

# Hydrogen bonds: relation between lengths and electron densities at bond critical points

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**Abstract.** The electron densities for a number of molecules with either inter- or intra-molecular hydrogen bonds are analyzed using the theory of atoms in molecules. The levels of theory used include second order Møller Plesset and density functional methods. The molecules investigated ranges from small molecules/ions to an alanine octa-peptide. The hydrogen bond length,  $BL$ , varies from 1.15 to 3.01 Å and  $\rho_b$ , the electron density at the bond critical point, spans the interval 0.0033 to 0.168 (au). We find that the data may be represented by the relation  $\rho_b = A \exp(-B \times BL)$ , where  $A$  and  $B$  are empirical constants. The relation is compared to a similar relation derived from solid state experiments. Since the  $\rho_b$  values are related to the bond strengths, this general relationship may useful for hydrogen bond studies.

**PACS.** 71.15.-m Methods of electronic structure calculations – 31.15.-p Calculations and mathematical techniques in atomic and molecular physics (excluding electron correlation calculations)

## 1 Introduction

The theory of *Atoms in Molecules* (AIM) has proved to be a very useful tool in describing electron densities in various systems and in extending the understanding of chemical bonding [1–10]. We believe it will be useful to investigate if the theory can support a simple, general relation between the bond critical point and a basic molecular parameter, like the bond length. We address this question in the case of hydrogen bonds. We consider systems with inter- and intra-molecular hydrogen bonding and find that the electron density at the bond critical points may be well represented by an exponential function of the bond length.

## 2 Theoretical details

### 2.1 Geometry determinations

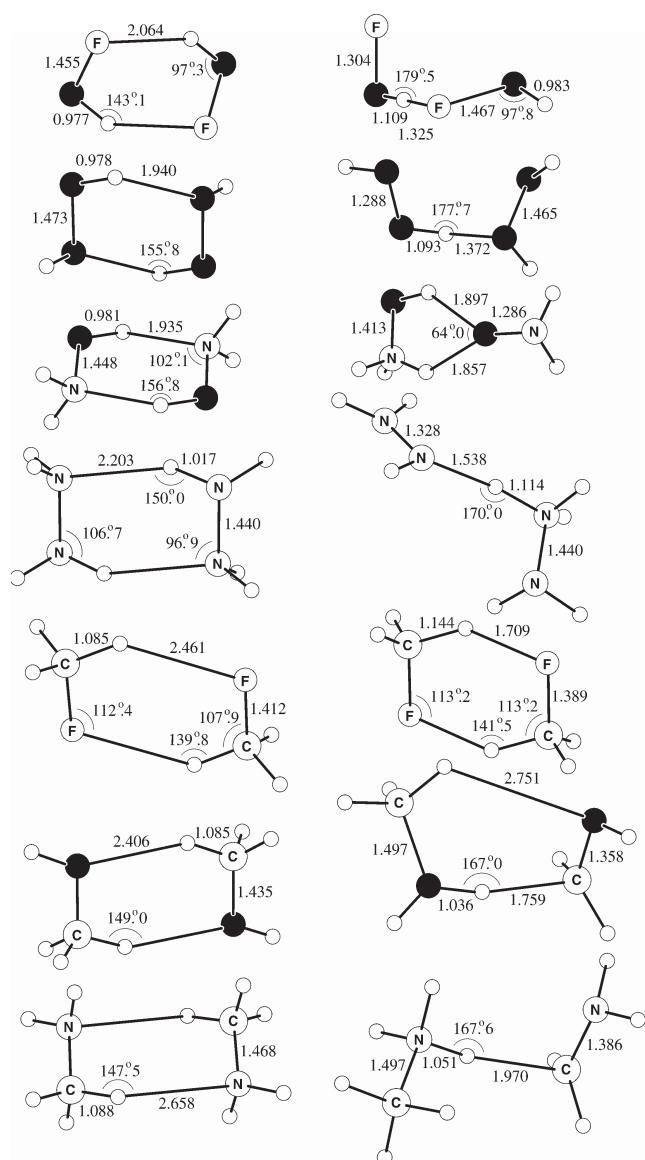
We consider inter-molecular, as well as intra-molecular hydrogen bonds. For convenience the inter-molecular hydrogen bonds are selected from systems which we have

