

# **INTERATOMIC DISTANCES FROM ATOMIC SIZES: INFLUENCE OF “EXTRA-BONDING” VALENCE ELCTRONS**

**P. Ganguly**

Physical Chemistry Division  
National Chemical Laboratory  
Homi Bhabha Road  
Pune 411021  
INDIA

## ABSTRACT

This article will be an attempt to explain the earlier universal features of the shortening of single-bond distances on introducing multiple bond character (*J. Am. Chem. Soc.*, **1995**, *115*, 1776). The shortening depends on the number,  $n_v$ , of—what we have termed—“extra-bonding” (instead of the usual “unsaturated”) valence electrons on each atom. The interatomic distance,  $d_{M-X}$ , between two atoms M and X (X being more electronegative) is given by  $d_{M-X} = CR_0^+(M)/F_S(M) + CR_0^-(X)/F_S(X)$ , where  $F_S$  is an universal atom-independent function of  $n_v$ , expressed by its spin,  $S$  ( $= n_v/2$ ).  $CR_0^\pm$  are sizes associated with the more electropositive M and more electronegative X atoms when  $n_v = 0$ . We propose a general model, which accounts for this empirical and unexpected universality and yields values of  $F_S$  close to that observed. This model simply extends the methodology (*J. Phys. Chem.*, **2000**, *104*, 8432) for the hydrogen molecule based on the application of the Bohr model to hydrogen-atom-like bonding precursor states for an universal condition,  $\mu = 0$ , for the chemical potential. The novelty in the present communication is to consider the magnetic analogue of the electrostatic Bohr model for hydrogen-like-atoms. We show that the term  $F_S = 1 + (2/\pi^2)\{S(S + 1)\}^{1/3}$ , where the term  $(2/\pi^2)$  comes from geometrical arguments. We then show how the term  $F_S$  may be used to obtain quantitative insights into recent debates including the gallyne bond order problem, fractional bond order, changes in atomic sizes with valence-states, spin-states and electronegativities especially of transition metal elements, bond-stretch isomerism. The bond order of oxygen molecule and its paramagnetism is discussed in a new light.

## I. INTRODUCTION

It has been realized from very early<sup>1,2</sup> that in the formation of a chemical bond between two atoms, each atom contributes one electron to the bonding electron pair to form a single bond. The presence of additional “unsaturated” valence electrons increases the bond order. The way the single bond distance changes on increasing bond order forms the basis of much of the discussions in the literature even if a quantified, atom-independent, universal description of this correlation is very elusive. Theoretical approaches that relate bond order to bond distance are based on atomic-specific considerations of electronic degrees of freedom, especially those of  $\pi$ -electrons<sup>3,4</sup> or by bond order potential methods<sup>4,5</sup>. One of the more successful empirical approaches has been the bond valence model<sup>6-8</sup> in which the valence of an atom is the sum of its bond valence, which in turn is correlated to the bond length through empirical relationships. The crucial feature is that one requires quantitative estimates of “single-bond” distances before one can correlate changes in bond length with changes in bond order.

Fairly reliable estimates of single-bond distances have been obtained from transferable “core” atomic sizes<sup>9-12</sup>. Irrespective of how a bond is formed, there exists a free-atom-like<sup>9, 12, 13</sup> universal chemical potential,  $\mu_{\text{univ}} = 0$  condition for an energy minimized, density optimized state. This helps to set a reference point for obtaining transferable parameters, such as a core atomic size,  $r_{\text{core}}$ , for the description of bond distances. This  $\mu = 0$  condition is a condition for free atoms so that one may expect<sup>12</sup> an atomic property to contribute to an understanding of the property of the molecule to which it belongs. An atomic size,  $CR$ , contributing to interatomic distances has been found<sup>10</sup> to be linearly related to  $r_{\text{core}}$  as  $CR = Cr_{\text{core}} + D$ . The parameters  $C$  and  $D$  are independent of the “ionic character of the bond” even if bond-formation may be consolidated by the creation of charges<sup>10, 12</sup> (Kosselion<sup>1</sup>). The interatomic distance,  $d_{MX}$ , of a  $M$ - $X$  bond of “single-bond” character is given in a “ball-and-stick” manner<sup>10, 12</sup> by

$$d_{MX} = [C_M r_{\text{core}} + C_X r_{\text{core}}]_{\text{“ball”}} + [D_M + D_X]_{\text{“stick”}} \quad (1)$$

where the atom-dependent “ball” dimensions and the “atom-independence” of the “stick” dimension is apparent. Changes in bond lengths due to changes in  $C$  and  $D$  would constitute a pristine example of the much sought after example of “bond stretch isomerism”<sup>14-16</sup>. This is not the primary topic for this communication. Instead, we focus on a new perspective<sup>9, 10</sup> on bond-order/bond distance relationship that is based on atom-independent expressions relating bond order to bond distance, when more than one (“extra-bonding”) valence electron is involved. Our first interest would be to find a simple, first principles, theoretical justification for the earlier observation<sup>9, 10</sup> of universal atom-independent extent of reduction in bond length with bond order in “multiply bonded” systems. We then show how this model gives useful insights into some general and current physico-chemical problems involving bond distances.

From an examination<sup>9, 10</sup> of interatomic distances of transition metal elements as a function of the nominal number of electrons,  $n_v$ , or their spin,  $S$  ( $= n_v/2$ ) due to electrons in the  $d$  shell (from their position in the periodic table) it has been noted that the extent of shortening of single bond distances due to an increase in bond order ( $= n_v + 1$ ) was best

fitted by a term  $F_S = 1, 1.16, 1.25, 1.32, 1.38$  and  $1.42$  for  $n_v = 0, 1, 2, 3, 4$  and  $5$ , respectively. The term  $F_S$  is seemingly an atom-independent universal quantity that describes changes in atomic size when there are  $n_v$  additional bonding (“extrabonding”) valence electron that is better recognized as “unsaturated” valence electrons. Because of such a shortening, eqn 1 becomes (for the general condition  $n_v(M) \neq n_v(X)$ )

$$d_{MX} = CR(M)/F_S(M) + CR(X)/F_S(X) \quad (2a)$$

$$= [C_{Mr_{core}}/F_S(M) + C_{Xr_{core}}/F_S(M)]^{\text{“ball”}} + [D_M/F_S(M) + D_X/F_S(X)]^{\text{“stick”}} \quad (2b)$$

Current wave-function-based quantum chemical methodologies have not anticipated such an universality. The interpretation<sup>17</sup> of the empirical quantity,  $F_S$ , and the way it may be applied to obtaining, what is known as, “multiple bond” distances will be presented in this communication. We obtain changes in atomic sizes as a function of valence state or spin state especially for transition metal elements and find a straightforward estimate of bond distances with fractional bond order—as implied in eqn 2b when  $F_S(M) \neq F_S(X)$ . We also comment on a few important issues related to bond order including that of an important exception, the oxygen molecule.

Earlier, we have accounted for the bond lengths of the hydrogen molecule—by applying the equation<sup>18</sup> ( $\epsilon_{\text{eff}}$  is an effective dielectric constant)

$$E_{\text{tot}} = (\hbar/r)^2/2m - e^2/\epsilon_{\text{eff}}r \quad (3)$$

to hydrogen-atom-like bonding “charge-transfer” quasi-particles (see Section III. 2) for the  $\mu = 0$  condition for the chemical potential for an energy-minimized, density optimized state. Such a quasi-particle approach effectively eliminates complications due to electron-electron interactions in current quantum chemical methodologies which have the same difficulties as a straightforward extension of the Bohr model to the two-electron, two-nuclei hydrogen molecule leads to the use of complex planetary orbits, which end up with singular, non-integrable and multidimensional Hamiltonians<sup>19,20</sup>. It is sufficient to visualize<sup>21</sup> eqn 2 as a one-dimensional equation (see eqn 3. 12 of Ref 22 and the discussions thereon) even if it is reminiscent of the electron in the hydrogen atom in its first Bohr orbit. In what follows, this approach is extended to systems with  $n_v$  “extra-bonding” valence electrons to obtain changes of bond distance with “bond order” ( $= n_v + 1$ ).

The interactions involving “charge” or “spin” degree of freedom may be viewed<sup>23</sup>—as far as obtaining the first Bohr energy of the hydrogen atom—in terms of a magnetic Bohr model. In this model a flux quantum is introduced into an area equivalent to that of the first Bohr orbit<sup>24, 25</sup> (see Sec II. 2). The interaction between the magnetic field thus generated and the magnetic moment of the electron is taken as the equivalent of a potential energy  $e^2/r$  and application of the virial theorem reproduces the energy,  $E_H$ , of the hydrogen atom. In this communication we have extended this “magnetochemical” Bohr-like model for hydrogen-atom-like bonding quasiparticles, to account for the universal changes in bond lengths with “bond order” in “multiple”-bonding systems. For this purpose we treat all atoms as pseudo hydrogen atoms, with the spins of the “extrabonding” valence electrons being located at their “nucleus”.

We are well aware that the approach adopted by us may seem antiquated in the context of the more demanding, complex and well-established Schrödinger-equation-based

methodologies. However, we insist (Section II) that we are providing, at worst, an analytical simplification<sup>26</sup> of the methodology for obtaining bond distances without necessarily contradicting the Schrödinger-equation-based results on atoms. Of particular importance is the importance of emphasizing a 2+1 dimensional approach (Sections II. 2-4) in the presence of an interaction and to use a concept of quasiparticles to describe interatomic distances in the context of a  $\mu = 0$  condition for the chemical potential (Section II. 5, 6). We introduce in the notion of “extrabonding” electrons (Section III.1, 2) and the “magnetic” Bohr model<sup>24, 25</sup> using planar orbits for the valence electron when we treat all atoms as pseudo hydrogen atoms (section III. 2). The “core” or “pseudo-nuclear” electron spins contribute (Sec III. 3) an additional interaction term,  $\zeta$ , such that the “ball” and “stick” sizes are scaled by  $(1 + \zeta)^{-1}$  or  $F_S = (1 + \zeta)$ . We find from a dimensionality argument (Sections III. 4-6) involving a flat 2D orbit that  $\zeta = (2/\pi^2)\{S(S + 1)\}^{1/3}$  such that  $F_S = 1 + \zeta$  which gives the values of  $F_S$  very close to that empirically found earlier. This simple and “first principles” demonstration/explanation of an empirical relationship has demonstrable advantages for understanding chemical systems in a straightforward and “portable” manner<sup>27</sup> (Section IV). This includes “fractional bond order”, valence- and spin-state- dependent sizes, electronegativity, spin-state transitions, impact on bond energies, “bond stretch isomerism” and find insights into the bond order of oxygen molecule and its paramagnetism.

## II. Magnetic Interactions and Atomic Sizes

II. 1. Bohr Orbits and Magnetic Fields. Eqn 3 may be treated as an equation of motion in 1D and may be obtained from the uncertainty principle itself<sup>22</sup>. The energy of the hydrogen atom,  $E_H$ , is obtained from the size,  $a_H$ , of the first Bohr radius. The Bohr radius may be looked upon as the quantum mechanical zero point motion perpendicular to a magnetic field line. An electron in a magnetic field  $B$  gyrates in a circular orbit perpendicular to the field with cyclotron radius  $\ell = |\hbar/eB|^{1/2}$  and with quantized Landau energy levels. It has been recognized<sup>28, 29</sup> that for high magnetic fields, magnetic confinement is perpendicular to the direction of the field that dominates the attractive binding to a proton. When  $\ell = a_H$  ( $\sim 53$  pm), the first Bohr radius, and one quantum of magnetic flux is present<sup>23</sup> in an area of the first Bohr orbit, the magnetic field,  $B^1_{Bohr} = m_e^2 e^3 / \hbar^3 \approx 2.4 \times 10^5$  T. For  $B > 2.5 \times 10^5$  T  $\sim B^1_{Bohr}$ , the Bohr radius becomes less than  $a_H$ . There is an increase in binding energy as the magnetic field increases since the electron is more likely to be found near its nucleus.

