

Transferable Atomic Sizes and Electron Density Profiles: Analysis of Bond Length Variations

Parthasarathy Ganguly*, Bhakti S. Kulkarni and Sourav Pal
Physical Chemistry Division, National Chemical Laboratory, Pune
411021, INDIA

Abstract. The total number of electrons, N , along a bond axis is obtained from electron density plots calculated using B3LYP DFT 6-311G** method or some gas-phase diatomic molecules, MX. The plots agree reasonably well with that expected from simple models using atom-specific transferable (“hub”) core atomic sizes and another (“axle”) size coupled to a pair of (bonding) electrons. The “axle” dimension is a simple multiple of a_H , the Bohr radius of the hydrogen atom. The N vs r plots around each atom are described by a simple hydrogen-atom-like function which could differ away (“out”) or towards (“in”) the M-X bond. Specifically $N_{in, out}(M, X) = (Z_{M, X} \pm 1) \exp(-r/B_{in, out})$ where the plus sign is associated with M and minus sign with X and $B_{in, out}$ varies with the atom.

1. Introduction

An important parameter in understanding molecular structure is the distance between atoms in a chemical bond. This distance is usually taken as a measure of the nature and strength of the interactions between the atoms. Because of this, the energy of a system becomes a critical parameter and equilibrium bond distances are calculated using a quantum chemical energy-minimization procedure for the whole molecule. Disappointingly, the actual calculation involves opaque (semi-empirical) and time-consuming mathematical calculations. Woolley (1976) has noted, “... *we might ... expect (quantum chemistry) ... to give a deductive account of the behavior of molecules in which molecular structure is a derived concept. Quantum chemistry however has not as yet achieved this result and instead the notion of molecular structure remains a stark mystery which, like revelation for some known theologians, is simply said to be demanded by the known facts.*” As mentioned by Hofmann (1998) (regarding the state-of-the-art in quantum chemical calculations) “... *in many interesting areas of chemistry we are approaching predictability, but... I would claim, not understanding*”.

Part of this “mystery” may be removed once real-space functions—as distinct from complex imaginary wave functions—are the only parameters used for quantifying our understanding of molecular structure. It has been recently found that a N -particle molecule may be represented by a shape function $\sigma(\mathbf{r})$, which is the density $\rho(\mathbf{r})$ per particle of the system (Ayers 2000, 2007). The shape function ($\equiv \rho(\mathbf{r})/N$) contains information about the particle density at various points in space. It is thus sufficient to

*Corresponding Author. Present address: Flat 8B, Mont Vert I, 140/1A Pashan-Sus Road, Pashan, Pune 411021, India. E-mail: patchug@gmail.com

obtain the value of any observable quantity even if it “contains no directly accessible information about the number of particles in the system”. Since an atom is a discrete entity with integer number of particles, these real-space functions may be just an atomic size. Usually, the empirical sizes used (see, for example, Etschmann and Maslen 2000) for describing inter-atomic distances are specific for the nature of the interaction—say, ionic character—which is, again, difficult to quantify.

Ganguly has examined (2008a) an alternative approach to inter-atomic distances using a single set of sizes, r_{nZ}^c (Ganguly 2008a, 2008b, Ganguly and Desiraju 2008) specific to each atom which do not depend on the “ionic character”. These sizes have been used to account for first order changes in inter-atomic distances between identical atoms without requiring changes in valence, bond order, spin-state and so on. The atomic sizes, obtained (Ganguly 2008b) from “...*more elementary particles (electrons and nuclei)*...” themselves become a molecular descriptor as far as molecular geometry is concerned without requiring knowledge about the final energy of the system. The molecular structure from such atomic sizes then becomes a “*derived concept*” (Woolley 1976).

One is interested in examining, say, similarity (Solà *et al* 1996, Geerlings and DeProft 2002, Bultnick and Carbó-Dorca R 2005, Borgoo *et al* 2007) between molecular descriptors such as electron density obtained from successful quantum chemical methods and simple real space atomic sizes. For example, a comparative analysis by means of quantum molecular similarity measures of density distributions derived from conventional *ab initio* and density functional methods have been used earlier (see Koch and Holthausen 2001). Similarly, a prediction of inter-atomic distances based on transferable atomic sizes should find a corresponding real-space interpretation derived from electron density maps which are obtained from the so-called *ab initio* quantum chemical calculations. It is possible, for example, to obtain a profile of the number of electrons, N_{el} , along a bond axis from an integration of theoretically calculated electron density contours. One then compares the calculated N_{el} vs r plot with that expected from atomic sizes. In the exact limit both the methods should reproduce the same molecular properties. In this communication we have calculated the electron density profile along the axis of some selected gas-phase diatomic MX bonds and have compared this profile with that expected from atomic sizes. This helps in understanding both the methodologies and removes thereby some opacity. At the same time one expects that the number profile of the N_{el} vs r plot in 1D obtained from DFT will be equivalent to the shape function, $\sigma(r)$ of Ayers (2000, 2007).

2. Atom-Specific and Atom-Independent Contributions.

2.1. “Hub” and “Axle” Sizes.

We use “core” atomic sizes, r_{core} , (considerably less than observed inter-atomic distances) instead of the more frequently used (see Etschmann and Maslen 2000) “ionic” or “covalent” sizes. It has been shown (Ganguly 2008a, 2008c) that these “core” sizes may be related to any property, P, through a property-dependent atomic size, CR_P , by

$$CR_P = C_P r_{nZ}^c + D_P. \quad (1)$$

where the environment- or P-invariant, atom-specific, size r_{nZ}^c has been obtained from first principles (Ganguly 2008b, see also Ganguly and Desiraju 2008) The nature of systematic variation in bond distances with first-order changes in the nature of the bonding interaction lies in the way the first order variations in C and D take place. Of interest is the way the changes in coefficients C and D is reflected in the density plots obtained by conventional and well established quantum computational methods.

The 1,2-inter-atomic distance, d_{MX} , of an M–X bond may be written in terms of “hub” and “axle” sizes

$$d_{MX} = \epsilon_{\text{eff}} \left[\left\{ C_M r_{nZ}^c(\text{M})/F_S(\text{M}) + C_X r_{nZ}^c(\text{X})/F_S(\text{X}) \right\} \text{“ball”} + (D_M/F_S(\text{M}) + D_X/F_S(\text{X})) \text{“axle”} \right] \quad (2)$$

The form of eqn 2 is similar to the form used earlier (Ganguly 1995a, 2000). The atomic size, r_{nZ}^c , have been obtained from a theoretical model with no adjustable parameters (Ganguly 2008a, 2008b, Ganguly and Desiraju 2008) . These values are close to the empirically tabulated values, r_G (Ganguly 1995a) or the theoretically evaluated Zunger-Cohen pseudo-potential valence s -electron orbital radii, r_s , obtained from the classical turning point (Zunger 1980). The value of the coefficients C and D in eqn 2 are separately expected to characterize the $\mu = 0$ condition (Ganguly 1993, 1995a, 2000; Politzer 1984) for the chemical potential. The term ϵ_{eff} is an effective dielectric constant (see Wadhera and Ghosh) which has values close to 1.05 (Ganguly 2008a, 2008c). The terms F_S accounts for a decrease in bond length when there are n_v “extrabonding” valence electrons on an atom. For example, the bond order is given by $(n_v + 1)$. The values of F_S is found (Ganguly 1995b) to be empirically given by $F_S = 1, 1.18, 1.26, 1.32, 1.38$ and 1.42 for $n_v = 0, 1, 2, 3, 4$, and 5 , respectively. In a theoretical formulation (Ganguly 2005) it is shown that $F_S = (1 + (2/\pi^2)(1 + \{S_v(S_v + 1)\})^{1/3})$ where $S_v = n_v/2$ and $F_S = 1.000, 1.184, 1.255, 1.315, 1.368$ and 1.418 for $n_v = 0, 1, 2, 3, 4$, and 5 , respectively. In what follows, we use these theoretical values.