studied before. They encompass: (i) dimers [11] and trimers [12] with hexagonal structure derived from small molecules where the electronegative atoms belong to the first period and (ii) their cations. The optimized geometries are obtained using Møller Plesset calculations at the MP2/6-31+G(d,p) level. The structures of the dimers and their cations are shown in Figure 1 while the trimers and cations are shown in Figure 2. All dimers are spin singlets whereas the cations are spin doublets. In order to have a wider range of hydrogen bond lengths for the data analysis we augmented the selected species with the anions  $\text{FHF}^-$  and  $\text{O}_2\text{HO}_2^-$ , which have short and symmetric hydrogen bonds of length 1.15 and 1.21 Å [13], respectively, at the MP2/6-31+G(d,p) level of theory. The geometry of all these species have also been optimized at the density functional level with a more extensive basis set [B3LYP/6-311++G(2d,2p)] to check that the findings are not specific to MP2 theory.

The intra-molecular hydrogen bonds are taken from two conformers of an alanine octa-peptide,  $\text{HCO}-(\text{Ala})_8-\text{NH}_2$ , with a helical structure. The peptide has previously been investigated [14] with density functional calculations (B3LYP) using the basis set 6-31G(d). We optimized the conformers at the level B3LYP/6-31G(d,p) in order to ensure that polarization effects are taken into account for all types of atoms. In Figure 3 we show a picture of one of

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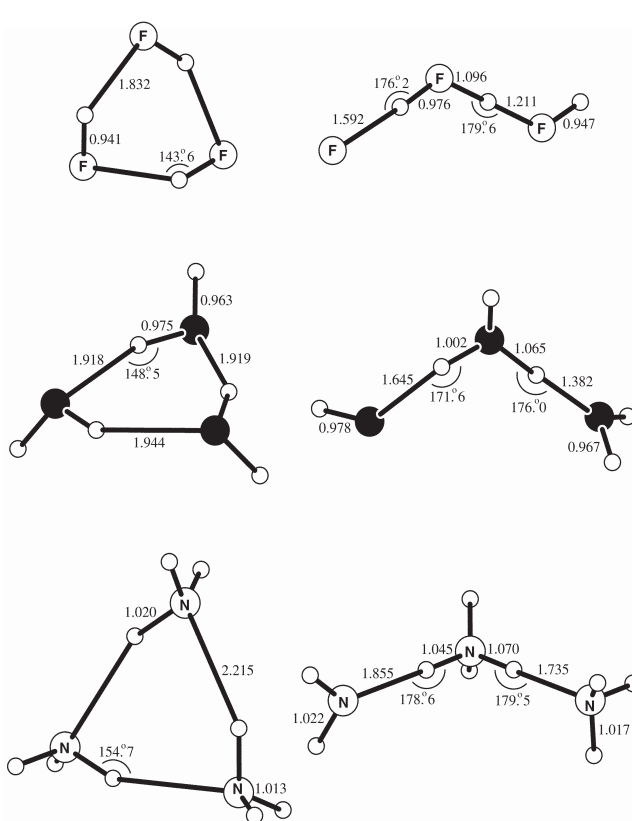


**Fig. 1.** Structures of hexagonal dimers (left column) and their cations (right column) calculated at the level MP2/6-31+G(d,p); ● indicates an oxygen atom and ○ indicates a hydrogen atom.

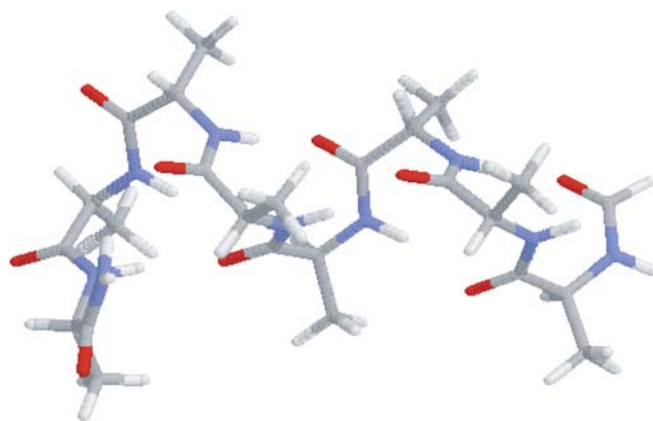
the octa-peptide conformers. All geometry optimizations are carried out using the Gaussian98 software [15].