II. 2. 2D Nature of Bohr Orbit. This section is meant to serve as a justification for the use of the “Bohr model” as an accurate approximation to, say, the Schrödinger equation. This is in the spirit of Dirac’s statement<sup>31</sup> that follows his more quoted phrase “... *the mathematical theory of a large part of physics and the whole chemistry are thus completely known.*” The so-called first Bohr radius,  $a_H$ , in the Schrödinger wavefunction approach, represents the radius of a sphere whose surface is iso-energetic with the solution of eqn 3 in an isotropic medium for an energy-minimized state. The important feature is that any real current induced on this surface in response to an external perturbation (say, a fluctuation in electron charge/spin density) would be an induced ring current. Such a current is expected to be dissipationless or persistent as long as there is no

inelastic scattering and phase coherence is maintained. The surface of the sphere then represents a barrierless region for the transport of an electron. It is this ring current that can be identified with the “Bohr orbit” especially when the perturbation is small. The equations governing the quantization of angular momentum as in a circular Bohr orbital<sup>21</sup> is expressed in eqn 3.

The use of a two-dimensional Bohr orbit<sup>30</sup> in a modern context may be justified—if only to allay more conservative apprehensions—if one considers a response to an external fluctuation or perturbation. The binding energy,  $E_H$ , of the hydrogen atom, as in the Balmer series, appears experimentally as a consequence of external an excitation when the electron is taken apart from its ground state. Any fluctuation in electric charge in an atom will cause integral changes in charge or spin in its own microscopic environment, since an electron cannot be fractured. By Faraday’s laws, a voltage is induced in a coil due to a change in its magnetic environment, say the appearance-disappearance of a spin or charge no matter how the change is produced. The induced voltage is such that, by Lenz’s law, it produces a current whose magnetic field (inside, say, a loop of wire) always acts to keep the magnetic flux in the loop constant. The ring current is expected to be perpendicular to the direction of perturbation in a (2+1)D system.

II. 3. Magnitude of Spin-Orbit Interaction. The interaction of the magnetic moment of an electron due to its spatial motion and its spin orientation is usually described as the spin-orbit interaction, which is considered to be small compared to electrostatic interaction energies. This is because the spin-orbit interaction is measured from the average of the orbital moment and gives thereby the deviation of the environment or the average orbital motion from spherical symmetry. The magnetic field arising from orbital motion is  $B^{\text{orb}} = \mu_0 e v / 4\pi r^2 = \mu_0 e L / 4\pi m r^3$  where  $L$  is the orbital angular momentum. The magnetic field is vanishingly small for a hydrogen electron in the 1s state with  $L = 0$ . In such an approximation a change in the spin-state is not expected to affect the orbital motion. The orbital function,  $\phi(r)$  and the spin function  $\chi$ , are then treated as independent factors and the wave function,  $\psi$  is then written in the customary product form,  $\psi = \phi(r)\chi$ .

In our case we take a flat Bohr-orbital motion, which is a limit of extreme anisotropy with each electron carrying a magnetic solenoid with it. The concept of an interaction between an orbiting charge and a magnetic flux in a tube giving rise to quantization is central to the ideas of the charge-flux-tube composite introduced by Wilczek<sup>32</sup>. We borrow from Wilczek’s description in which the electron “orbits around, but does not penetrate, a solenoid”. The interaction energy (see Appendix),  $-m_e e^4 / \hbar^2$  of the magnetic moment (one Bohr magneton,  $e\hbar/2m_e$ ) of the electron with  $B^1_{Bohr}$  the high magnetic field ( $> 10^5$  T) may be taken<sup>23</sup> as the magnetic equivalent of the potential energy. The energy  $\hbar^2/2m_e a_H^2$  is the kinetic energy, satisfying the virial theorem, and giving the total energy as  $-\hbar^2/2m_e a_H^2 = E_H$ , the energy of the hydrogen atom. The expression for the energy is equivalent to the energy obtained from electrostatic interactions that stabilize the Bohr atom. It is not additional interaction energy.

II. 4. Electron-Electron Interaction in 2DEG. This section is introduced for sake of completeness (hopefully). The effect of a magnetic field on a two-dimensional gas

(2DEG) of electrons manifests itself most clearly in the Quantum Hall Effect<sup>33, 34</sup> (QHE) and more startlingly in the fractional quantum Hall effect<sup>34c</sup>. According to the currently accepted theories<sup>33, 34</sup> of QHE, the energy spectrum of a 2DEG in the presence of a strong perpendicular magnetic field,  $B$ , consists of highly degenerate Landau levels. The solution of the Schrödinger equation for a 2D gas of electrons in a strong perpendicular magnetic field,  $B$ , gives eigenvalues of an harmonic oscillator,

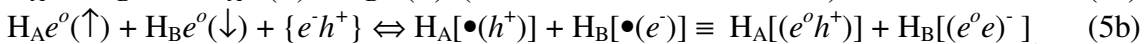
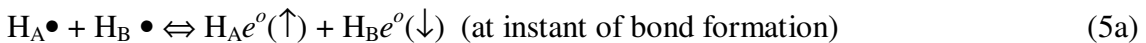
$$\epsilon_i = (n + 1/2)\hbar\omega_c$$

where  $n = 0, 1, 2, 3 \dots$  correspond to the different Landau levels.  $\omega_c (= eB/m)$  is the cyclotron frequency which has no dependence on the size of the Landau levels. Since the electron's trajectory in the 2DEG in the presence of an external magnetic field is in spiral orbits perpendicular to the direction of the field, Laughlin's single particle wave functions<sup>34</sup> are necessarily eigenfunctions of orbital angular momentum. In the localized electron limit, one obtains a real-space picture of Landau levels as two-dimensional rings with quantized energy levels. In the limit of the ground state ( $n = 0$  in the above equation), the scheme for the Landau levels resembles the Bohr model<sup>26, 35</sup> of two-dimensional planetary orbit. Ganguly<sup>23</sup> has examined some of these concepts in the context of the electron-electron interactions in the chemical bond.

II. 5. Instant of Bond Formation. One of the crucial steps in the atom-bond transition is the “knitting” of two radicals into a spin-less chemical bond. Turro and coworkers<sup>36</sup> have discussed how conservation of spin imposes “a complicated, coincidental, and coordinated choreography or hyperdynamics which integrates the spin, chemical, molecular and rotational motions of the pair within the overall restricted space available to it”. A “severe” constraint due to complications on “spin stereochemistry” is imposed due to the principle of conservation of angular momentum<sup>36</sup>. Being based on a fundamental principle, such choreography is expected to accompany all the dancing spins that form a spin-paired singlet bond, including that of the hydrogen molecule formed from two hydrogen atoms. The crucial aspect of the model is that the spins be aligned antiparallel to each other “at the *instant* of a bond formation”<sup>36, 37</sup> (italics due to the author) between two doublet radicals (or electrons) on two atoms (M and X, for example)  $M(\bullet) + X(\bullet)$  (“biradical”)  $\rightarrow [e^o(\uparrow)_M + e^o(\downarrow)_X]_{S=0}$  (4)

The probability of finding that instant when the two spins on different atoms have an antiparallel orientation will be then dictated by the spatial geometry in which the bond is being formed.

II. 6. Bonding Spinless Quasiparticles. In the formation of hydrogen molecule itself the two radicals of eqn 4 are the two  $H\bullet$  atoms. For the formation of the “ordinary” bond length ( $\sim 74$  pm) of the hydrogen molecule we have proposed that a spin-paired singlet state (eqn 5a) is transformed in charge-transfer step to bonding spin-less quasi-particles (eqn 5b) in the presence of a spin-less electron-positron pair,  $\{e^-h^+\}$ , representing an interaction



We will use eqn 5 as a typical bond-forming interaction involving (Kosselian<sup>1</sup>) charge-transfer before bond formation. We identify the bonding electron as that electron whose

spin is located and annihilated by a spin-pairing process, such as to initiate the charge-transfer process<sup>12</sup>.

Once the bond is formed and an energy-minimized density-optimized states is reached, the bonding quasi-particle states,  $H^+[(e^o h^+)]$  and  $H^+[(e^o e^-)]$  are defined and written simply as  $(e^o e^-)$  and  $(e^o h^+)$ . These particles are different from the so called effective mass-particle complexes (complexes A and B of Lampert<sup>38</sup>) or trions<sup>39</sup>. In general quasiparticles are created as part of an emergent phenomenon<sup>34</sup> as a collective effect of a large number of particles and do not depend on the details of the causal equations of motion. In this case, the bonding quasiparticles are defined for the  $\mu = 0$  condition<sup>12</sup>. These quasiparticles appear only as a consequence of the quantum phase transition that marks the atom-bond transition<sup>12, 40</sup> and viewed as a “bound-unbound” transition similar to a metallization process<sup>40</sup>.

The bonding quasiparticles  $H^+[(e^o h^+)]$  or  $H^+[(e^o e^-)]$  have been treated<sup>12</sup> as Bohr like atoms with the composite charges  $e^o h^+$  and  $e^o e^-$  being in Bohr-like orbits around a  $H^+$  nucleus to give “Bohr sizes”  $a^{ee}_H (= 2\varepsilon_{\text{eff}} a_H \sim 111 \text{ pm}$  where  $a_H \sim 53 \text{ pm}$  and  $\varepsilon_{\text{eff}} (\sim 1.05)$  is an effective dielectric constant ) and  $a^{eh}_H (-4\varepsilon_{\text{eff}} a_H/3 \sim -37 \text{ pm})$ , masses  $m^{ee}_H (= m_o/2$ ,  $m_o$  being the mass of the free electron) and  $m^{eh}_H (= 3m_o/2)$  and energies,  $E_H^{ee} = -E_H/2$  and  $E_H^{eh} = -3E_H/2$  where  $-E_H$  is the first Bohr energy of the hydrogen atom. The total energy  $E_{\text{tot}} = E_H^{ee} + E_H^{eh} = -2E_H$  satisfying thereby the  $\mu = 0$  condition<sup>12</sup>. The “stick” dimension is then given for “charge-transfer” interactions by

$$D^+ + D^- = 4\varepsilon_{\text{eff}} a_H/3 = 74 \text{ pm} \approx d_{H-H} \quad (5c)$$

where  $d_{H-H}$  is the “ordinary” bond length of the hydrogen molecule. It is because of this that it has been suggested that all atoms may be treated as pseudo hydrogen atoms with atom-dependent “core” sizes, and a hydrogen-atom-like valence electron. Since the quasi-particle states,  $(e^o e^-)$  and  $(e^o h^+)$  lose their identity when they are taken apart<sup>34c</sup>, the sizes  $CR^\pm$  are also defined once a bonding interaction is defined at  $\mu = 0$ . They may have no role in defining non-bonded distances between rare-gas atoms, for example.

