}$ ,  $r_{\text{C-H}}^{(n)}$ ) and molecular electrostatic potentials ( $V_{\text{N}}^{(n-1)}$ ,  $V_{\text{H}}^{(n-1)}$ ). See text.

Table 3

HF/6-31+G(d) ab initio calculated molecular electrostatic potentials at the end nitrogen ( $V_N^{(n)}$ ) and hydrogen ( $V_H^{(n)}$ ) atom for the hydrogen-bonded  $(\text{HCN})_n$  clusters studied. All values are in a.u.

$n$	$V_N^{(n)}$	$V_H^{(n)}$
1	-18.3230	-0.9559
2	-18.3464	-0.9331
3	-18.3543	-0.9252
4	-18.3579	-0.9215
5	-18.3599	-0.9196
6	-18.3611	-0.9183
7	-18.3619	-0.9175

parameters are defined in Fig. 1. The infrared frequency shift of the C–H bond stretch ( $\Delta\nu_{\text{C-H}}^{(n)}$ ) is also given in the Table 2. The non-linear dependencies of  $r_{\text{N}\cdots\text{H}}^{(n-1)}$ ,  $\Delta r_{\text{C-H}}^{(n)}$ , and  $\Delta\nu_{\text{C-H}}^{(n)}$  versus  $n$  are discussed in detail in the paper of King and Weinhold [20] and therefore will not be given here. We would like to mention however, that there exist almost perfect linear relations between the energy of hydrogen bond formation and  $r_{\text{N}\cdots\text{H}}^{(n-1)}$ ,  $\Delta r_{\text{C-H}}^{(n)}$ , and  $\Delta\nu_{\text{C-H}}^{(n)}$ . All these dependencies can, of course, be expected, though the obtained results for the linear regression coefficients are impressive: 0.9977, 0.9993 and 0.9989, respectively.

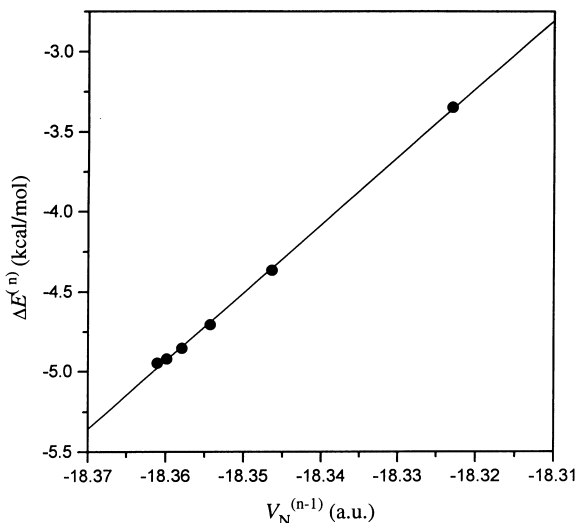


Fig. 2. Dependence between the energy of hydrogen bond formation ( $\Delta E^{(n)}$ ) and the molecular electrostatic potential at the end nitrogen atom ( $V_N^{(n-1)}$ ) for the hydrogen-bonded  $(\text{HCN})_n$  clusters studied,  $n = 2, 3, 4, 5, 6, 7$ .

### 3.3. Molecular electrostatic potential and hydrogen bonding

The HF/6-31 + G(d) ab initio calculated molecular electrostatic potentials at the end nitrogen ( $V_N^{(n)}$ ) and hydrogen ( $V_H^{(n)}$ ) atom for the hydrogen-bonded  $(\text{HCN})_n$  clusters studied are presented in Table 3. These quantities are also defined in Fig. 1. As mentioned above, the absolute values of the energy of formation of the last hydrogen bond increase non-linearly with increased cluster size and tend asymptotically to a given value. It can be seen from Table 3 that the absolute values of the molecular electrostatic potential at the end nitrogen atom ( $|V_N^{(n)}|$ ) also increase non-linearly with  $n$ . On the contrary, the absolute values of molecular electrostatic potential at the end hydrogen atom ( $|V_H^{(n)}|$ ) decrease non-linearly with increased  $n$ . It can also be noted that the higher is  $|V_N^{(n)}|$ , the smaller is  $|V_H^{(n)}|$  and there is a perfect linear correlation between these two quantities ( $R = 0.99997$ ).

Fig. 2 represents the dependence between  $\Delta E^{(n)}$  and  $V_N^{(n-1)}$ . The respective linear regression result is:

$$\Delta E^{(n)} = 42.5310(\pm 0.6031)V_N^{(n-1)} + 775.9393(\pm 11.0677) \quad (2)$$

$$n = 6, R = 0.9996, SD = 0.0195$$

The linear regression coefficient is indeed very high and reveals a perfect linear dependence between  $\Delta E^{(n)}$  and  $V_N^{(n-1)}$ . The relation found, clearly shows that the molecular electrostatic potential can adequately describe the co-operative effects in hydrogen bonding. When  $n$  is small, with increasing the cluster size molecular electrostatic potential at the end nitrogen atom becomes more negative. Consequently, the participation of that atom in formation of new hydrogen bond becomes more favourable. For higher  $n$  there is a gradual saturation,  $V_N^{(n)}$  becomes approximately constant value and consequently the energies of all new formatted hydrogen bonds become approximately equal.