It has been suggested (Ganguly 2008a, 2008c) that changes in bond lengths due to changes in C and D (or “hub” and “axle”) sizes constitute a natural example of “bond stretch isomerism” (Stohrer and Hoffmann 1972a, 1972b; Parkin 1993; Rohmer and Bènard 2001). The coefficients C and D in eqn 2 may vary from bond to bond but the extent of variation is limited to a few specific values characteristic of a given bonding description. It has been shown (Ganguly 2008a, 2008c) it has been shown that the values of C_M and C_X can take “charge-transfer” or “neutral” values. In the case of “charge-transfer” descriptions, the atom with the smaller value of r_{nZ}^c is usually associated with the negative charge (Ganguly 1995a). The “charge-transfer” values are $C_M = C_1^+ \sim 2.144$ and $C_X = C_1^- \sim 2.300$, the subscript 1 denoting $\epsilon_{\text{eff}} = 1$ in eqn 2. The “neutral” values of C are integer values of $C = 1, 2 \dots$ etc. We sometime require $C = 1.5$ which may be interpreted as an average of $C = 1$ and $C = 2$. The “axle” dimension is usually the “ordinary” bond length, d_{H-H} (~ 74.2 pm), of the hydrogen molecule. In a charge-transfer” description it is given as (Ganguly 2000), $d_{H-H} = \epsilon_{\text{eff}}(D_1^+ + D_1^-) = \epsilon_{\text{eff}}4a_H/3 \sim 74.2$ pm when $\epsilon_{\text{eff}} \sim 1.05$. The “elongated” bond length of the hydrogen molecule (~ 106 pm $\sim (D_M + D_X) = 2a_H$) is often the “axle” dimension when the “hub” dimensions are neutral (Ganguly 2008a, 2008c).

2.2. “Resident” and “Peripatetic” Bonding valence Electrons.

The core atomic size, $r_{nZ}^c(\eta)$ for an atom in row η ($= (n - 1)$ where n is the principal quantum number) has been obtained as the sum of contributions from a valence-shell s - and p -electron size, r_{nv} , and an inner-shell size, $r_{RG(\eta-1)}$, with

$$r_{nZ}^c(\eta) = r_{nv} + r_{RG(\eta-1)} \quad (3)$$

An atomic size, $\{r_{nZ}^c(\eta)\}^*$, has been obtained (Ganguly 2008a) as

$$\{r_{nZ}^c(\eta)\}^* = r_{nv} + 0.5r_{RG(\eta-1)} \quad (4)$$

There is a good correlation between the inverse of the Pauling electronegativity, χ_P^{-1} , and $\{r_{nZ}^c(\eta)\}^*$ with $\chi_P^{-1} = 1.021(0.016\{r_{nZ}^c(\eta)\}^*)$ ($R > 0.98$, $SD = 0.06$) for s - and p -block main group elements.

It is found that atoms with $\{r_{nZ}^c(\eta)\}^* > 0.5$ are metallic at NTP (Ganguly 2008a). Since an atom of an element cannot be metallic by itself, the implication of the condition $\{r_{nZ}^c(\eta)\}^* \geq 0.50$ a.u. for an atom of a metallic element is that the condition for metallization of an M-X bond is

$$\{r_{nZ}^c(\eta)\}^*(M) + \{r_{nZ}^c(\eta)\}^*(X) \geq a_H \quad (5)$$

We find that eqn 5 is a useful criterion, especially in the context of changes in bond lengths of gas-phase and solids of compounds of metallic elements. When eqn 5 is not satisfied the bonding valence electrons are termed as “resident” while when eqn 5 is satisfied the bonding valence electrons are considered “peripatetic”. This classification is helpful in finding the conditions for which “charge-transfer” or “neutral” parameters for C_M and C_X may be used for gas-phase MX compounds. Usually, we find “resident” bonding valence electrons require “charge-transfer” “hub” sizes, while “peripatetic” bonding valence electrons require “neutral” “hub” sizes for describing bond lengths in gas-phase MX compounds.

3. DFT Method

Reliable prediction of molecular structures from geometry optimizations is now routinely carried out using Hartree-Fock approaches using methods (Møller and Plesset 1934) based on n^{th} order Møller-Plesset (MP_n) perturbation theory (“... a very successful and well-accepted black box treatment of virtually any problem in organic chemistry...” see Koch and Holthausen, 2001). The other method is that using density functional theory (DFT) methods (Koch and Holthausen, 2001). Both of these give an expected accuracy of ± 2 pm or better. The main advantage of the density functional method (DFT) is that it exploits the knowledge that non-relativistic Coulomb systems differ only by their potential. The basic variable is the three-dimensional electron density $\rho(\mathbf{r})$ instead of the complicated many-variable ($4N$ variables for N number of electrons) wavefunction. Among the parameters that are important are

- The electron density determines the probability of finding any of the N electrons within volume element $d\mathbf{r}$.
- The electron density is a non-negative function of only the three spatial variables which vanishes at infinity and integrates to the total number of electrons.
- The gradient of the electron density has a cusp because of a discontinuity in the function at any position of the atom.

d) There is an asymptotic exponential decay of $\rho(r)$ ($\sim \exp[-2\sqrt{(2I)|r|}$ where I is the exact ionization energy) for large distance.

The exact knowledge of $\rho(r)$ implies knowledge of the wave function and the potential, and hence of all other observables. The DFT method is now routinely applied to calculate energy-minimized parameters of molecules and solids. The link to an exact DFT theory is the exact exchange-correlation energy functional. This functional is unknown and the basic (Hohenberg-Kohn) theorem of this theory does not address itself to obtaining the explicit construction of these functionals. *“On top of it there is no hope, at least up to our present knowledge in DFT, to find such an explicit density functional in the next future”* (Capelle 2006). In the absence of this exact knowledge, the DFT methodology relies on approximate and semi empirical functionals (*“... chemists start to use approximate density functional theory and take advantage of black box implementations in modern programs without caring too much about the theoretical foundations and – more critically – limitations of the method ...”* from Koch and Holthausen, 2001). For the present purpose, state-of-the-art DFT methods should be sufficient to obtain at least an empirically accurate density profile that is sufficient for the present purpose of comparing density profiles at least or simple systems.

We have carried out all calculations with the DFT B3LYP/6-311G** (6-311G basis set is a triple valence basis set where the valence orbitals are split into three functions) functionals which have been demonstrated to be successful in many chemical applications, including open-shell transition-metal chemistry. The connection with an atomic size comes through the local density approximation (LDA) which is used for closed shell systems with no spin polarization. The LDA represents the dependence of the correlation energy density per electron of the homogeneous electron gas model on the Wigner radius $r_s(\text{Wigner}) (= (4\pi\rho/3)^{-1/3})$. In generalized gradient approximation (GGA) or inhomogeneous systems, information about the gradient of the charge density supplements information on the local density approximation (LDA). The most successful exchange functional in chemical applications is Becke's three parameter (B3) hybrid functional which mix (Runge and Gross 1984) a fraction of Hartree-Fock exchange into the DFT exchange functional (other mixtures are also possible). In Becke's adiabatic connection formula, Becke mixed Hartree-Fock exchange or fully interacting systems with the non-interacting Kohn-Sham reference system in the DFT method. In this linear interpolation method there is an equal admixture of exact exchange and the LSD formalism of DFT. In Becke's three parameter (B3) method (see Becke 1993), the construction of hybrid functional involves a certain amount of empiricism (by including fitting terms which reproduce the conventional electron correlation energies of closed-shell atomic systems He, Li⁺, Be²⁺, Be, B⁺, Ne, Mg, Ar) in the choice of functionals that are mixed and in the optimization of the weight factors given to the HF and DFT terms. Despite these drawbacks the B3 functional is the most successful exchange functional in chemistry especially when combined with the Lee-Yang-Parr correlation functional (1988). The Lee-Yang-Parr method modifies Colle-Salvetti expression (Colle and Salvetti 1975, 1983) of the correlation energy density (hybrid of electron density and second order Hartree-Fock density matrix) by involving the density with local kinetic

energy density. The resulting B3LYP method has been often considered as an *ab initio* method despite its empirical content (Koch and Holthausen 2001).