We may exploit the  $\mu = 0$  condition in a different way so as to get further insights especially regarding the way the spins of the “extra-bonding” valence electrons are coupled (or decoupled) from that of the bonding electron (see Section III. 5). We also use this opportunity to assert the importance of the “one-third effect”<sup>23</sup> ( $|D^+|/|D^-| = 1/3$ ) that arises from the electron-electron interaction in a chemical bond. From considerations of conservation of total angular momentum, we must assume that the composite particles  $H^+(e^o h^+)$  and  $H^+(e^o e^-)$  are spin-less if the electron-hole pair  $\{e^- h^+\}$  (representing the interaction) is also assumed to be spin-less with the electron and its hole having equal and opposite spins that add up to the original zero spin interaction. We consider the composite of the  $e^o$  neutral electrons (“chargeless spinon”) with spin  $1/2$  attached to solenoids of orbiting charges such as  $e^-$  in  $H^+(e^o e^-)$  and  $h^+$  in  $H^+(e^o h^+)$  that create magnetic fields,  $H_0^{e^-}$  and  $H_0^{h^+}$ . These fields are created by confining one flux quantum in an area equivalent to that of first Bohr orbits of  $e^-$  and  $h^+$ . The magnetic interaction energy of  $H_0^{e^-}$  with the magnetic moment,  $\mu^- (= e\hbar/2m_e^-)$ , of  $e^o$  in the quasiparticle  $(e^o e^-)$ , is given by<sup>29</sup>

$$-H_0^{e^-} \cdot \mu^- = -((m^-)^2 e^3/\hbar^3) \cdot (e\hbar/2m_e^-) = -(m^-)^2 e^4/\hbar^2/2m_e^- = -m_o e^4/2\hbar^2 \quad (6)$$

The mass of the  $e^o$  electron is  $m_e^-$  and  $m^-$  is the mass of the orbiting electron charge,  $e^-$ , in the composite particle ( $e^oe^-$ ). We let  $m^- = m_e^- = m_o$ , the mass of the free electron, such that  $(1/m^- + 1/m_e^-) = 2/m_o = 1/m^{ee}_H$  where  $m^{ee}_H$  is the mass of the composite article ( $e^oe^-$ ). We require

$$E^{ee}_H + E^{eh}_H = -(H_0^{e^-} \cdot \mu^- + H_0^{h^+} \cdot \mu^+) = -m_o e^4 / \hbar^2 = -2E_H \quad (7)$$

In order to satisfy the  $\mu = 0$  condition for the quasiparticles. Because of this, the magnetic interaction energy of  $H_0^{h^+}$  with the magnetic moment,  $\mu^+$  ( $= e\hbar/2m_e^+$ ), of  $e^o$  in the quasiparticle ( $e^oh^+$ ), is required to be given by

$$-H_0^{h^+} \cdot \mu^+ = -((m^+)^2 e^3 / \hbar^3) \cdot (e\hbar/2m_e^+) = -(m^+)^2 e^4 / \hbar^2 / 2m_e^+ = -3m_o e^4 / 2\hbar^2 \quad (8)$$

where  $m_e^+$  is the mass of the  $e^o$  electron, and  $m^+$  is the mass of the orbiting electron charge,  $h^+$ , in the composite particle ( $e^oh^+$ ). We let  $m^+ = m_e^+ = 3m_o$ , the mass of the free electron<sup>41</sup>, such that  $(1/m^+ + 1/m_e^+) = 2/3m_o = 1/m^{eh}_H$ , where  $m^{eh}_H$  is the mass of the composite article ( $e^oh^+$ ). Eqn 7 is then satisfied using the virial theorem and kinetic energies obtained from Bohr radii  $a^{ee}_H$  and  $a^{eh}_H$  with masses  $m_o/2$  and  $3m_o/2$  of the quasiparticles ( $e^oe^-$ ) and ( $e^oh^+$ ), respectively.

## II. Influence of Extra-bonding Valence Electrons.

III. 1. Nature of “Extra-Bonding” Electrons. The choice of the term “extra-bonding” electrons implies that we have to distinguish them not only from the “bonding electron” but also from core “unpaired” electrons, which do not participate in the bonding. The “extra-bonding” electrons contribute to changes in bond distances in “multiple bonds” and also contribute to changes in atomic sizes due to change in spin- and oxidation-states as we shall see later. The “extra-bonding” valence electrons are not part of the spinless bonding quasi-particles, ( $e^oe^-$ ) or ( $e^oh^+$ ) and consequently their spins may be de-coupled from that of the bonding valence electron. In an isolated atom, energy levels of the “extra-bonding” valence electrons and the bonding electron are degenerate. The degeneracy is lifted once the spin of the bonding electron is, say, converted to spinless charged precursor quasi-particle states, ( $e^oe^-$ ) and ( $e^oh^+$ ) and any magnetic field due to their motion is not pinned to any bond axis or vice versa (see Section III. 6) and may be continuously changing even if the actual bond-axis is fixed. Such a distinction between bonding and “extrabonding: states resembles in some way the distinction between  $\sigma$ -bonding (orbitals oriented along bonding axis) and  $\pi$ -electrons (orbitals oriented away from the bonding axis) that is used in conventional chemical terminology. The spin-conserving constraints due to spin-charge conversion (eqn 5) are not necessarily applicable to the additional “extra-bonding” valence electrons<sup>42</sup>. In this sense they need not participate in the “bound-unbound” transition that characterizes the bonding electrons in bonded atoms.

III. 2. On the Application of the Magnetic Bohr Model. The coupling of the spin of an electron with the magnetic field due to orbital motion (Sec II. 4) is important for this paper. Theoretically calculated values of core radius of an isolated atom, such as the Zunger-Cohen orbital radii, take into account the additional exchange and correlation effects in determining core atomic sizes when there are,  $n_v$ , “unpaired” “extra-bonding” valence electrons with a spin  $S (= n_v/2)$  in the “core”. However, these calculations do not account for changes in size in the presence of an external field, including the influence of

a spin-pairing chemical reaction field. We propose that it is this external field accounts for the magnitude of  $F_S$ .

Just as one has the “magnetic equivalent” of the electrostatic binding energy of an electron in hydrogen atom, one may also consider the bonding electrostatic field to be represented by the equivalent of a magnetic field. When one quantum of flux is enclosed in one Bohr orbit, the interaction of the magnetic field,  $B^1_{Bohr}$ , thus generated with the magnetic moment of one Bohr magneton of the electron is the equivalent electrostatic attractive energy for an electron in a Bohr orbit<sup>23</sup> (see Appendix). The magnetic interaction energy may therefore be set in  $e^2/a_H^*$  units, for Bohr-like atoms with a Bohr radius,  $a_H^*$ . A novel feature appears when we consider the electron-electron interaction in a chemical bond (see Section II. 6). Some of these effects of electron-electron interactions in 2DEG due to a magnetic field mark the quantum phase transitions<sup>34</sup> in the Fractional Quantum Hall Effect.

In the way the “ball-and-stick” model has been used to describe interatomic bonded distances in eqn 5c all atoms may be treated as pseudo hydrogen atoms. One may consider the number,  $n_v$ , of “extra-bonding” valence electrons with its spin  $S (= n_v/2)$  to be associated with its parent atom but treated as extra valence electrons interacting through their spin with the bonding electrons. There are additional interactions present when there are additional magnetic moments involving the spin,  $S(n_v)$ , of  $n_v$  “extra-bonding” valence electrons. These “extra-bonding” valence electrons of an atom contribute to an internal magnetic field,  $H_{int}$ . Thus if  $H_0$  is a magnetic field that is associated with the bonding electrons (see section III. 6) the total magnetic field,  $H_{tot}$ , by the valence electron of an atom due to bond formation is given by

$$H_{tot} = H_0 + H_{int} \quad (9)$$

It is the additional internal “magnetic field”,  $H_{int}$ , due to the “extra-bonding” electrons that contributes to a decrease in the size of the bonding quasiparticles (see also sec II. 1). For convenience, and without loss of generality, we consider the  $n_v$  “extrabonding” electrons to belong to the element, M, in the M-X bonds.

### III. 3. Magnetic Influence of “Extra-Bonding” Electrons.

*III. 3. a. Valence Electron.* We consider the interactions due to the spin,  $S(n_v)$ , of the “extra-bonding” valence electrons as an additional term,  $\zeta$ , that contributes to the attractive energy in units of  $e^2/r$ . We may therefore write the attractive energy as  $(1 + \zeta)e^2/r$  such that the total energy becomes

$$E_{tot} = (\hbar/r)^2/2m - (1 + \zeta)e^2/r \quad (10)$$

A stationary state is then reached in the Bohr model with  $r_{eq}$  being given by

$$r_{eq} = \hbar^2/(1 + \zeta)me^2 = a_H/(1 + \zeta) \quad (11)$$

Such a reduction in the Bohr radius by  $(1 + \zeta)$  is expected for the hydrogen-atom-like quasi-particles,  $(e^o e^-)$  and  $(e^o h^+)$ , as well. The relation between  $F_S$  and  $(1 + \zeta)$  is expected to follow. It is known empirically from the way the correction  $F_S$  has been applied in eqn 3 that the reduction in lengths due to the “extra-bonding” valence electrons affects both the “ball” as well as the “stick” to the same extent. We may therefore use<sup>43</sup> the identify  $F_S = (1 + \zeta)$ .

III. 3. b. *Core Size.* For a given atom, the nodal point serves to define a core size,  $r_{core}$ , such as the Zunger-Cohen orbital radii<sup>44</sup> or the outer most nodal point<sup>45</sup> of the valence electron wave function. This nodal point separates core regions from valence regions at a distance  $r_h$  from the nucleus. Because of the vanishing probability of finding an electron at the nodal point,  $r_h$ , serves as a location of a positive charge (or hole). This positive charge at  $r_h$  attracts the valence electron and is repelled by an effective positive nuclear charge. We may take  $r_{core}$  as that point at which attractive and repulsive forces cancel each other, as in the Zunger-Cohen radii<sup>44</sup>. For a given atom-independent valence size,  $r_{val}$  (say, the Bohr radius of the hydrogen-atom-like valence electron), the size  $r_h$  ( $\equiv r_{core}$ ), is well defined relative to  $r_{val}$  for the condition corresponding to  $\mu_{univ} = 0$ . Since the dimension of the “stick” is fixed and single charges are involved the ratio of the valence and core lengths is expected to be characteristic of the atom. We assume it to be a constant for a  $\mu = 0$  condition such that

$$r_{val}/r_h = \text{constant} \quad (13)$$

for a given atom. A change by  $(1 + \zeta)$  of the valence size will correspondingly lead to a reduction in the core size once the  $\mu = 0$  condition is maintained.

III. 4. Relationship between  $\zeta$  and  $S$ . The changes in the length scale because of the additional interaction term,  $\zeta$ , due to the *internal exchange field* of the “extra-bonding” valence electron is expected<sup>17</sup> to be a smooth function of  $S$ , with  $\zeta = 0$  when  $S = 0$ . Because of the two-dimensional orbit, the internal field should be proportional to the spin density in two-dimensions which we take to be proportional to  $n_v^{2/3}$  or proportional to  $\langle S^2 \rangle^{1/3}$ . The expectation value of the total spin,  $\langle S^2 \rangle$  should equal  $S(S+1)$  if there is no spin contamination and  $S = n_v/2$ . We thus obtain

$$\zeta \propto H_{int} \propto n_v^{2/3} \propto \{S(S+1)\}^{1/3} \quad (14a)$$

or

$$\zeta = C_\zeta \{S(S+1)\}^{1/3}. \quad (14b)$$

The term  $F_S$  is then given by

$$F_S = 1 + \zeta = [1 + C_\zeta \{S(S+1)\}^{1/3}]. \quad (15)$$

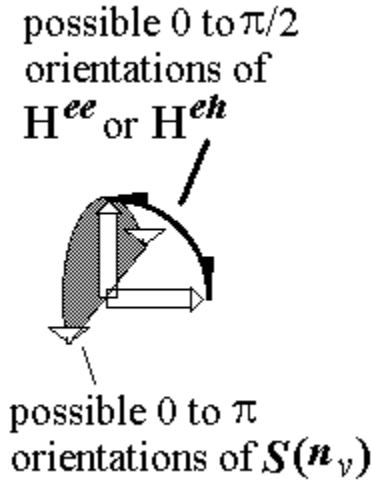
The extent of reduction is empirically given by the magnitude of  $F_S$ . When we assume  $C_\zeta = 0.2$ , we obtain the calculated value  $F_S(\text{calcd}) = 1.18, 1.25, 1.31, 1.36$  and  $1.41$  for or  $S = 0, 1/2, 1, 3/2, 2$  and  $5/2$ , respectively, which is within 2% of that observed<sup>9, 17</sup> empirically. It only remains to provide an estimate that justifies  $C_\zeta \approx 0.2$ . We examine one possible explanation. This *internal field*,  $H_{int}$ , is due to the coupling of the *external exchange field*,  $H_0$ , with spin,  $S$  and magnitude  $(S(S+1))^{1/2}$ . This exchange field is due primarily to opposite charges in essentially two-dimensional orbits.

The dimensionality arguments above for obtaining eqn 14 is consistent with that used by us<sup>12</sup> to account for the binding energy,  $D_{H-H}$ , of the (“ordinary”) hydrogen molecule using a Bohr model for the quasiparticles  $(e^o e)^-$  and  $(e^o h)^+$  hydrogen-atom-like orbits around hydrogen nucleus. The  $\mu = 0$  stationary state of the bond in which the quasiparticles exist is obtained by the liberation of a binding energy due to attractive electrostatic interaction between electron-hole pair. The bond energy,  $D_{H-H}$ , in this case should be close<sup>12</sup> to the maximum electron-hole excitonic binding energy,  $E_{exc}^{max} \approx 6.8$  eV instead of the observed  $D_{H-H} \approx 4.45$  eV  $\approx 2E_{exc}^{max}/3$ . The difference of  $\sim E_{exc}^{max}/3$  has

been attributed<sup>46</sup> to a loss of a translational degree of freedom at the instant of bond formation in the one-dimensional chemical bond in the hydrogen.