## 2.2 Topological properties analysis

The topological properties of the electron density distributions are studied using the theory of “Atoms In Molecules” (AIM) [16]. The total electron density  $\rho(\mathbf{r})$  is calculated from the wave function of the equilibrium geometry of the various species. The topological properties of  $\rho(\mathbf{r})$  are characterized by its critical points where  $\nabla\rho(\mathbf{r}) = 0$ . The presence of a bond critical point (BCP) at  $r = r_b$  between two atoms is ‘a universal indicator of bonded interactions’ and the electron density,  $\rho_b$ , at the critical point is re-



**Fig. 2.** Structures of hexagonal trimers (left column) and their cations (right column) calculated at the level MP2/6-31+G(d,p). The symbols are explained in Figure 1.



**Fig. 3.** Structure of a helical conformer of the alanine octa-peptide.

lated to the bond strength or bond order [17–19]. The theory has been used extensively for studies of chemical bonding [20–25]. The topological properties of  $\rho(\mathbf{r})$  are analyzed using the programs AIMPAC [26]/AIM98PC [27]. In Tables 1–4 we list the  $\rho_b$  data along with the length of the hydrogen bond,  $BL$ , for the various species. We note that the oxygen atoms in the octa-peptide, typically, are involved in two hydrogen bonds (bifurcated), which differ by a factor of around 4 in the  $\rho_b$  values (Tab. 4). In Figures 4–6 we show plots of the Laplacian of electron

**Table 1.** Some topological properties of electron density for hydrogen bonds in the dimers and their cations shown in Figure 1 calculated at the MP2/6-31+G(d,p) and B3LYP/6-311++G(2d,2p) levels of theory with the latter data enclosed in parenthesis.  $BL$  (Å) is the length of the hydrogen bond and  $\rho_b$  (au) is the electron density at the bond critical point.

Species	$BL$ dimer	$\rho_b$ dimer	$BL$ cation	$\rho_b$ cation
HOF	2.064 [1.994]	0.0171 [0.0193]	1.325 [1.297]	0.0939 [0.1135]
H <sub>2</sub> O <sub>2</sub>	1.940 [1.936]	0.0239 [0.0262]	1.372 [1.265]	0.1019 [0.1501]
H <sub>2</sub> NOH	1.935 [1.925]	0.0295 [0.0325]	1.897 [1.937]	0.0270 [0.0169]
			1.857 [1.852]	0.0296 [0.0300]
H <sub>4</sub> N <sub>2</sub>	2.303 [2.261]	0.0186 [0.0161]	1.538 [1.548]	0.0771 [0.0781]
H <sub>3</sub> CF	2.461 [2.535]	0.0077 [0.0070]	1.709 [1.505]	0.0442 [0.0926]
H <sub>3</sub> COH	2.406 [2.546]	0.0100 [0.0073]	1.759 [1.669]	0.0460 [0.0655]
			2.751	0.0054
H <sub>3</sub> CNH <sub>2</sub>	2.658 [2.865]	0.0078 [0.0053]	1.970 [1.873]	0.0298 [0.0435]

density,  $\nabla^2\rho_b$ , for a molecule with short-, long- and bifurcated hydrogen bonds. These figures illustrate some features of the charge distribution around the hydrogen bond. Particularly, it is quite interesting that Figure 4 shows that  $\nabla^2\rho_b$  is very negative in the neighbourhood of the H-atom in this strong hydrogen bond.