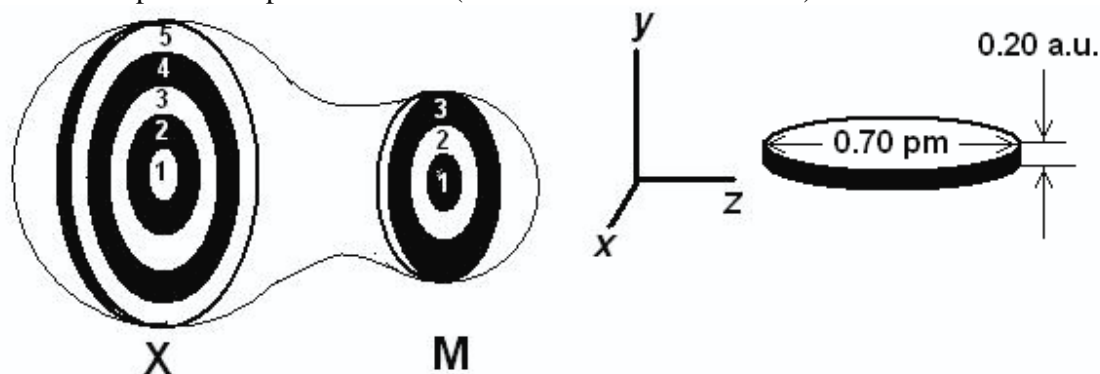


Fig 1. Schematic diagram of counting the number of electrons in a thin slice perpendicular (xy plane) to the bond axis (z -axis). Two such slabs are shown. The thickness and diameter of the slabs used in this are shown on the right. The concentric circles shown in each slab show iso-density contours. The integration may be carried out contour by contour for each slab or from the variation in calculated density across the slab

The energy-minimized geometry obtained by us with the B3LYP method for these diatomic molecules are in agreement with those reported earlier (Fossgard *et al* 2003). After we have obtained the energy-minimized geometry by these DFT B3LYP calculations, we have calculated an electron number profile across the bonding axis from the electron density plots. We then slice the electron density plots into thin circular slabs (Fig 1) in the xy plane along the bond axis (z -axis). For the results reported in this article, the width of the slab is 0.2 a.u. and the diameter of the circular slab is 0.7 pm. The number of electrons, N_i in each slab is integrated out from the density profile. The total number of electrons as a function of distance from some reference point is then obtained. These N vs r profiles along a bond axis is then used to compare the values of N expected from the use of “hub and axle” size parameters of eqn 2 to match observed distances of some gas-phase MX compounds. This simple exercise does not seem to have been done earlier.

4. Results and Discussion.

4. 1. General Trends.

We have shown in Fig 2 the changes in the value of the number of electrons, N_{el} , calculated by the DFT method vs the distance, r , from the M nucleus (located at $r = 0$) along the M-X bond axis for chlorine, Cl_2 , sodium fluoride, NaF, potassium fluoride, KF, and magnesium oxide, MgO. Characteristic of all these plots is a large slope near the nuclear positions (“hub” feature) and a fairly flat region between the atoms (“axle” feature). We have also shown in Table 1, the way the various observed (Lide 2007, see Hargittai, 2000 for a review) gas-phase M-X distances in MX compounds has been fitted to eqn 2 using the “hub” atomic sizes, r_{nz}^c , for M and X atoms (listed in Table 1) and the values of C_M , C_X and D (listed in the column named as $C_M C_X D_{MX}$). We have shown by $N \times R$ boxes in Fig 2 the (self-explanatory) way the sizes, R , and the number

of electrons, N , vary in this “hub-and-axle” representation. Here $R_M = C_M r_{nZ}^c(M)$, $R_X = C_X r_{nZ}^c(X)$ and $R_{\text{bond}} \equiv D = na_H$, and N_M , N_X and N_{bond} are the number of electrons associated with M , X and the “axle” ($= D = \{D_M + D_X\}$), respectively. We find that $N_{\text{bond}} = 2$ in all cases. More interestingly, $N_M = (Z_M - 1)$, $N_X = (Z_X + 1)$, Z_M and Z_X being the atomic numbers of M and X atoms when $M \neq X$. In the

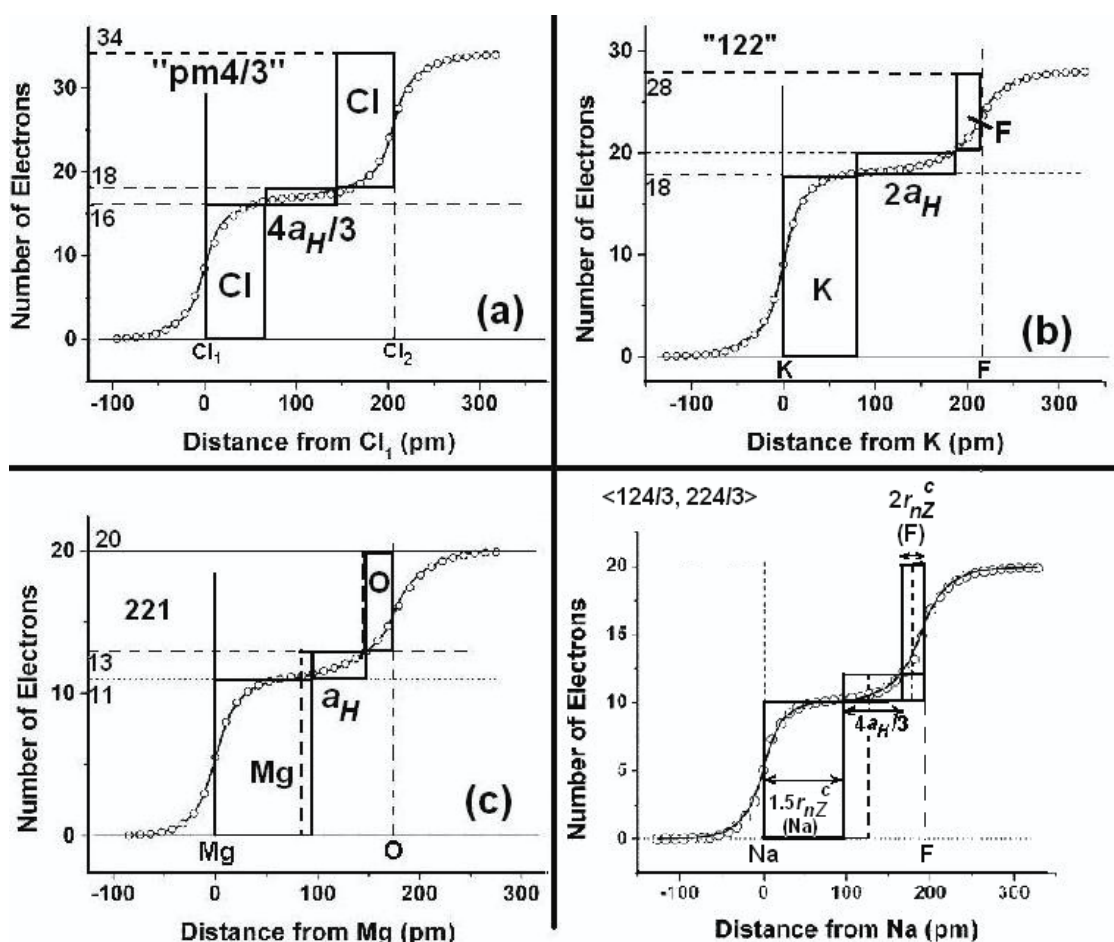


Fig 2. Plots of the values of the number of electrons, N , calculated by the DT B3LYP/6-311G** method for various gas-phase MX compounds vs the distance, r , from the M atom: (a) Cl_2 ; (b) KF ; (c) MgO ; (d) NaF . $N \times R$ boxes show the way the sizes, R , and the number of electrons, N , vary in a “hub-and-axle” representation. $R_M = C_M r_{nZ}^c(M)$, $R_X = C_X r_{nZ}^c(X)$ and $R_{\text{bond}} \equiv D = na_H$ as given in Table 1. $N_M (= (Z_M - 1))$, $N_X (= (Z_X + 1))$, $N_{\text{bond}} = 2$, are the number of electrons associated with M , X and the “axle” Circles: Calculated values of N vs r using eqn and parameters in Table 2.