**III. 5. Value of  $C_\zeta$ .** Once the composite particles,  $(e^o e^-)$  and  $(e^o h^+)$ , themselves are taken to be spinless, the orientation of the orbital magnetic<sup>47</sup> fields,  $H^{ee}$  and  $H^{eh}$  (see Sec II. 6), are not necessarily correlated to the direction of the spin associated with the neutral spinon,  $e^o$ , within the two quasiparticles. The direction of the orbital magnetic fields,  $H_0^{e^-}$  and  $H_0^{h^+}$ , are also expected to be independent of each other. Because of this one may also consider the spins on the  $n_v$  “extra-bonding” electrons to be de-phased or decoupled from that of  $H^{ee}$  or  $H^{eh}$ . If such a dephasing was complete one would expect that  $C_\zeta = 0$  while in the absence of any dephasing one could expect  $C_\zeta = 1$ .

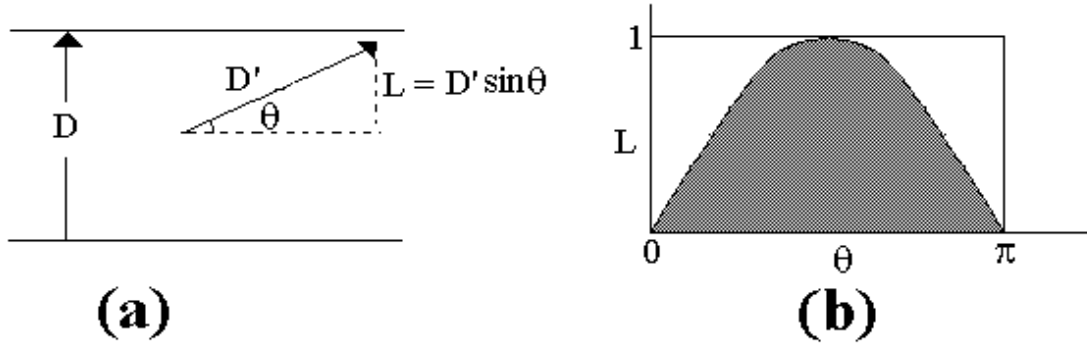
Although,  $H^{ee}$  and  $H^{eh}$  are decoupled from  $S(n_v)$  their mutual fields are expected to be oppose each other. One may expect the two bonded atoms to be immersed in a magnetic field of opposite orientations (reminiscent of the “staggered” magnetic field in antiferromagnets) and aligned along an axis parallel to  $H_0$  in eqn 9. At the same time the bonding quasiparticles have no separate existence by themselves and exist only in the context of bond formation. The consequence is that the dephasing is such that it allows (Fig. 1) a canting of  $S(n_v)$  away from the spin-pairing axis over all angles from 0 to  $\pi$  with respect to the spin-axis (determined by  $H_0$ , not shown) just as  $H^{ee}$  or  $H^{eh}$  can vary from 0 to  $\pi/2$ . Otherwise, the relative orientation of  $S(n_v)$  with respect to that of  $H^{ee}$  or  $H^{eh}$  is random<sup>48</sup> within the given hemisphere with oppositely polarized spin axes.



**Fig. 1.** Illustrating the possible orientations of the magnetic field,  $H^{ee}$  or  $H^{eh}$  due to an orbiting charge (indicated by long arrows) and the spin  $S(n_v)$  due to “extra-bonding” valence electrons (indicated by shorter or broader arrows) when the spin of the valence bonding electron is converted to charge at the instant of bond formation.

In the best spirit of phenomenology, we shall try to use all available geometrical hindsight to justify the empirical observation that  $C_\zeta \approx 0.2 \approx 2/\pi^2$  instead of, for example,  $C_\zeta \approx 0.2 \approx 2^{2/3}/2^3$ . In obtaining the value of  $C_\zeta$  we do not need to consider the magnitude of the spin  $S$  or that of the magnetic field due to the orbiting charge. One requires the probability,  $p(\text{orient})$ , that the magnetic moment,  $\mu(n_v)$ , due to the  $n_v$  “extra-bonding”

valence electrons is aligned antiparallel (just as the bonding valence electron) to  $H_0$  due to the orbiting charge (solenoid) as defined in Section III. 2.



**Fig. 2.** (a) Illustrating the definition of  $L$ , the component of the vector  $\mathbf{D}'$  that is parallel to  $\mathbf{D}$ ,  $\theta$  being the angle that  $\mathbf{D}'$  makes with  $\mathbf{D}$ . (b) Line defining the shaded area is the value of  $\sin\theta$  for various values of  $\theta$ . The area under the line gives  $\sin\theta$  when integrated between  $0$  and  $\pi$ .

We consider two unit vectors,  $\mathbf{D}$  and  $\mathbf{D}'$  in the diagram shown (Fig. 2a) as in the Buffon needle problem<sup>49</sup>. The component of  $\mathbf{D}'$  aligned parallel to  $\mathbf{D}$  is given by  $L = D' \sin\theta$ . The average value of  $L$ ,  $\langle L \rangle_{0,\pi}$ , for  $0 \leq \theta \leq \pi$ , obtained by integrating  $\sin\theta$  between  $0$  and  $\pi$ , is given by  $\langle L \rangle_{0,\pi} = 2$  (shaded area of Fig. 2b). As in the Buffon needle problem, the probability,  $p_{//}$ , that  $L$  is parallel to  $\mathbf{D}$  is then given by  $p_{//} = 2/\pi$ . From this reasoning, we may obtain from Fig. 1b, the probability,  $p(\text{orient})$ , that  $H_{\text{ext}}$  is parallel to  $S_M$  as  $p(\text{orient}) = (1/2)(p_{//})^2 = 2/\pi^2$ . We thus obtain  $C_\zeta = p(\text{orient}) = 2/\pi^2$ . The value of the interaction term,  $\zeta$ , due to the additional spin,  $S$ , of the “extra-bonding” valence electrons then satisfies the empirically observed relation<sup>41</sup>,

$$F_S = (1 + \zeta) = 1 + (2/\pi^2)\{S(S + 1)\}^{1/3} \quad (14)$$

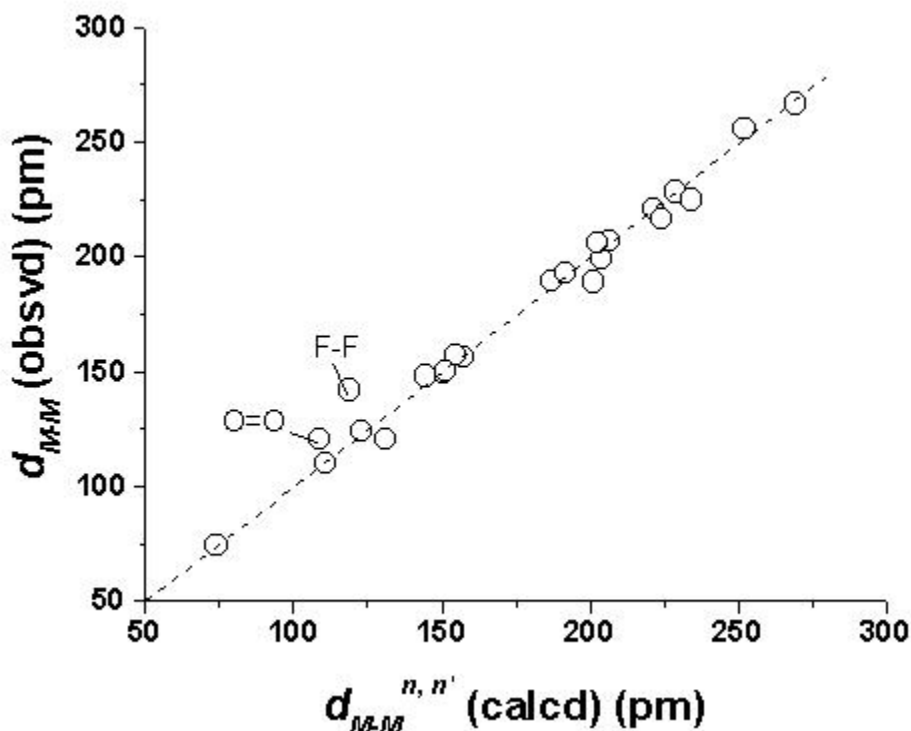
## IV. Some Consequences

**IV. 1. Bond Distances.** The role of  $F_S$  in the context of changes in interatomic distances with bond order has been discussed earlier<sup>9, 10</sup> using calculated Zunger-Cohen orbital radii values<sup>44</sup>,  $r_s$ , which are substantially larger than the empirical size,  $r_G$ , obtained later<sup>10</sup>, especially for the first main row elements such as C, N, O and F. For gas-phase  $MM'$  compounds<sup>50</sup> between atoms of insulating elements (at NTP), the M-M distance has been calculated (Table 1) using the relationship reported in Ref 10 and Ref 12 (where  $\epsilon_{\text{eff}} = 1.05$  in eqn 15) and written as

$$d_{M-M'} = \epsilon_{\text{eff}} \left[ \{2.13r_G(M) - 35.3\}/F_S(M) + \{2.37r_G(M') + 105.8\}/F_S(M') \right] \quad (15)$$

with  $r_G$  being taken from Ref 10. The plots of observed values of  $d_{M-M'}$  versus that calculated using eqn 15 and  $\epsilon_{\text{eff}} = 1.05$  is shown in Fig 3, for fitted  $n_v$  values as given in Table 1. These results are discussed in another communication. It is rather satisfying that the unexpected universal correlation between single-bond interatomic distance,  $d_{M-X}$ , and multiple bond distances,  $d_{M-X}(n_v) = d_{M-X}/F_S$  ( $F_S(M) = F_S(X)$  in eqn 3) may be so simply explained in terms of a universal “magnetic model of the Bohr atom”. The universality of

these relationship appears from the requirement of  $\mu = 0$  for the stationary state<sup>12</sup>. From the arguments in Sec III 3, the extent of changes in the “stick” and “ball” sizes is the same such that eqn 3 is justified. There is an universal change in bond distances of atoms as a function of the number,  $n_v$ , of “extra-bonding” valence electrons for a given bonding interaction (given values of  $C_M$ ,  $C_X$  and  $[D_M + D_X]$  in eqn 3).

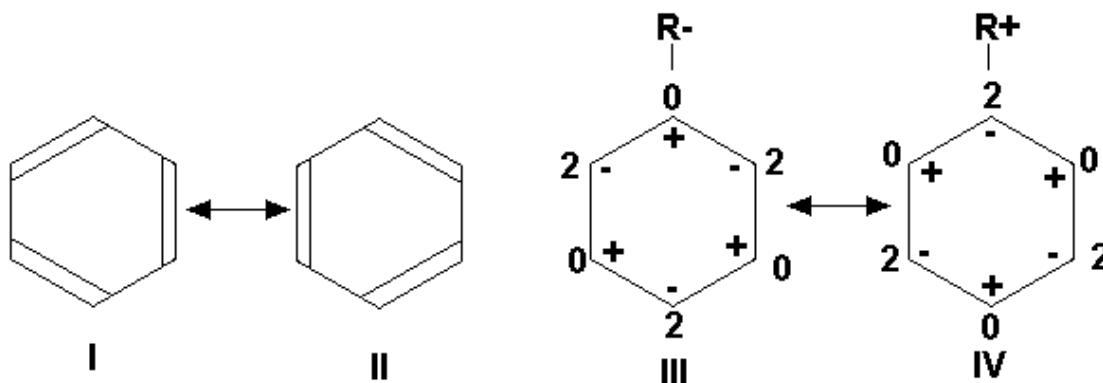


**Fig 3.** Plots of observed M-M' distance,  $d_{M-M'}$ (obsvd), in gas-phase MM' compounds (from Ref 50) *versus* calculated values of  $d_{M-M'}$ (calcd) using eqn 15, with  $\epsilon_{\text{eff}} = 1.05$  and  $n_v$  values of M and M' as given in Table 1. The values of  $r_G$  are taken from Ref 10.