### 3 Results

Our data set includes 29 inter- and 27 intra-molecular hydrogen bonds. The  $\rho_b$  data cover the range from 0.168 to 0.0033 (au) while the  $BL$  data span the interval from 1.15 to 3.01 Å. The inter-molecular hydrogen bond data in Table 1 cover the widest region. It appears from this table that there are some pairs of molecules with similar  $BL$  values, where the one with the shorter  $BL$  also has the lower  $\rho_b$  value. However, the overall trend of the data is a decrease of  $\rho_b$  with increasing  $BL$ . We have analyzed the dependency by fitting an exponential function,  $A \exp(-B \times BL)$  to the data. We find that  $A = 2.71$  (au) and  $B = 2.40 \text{ Å}^{-1}$  give a good fit with  $\text{RMS} = 2.16 \times 10^{-3}$  for the MP2 data. When the same function is fitted to the DFT data we find  $A = 2.77$  (au) and  $B = 2.37 \text{ Å}^{-1}$  with  $\text{RMS} = 2.53 \times 10^{-3}$ . The intra-molecular data (Tab. 2) are basically clumped together in two small regions: ( $0.019 < \rho_b < 0.016$ ;  $2.05 < BL < 2.33$ )

**Table 2.**  $\rho_b - BL$  data for the hydrogen bonds in the trimers and their cations shown in Figure 2 calculated at the MP2/6-31+G(d,p) and B3LYP/6-311++G(2d,2p) levels of theory. The symbols are defined in Table 1.

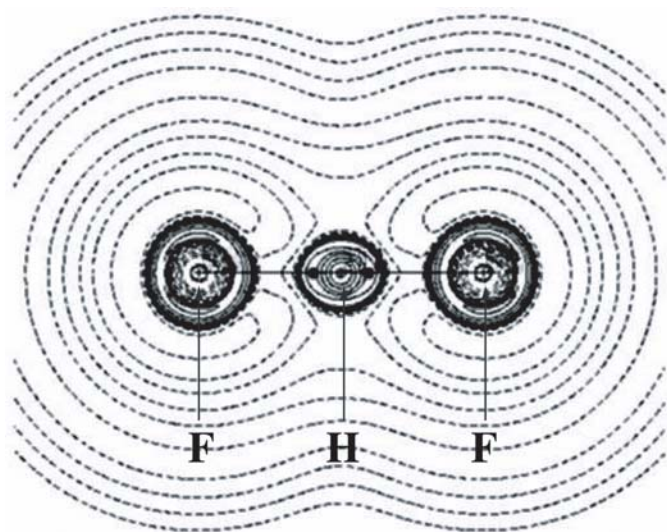
Species	$BL$ trimer	$\rho_b$ trimer	$BL$ cation	$\rho_b$ cation
HF	1.832 [1.765]	0.0272 [0.0325]	1.592 [1.566]	0.0437 [0.0495]
			1.211 [1.218]	0.1321 [0.1351]
H <sub>2</sub> O	1.944 [1.934]	0.0233 [0.0256]	1.645 [1.616]	0.0470 [0.0538]
	1.919 [1.909]	0.0239 [0.0273]	1.382 [1.388]	0.0958 [0.0972]
	1.918 [1.909]	0.0252 [0.0274]		
NH <sub>3</sub>	2.215 [2.251]	0.0179 [0.0161]	1.855 [1.828]	0.0359 [0.0396]
			1.735 [1.716]	0.0506 [0.0546]

**Table 3.**  $\rho_b - BL$  data for the hydrogen bonds in FHF<sup>-</sup> and O<sub>2</sub>HO<sub>2</sub><sup>-</sup> calculated at the MP2/6-31+G(d,p) and B3LYP/6-311++G(2d,2p) levels of theory. The symbols are defined in Table 1. The experimental value for  $BL$  in FHF<sup>-</sup> is 1.139 Å [K. Kawaguchi, E. Hirota, J. Chem. Phys. **87**, 6838 (1987)].