case of NaF , the Na-F distance may be equally well fitted by $C_M = 2$, $C_X = 1$ and $D_{MX} = a_H$ (indicated by broken lines of $R \times N$ boxes in Fig 2d) in eqn 3 or by $C_M = 1.5$, $C_X = 2$ and $D_{MX} = 4a_H/3$ in eqn 3 (indicated by full lines of $R \times N$ boxes in Fig 2d). It is apparent from Fig 2d and Table 1 that the best agreement between DFT projections and atomic

sizes is obtained for NaF with $C_M C_X D_{MX} \equiv 1.5, 2, 4/3$. This helps in finding the right values of $C_M C_X D_{MX}$.

Table 1. Calculated and Observed M-X Distance in some Gas-Phase M-X Compounds

M-X	d_{MX} (pm)		r_{nZ}^c (a.u.) ^b		$C_M C_X D_{MX}^s$	$(r_{nZ}^c)^*$ (a.u.) ^c		d_{MX}^{CCD} (calcd) ^d (pm)	$d_{ob}/d_{cal} = R_{oc}^e$	
	B3LYP [#]	Obsvd ^a	M	X					CCD	pm4/3
H ₂	74.7	74.1	0	0	pm4/3	--	--	70.5	1.051	1.051
(F ₂)	140.5	141.2	0.26	0.26	pm4/3	0.20	0.20	131.6	1.073	1.073
F ₂	140.5	141.2	0.26	0.26	1,1.5,2	0.20	0.20	140.2	1.007	1.073
Cl ₂	205.7	198.8	0.53	0.53	pm4/3	0.34	0.34	195.1	1.016	1.019
FH	92.0	91.7	0.26	0	1.5,-,2	0.20	--	91.1	1.006	0.917
IH	162.6	160.9	0.74	0	pm4/3	0.44	--	154.4	1.041	1.041
(MgO)	176.0	174.9	0.88	0.28	2,2,1	0.69	0.22	175.6	0.996	0.856
MgO	176.0	174.9	0.88	0.28	(pm4/3) ₁ ^f	0.69	0.22	173.4	1.009	0.856
LiF *		156.4	1.04	0.26	1,2,2	1.00	0.20	153.0	1.022	0.711
NaF *	191.1	192.6	1.18	0.26	1.5,2,4/3	0.99	0.20	191.5	1.006	0.816
(NaF) *		192.6	1.18	0.26	2,1,1	0.99	0.20	191.7	1.005	0.816
KF *	213.3	217.2	1.46	0.26	1,2,3,2	1.05	0.20	210.5	1.031	0.811
LiH *	159.3	159.5	1.04	0	1,2,3,2	1.00	--	160.8	0.992	0.846
Lil *		239.2	1.04	0.74	1,2,2	1.00	0.44	239.1	1.000	0.859

[#]: calculated using B3LYP DFT 6-311G** method. ^s: $C_M C_X D_{MX}$ gives values of C_M , C_X and D_{MX} (in a_H units) in eqn 3; pm4/3 are “charge-transfer” sizes obtained with $p = 2.144$, $m = 2.30$, and $D_{MX} = 1.333$. ^a: Inter-atomic Distances are obtained from Lide (2007) and Hargittai (2000). ^b: theoretical sizes obtained from a simple model (eqn 5); ^c: Theoretical sizes obtained from eqn 6; ^d: Calculated distances using eqn 3; ^e: Ratio of observed and calculated distances using $C_M C_X D_{MX}$ values (CCD) or “charge-transfer” values (pm4/3); ^f: (pm4/3)₁ indicates the value of (pm4/3)/1.18 which is expected shortening when $n_v = 1$.

4. 2. Case of Fluorine Atoms.

The second important point is to find a justification for the conditions when “charge-transfer” or neutral sizes may be used. In general, when the condition for “metallization” of a bond (eqn 5) is not satisfied, one requires charge-transfer sizes to fit the observed inter-atomic distances in general (including compounds outside this study). This is generally what is observed when examining the M-X distances in all the gas-phase diatomic MX compounds. Among the no exceptions to this rule (Table 1) are fluorine molecule, F₂, as well as hydrogen fluoride (which we have written as FH, to emphasize F as the atom to be associated with a positive “charge-transfer” size).

It is well known that large errors in calculated energies by Hartree-Fock or by LDA methods for the fluorine molecule which “... *formally contains a single bond, ... are somewhat irritating...*” (Koch and Holthausen 2001). Such errors are corrected (Koch and Holthausen 2006) by including correlation energy terms in HF methods (such as MP2) or by including gradient dependencies explicitly.

From simple chemical insights based on the periodic table, it requires more energy to associate a positive charge with the fluorine atom since it prefers to adopt the filled shell configuration of F^- . As a result, the fluorine atoms prefer the “neutral” sizes. In FH itself we find that the electron density profile is best given by that of an electronic

Table 2. Parameters of fits to the exponential decay of electron density from atom positions M and X of M-X bond in diatomic gas-phase MX molecules (B in pm).

M-X	M				X				ϵ_{eff}^a
	in		out		in		out		
	N_{in}	B_{in}^M	N_{out}	B_{out}^M	N_{in}	B_{in}^X	N_{out}	B_{out}^X	
H ₂	0.5	36	0.5	28	0.5	36	0.5	25	1.05
Cl ₂	8.5	21	8.5	25	8.5	21	8.5	25	1.055
FH	0	-	0	-	5.5	23.5	4.5	32	1.015
LiF	1	12	1	16	5.5	26	4.5	28	1.022
NaF	5	16	5	21	5.5	28	4.5	25	1.006
KF	9	18	9	22	5.5	32	4.5	25	1.011
IH	0.5	12	0.5	18	26.5	20	26.5	24	1.041
Lil	1	12	1	18	26.5	24	27.5	32	1.001
LiH	1	16	1	16	0.85	64	1.15	58	1.05
MgO	5.5	17	5.5	17	4	36	5	26	1.015

^a: Ratio of observed and calculated distance.

configuration $H^+(F^-)$ (Fig 3) with $C_H C_F D_{HF} = --, 2.3, 2$, which would correspond to “charge transfer” negative size for F and an “axle” size of $2a_H$. This does not give the right distance (calcd distance ~ 105 pm as compared to observed 92 pm) but the RxN box