We note that in agreement with established notions, the bond order in heavy elements does not exceed 2 in these cases. There are significant differences regarding the calculated F-F and O=O ( $n_v = 1$ ) distances using eqn 15 and the observed distances. This feature will be discussed later (Section IV 7). In our method, there could be further small changes in bond distances due to environment-dependent changes (not taken into account here) in  $\epsilon_{\text{eff}} (\geq 1)$  for given  $n_v$ . Instead of making correlations<sup>51</sup> between bond reactivity through bond distance and bond order, we may, for example, associate greater reactivity with larger values of  $\epsilon_{\text{eff}}$ . Unusual bond orders have been recently proposed<sup>52</sup> for S-S bonds ( $\sim 2.4$ ) and I-I bonds ( $\sim 1.3$ ) in  $S_2I_4(MF_6)_2$  (M = As, Sb) using Pauling bond order. We find that the “double bond” ( $n_v = 1$ ) character of the S-S bond and the “single-bond” character of the I-I bond is retained once changes in  $\epsilon_{\text{eff}}$  is taken into account. The so-called “triple-bond” Ga-Ga distance reported by Robinson’s group<sup>53</sup> would in our analysis correspond to  $d_{Ga-Ga} = 231.9^{11}_{1.067}$  (for  $r_G = 0.78$  a.u.) which indicates double-bond character at best using eqn 15. A recent study by Hardman *et al*<sup>54</sup> of the dimeric  $Na_2(\text{Ar}'GaGa\text{Ar}')$  (Ar' =  $C_6H_3-2,6-(\text{Dipp})_2$ , Dipp =  $C_6H_3-2,6-(i\text{-Pr})_2$ ) with a trans-bent CGaGaC core had Ga-Ga bond length was found to be 234.7 pm, which is consistent

with  $n_v=1$  and  $\epsilon_{\text{eff}} = 1.081$  (eqn 15). The Ga-Ga distance<sup>54</sup> in  $(\text{GaAr}')_2$  of 262.7 pm is consistent with single-bond distances ( $F_S = 1$ ) using eqn 15 and  $\epsilon_{\text{eff}} = 1.025$ .

**IV. 2. Fractional Bond Order.** Another important advantage in the present approach is that changes in bond length due to the presence of “extra-bonding” valence electron may be obtained using various values of  $n_v$  or  $F_S$  for the two atoms forming a given bond. The concept of “fractional bond order” may now be rationalized without requiring resonance structures. Examples of such fractional bond order due to different values of  $n_v$  are given in Table 1. Experimental validation of such conjectures is awaited. We note that there could be changes of  $n_v$  only by integral numbers so that changes in the bond distance,  $d_{MX}^{n,n'} \epsilon$ , (the superscripts  $n$  and  $n'$  are values of  $n_v$  on M and X, respectively, and the subscript,  $\epsilon$ , being the value of  $\epsilon_{\text{eff}}$ ) can only be due to changes in  $\epsilon_{\text{eff}}$  for given  $n$  and  $n'$ .



Of special interest are the changes in  $\pi$ -electron bond order<sup>3</sup>. We speculate on some aspects below. For example, the average value of  $n_v$  per carbon atom is unity in ethylene and benzene. The bond distance in ethylene is written as  $d_{C-C} = 133.9^{11}_{1.077}$ , while in benzene it is an average of “single” bond and “double” bond distances because of the involvement of resonance structures (I and II) which we write as  $d_{C-C} = 139.9^{<00,11>}_{1.032} \equiv (151.5^{00}_{1.032} + 128.4^{11}_{1.032})/2$ . We introduce an alternative way to describe the structure of benzene that involves dynamic fluctuations involving structure III and IV ( $\mathbf{R-} = \mathbf{R+} = \text{H}$ ) in which there are alternation of  $n_v = 2$  and  $n_v = 0$  between the six carbons atoms. In this case the C-C bond distance of benzene is described as  $d_{C-C} = 139.9^{<02,20>}_{1.06}$ . The lower value of  $\epsilon_{\text{eff}}$  calculated for these benzene structure is case as compared to ethylene indicates a lower reactivity of benzene. Among other possible virtues in this conjecture could be the following:

- i) the different reactivity of a simple double bond ( $n_v = 1$ ) and that in benzene ( $n_v = 2$  or 0) is indicated.
- ii) The ortho- and para- positions are distinguished from the meta positions in III-IV once a substitution (electron donating  $\mathbf{R-}$  (III) or electron withdrawing  $\mathbf{R+}$  (IV)) is made in the ring.
- iii) The structures III and IV have intra-site “spin-pairing” of the “extra-bonding” ( $n_v = 2$ ) electrons similar to lone-pair electrons which do not contribute to binding energies. The small contribution to binding energy by the three “double” bonds in benzene in the valence bond structures I and II as compared to cyclohexene has been attributed to a “resonance energy” that accounts for aromaticity.

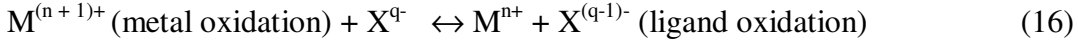
IV. 3. Changes in Electronegativity. Since the value of the core radius,  $r_{core}$ , changes inversely with  $n_v$  or  $F_S$  one would expect the electronegativity of an atom to increase with increasing  $F_S$ . This would account for the tendency of the electronegativity of transition metal elements in a series to show a maximum electronegativity in Pauling's scale<sup>55/37</sup> (after normalizing with respect to the core radius such as the orbital radius,  $r_s$ ) in the middle of the series. These elements are likely to have the maximum number of unpaired valence electrons. It is also to be noted that in the context of the Principle of Maximum Mechanical Hardness<sup>10</sup>, the element with the smaller value of the core atomic size is that associated with a negative charge as far as interatomic distances are concerned (more "spatially electronegative"). The relevant core radius determining the direction of polarity of a bond now is  $r_{core}/F_S$ . Transition metal elements of the same row are therefore expected to have the electronegativity enhanced by  $F_S$ . The enhancement with respect to that expected for a given size is expected to be a maximum for elements such as Mn, Tc, Re, which are expected to have nominally half-filled  $d$  levels.

IV. 3. Bond Energies. It is not expected that one would obtain changes in bond energies with  $n_v$  in as straightforward a manner in our as one thinks one obtains<sup>12</sup>, for example, the bond energy of the hydrogen molecule or the heat of formation of M-X bonds in simple binary compounds. One would expect that the changes in bond-energy due to changes in bond length would also scale as  $F_S$  or  $(1 + \zeta)$ . We have not found this to be true in most cases. Moreover, our model may not require it to be so. Our "size eigenvalue" approach gives the ground-state bond length and does not purport to give bond strengths in the conventional energy eigenvalue approaches (as yet). For example, we may obtain the Be-Be bond length ( $\sim 229$  pm in basal plane of hcp structure<sup>56</sup>) in Be in a straightforward manner ( $r_{core} = r_G = 0.59$  a.u.,  $d_{Be-Be} = 221$  pm from eqn 3,  $F_S = 1$ ) even if the energy eigenvalue of  $Be_2$  requires special quantum treatment<sup>57</sup>. In the case of carbon-carbon bonds, we find (empirically) that the bond energy scales roughly as  $F_S^4$ .

We draw attention to at least one theoretical calculation, which is consistent with the result that the energy should scale linearly as  $F_S$ . Gunnarsson and Jones<sup>58</sup> have estimated the change in the interelectronic exchange interaction,  $\Delta E_{x, int}(n)$ , when a  $3d$  electron interacts with a  $3d^n$  configuration. They find that for the spin-polarised  $3s\downarrow 3p\downarrow^3 3d\downarrow^n$  system ( $n < 5$ ) in which the  $s$  and  $p$  orbitals are half-filled,  $\Delta E_{x, int}(n)$  is given by  $\Delta E_{x, int}(n) = E_{x, int}(3s\downarrow 3p\downarrow^3 3d\downarrow^{n+1}) - E_{x, int}(3s\downarrow 3p\downarrow^3 3d\downarrow^n) - E_{x, int}(3d\downarrow)$ . The relative changes in  $\Delta E_{x, int}(n)$  for  $n = 1, 2, 3$  and  $4$  relative to that for  $n = 0$  is, respectively, 1.12, 1.23, 1.38 and 1.42 in the  $X_\alpha$  approximation, and 1.14, 1.17, 1.29 and 1.38, respectively, in the HF approximation. These values are close to the values of 1.18, 1.25, 1.31 and 1.37 calculated for  $F_S$  from Eqn. 14. These results do suggest that the changes incorporated in  $F_S$  takes into account the changes in exchange energies due to the interaction between the unpaired valence  $s$ -electron and the other unpaired electrons. On the other hand, the relative changes in the interaction energy,  $\Delta E_x^{ds} (= E_x(3d^n 4s) - E_x(3d^n) - E_x(4s))$  for  $n = 1, 2, 3, 4$  and  $5$  for the filled  $s$  and  $p$  shells, the changes<sup>40</sup> in  $\Delta E_x^{ds}$  as a function of the number of  $d$  electrons do not follow the changes in  $F_S$ .

IV. 4. Changes in Atomic Sizes with Valence State. The Shannon-Prewitt radii<sup>59</sup> of ionic sizes are complicated because of the coordination number dependence. There does not

exist a truly reliable size for high valence states since there could be complications due to the problem of ligand-oxidation vs metal-oxidation<sup>60</sup>



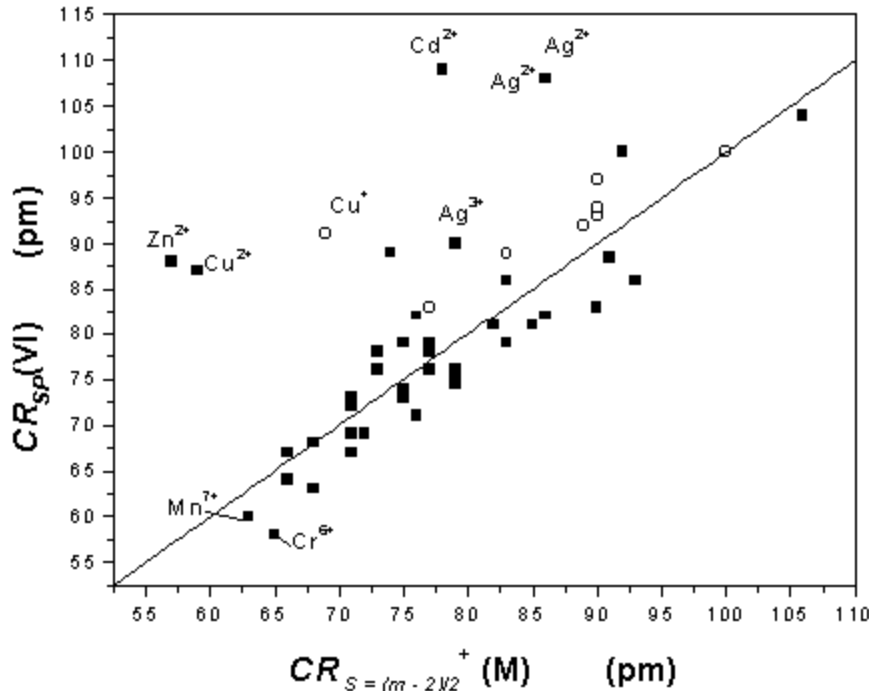
Some of these problems may be minimized in certain cases such as in Ti and V oxides in which the metal valence states are<sup>61</sup> well above the valence band. Finally, the assignments of the actual valence state for which  $n_v = 0$  (no “extra-bonding” electrons), is not always unambiguous. The conventional electronic configuration of these transition metal elements has the  $s^2$  configuration (except for Cu, Ag, Au; one may consider the  $s^1 d^{10}$  configuration for the  $S(n_v) = 0$  state for these atoms) for the outermost valence electrons. For the present purpose, we therefore consider the divalent state of the  $d$ -block elements to correspond to the  $n_v = 0$  state with a size  $CR_0^+$ .