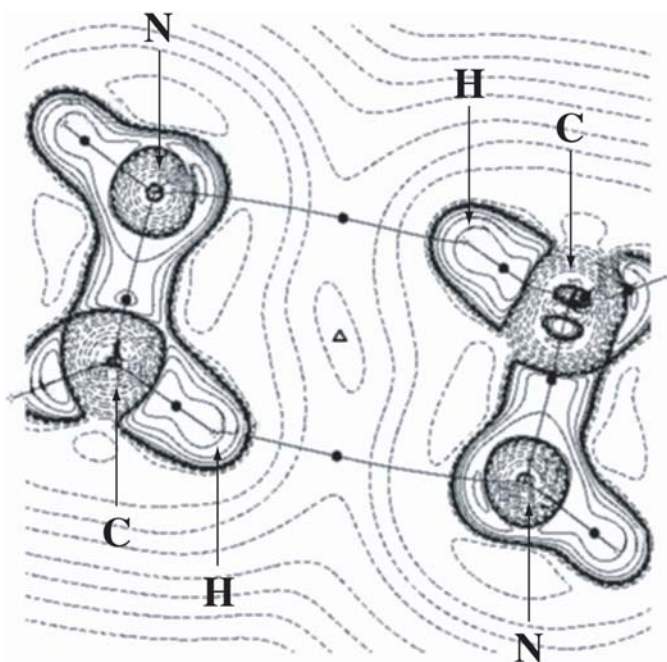
Species	$BL$	$\rho_b$
FHF <sup>-</sup>	1.150 [1.148]	0.169 [0.178]
O <sub>2</sub> HO <sub>2</sub> <sup>-</sup>	1.214 [1.217]	0.176 [0.176]

**Table 4.** Bond lengths,  $BL(i)$  (Å), and electron densities at the bond critical points,  $\rho_b(i)$  (au)  $i = 1, 2$  for hydrogen bonds in two conformers of an alanine octa-peptide. O and N denote the type of acceptor-atom. O<sub>b</sub> indicates that the O-atom participate in a bifurcated hydrogen bond.

	$BL(1)$	$\rho_b(1)$	$BL(2)$	$\rho_b(2)$
O <sub>b</sub>	2.084 2.931	0.0182 0.0039	O <sub>b</sub>	2.084 2.931
O <sub>b</sub>	2.103 2.796	0.0177 0.0048	O <sub>b</sub>	2.141 2.909
O <sub>b</sub>	2.111 2.818	0.0174 0.0045	O <sub>b</sub>	2.121 2.858
O <sub>b</sub>	2.137 2.069 3.012	0.0173 0.0187 0.0033	O <sub>b</sub>	2.108 2.838
O	2.186	0.0158	O <sub>b</sub>	2.145 2.792
O <sub>b</sub>	2.126 2.922	0.0167 0.0038	O <sub>b</sub>	2.114 2.890
			O	2.147
N	2.327	0.0167		
N	2.874	0.0055		

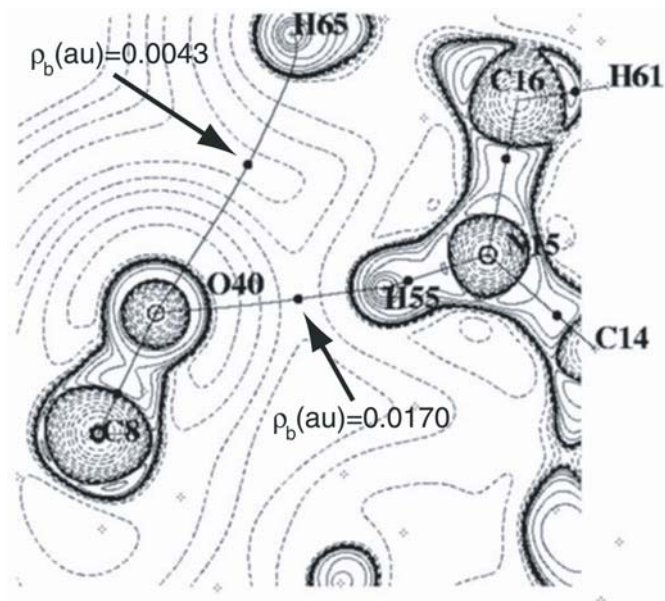


**Fig. 4.** Contour plot of  $\nabla^2\rho$  for the anion  $\text{FHF}^-$  with a strong hydrogen bonding; ● indicates the position of the bond critical point.



**Fig. 5.** Contour plot of  $\nabla^2\rho$  for the hexagonal  $\text{H}_3\text{CNH}_2$  dimer with weak hydrogen bonding; ● and Δ indicate the position of the bond critical point and the ring critical point of the electron density distribution, respectively. The plot is taken in the plane defined by the atoms forming the hydrogen bond (CH...N). The nuclei are denoted by crosses + (or open crosses -).