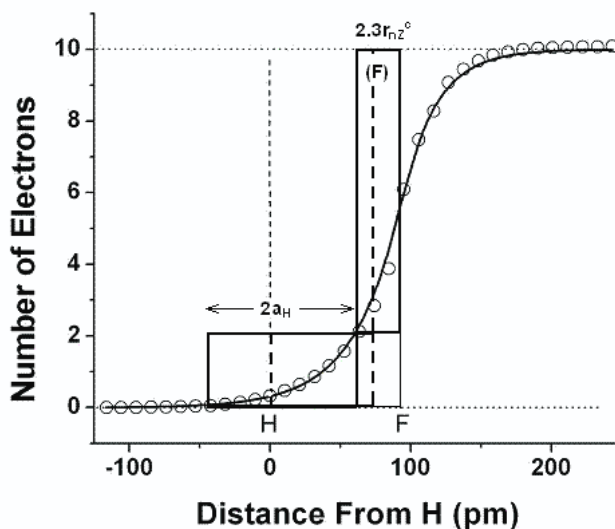


Fig 3. Number of Electrons vs distance from hydrogen atom in HF. Circles calculated from the DFT method. The full line corresponds to the fit with parameters in Table 2. The RxN, boxes with full lines correspond to $C_H C_F D_{HF} = --, 2.3, 2$ ($r_{\text{core}}(H) = 0$, so that C_H is not defined) while the boxes of broken lines correspond to $C_H C_F D_{HF} = --, 1.5, 4/3$.

diagram matches the electron count obtained from the DFT B3LYP calculation. One may then visualize HF as a F⁻ species with a bare proton embedded in its electron cloud. On the other hand, $C_F C_H D_{FH} = 1.5, -, 4/3$ matches the distance but not the electron count. This agreement of the DFT-calculated N_{el} vs r plot and the disagreement of the observed inter nuclear distance in HF with the 1.5,-,4/3 parameters for C_M, C_X, D_{MX} could suggest that the electron cloud around the proton is distorted. Such a distortion could contribute to “... *abnormally high values for the dielectric constant for many hydrogen-bonded substances ... due to the ‘atomic polarization’ of the proton in the bond.*” (Latimer 1950, see also Latimer and Rodebush 1920)

4. 3. Fitting Electron Number Profile with Hydrogen-Atom-Like Functions.

The nature of the calculated changes in N_{el} is a consequence of the DFT method employed and need not necessarily be a representation of the actual changes in the number of electrons. From the DFT calculations, the final density vs r profile (or N_{el} vs r profile) is one which corresponds to an energy-minimized state for the M-X molecule. Since an electron cannot be fractured, any non-integral N_{el} , is usually related only to the probability of finding N electrons at a given point from the nucleus along the bond axis. How this probability appears in DFT is only a matter of philosophical conjecture (involving, say, the uncertainty principle or fluctuations) even if it is not inconsistent with a wave functional formalism. In the DFT methodology, of course, there is no characteristic size that can be associated with “hub” or “axle” dimensions. However, the satisfying “quantum similarity” of the molecular descriptor part ((Solà *et al* 1996, Geerlings and DeProft 2002, Bultnick and Carbó-Dorca R 2005, Borgoo *et al* 2007, Geerling *et al* 2003, 2004) is that one finds a one-to-one mapping (with few important exceptions such as HF) of the inter-atomic distance as seen from the DFT “continuous” density profile and the “hub-and-axle” components, C_M, C_X, D_{MX} (eqn 2).based on discrete atomic sizes. It is as if the entire machination involved in the complex (opaque or “black box”) DFT B3LYP methodology is simply to reproduce what can be obtained simply from atomic sizes.

In our analysis of the diatomic molecules, where we associate $N_{bond} = 2$, we have taken the “hub” size, Cr_{nZ}^c , of the M (or X atom) in hetero-atomic MX bonds ($M \neq X$) to be the size that marks the point within which there are $(Z_M - 1)$ electrons of the M atom (or $(Z_X + 1)$ electrons of the X atom). The decay of the number of electrons, N_{el} , with distance from any nucleus (M or X) of an M-X bond away (“out”) or towards (“in”) the bond is nearly exponential. The decay from any nucleus is actually given by

$$N = N_{in,out} \exp(-r/B_{in,out}) \quad (6)$$

$B_{in, out}$ and $N_{in,out}$ are atom-specific constants, which describing the decay away (“out”) or towards (“in”) the bond. One may consider the M or X atom to be located at the origin and the value of r is measured along the M-X bond axis. The actual form of the N vs r plot is then given by (B^M and B^X are values of B for M and X, respectively)

$$N = N_{in}(M)\exp(-|r|/B_{in}^M) + N_{out}(M)\exp(-|r|/B_{out}^M) + N_{in}(X)\exp(-|r|/B_{in}^X) + N_{out}(X)\exp(-|r|/B_{out}^X) \quad (7)$$

For the MX compounds ($M \neq X$) described in this communication we find (Table 2) $N_{in} = N_{out} = (Z \pm 1)$ where Z is the atomic number, and the + and – sign is applicable to the X

and M atom, respectively. The observed dependence of $N_{in,out}$ on Z indicates that the size of M is to be associated with one positive charge ($N_{in,out}(M) = Z_M - 1$) and the size of X with a negative charge ($N_{in,out}(X) = Z_X - 1$). Equation 6 has the typical form of hydrogen 1s-like Slater-type-orbital usually expressed as $(Nr^{n-1}\exp[-\zeta r]Y_{lm}(\Theta, \phi))$, where N is a normalization factor, n corresponds to the principal quantum number, the orbital exponent is termed ζ , and Y_{lm} are the usual spherical harmonics that describe the angular part of the function.

4. 4. Li-X Compounds.

We have compared in Fig 4 the changes in the N vs r plots of some LiX compounds. The N vs r plots seem to be exactly superimposed around the Li atom away (out) from the Li-X bond. It is seen from the values tabulated in Table 1 that the value of the “hub” coefficient, C_{Li} , of Li in the LiX compounds are the same ($C_{Li} = 1$). The values of B_{out}^{Li} also changes little (Table 2). There is considerable difference in the N_{el} vs r plots between the various LiX compounds near Li in the bonding (in) region. This is likely to be due to contributions to the electron number by X atoms. For example, in LiH the large value of B_{in}^H ($= 64$ pm) leads to a large contribution from the hydrogen atom to Li. As a result $N_{in}(Li)$ is increased to 1.15 (from 1) and $N_{in}(H)$ is decreased to 0.85 from 1 (Table 2). This is reflected in the plot in Fig 4 where the number of electrons at $r = +r_n^c$ is ~ 2.15 . The value of B_{in}^{Li} is ~ 12 pm for $X = F$ and $X = I$ and $B_{in}^{Li} \sim 16$ pm for $X = H$ (Table 2). The value of $N_{in}(Li) = N_{out}(Li) = 1 = (Z_{Li} - 1)$ for LiF and LiI. This is consistent with the participation of the third electron of Li in the bond formation. It is as if both LiF and LiI are to be treated as Li^+X^- . Using the method of Quantum

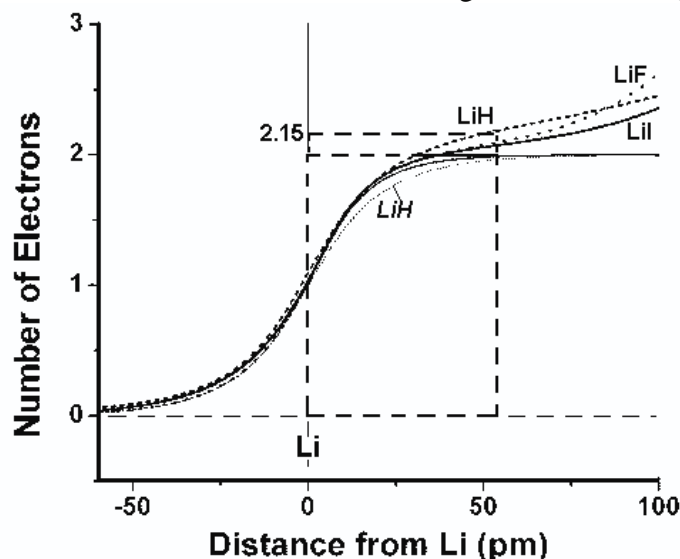


Fig 4. Plots of Number of Electrons vs distance from Li atom in some LiX compounds ($X = H, F, I$). In the bottom of the figure the contribution of Li atoms ($C_{Li} = 1$ for all compounds). The rectangular dashed box gives the RxN box.