Despite the above limitations, we find that  $F_S$  becomes important in describing sizes of transition metal elements for various valence states. First of all, we find that for the (high-spin) transition metal elements

$$CR_0^+ \approx CR_{SP(VI)_{\text{oct}}} \quad (17a)$$

where  $CR_{SP(VI)_{\text{oct}}}$  is the Shannon Prewitt Crystal Radius<sup>59</sup> for divalent transition metal atoms in six-fold coordination. When the valence state is increased to  $m (> 2)$ , the value of  $n_v = (m - 2)$  (or spin  $S = (m-2)/2$ ) which contributes additionally to bonding to be treated as spin-less “extra-bonding” valence electrons. Thus, for the  $M^{m+}$  state the relevant atomic size is given by

$$CR_{[S=(m-2)/2]}^+(M^{m+}) = CR_0^+(M)/F_{[S=(m-2)/2]} \quad (17b)$$



**Fig. 4.** Plot of the Shannon-Prewitt crystal radii (from Ref 59) in octahedral coordination,  $CR_{SP(VI)_{\text{oct}}}(M^{m+})$ , for various oxidation states,  $m^+$ , of transition metal atoms versus  $CR_{[S=(m-2)/2]}^+(M^{m+})$ , the atomic size calculated from eqn 1 ( $C^+ = 2.24$ ,  $n_v = m - 2$  and  $r_{\text{core}} = r_G$  of Ref 10) of the transition metal elements. The circles correspond to that observed for the divalent state. The straight line is given as a guide to the eye.

The Shannon-Prewitt size,  $CR_{SP(VI)_{oct}}(M^{m+})$ , of the  $d$ -block elements,  $M^{m+}$ , in octahedral coordination decreases with valence,  $m$ , as shown in Fig 3 (see also Table 2). It can be seen that the relationship,  $CR_{[S=(m-2)/2]}^+(M^{m+}) \approx CR_{SP(VI)_{oct}}(M^{m+})$ , holds fairly well in most cases those of Cu, Ag, Zn for which the  $S(n_v) = 0$  state is perhaps more difficult to define unambiguously. The trends in atomic sizes as a function of the oxidation state are satisfying given the empirical nature of the Shannon sizes and the consequent uncertainties. The other exceptions are the elements in high oxidation state such as  $Cr^{6+}$  and  $Mn^{7+}$ . For these high oxidation states there may be complications due to ligand oxidation as in eqn 15.

IV. 5. Spin-State Transitions. In the high-spin state the unpaired electrons may be treated as “core” electrons such as the  $f$  electrons and do not participate in bonding interactions and do not contribute to  $n_v$ . When  $n_v$  of these electrons are spin-paired into a low-spin state for the same valence state, we may treat them as “extra-bonding” electrons. This would be qualitatively consistent with stronger metal-ligand bonding. The high-spin to low-spin conversion would then lead to an increase in  $n_v$ . For example, in the conversion of high-spin  $Fe^{2+}(HS)$  with four unpaired  $d$  electrons to diamagnetic low-spin  $Fe^{II}(LS)$ , the spins of two electrons are effectively flipped. The value of  $n_v = 2$  in this case and  $S(n_v) = 1 = \Delta S/2$ , where  $\Delta S$  is the change in the value of the spin in the conversion high-spin states to low-spin states.

We have shown in Table 2 the calculated ratio,  $F_S(M)/F_S(M')$ , of the changes in atomic size on going from a high-spin state,  $M$ , to the corresponding low-spin state,  $M'$ , and have compared it with the ratio of the corresponding Shannon sizes. The ratio of the Shannon radii<sup>59</sup> (Table 1) of high-spin  $Fe^{2+}$  to low-spin  $Fe^{II}$  in six-fold coordination is 1.22 which is close to the value of  $F_S = 1.26$  for  $S = 1$  or  $n_v = 2$ . The trivalent state of Fe is expected to be an  $n_v = 1$  state ( $m = 3$  a  $S = 1/2$  state ( $n_v = 1$ )). The transition from high-spin  $Fe^{3+}$  to low-spin  $Fe^{III}$  is then expected to be a transition from a  $n_v = 1$  state to an  $n_v = 3$  state (two additional spins are flipped)  $S = 1/2$  state ( $F_{S=1/2} = 1.18$ ) to an  $S = 3/2$  state ( $F_{S=3/2} = 1.31$ ). The ratio of the Shannon sizes (Table 2) of high-spin  $Fe^{3+}$  ( $n_v = 1$ ,  $F_S = 1.18$ ) to that of low-spin  $Fe^{III}$  ( $n_v = 3$ ,  $F_S = 1.31$ ) in six-fold coordination is 1.14 as compared to the value of 1.11 expected from the ratio of the corresponding values of  $F_S$ . The ratio of Shannon size on going from high-spin  $Co^{3+}$  to low-spin  $Co^{III}$  is nearly 1.10 and is close to the expected value of 1.11. In the case of high-spin  $Mn^{2+}$  ( $n_v = 0$ ) to low-spin  $Mn^{2+}$  ( $n_v = 2$ ) (Table 2) one expects the high-spin/low-spin radius ratio to be 1.25 as compared to the tabulated Shannon-Prewitt value<sup>59</sup> of  $\sim 1.20$ . The high-spin/low-spin radius ratios are decreased considerably from the expected values for the late transition metal elements such as trivalent Ni. This is not necessarily a refutation of the model and may reflect changes in sizes of ligand due to ligand oxidation<sup>60</sup> (eqn 15).

#### IV. 6. Bond-Stretch Isomerism.

The above interpretation of multiple bond distances is useful in clarifying the extremely interesting concept<sup>14-16</sup> of bond-stretch isomerism which is in which molecules may differ only in the length of one or several bonds between identical atoms. Changes in bond-lengths due to changes in valence state (involving changes in  $F_S$ ) are not bond stretch

isomers. By the same argument, changes in bond distance due to changes in spin-state are not strictly bond stretch isomers—it loses the appealing “special intrigue” associated with the name of bond-stretch isomers<sup>15e/6c</sup>—even if it has been suggested that there can be no bond-stretch isomer without a spin-state isomer<sup>15b-15d</sup>. One requires demonstrating that there are changes in bond distance between two atoms without changes in spin-or valence-state or bond order. Such changes can be brought about solely by changes in  $C$  and  $D$  in eqn 1 or 3.

A case of “bond-stretch isomerism” could be found for the example of the extremely short bond in the isolated  $\text{Cr}_2$  dimer<sup>16</sup> as compared to that in the elemental metal. We find that the short bond-distance<sup>16, 62, 63</sup> of  $\sim 168$  pm in the  $\text{Cr}_2$  dimer and the longer Cr-Cr distance of  $\sim 250$  pm in the solid<sup>56</sup> could be attributed to changes in both  $C$  and  $D$  terms (eqn 1 or 3) for a fixed value of  $F_S$  ( $= 1.37$  for  $n_v = 4$  consistent with the position of Cr in the periodic table). The long Cr-Cr distance in crystals is consistent with  $F_S = 1.37$  ( $n_v = 4$ ),  $r_G(\text{Cr}) = 1.07$  a.u. and  $\epsilon_{\text{eff}} = 1.052$  in eqn 15 which is what is normally expected. The short Cr-Cr distance in the dimer cannot be obtained from eqn 15 unless changes in  $C$  and  $D$  are made. This satisfies, in our opinion, the criterion for “bond-stretch isomerism”.

The size of the “stick” has been taken as the “ordinary” bond length of hydrogen molecule in the “charge transfer” expression for interatomic distances (eqn 15). The hydrogen-hydrogen distances in dihydrogen complexes have an “elongated” hydrogen-hydrogen bond distance<sup>64</sup>. Some of these have distances of  $\sim 105$  pm which is close to  $2a_H$ , the sum of the Bohr size of the hydrogen atom. The “ordinary” and “elongated” hydrogen-hydrogen distances may be taken as a fundamental example of “bond-stretch isomerism” even if they have not been mentioned as such in the literature. In the context of the “ball-and-stick” model of eqn 2 we find that we may write Cr-Cr distance of  $\sim 168$  pm in the  $\text{Cr}_2$  dimer with  $C(\text{M}) = C(\text{M}') = 1$  and the “stick” dimension as  $2a_H$  such that

$$d_{\text{Cr-Cr}}(\text{dimer}) = \epsilon_{\text{eff}}(2r_G(\text{Cr}) + 2a_H)/F_S(\text{Cr}) \quad (18)$$

$$= 168 \text{ pm } (r_G(\text{Cr}) = 1.07 \text{ a.u.}, n_v = 4 \text{ and } \epsilon_{\text{eff}} = 1.08)$$

Using a modified general valence bond method, which corrects one-center self Coulomb integrals to match experimental quantities, Goodgame and Goddard<sup>65</sup> have found a double well for the potential energy curve of the ground state of the diatomic dimer of chromium,  $\text{Cr}_2$ . There is a shallow outer minimum around 306 pm and a sharp inner minimum around around 160 pm. The longer bond is a single bond (in our methodology the single bond Cr-Cr distance would be  $\sim 340$  pm when  $F_S = 1$  in eqn 15) involving 4s electrons with the electrons of the  $d$  shell being coupled antiferromagnetically. In the shorter bond the  $d$  electrons are involved in covalent bonding. The mechanism proposed by Goodgame and Goddard<sup>65</sup> for changes in Cr-Cr distance<sup>62, 63</sup> in  $\text{Cr}_2$  dimer would translate to changes in  $F_S$  in our model.

It is extremely satisfying that a non-trivial problem of the bond length contraction in  $\text{Cr}_2$  dimer as compared to that in the crystal is obtained in such a facile and self-consistent manner without recourse to lengthy calculations<sup>65, 66</sup> and despite considerable skepticism regarding the concept. Changes in bond distances due to changes in  $C$  and  $D$  seems to be quite readily account for many unusual bond distances. The Mo-Mo distance of 193 pm

(see Ref 65) in the Mo<sub>2</sub> dimer may be obtained using the “ordinary” H-H bond distance with

$$d_{Mo-Mo}(\text{dimer}) = \epsilon_{\text{eff}}(2r_G(\text{Mo}) + 4a_H/3)/F_S(\text{Cr}) \quad (19)$$

$$= 168 \text{ pm } (r_G(\text{Mo}) = 1.19 \text{ a.u.}, n_v = 0 \text{ and } \epsilon_{\text{eff}} = 1.014)$$

A very short Fe-Ga distance of 222.5 pm reported by Robinson’s group<sup>67/70</sup> is also quite extraordinary. From eqn 15 the Fe-Ga single bond distance is expected to be 303.5 pm (for  $\epsilon_{\text{eff}} = 1.05$ ). The observed shortening of the Fe-Ga distance would require, for example,  $F_S(\text{Fe}) = F_S(\text{Ga}) \sim 1.37$  which means that  $n_v$  is close to three or four which is unlikely<sup>68</sup>. In the spirit of “bond stretch isomerism”<sup>14-16</sup> we write

$$d_{Fe-Ga} = \epsilon_{\text{eff}}[\{r_G(\text{Fe})/F_S(\text{Fe}) + 2.37r_G(\text{Ga})/F_S(\text{Ga})\}^{\text{“ball”}} + \{2a_H/(F_S(\text{Fe}) + F_S(\text{Ga}))\}^{\text{“stick”}}] \quad (20)$$

The Fe-Ga bond length is given by  $F_S(\text{Fe}) = F_S(\text{Ga}) = 1.18$  ( $n_v = 1$ ) for  $r_G(\text{Fe}) = 1.07$  a.u. and  $r_G(\text{Ga}) = 0.78$  a.u. and  $\epsilon_{\text{eff}} = 1.01$ . Hardman *et al*<sup>54</sup> had shown that certain 1,2-diiodo-1,2-diaryldigallane compounds had planar ICGaGaCI core arrays with Ga-Ga distances of  $\sim 249$  pm. This distance is too short for single bonds using eqn 15 ( $d_{Ga-Ga} \approx 256$  pm for  $\epsilon_{\text{eff}} = 1$  and  $n_v = 0$  or  $F_S = 1$ ). On the other hand a Ga-Ga distance of 249 pm is consistent with eqn 20 with  $F_S(\text{Fe}) = F_S(\text{Ga}) = 1$  and  $\epsilon_{\text{eff}} = 1.021$  which is another kind of “single bond”. It is seen from the extensive experimental work of Power’s group that the Ga-Ga bond distance shows Ga-Ga distances of  $2.63 \pm 0.03$  pm (“single bond” eqn 15),  $2.52 \pm 0.04$  pm (“single bond, eqn 20) and  $2.35 \pm 0.01$  pm (“double bond” eqn 15) which shows an environment-independence of the bond length for the given bonding descriptions. A correlation between bond types and reactivity can now be made with more confidence.