It was interesting to also study the dependence between  $\Delta E^{(n)}$  and the molecular electrostatic potential at the other atom participating in hydrogen bond formation: the end hydrogen atom of each cluster. In the light of the fact mentioned above that

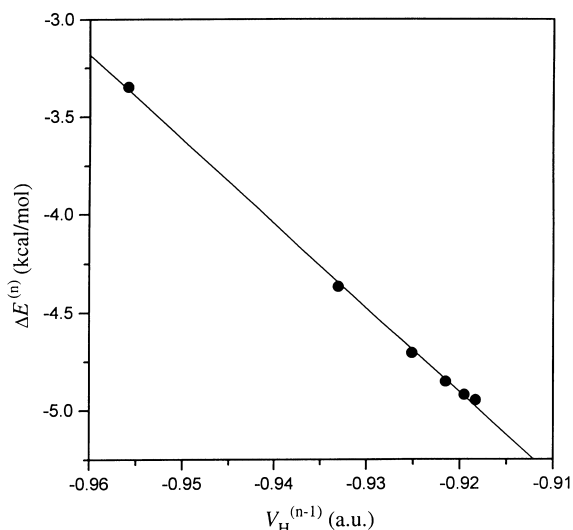


Fig. 3. Dependence between the energy of hydrogen bond formation ( $\Delta E^{(n)}$ ) and the molecular electrostatic potential ( $V_H^{(n-1)}$ ) at the end hydrogen atom for the hydrogen-bonded  $(\text{HCN})_n$  clusters studied,  $n = 2, 3, 4, 5, 6, 7$ .

there is perfect linear relation between  $V_N^{(n)}$  and  $V_H^{(n)}$ , a linear dependence can be expected. Indeed, as can be seen from Fig. 3 there is an excellent correlation between  $\Delta E^{(n)}$  and  $V_H^{(n-1)}$ . The linear regression result is:

$$\Delta E^{(n)} = 43.1213(\pm 0.7436)V_H^{(n-1)} - 44.5794(\pm 0.6908) \quad (3)$$

$$n = 6, R = 0.9994, SD = 0.0237$$

The obtained linear regression coefficient is again very high. It can be stated that there exist perfect linear dependencies between  $\Delta E^{(n)}$  and  $V_N^{(n-1)}$ , as well as between  $\Delta E^{(n)}$  and  $V_H^{(n-1)}$ . As expected, the trends of changes of the molecular electrostatic potentials of nitrogen and hydrogen atom are opposite reflecting the different role of the two atoms in the process of hydrogen bonding. The more negative the molecular electrostatic potential of the electron donating atom is, the higher is its ability to form hydrogen bonds. On the contrary, the less negative the molecular electrostatic potential of the electron accepting atom is, the higher is its ability to form a hydrogen bond. The addition of new HCN molecules to the cluster leads to increased ability for new

hydrogen bond formation at both ends: through the end nitrogen atom and through the end hydrogen atom. This tendency continues until saturation is reached and the addition of new HCN molecules no more leads to further changes in the ability of the cluster to grow.

The linear dependence between  $\Delta E^{(n)}$  and  $V_N^{(n-1)}$ , as well as between  $\Delta E^{(n)}$  and  $V_H^{(n-1)}$  are in accord with our previous results concerning series of carbonyl and nitrile derivatives [18,19]. The relations established in the present study show once again that the molecular electrostatic potential can be successfully used to predict the ability of molecules to form hydrogen bonds. In our previous studies it has been demonstrated for series of different electron donor molecules that the energy of hydrogen bonds can be rationalised in terms of molecular electrostatic potential at the electron donating atom that takes part in the hydrogen bond formation. According to the present results, the energy of hydrogen bond formation can be rationalised in terms of the variation of the molecular electrostatic potentials of both electron donor and electron acceptor atoms participating in the interaction.

The above discussed linear dependencies between the interaction energy and molecular electrostatic potentials at the atoms participating in hydrogen bond formation do not imply that the electrostatic forces are the only factor reflecting the process of hydrogen bonding. It is well known that there are a number contributions to the interaction energy: electrostatic energy, polarisation energy, exchange repulsion, charge transfer energy, and dispersion energy [1,2]. However, the linear relations found, convincingly demonstrate that the ability for hydrogen bonding can be explained in terms of a simple and accurately defined molecular quantity: the molecular electrostatic potential, a quantity that can be obtained both theoretically and experimentally. The linear dependence between  $\Delta E^{(n)}$  and  $V_N^{(n-1)}$ , as well as between  $\Delta E^{(n)}$  and  $V_H^{(n-1)}$  clearly shows that the molecular electrostatic potential at atomic sites can be used as a reactivity index for the process of hydrogen bonding.

#### 4. Conclusions

The ab initio HF/6-31 + G(d) study of  $(\text{HCN})_n$  clusters confirms the known linear relations between

the energy of hydrogen bond formation ( $\Delta E^{(n)}$ ) and: (1) the last formed hydrogen bond length ( $r_{N\cdots H}^{(n-1)}$ ); (2) the change of the neighbouring C–H bond length ( $\Delta r_{C-H}^{(n)}$ ); and (3) its characteristic vibrational frequency shift ( $\Delta \nu_{C-H}^{(n)}$ ).