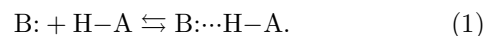
and ( $0.0055 < \rho_b < 0.0033$ ;  $2.79 < BL < 3.01$ ). The smallness of the regions allows these data to be well represented by a linear function  $\rho_b = 0.0532 - 0.0170BL$ . The data can also support an exponential  $BL$ -dependence and when inter- and intra-molecular data are analyzed collectively we find  $A = 2.61$  (au) and  $B = 2.38 \text{ \AA}^{-1}$  with  $\text{RMS} = 2.23 \times 10^{-3}$ . This function is displayed in Figure 7 along with the data.



**Fig. 6.** Contour plot of  $\nabla^2\rho$  of a bifurcated hydrogen bond in a conformer of alanine octa-peptide. Bond paths are denoted by lines, bond critical points are denoted by solid circles ● and the nuclei are denoted by crosses + (or open crosses -). The plane of the figure is defined by the atoms forming the bifurcated hydrogen bond (O40, H65 and H55).

## 4 Discussion

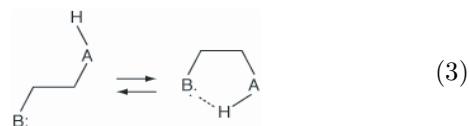
The determination of energy associated with hydrogen bonds,  $E_{HB}$ , is relatively straightforward for inter-molecular interactions such as:



It is computable as

$$E_{HB} = E(\text{B} \cdots \text{H}-\text{A}) - \{E(\text{B}) + E(\text{H}-\text{A})\} \quad (2)$$

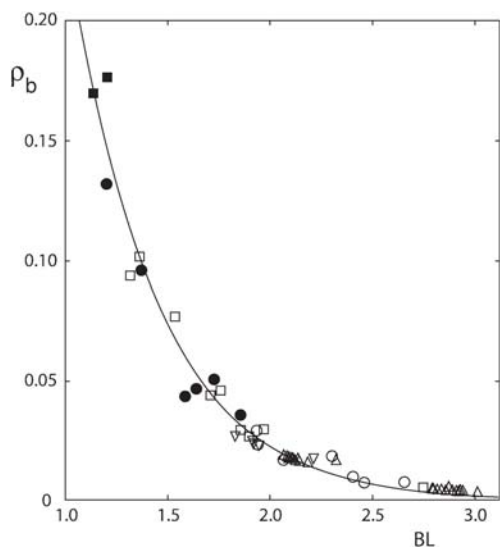
with the inclusion of zero point vibrational correction as well as the calculated basis set superposition error (BSSE). However, the energy associated with intra-molecular hydrogen bond



is not easily calculable because  $E_{HB}$  incorporates both the energy of conformational change as well as the energy associated with the hydrogen bond formation.

For a long time, the  $\text{B} \cdots \text{H}-\text{A}$  bond length ( $BL$ ) was used as an arbitrary measure for hydrogen bond stability. Within the AIM theory the magnitude of the electron density computed at the bond critical point ( $r_b$ ) was regarded as a more appropriate measure of hydrogen bond strength.

We expect the hydrogen bond strength to be associated with the local potential energy density at the bond



**Fig. 7.** Electron densities at bond critical points,  $\rho_b$  (au), versus the hydrogen bond lengths,  $BL$  ( $\text{\AA}$ ), for various species with inter- and intra-molecular hydrogen bonding. The data for the species with inter-molecular hydrogen bonding are calculated at the MP2/6-31+G(d,p) level of theory and encompass neutral dimers (O); cations of dimers ( $\square$ ); neutral trimers ( $\nabla$ ); cations of trimers ( $\bullet$ );  $\text{FHF}^-$  ( $\blacksquare$ ) and  $\text{O}_2\text{HO}_2^-$  ( $\blacksquare$ ). The data for the octa peptide with intra-molecular hydrogen bonding ( $\Delta$ ) are calculated at the B3LYP/6-31G(d,p) level of theory. The full line is the function  $2.61\exp(-2.38BL)$ .