**IV. 7. The Paramagnetism of Oxygen.** As seen from Table 1, the fitting of the O-O distance in oxygen molecule to a double bond using eqn 15 ( $F_S = 1.18$ ,  $n_v = 1$ ) requires too high a value of  $\epsilon_{\text{eff}}$ , which is inconsistent with the low reactivity of triplet oxygen. The question occurs whether we require a “double” bond character at all. For example, the O-O distance may be fitted quite close to a single bond distance with  $\epsilon_{\text{eff}}$  being close to 1.00. This “single bond” description has an advantage in describing the paramagnetic properties of oxygen, self consistently within our model. We have described in Sections IV 4 and IV 5, the “extrabonding” electrons as contributing to chemical bonding and thereby requiring to be distinguished from “core” unpaired or paramagnetic electrons that do not contribute to bonding. In this case, the paramagnetism of oxygen would be inconsistent with the expected value  $n_v = 1$ . Instead we may consider the  $n_v = 1$  description to be valid for singlet oxygen.

## V. Conclusions

The application of the Bohr model to chemical bonding is routinely viewed with considerable suspicion (perhaps justifiably in the way it has been applied so far). We have stressed that we use the Bohr model as a simple approximation to obtain useful insights. It is especially useful when we apply the model to hydrogen or pseudohydrogen atoms using bonding spinless quasiparticles, ( $e^{\circ}e^{-}$ ) and ( $e^{\circ}h^{+}$ ). These particles have been examined<sup>12</sup> earlier in terms of the electrostatic Bohr model to obtain the interatomic distance of the hydrogen molecule in a simple manner. We emphasize the consequences

of a two-dimensional Bohr orbit in Section II especially in the way magnetic fields influence Bohr orbits, and the magnitude of the spin-orbit interaction in 2D orbit. Since the composite particles are spinless, the Bohr orbits of these composite particles are not fixed to a spin axis.

We next analyze (Section III) the influence of the number  $n_v$  of “extra-bonding” valence electrons, which do not participate in the spin-charge inter-conversion (eqn 5) at the instant of bond formation. We analyze the spin orbit interaction in the composite particles due to the orbital magnetic field,  $H_0^-$  and  $H_0^+$  ( $n_v = 0$ ), of the charges  $e^-$  and  $h^+$  acting on the spin of the electron  $e^o$ . The interaction of the spin,  $S(n_v)$ , of these extra-bonding electrons with the orbital magnetic field generates an internal magnetic field  $H_{\text{int}}$ . We argue that  $H_{\text{int}} \propto n_v^{2/3} \propto (S(S+1))^{1/3}$  when we consider the density of the  $n_v$  “extrabonding valence electrons in a 2D orbit. The contribution of these internal field leads to an increased interaction energy and a reduction in the Bohr size by a term  $F_S \approx [1 + 0.2(S(S + 1))^{1/3}]$ . The value of  $F_S$  obtained in this model fits well with that obtained earlier empirically<sup>17</sup>. This interpretation is based on a simple two-dimensional Bohr-like model, accurate, transparent, portable and internally consistent. This should overcome its major drawback, which is that it does not require the complicated mathematics of wave-function-based approaches.

In the last section (Section IV) we show how these values of  $F_S$  may be used to interpret changes in atomic sizes with changes in valence- or spin-state of transition metals as well as their electronegativities. They also account for changes in bond distance with bond order including “fractional bond order”. The role of  $F_S$  in systems exhibiting bond-stretch isomerism has been discussed and it is suggested that the pristine example of this phenomenon should not involve change in interatomic distances due to  $F_S$ . Our analysis throw insights into recent debates on bond order and bond distances<sup>52, 53, 67, 68</sup>, bond-stretch isomerism including the very short bond distance in the  $\text{Cr}_2$  dimer<sup>16</sup>, changes of atomic size with valence state or spin-state of transition metal atoms, and finds a new explanation to account for the bond length and paramagnetism of oxygen molecule.

Our description of bond-distance changes due to the influence of  $n_v$  “extrabonding” electrons per atom is different from the definition which states<sup>69, 70</sup>, for example, that “... a co-valent bond consists of an electron pair which is localized on only two atoms, and a triple bond is defined by three covalent bonds connecting two atoms. ...”. Our approach does not require the “extra-bonding” valence electron to contribute to bonding in the above sense. The impact of “extra-bonding” electrons—as quantified by  $F_S$ —is derived from an individual atom rather than a bonding pair of electrons. It is more in the spirit of the atom-in-molecule approach<sup>70</sup>, which uses atoms as proper open systems with transferable properties.

## Acknowledgment

The author thanks the authorities of the CSIR for very generously providing an Emeritus Grant for sustenance and the authorities of the National Chemical Laboratory, Pune for desk space and restricted Library facilities. He would also like to thank Dr. Carlo Taliani

of ISMN, Bologna, for valuable encouragement and facilities Professor Peter Nozar of ISMN, Bologna, for some early discussions.

## Appendix

### A.1. Magnetic Bohr Model.

We consider a flat Bohr orbit containing one flux quantum and one electron. For a magnetic field,  $B$ , and a circular coil area,  $A$ , the total magnetic flux,  $\Phi = BA$ . If the radius of the coil is  $\ell$  so that  $A = \pi\ell^2$ , and  $\Phi = S\phi_o$  for a total number,  $n_\Phi = S$ , of flux quantum,  $\phi_o = h/e$ , we obtain<sup>71</sup>

$$B = n_\Phi h/e\pi\ell^2 = 2 n_\Phi (\hbar/e\ell^2) \quad (\text{A1})$$

We identify the magnetic length<sup>72</sup>,  $\ell$ , with the first Bohr radius,  $a_H$ , such that  $A = \pi a_H^2$ , and the magnetic field corresponding to the first Bohr orbit,  $B^1_{Bohr} = hS/e\pi a_H^2$ . The interaction energy<sup>72</sup>,  $\epsilon_o = B^1_{Bohr}\mu_B$ , of the magnetic field  $B^1_{Bohr}$ , aligned antiparallel with the magnetic moment of the electron of one Bohr magneton,  $\mu_B$ , is given by

$$\epsilon_o = B^1_{Bohr}\mu_B = -\hbar^2 S/m a_H^2 = -me^4 S/\hbar^2 = E_H \quad (\text{A2})$$

when  $S = 1/2$  and  $E_H$  is the total energy (potential + kinetic) of the hydrogen atom in the Bohr model. The energy  $\hbar^2/2m_o a_H^2$  is the kinetic energy ( $= \epsilon_T$ ) of the electron so that the potential energy ( $= \epsilon_V$ ) may be equated to an energy  $-\hbar^2/m_o a_H^2$  such that the energy  $B^1_{Bohr}\mu_B = -\hbar^2/2m_o a_H^2$  ( $= \epsilon_T + \epsilon_V$ ) satisfies the virial theorem. The value of the Bohr radius,  $a_H$ , used in Eqn. (A2) is obtained a priori from the Bohr model using an electrostatic Coulomb interaction potential energy term. *The consequence of the above seems to be that the Bohr size,  $a_H$ , is a fundamental magnetic length that can be associated with an electron orbit containing one flux quantum per unit area..*

The solution of the Schrödinger equation for a 2D gas of electrons in a strong perpendicular magnetic field,  $B$ , gives eigenvalues of an harmonic oscillator

$$\epsilon_i = (n + 1/2) \eta \omega \quad (\text{A3})$$

where  $n = 0, 1, 2, 3, \dots$  correspond to the different Landau levels.  $\omega_c$  ( $= eB/m$ ,  $e$  being the charge of an electron) is the cyclotron frequency which has no dependence on the size of the Landau levels. The energy  $\epsilon_o = B^1_{Bohr}\mu_B = \hbar e B^1_{Bohr}/2m_e$  is the energy for the  $n = 0$  level in eqn A3 and in this sense the Bohr energy,  $E_H$ , for the hydrogen atom may be taken as a zero point energy.

## REFERENCES AND FOOTNOTES

1. Kossel, W., *Ann. Phys.*, **1916**, 49, 229
2. Lewis, G N., *Chem. Rev.* **1924**, 1, 231. "...every electron in a molecule ... in orbital motion ... must be regarded as a small magnet. ... the basic fact of chemistry is ... that two isolated electronic orbits or magnets tend to couple with one another so as to eliminate their magnetic moments. ... the pair which is formed is the joint property of two atoms and is known as the chemical bond".
3. Coulson, C. A., *Chem. Soc., Spec. Publ.*, **1958**, 85; see, for example, Murrell, J. N., Kettle, S. F. A., Tedder, J. M., *The Chemical Bond*, John Wiley and Sons, New York, 1978

4. Grunenberg, J., Goldberg, N., *J. Am. Chem. Soc.* **2000**, *122*, 6045-6047; ... *higher the quality of the molecular orbital wave function, the less their clarity.* ...
5. D.G. Pettifor, *Phys. Rev. Lett.*, **1989**, *63*, 2480; Pettifor, D. G., Finnis, M.W., Nguyen-Manha, D., Murdick, D.A., Zhou, X.W., Wadley, H.N.G., *Materials Science and Engineering*, **2004**, *A365*, 2–13
6. O'Keeffe, M.; Brese, N.E.J. *Am. Chem. Soc.* 1991, **113**, 3226-9
7. Brown, I. D. *Acta Crystallogr.* **1992**, *B48*, 553
8. Burdett, J. K., Hawthorne, F. C., *American Mineralogist*, **1993**, *78*, 884-892
9. Ganguly, P., *J. Am. Chem. Soc.*, **1995**, *117*, 2656
10. Ganguly, P., *J. Am. Chem. Soc.*, **1995**, *117*, 1776
11. Ganguly, P. *J. Am. Chem. Soc.*, **1993**, *115*, 9287
12. Ganguly, P., *J. Phys. Chem.*, **2000**, *104*, 8432
13. see Politzer, P. Jin, P. and Murray, J. S., *J. Chem. Phys.*, **2002**, *117*, 8197 for a recent discussion and earlier works
14. Stohrer, W.-D. and Hoffmann, R., *J. Am. Chem. Soc.*, **1972**, *94*, 779, 1661
15. (a) Jean, Y., Lledos, A., Burdett, J. K., Hoffmann, R., *J. Am. Chem. Soc.*, **1988**, *110*, 4506; (b) Kölle, U., Kossakowski, J., Klaff, N., Wesemann, L., Englert, U., Heberich, G. E., *Angew. Chem. Intl. Edn.*, **1991**, *30*, 690; (c) Parkin, G., *Chem. Rev.*, **1993**, *93*, 887; (d) Gütllich, P., Goodwin, H. A., Hendrickson, D. N., *Angew. Chem. Intl. Edn.* **1994**, *33*, 425; (e) Parkin, G., Hoffmann, R., *Angew. Chem. Intl. Edn.* **1994**, *33*, 1462
16. Rohmer, M.-M., and Bénard, M., *Chem. Soc. Rev.*, **2001**, *30*, 340
17. The interpretation of chemical reactivity based on molecular structure will depend on the understanding/interpretation of  $F_S$ . In the first empirical fit (see Ref 9/17) of  $F_S$  to the number,  $n_v$ , or spin,  $S$  ( $= n_v/2$ ), of “extra-bonding” valence electrons, it was thought that since  $F_S = 1.19[S(S+1)^{0.08}]$  ( $\approx (2\ln 2)^{1/2}[S(S+1)]^{1/4\pi}$ ) gives  $F_S > 1$  when  $S \neq 0$ . Because of this, it was thought (see Ref. 10/3) that the mechanisms of interactions which define the orbital radius is different for the  $S = 0$  and  $S > 0$  situations. An interpretation of  $F_S$  based on this rationale has not been successful
18. See Feynman, R. P. *The Feynman Lectures on Physics*, Vol. III, Quantum Mechanics; Addison-Wesley Publishing Co.: Reading, MA, 1965, pp 2: 5, (Indian Edition).
19. see López-Castillo, A., *Phys. Rev. Letts.*, **1996**, *77*, 4516 and references therein
20. Tanner, G., Richter, K. and Rost, J-M., *Rev. Modern Phys.*, **2000**, *72*, 497; the failure of the Bohr model and the way the Schrodinger methodology may be made to work for two-electron atom is discussed in this article
21. In isotropic 2D space the locus of the solutions of the energy minimized state would trace a circular (Bohr) orbit that satisfies eqn 2 with  $(\hbar/r)$  defining an angular momentum that is applicable to a Bohr-like model
22. see L. Spruch, *Revs. Mod. Phys.* **63**, 153 (1991) and references therein.
23. see Ganguly, P., *Proc. Indian Acad. Sci. (Chem. Sci.)*, **2001**, *113*, 415
24. Throughout this paper we will be referring to Bohr radii as solutions of eqn 3 which minimizes the energy. Eqn 3 may be viewed as a one-dimensional equation as far as obtaining a Bohr size,  $a_H$ , is concerned. A Bohr orbit of area given by  $\pi a_H^2$  is necessary to define a magnetic field due to a quantum of flux being trapped in this area.
25. Although the Bohr model is considered primitive when applied to chemistry, its main conclusions remains valid in several areas of modern physics, the most persistent area

being perhaps the area of Rydberg atoms (see Gallagher T F *Rydberg atoms* (Cambridge: University Press. **1994**) chap. I and II).