Molecular Similarity Measures of Density (QMSM), Solà *et al* (1996) have shown that in the presence of correlation, the overall effect is to reduce the ionicity of the Li-F bond with the density from the fluorine non-shared electron pairs being pushed into the

bonding region and in the lithium atom. We are unable to find support for such a conclusion in our analysis.

4. 5. M-F Compounds.

In the case of M-F compounds (M = H, Li, Na, K) the electron density vs distance plots near the fluorine atom are shown in Fig 5. From the fitting parameters of Table 2 it can be seen that B_{in}^F (eqn 7) increases from 23.5 pm for M = H to 32 pm for M = K while B_{out}^F decreases from 32 pm for M = H to 25 pm for M = K. do not change with the M atom. The value of C_F of F in MF compounds (M = H, Li, Na, K) changes slightly with changes in M. The fits in Fig 5 show $C_F = 2$ for M= Li and Na and $C_F = 2.3$ or M = H and K in Fig 5. However, there are considerable changes in the “axle” dimensions for NaF ($D_{NaF} = 4/3$) while $D_{MF} = 2$ for M = I, Na and K (Table 1). One does not expect much changes in the density profile for the same element near the core (“hub”) since the basis set (the 6-311G** part) is not changed (see Curtiss *et al*, 1993). The small but important changes changes in the N_{el} contribution probably arises from the changes in the way the B3 part of the B3LYP method is handled.

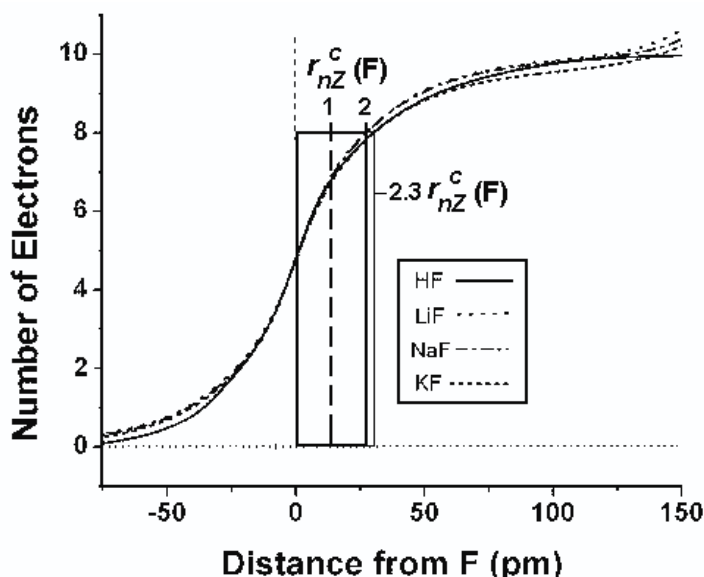


Fig 7. Plots of Number of Electrons vs distance from F atom in some M-F compounds (M = H, Li, Na, K). The rectangular dashed box gives the RxN box, for N = 8 and R = $C_F r_{nZ}^c$ or $C_F = 1, 2$ and 2.3 .

4. 6. Hydrogen Molecule.

In the case of the hydrogen molecule, H_2 , itself the normal H-H bonded distance of 74 pm is obtained from a charge-transfer value for $D_{MX} = 4/3$. The best fits to eqn 7 are given in Table 2. The actual nature of the best fit is not very satisfactory (Fig 6) with a “kink” in the centre of the bond which we are unable to smoothen by changing parameters in eqn 7. The value of N_{in} and N_{out} would indicate that there is an average of one electron per hydrogen atom. This would be inconsistent with a “charge-transfer” model unless we assume that the electron number is a time- averaged number. Such time-averaged values of $N_{in,out}$ are require for homoatomic molecules such as chlorine

(see chlorine in Fig 2a in which the RxN box for chlorine atom is the average value of $2.22 = (C^+ + C^-)/2$). Another way of fitting the distance is to take the origin at the central of the H-H bond and calculate the electron number for the hydrogen bond as from the equation

$$N = N_{in}(HH)\exp(-|r|/B_{in}^{HH}) + N_{out}(HH)\exp(-|r|/B_{out}^{HH}) \quad (10)$$

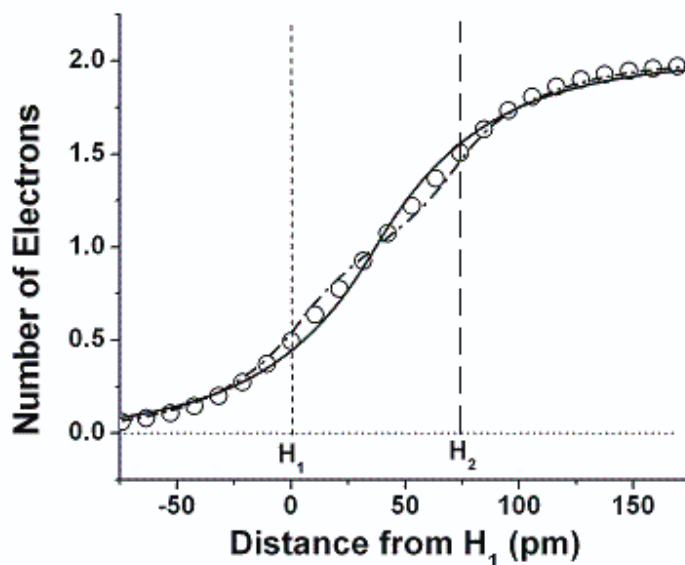


Fig 6. Plot of Electron number vs r for hydrogen molecule. Circle: from DFT method; dahed-and-dotted line: from eqn 9 using parameters in Table 2. Continuous line: From eqn 10 with origin at centre of bond with $N_{in}^{HH} = N_{out}^{HH} = 1$ and $B_{in}^{HH} = B_{out}^{HH} = 45$ pm obtained from best fit ($R > 0.999$, $SD < 0.035$).

4.7. “Metallization” and Bond Lengths.

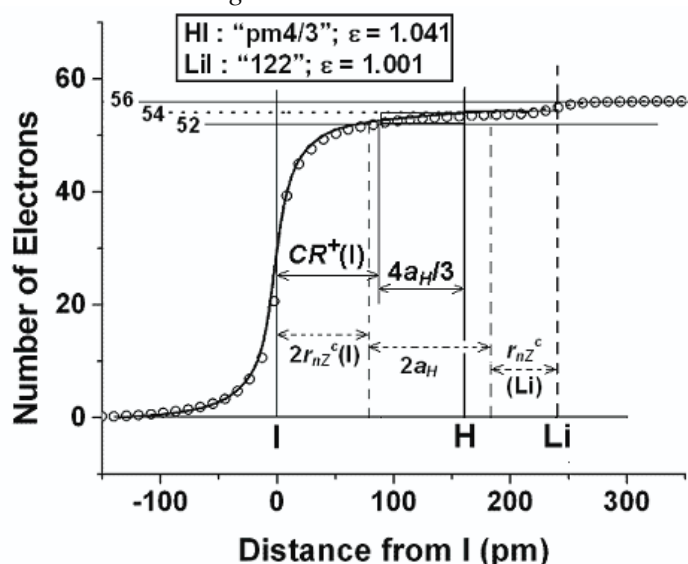


Fig 7. Plots of Electron Number, N , vs distance, r , from the iodine atom in IH (iodine is associated with the positive charge) and LiI.