critical point, i.e.,

$$E_{HB} \sim V(r_b) = \nabla^2 \rho_b - 2G(r_b). \quad (4)$$

Recently, Abramov [9] recommended the following relationship for  $G(r_b)$ , which is regarded as the local electronic kinetic energy density,

$$G(r_b) = (3/10)(3\pi^2)^{2/3} \rho_b^{5/3} + (1/6)\nabla^2 \rho_b. \quad (5)$$

After substituting  $G(r_b)$  in the expression of  $V(r_b)$  we can see that  $E_{HB}$  is related to  $\rho_b$  and  $\nabla^2 \rho_b$

$$E_{HB} \sim V(r_b) = -(3/5)(3\pi^2)^{2/3} \rho_b^{5/3} + (2/3)\nabla^2 \rho_b. \quad (6)$$

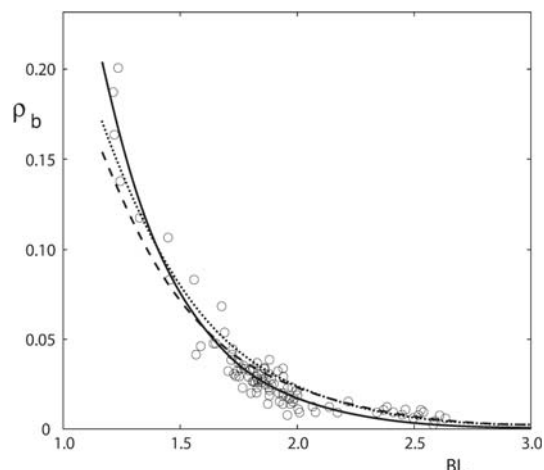
In this sense we may consider the following functional relationship for  $E_{HB}$

$$E_{HB} = F(\rho_b, \nabla^2 \rho_b). \quad (7)$$

One may argue that this relationship is too simplistic as the emphasis is given only to the density  $\rho_b$  and its Laplacian. It is possible that the elongation of the density, as measured by  $\lambda_3$ , may also play a role in the functional dependence [10]

$$E_{HB} = F(\rho_b, \nabla^2 \rho_b, \lambda_3). \quad (8)$$

Each of these quantities ( $\rho_b$ ,  $\nabla^2 \rho_b$  and  $\lambda_3$ ) is expected to vary with hydrogen bond length:  $BL$ . In this paper we studied the variation of  $\rho_b$  with  $BL$  by fitting analytic



**Fig. 8.** Experimental  $\rho_b$  (au) –  $BL$  ( $\text{\AA}$ ) data (o). The full line [ $\rho_b(\text{au}) = 6.78\exp(-2.99BL)$ ] is derived by fitting an exponential function to the data. Dashed- and dotted-lines are similar functions derived from theoretical calculations on molecules/ions at the MP2/6-31+G(d,p) and B3LYP/6-311++G(2d,2p) levels, respectively.

functions to 56 hydrogen bond data points. We find that  $\rho_b$  at the critical point in hydrogen bonds in molecules may be well represented by an exponential function of the bond length.

Espinosa et al. [28] have made a very thorough analysis of experimental  $\rho_b$  values pertaining to hydrogen bonding in the solid state. They considered 85 bonds that had been obtained using various experimental techniques. The vast majority of their data had  $BL$  values in the interval 1.6–2.6  $\text{\AA}$ . In order to have a wider  $BL$ -range for the data analysis we have added 11 newer experimental data to the data set. The new data are from studies of L-tryptophan formic acid complex [2], dimethyl ammonium hydrobis squarate [29], benzoylacetone [30] and potassium hydrogenoxalate [31]. With this addition the  $BL$  values extend to 1.217  $\text{\AA}$ . When the exponential function is fitted to these data we find  $A = 6.78$  (au) and  $B = 2.99 \text{\AA}^{-1}$  with  $\text{RMS} = 6.61 \times 10^{-3}$ . In Figure 8 we show the fit to the experimental data along with the exponential functions derived theoretically from electron structure calculations on simple molecules. It appears that the exponential function gives a good representation of the trend of the experimental data. The two functions derived from electron structure calculations agree well with the experimental data in a region of  $BL$  from around 1.6 to 2.2  $\text{\AA}$ . For larger values the experimental  $\rho_b$  data seem to decay faster than predicted by the functions. In contrast, for short bond lengths the  $\rho_b$  values exceed the theoretical functions.

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