An excellent linear dependence is found between the energy of hydrogen bond formation ( $\Delta E^{(n)}$ ) and the molecular electrostatic potential at the end nitrogen atom ( $V_N^{(n-1)}$ ). A perfect linear relation also exists between  $\Delta E^{(n)}$  and the molecular electrostatic potential at the end hydrogen atom ( $V_H^{(n-1)}$ ). These dependencies show that the molecular electrostatic potential can be successfully used to predict the ability of molecules to form hydrogen bonds. It can be stated that the energy of hydrogen bond formation can be predicted from the molecular electrostatic potentials of both electron donor and electron acceptor atoms participating in the interaction. In general, the results obtained indicate that the molecular electrostatic potential at atomic sites can be used as a reactivity index reflecting the ability of molecules to participate in hydrogen bonding.

## References

- [1] P. Schuster, in: P. Schuster, G. Zundel, C. Sandorfy (Eds.), *The Hydrogen Bond. I. Theory*, North-Holland, Amsterdam, 1976, p. 25.
- [2] K. Morokuma, K. Kitaura, in: P. Politzer, D.G. Truhlar (Eds.), *Chemical Applications of Atomic and Molecular Electrostatic Potentials*, Plenum Press, New York, 1981, p. 215.
- [3] P. Kollman, in: P. Politzer, D.G. Truhlar (Eds.), *Chemical Applications of Atomic and Molecular Electrostatic Potentials*, Plenum Press, New York, 1981, p. 243.
- [4] U. Singh, P. Kollman, *J. Chem. Phys.* 80 (1984) 353.
- [5] A. Buckingham, P. Fowler, J. Hutson, *Chem. Rev.* 88 (1988) 963.
- [6] M. Benzel, C. Dykstra, *J. Chem. Phys.* 78 (1984) 4052.
- [7] M. Spackman, *J. Chem. Phys.* 85 (1986) 6587.
- [8] R. Bonaccorsi, C. Petrongolo, E. Scrocco, J. Tomasi, *Theor. Chim. Acta.* 20 (1970) 331.
- [9] P. Hobza, R. Zahradnik, *Chem. Rev.* 88 (1988) 871.
- [10] P. Rendell, G. Backsay, N. Hush, *Chem. Phys. Lett.* 117 (1985) 400.
- [11] S. Scheiner, *Rev. Comput. Chem.* 2 (1991) 165.
- [12] S.R. Gadre, S.S. Pundlik, *J. Phys. Chem. B* 101 (1997) 3298.
- [13] G. Naray-Szabo, G. Ferenczy, *Chem. Rev.* 95 (1995) 829.
- [14] N. Sokolov, *J. Mol. Struct.* 436/437 (1997) 201.
- [15] P. Kollman, J. McKelvey, A. Johansson, S. Rothenberg, *J. Am. Chem. Soc.* 97 (1975) 955.
- [16] G. Leroy, G. Louterman-Leloup, P. Ruelle, *Bull. Soc. Chim. Belg.* 85 (1976) 205.
- [17] P. Politzer, J.S. Murray, *Rev. Comput. Chem.* 2 (1991) 273.
- [18] P. Bobadova-Parvanova, B. Galabov, *J. Phys. Chem. A* 102 (1998) 1815.
- [19] B. Galabov, P. Bobadova-Parvanova, *J. Phys. Chem. A* 103 (1999) 6793.
- [20] B.F. King, F. Weinhold, *J. Chem. Phys.* 103 (1995) 333.
- [21] D.J. Nesbitt, *Chem. Rev.* 88 (1988) 843.
- [22] J.A. Pople, A.P. Scott, M.W. Wong, L. Radom, *Isr. J. Chem.* 33 (1993) 345.
- [23] S.F. Boys, F. Bernardi, *Mol. Phys.* 19 (1970) 553.
- [24] F.B. van Duijneveldt, J.G.C.M. van Duijneveldt-van de Rijdt, J.H. van Lenthe, *Chem. Rev.* 94 (1994) 1873.
- [25] S.S. Xantheas, *J. Chem. Phys.* 104 (1996) 8821.
- [26] M.J. Frisch, G.W. Trucks, M. Head-Gordon, P.M.W. Gill, M.W. Wong, J.B. Foresman, B.G. Johnson, H.B. Schlegel, M.A. Robb, E.S. Replogle, R. Gomperts, J.L. Andres, K. Raghavachari, J.S. Binkley, C. Gonzales, R.L. Martin, D.J. Fox, D.J. Defrees, J. Baker, J.J.P. Stewart, J.A. Pople, *GAUSSIAN 92*, Revision E.1; Gaussian, Inc.: Pittsburgh, PA, 1992.
- [27] P. Politzer, in: P. Politzer, D.G. Truhlar (Eds.), *Chemical Applications of Atomic and Molecular Electrostatic Potentials*, Plenum Press, New York, 1981, p. 7.