As mentioned earlier, we consider eqn 5 to represent the “criterion” for itinerancy or—what we have termed as—“peripatetic” nature of the bonding pair of valence electrons. The rationalization for this criterion is based primarily on the probability of charge-transfer with conservation of spin from one site to another (Ganguly 2008c, see also Ganguly 2004). It can be seen from Table 1 that “neutral” values appear in C_M , C_X , when eqn 5 is satisfied. We have compared in Fig 7 the N vs r plots of HI (not satisfying eqn 5, Table 1) and LiI (satisfying eqn 5, Table 1). The fits to the electron number by RxN boxes for HI (full lines) is consistent with a “charge-transfer” pm4/3 formulation, while for LiI (broken lines) one requires “neutral” “221” configuration for the RxN boxes.

4. 7. Double Bonds.

It is of interest to examine the variation in the N_{el} vs r plots when there is a double bond. Of particular interest to us is the case of MgO. According to the constraints of eqn 5, MgO does not satisfy the constraint of eqn 5 and hence the bond-distance should be given by “charge-transfer” values of $C_{Mg}C_{O}D_{MgO}$. In MgO there are one “unsaturated” (or “extra-bonding”) valence electron ($n_v = 1$ as per the notation in Ganguly 1995b) per atom. The “single bond” distance is expected to be reduced by nearly 1.18 in this case. From Table 1 we see that the Mg-O distance can be given by either $C_{Mg}C_{O}D_{MgO} = 2,2,1$ or $C_{Mg}C_{O}D_{MgO} = (\text{pm}4/3)/1.18 \equiv (\text{pm}4/3)_1$. It is seen from Fig 4c that a better fit of the N vs r plots to RxN boxes is obtained with the $(\text{pm}4/3)_1$ than with 2,2,1. The better fit using “charge-transfer” pm4/3 sizes is consistent with the “insulating” nature of the Mg-O bond with eqn 5 not being satisfied in the case of MgO.

4. 8. Compounds of Hydrogen.

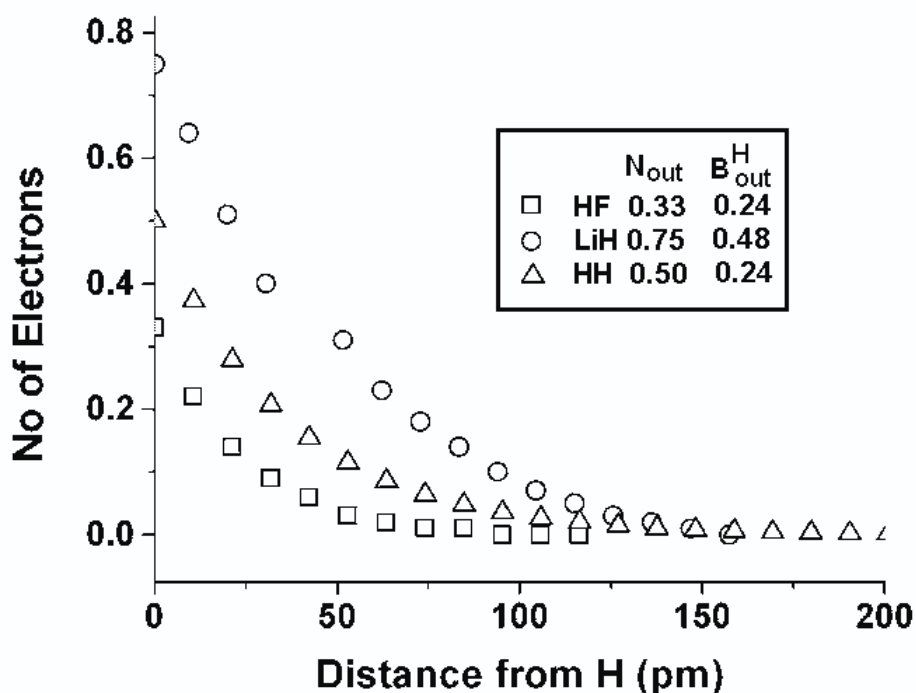


Fig 8. Plots of the electron number *versus* the distance, r , away (into vacuum) from the H nucleus for HF, LiH and Hydrogen molecule. Inset show the values of N_{out} and $B_{\text{out}}^{\text{H}}$ for the best fit (not shown) to the expression $N_{\text{el}} = N_{\text{out}}\exp(-|r|/B_{\text{out}}^{\text{H}})$ for the decay of N_{el} with r .

The contributions to N_{el} *vs* r in the “axle” region are difficult to assess. Since the “axle” region is related to the bonding in hydrogen molecule in our model (Ganguly 1993, 1995a, 2000), we may assess the “axle” contribution by examining the changes in N_{el} *vs* r around the H atom in compounds of hydrogen. We have shown in Fig 8 the changes in the number of electrons as a function of the distance away (into vacuum) from the hydrogen nucleus in LiH, HF and hydrogen molecule. There is an exponential decay of the number of electrons away from the hydrogen nucleus of the form $N_{\text{el}} = N_{\text{out}}\exp(-|r|/B_{\text{out}}^{\text{H}})$ (eqn 7). The nature of the changes in N_{out} and $B_{\text{out}}^{\text{H}}$ for the various compounds is shown in the inset of Fig 8. The value of N_{out} may be taken as a measure of the electron density at the H nucleus. For example in hydrogen molecule $N_{\text{out}} = 0.5$ and indicates that there is a sharing of 0.5 electrons per hydrogen atom in the bonding region of H_2 so that the chemical bond in H_2 may be considered to be fully covalent as expected. This would seem to be quite at variance with the “charge-transfer” description of the bond length ($d_{\text{H-H}} = \epsilon_{\text{eff}}(D^+ + D^-) \approx 1.05(-2a_{\text{H}}/3 + 2a_{\text{H}})$) for the hydrogen molecule (Table 1). It is, of course, apparent that the DFT calculations do not specifically distinguish between the spatial locations of the two hydrogen atoms in the hydrogen molecule. The density would only give a spatially averaged (as well as time-averaged) value of the electron density.

The value of N_{out} for HF (0.33) and for LiH (~0.75) shows, respectively, a depletion and growth of the number of electrons at the hydrogen nucleus relative to that in the hydrogen molecule. In this sense it is consistent with this interpretation of the Laplacian $\nabla^2\rho_{\text{BCP}}$ of the electron density at the bond critical point in Bader’s picture (Bader 1963; Bader and Jones 1963 Bader and Beddall 1971, 1972; Bader *et al* 1971; Bader 1990). The Laplacian $\nabla^2\rho_{\text{BCP}}$ of the electron density function, ρ , at the bond critical point is negative for HF (covalent bond-shared interaction) and is positive for LiH showing electron depletion.

Bader’s “Atoms in Molecules” approach may be regarded as a theory that retrieves chemical insight from modern *ab initio* wave functions. Thus, a molecule is partitioned into real-space topological “objects” (atomic basins) by means of zero-flux (inter-atomic surfaces) that are obtained from the gradient vector field of the density. The importance of this partitioning is that it enables any property of a molecule to be separated into atomic contributions by integrating the property over each atomic basin. The bond path is the ridge of electron density between the bonded atoms. The bond critical point is the point of minimum density along this bond path, where the inter-atomic surface cuts the bond path. The atomic fragments obtained at a point where the electron density is a minimum along the internuclear axis in Bader *et al*’s gained acceptability when virial fragments were obtained (Bader and Bedall 1972; see Popelier *et al* 2000) with the primary concern being to obtain a well-defined energy. Bader’s approach is based on the Hellmann-Feynman theorem (Hellmann 1937; Feynman 1939), according to which the distribution

of electronic density in the molecule determines the forces acting on the nuclei, which in turn define the geometry of the molecule in question. The Hellmann-Feynman theorem has also been used by Politzer (1984) to argue for the $\mu = 0$ condition for the stationary state of a molecule. In our approach (Ganguly 1993, 1995a, 2000, 2008a, 2008c), the “hub” and “axle” (see eqn 2) regions are obtained from considerations of stationary points which correspond to a $\mu = 0$ condition for the chemical potential. This $\mu = 0$ approach seems to be a simpler construct for obtaining atomic fragments.

6. Other General Comments.

The decay of N_{el} from a nucleus as $N_{out}\exp(-r/B_{out})$ into vacuum or its growth as $N_{in}(1-\exp(-r/B_{in}))$ into the bonding region is a somewhat surprising feature. Such changes in N_{el} are consistent with natural hydrogen-atom-like orbitals which have $1s$ wave functions that behave as $\phi_{1s} = A\exp(-Br)$. The probability of finding an electron in the wave-function formalism is ϕ_{1s}^2 . We may then write a “pseudo” $1s$ wave function as $\{\phi_{1s}\} = \exp(-R)$ and $N_{el} = \{\phi_{1s}\}^2 \propto \exp(-2R)$. In quantum mechanical calculations, the natural orbitals are difficult to integrate. Instead Gaussian functions, g , are used. The essential behaviour of g is that r is squared, with $g = x^l y^m z^n \exp(-\alpha r^2)$ where $l = m = n = 0$ for s -type orbitals and l or m or $n = 1$ for p -type orbitals, etc. Moreover, the asymptotic exponential decay is expected only at large distances from the nuclei. It is therefore revealing that after all the rigorous calculations involved in the (“black box”⁶) B3LYP method, the final result should result in the changes in N_{el} being so similar to that expected for hydrogen-like natural orbitals. It is as if all the electrons are to be treated as independent “ $1s$ ” hydrogen-like electrons. This is characteristic of a state in which there are no residual interactions between the particles one another. Such a state is consistent with a description of free electrons in free atoms and is consistent with a $\mu = 0$ condition for a molecule at rest in a minimum energy state.

7. Conclusions

We have outlined in this communication how molecular descriptors obtained from density functional theory and that obtained from atomic sizes give equivalent results regarding molecular geometry of diatomic molecules. The interatomic distance, d_{MX} , of a diatomic molecule, MX, has been written in terms of atomic sizes, r_{nZ}^c , as

$$d_{MX} = \epsilon_{eff}(C_M r_{nZ}^c(M) + C_X r_{nZ}^c(X) + D_{MX})$$

ϵ_{eff} is an environment-dependent dielectric constant that is a (empirical function) of the atomic sizes and is close to unity. The bond distance is thus partitioned into (“hub”) components $(C_M r_{nZ}^c(M) + C_X r_{nZ}^c(X))$ and an “axle” component D_{MX} . The interatomic distance thus depends on the values of C_M , C_X and D_{MX} , which we find depend on the nature of the atoms constituting the bond (eqn 5). Thus there could be “charge transfer” or “neutral” descriptors for C_M , C_X and D_{MX} . The molecular descriptor that we use from the DFT (B3LYP-611G**) calculations is the 1D profile of the number of electrons, N_{el} , with distance, r , along the bonding axis. We find that this DFT N_{el} vs r “number profile” corresponds very well with the way the bond distances are partitioned into the “hub” and “axle” components both in terms of the number of electrons as well as size.

The diatomic molecules used in this study provide some examples of the different combinations of “hub” and “axle” components that contribute to bond distances. The “number profile” for each atom has the typical form of simple hydrogen 1s-like Slater-type-orbital with coefficients (eqn 7) that are dependent on the nature of the molecule. Given this exponential dependence, the ‘number profile’ may be reverses-constructed given the “hub and axle” components. The 1D “number profile” thus holds information on the total number of electrons and, in this sense, is a simpler version of the “shape function” (Ayers 2000, 20007; De Proft *et al* 2004) which is the 3D profile of the density per particle. The current approach seems to solve in a considerable way one (number 9) of the fourteen major problems in DFT posed by Parr (2005) recently. This problem requires finding a simple way to “... *predict bond lengths from the properties of the atoms being bound, without using wavefunctions*”. This property of the atom that is relevant is its core atomic size, r_{nZ}^c .

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Table 1. Calculated and Observed M-X Distance in some Gas-Phase M-X Compounds

M-X	d_{MX} (pm)		r_{nZ}^c (a.u.) ^b		$C_M C_X D_{MX}^{\$}$	$(r_{nZ}^c)^*$ (a.u.) ^c		d_{MX}^{CCD} (calcd) ^d (pm)	$d_{ob}/d_{cal} = R_{oc}^e$	
	B3LYP [#]	Obsvd ^a	M	X					CCD	pm4/3
H ₂	74.7	74.1	0	0	pm4/3	--	--	70.5	1.051	1.051
(F ₂)	140.5	141.2	0.26	0.26	pm4/3	0.20	0.20	131.6	1.073	1.073
F ₂	140.5	141.2	0.26	0.26	1,1.5,2	0.20	0.20	140.2	1.007	1.073
Cl ₂	205.7	198.8	0.53	0.53	pm4/3	0.34	0.34	195.1	1.016	1.019
FH	92.0	91.7	0.26	0	1.5,-,2	0.20	--	91.1	1.006	0.917
IH	162.6	160.9	0.74	0	pm4/3	0.44	--	154.4	1.041	1.041
(MgO)	176.0	174.9	0.88	0.28	2,2,1	0.69	0.22	175.6	0.996	0.856
MgO	176.0	174.9	0.88	0.28	(pm4/3) ₁ ^f	0.69	0.22	173.4	1.009	0.856
LiF *		156.4	1.04	0.26	1,2,2	1.00	0.20	153.0	1.022	0.711
NaF *	191.1	192.6	1.18	0.26	1.5,2,4/3	0.99	0.20	191.5	1.006	0.816
(NaF) *		192.6	1.18	0.26	2,1,1	0.99	0.20	191.7	1.005	0.816
KF *	213.3	217.2	1.46	0.26	1,2.3,2	1.05	0.20	210.5	1.031	0.811
LiH *	159.3	159.5	1.04	0	1,2.3,2	1.00	--	160.8	0.992	0.846
Lil *		239.2	1.04	0.74	1,2,2	1.00	0.44	239.1	1.000	0.859

[#]: calculated using B3LYP DFT 6-311G** method. ^{\$}: $C_M C_X D_{MX}$ gives values of C_M , C_X and D_{MX} (in a_H units) in eqn 3; pm4/3 are “charge-transfer” sizes obtained with $p = 2.144$, $m = 2.30$, and $D_{MX} = 1.333$. ^a: Inter-atomic Distances are obtained from Res 24 and 25. ^b: theoretical sizes obtained from a simple model (eqn 5); ^c: Theoretical sizes obtained from eqn 6; ^d: Calculated distances using eqn 3; ^e: Ratio of observed and calculated distances using $C_M C_X D_{MX}$ values (CCD) or “charge-transfer” values (pm4/3); ^f: (pm4/3)₁ indicates the value of (pm4/3)/1.18 which is the expected shortening when $n_v = 1$.

Table 2. Parameters of fits to the exponential decay of electron density from atom positions M and X of M-X bond in diatomic gas-phase MX molecules (B in pm).

M-X	M				X				ϵ_{eff}^a
	in		out		in		out		
	N_{in}	B_{in}^M	N_{out}	B_{out}^M	N_{in}	B_{in}^X	N_{out}	B_{out}^X	
H ₂	0.5	36	0.5	28	0.5	36	0.5	25	1.05
Cl ₂	8.5	21	8.5	25	8.5	21	8.5	25	1.055
FH	0	-	0	-	5.5	23.5	4.5	32	1.015
LiF	1	12	1	16	5.5	26	4.5	28	1.022
NaF	5	16	5	21	5.5	28	4.5	25	1.006
KF	9	18	9	22	5.5	32	4.5	25	1.011
IH	0.5	12	0.5	18	26.5	20	26.5	24	1.041
Lil	1	12	1	18	26.5	24	27.5	32	1.001
LiH	1	16	1	16	0.85	64	1.15	58	1.05
MgO	5.5	17	5.5	17	4	36	5	26	1.015

^a: Ratio of observed and calculated distance.