26. “A sort of principle of least effort, or Occams’ maxim, which is usually followed in quantum mechanics (as in most other things), may be stated as *we only work hard enough to bring about the desired result and no harder*. Thus we usually carry a quantum-mechanical calculation only to the level of sophistication necessary to answer the question at hand and no further.” From Royer, D. J., *Bonding Theory*, McGraw Hill, p 149

27. Hoffmann, R., *J. Mol. Struct. (THEOCHEM)* **1998**, 424, 1).

28. see Rau, A. R. P., Mueller, R. O., Spruch, L., *Phys. Rev. A*, **1975**, 11, 1865 and references therein

29. see Lai, D., *Revs. Mod. Phys.*, **2001**, 73, 630

30. It is quite likely that such considerations have been made in the primordial soup that gave birth to the foundations of quantum mechanics. The author has not been able to cite/find a source for the above.

31. Dirac, P. A. M., *Proc. Roy. Soc.*, (London), 714. *The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.*

32. Wilczek, F., *Phys. Rev. Lett.*, **1982**, 48, 1144; *Phys. Rev. Lett.*, **1982**, 48, 1146;

Wilczek, F.; Zee, A., *Phys. Rev. Lett.*, **1983**, 51, 2250

33. Prange, R. E. and Girvin, S. M. (eds) 1987 *The quantum Hall effect* (New York, Berlin, Heidelberg: Springer-Verlag); Chakraborty, T. and Pietiläinen, P., 1995 *The quantum Halleffects: Fractional and integral* (Berlin, Heidelberg: Springer-Verlag); Tsui, D. C., Störmer, H. L. and Gossard, A. C., *Phys. Rev. Lett.* **1982**, 48, 1559

34. (a) Laughlin, R. B., *Phys. Rev.* **1983**, B27, 3383; (b) Laughlin, R. B., *Phys. Rev. Lett.* **1983**, 50, 1395; (c) Laughlin, R. B. *Revs. Modern Phys.*, **1999**, 71, 863 and references therein

35. The effect of anisotropy and magnetic fields on the reactivity of high Rydberg states is an emerging area (see for example, Clark, W. and Greene, C. H., *Rev. Modern Phys.* **1999**, 71, 821; Bartsch, T., Schippers, T., Müller, A., Brandau, C., Gwinner, G., Saghiri, A. A., Beitelspacher, M., Greiser, M., Schwalm, D., Wolf, A., Danared, H. and Dunn, G. H., *Phys. Rev. Lett.*, **1999**, 82, 3779)

36. Turro, N. J., Buchachenko, A. L., and Tarasov, V. F., *Acc. Chem. Res.*, **1995**, 28, 69

37. This *instant* of spin-pairing characterizes the instant of a quantum phase transition as an unpredictable emergent phenomenon (see Ref 34c). To quote T. S. Eliot, “*What will the spider do/ Suspend its operations, will the weevil Delay?/ De Bailhache, Fresca, Mrs. Cammel, whirled/ Beyond the circuit of the shuddering Bear/ In fractured atoms.*”

38. Lampert, M. A., *Phys. Rev. Lett.* **1958**, 1, 450

39. Kheng, K., Cox, R. T., d’Aubigne, Y. M., Bassani, F., Saminadayar, K. and Tatarenko, S., *Phys. Rev. Lett.* **1993**, 71,1752

40. It is not customary to consider metallization of a few particles. However, as discussed in Ref. 12, the constraints on metallization involve local atomic parameters without

requiring directly the many-body interactions. This is true for Mott's model for Thomas Fermi screening, or the Mott-Hubbard criterion for the on-site correlation. The well-established description of metallic electrons in a magnetic field also does not require directly a many-electron character.

41. The magnetic moment  $\mu^+$  of the  $e^o$  particle is  $e\hbar/2(3m_o) \equiv (e/3) \hbar/2m_o$  is identical to the magnetic moment of a particle carrying a fractional charge  $e/3$ . This fracturing of charge due to electron-electron interaction in a chemical bond has been discussed elsewhere. (see Ref 15)

42. It seems to us that this is an un-treaded area as far as conservation of total angular momentum is concerned. Some of the restrictions could be lifted if, as in an adiabatic approximation, the spin angular momentum of the "extra-bonding" electrons is not defined within the time-scale of the interactions.

43. We have not yet found occasion to consider  $\zeta < 0$ .

44. see A. Zunger, A. , *Phys. Rev. B*, **1980**, 22, 5839 and references therein

45. See Zhang, S. B., Cohen, M. L., Phillips, J. C., *Phys. Rev. B*, **1987**, 36, 5861 and references therein

46. An objection to such dimensionality arguments is that the bond-dissociation energy has contributions from the nuclear as well as the electronic part when using the Schrödinger wave function approach. Because of this the actual electronic contribution is required to be nearly 4.75 eV, which is much larger (by  $\sim$  than  $2E_{exc}^{max}/3$ . We do not take this objection with much alarm as we contend that our model is characterized by a free-atom-like stationary state condition,  $\mu = 0$ , for the chemical potential. A two-dimensional Bohr orbit cannot account for this increase. The nuclear contribution comes from the zero-point energy arising from the constraints due to the uncertainty principle. The Bohr-model approximation of Ganguly employs hydrogen-atom-like quasi-particles. The reduced masses of the quasi-particles in a center-of-mass approximation are used and the effect of nuclear mass is neglected. In such an approximation, it does not seem necessary to include the zero-point energy due to nuclear motion.

47. One expects  $H^{ee} = (m_{H}^{ee})^2 e^3/\hbar^3$  and  $H^{eh} = (m_{H}^{eh})^2 e^3/\hbar^3$ . Since  $m_{H}^{ee}/m^- = m_{H}^{eh}/m^+ = 1/2$ , the ratios  $H^{ee}/H_0^{e^-} = H^{eh}/H_0^{h^+} = 1/4$ .

48. The magnitude of the magnetic field due to a magnetic flux in a Bohr radius is extremely large ( $\sim 10^{10}$  T). The random orientations of the spin of the "extra-bonding" valence electron are therefore not likely to be due to a thermal effect. There needs to exist a more fundamental atomic microscopic reason that could be related to several other factors such as spin-charge decoupling; randomization due to 2D Bohr orbits in 3D space and so on that we have discussed in section III. 2.

49. see [web sites www.riskglossary.com/articles/monte\\_carlo\\_method.htm](http://www.riskglossary.com/articles/monte_carlo_method.htm),

<http://www.mste.uiuc.edu/reese/buffon/buffon.html> and

<http://www.angelfire.com/wa/hurben/buff.html>, for example.

50. Interatomic distances are obtained from *CRC Handbook of Chemistry and Physics*, 61st ed., Weast, R. C., Ed.; CRC Press: Boca Raton, 1980; F-221

51. see, for example, Scott, L. T., *Pure & Appl. Chem.*, **1996**, 68, 291-300, L. T. Scott, L. T., Roelofs, N. H., Tsang, T. H., *J. Am. Chem. Soc.*, **1987**, 109, 5456-61

52. Brownridge, S., Cameron, T. S., Du, H., Knapp, C., Köppe, R., Passmore, J., Rautiainen, J. M. and Schnöckelgave, H., *Inorg. Chem.*, **2005**, 44, 1660 -1671

53. Su, J.-R., Li, X.-W., Crittendon, C., Robinson, G. H., *J. Am. Chem. Soc.*, **1997**, *119*, 5471–5472
54. Hardman, N. J, Wright, R. J., Phillips, A. D., Power, P. P., *J. Am. Chem. Soc.*, **2003**, *125*, 2667-79
55. Pauling, L., *The Nature of the Chemical Bond*, Oxford & IBH Publishing Co., Calcutta, 1969, Chapter III, Table 3.8
56. Wyckoff, R. W. G., “Crystal Structure”, 2<sup>nd</sup> Edition, Vol 1., Chapter II and III, Interscience Publishers, 1963
57. See, for example, Kutzler, F. W., and Painter, G. S., *Phys. Rev. B*, **1992**, *45*, 3236
58. Gunnarsson, O.; Jones, R.O., *Phys. Rev. B*, **1985**, *31*, 7588
59. Shannon, R. D., Prewitt, C. T., *Acta Cryst.*, **1969**, *B25*, 925; Shannon, R. D., *Acta Cryst.*, **1976**, *A32*, 751
60. See Ganguly, P., and Hegde, M. S. *Phys. Rev. B: Condens. Matter*, **1988**, *37*, 5107 and references therein; Hegde, M. S.; Ganguly, P. *Phys. Rev. B: Condens. Matter*, **1988**, *38*, 4557
61. Mizushima, M., Tanaka, M., Asai, A., Iida, S., Goodenough, J. B., *J. Phys. Chem. Solids*, **1979**, *40*, 1129
62. Michalopoulos, D. L.; Geusic, M. E.; Hansen, S. G.; Powers, D. E.; Smalley, R. E. *J. Phys. Chem.* **1982**, *86*, 3914
63. Riley, S. J.; Parks, E. K.; Pobo, L. G.; Wexler, S. *J. Chem. Phys.* **1983**, *79*, 2577
64. (a) Heinekey, D. M. and Oldham, Jr, W. J., *Chem. Rev.*, **1993**, *93*, 913-928); (b) Kubas, G. J., Ryan, R. R., Swanson, B. I., Vergamini, P. J., Wasserman, H. J., *J. Am. Chem. Soc.* **1984**, *106*, 451; (c). Heinekey, D. M. and Oldham, Jr., W. J., *Chem. Rev.* **1993**, *93*, 913; (d) Sabo-Etienne, B. and Chaudret, B., *Chem. Rev.*, **1998**, *98*, 2077 ; (e) Esteruelas, M. A. and Oro, L. A., *Chem. Rev.* **1998**, *98*, 577
65. Goodgame, M. M., Goddard, W. A., *Phys. Rev. Lett.*, **1985**, *54*, 661
66. Dachsels, H., Harrison, R. J. and Dixon, D. A., *J. Phys. Chem. A* **1999**, *103*, 152; this paper emphasized the record-breaking length of the required CI calculation with the title being “Multireference Configuration Interaction Calculations on Cr<sub>2</sub>: Passing the One Billion Limit in MRCI/MRACPF Calculations”.
67. J. Su, J., Li, X.-W., Crittendon, R. C., Campana, C. F., Robinson, G. H., *Organometallics*, **1997**, *16* , 4511–4513
68. Cotton, F. A., Cowley, A. H., Feng, X., *J. Am. Chem. Soc.*, **1998**, *120*, 1795
69. Klinkhammer, K. W., *Angew. Chem. Int. Engl.*, **1997**, *36*, 2320
70. See Molina, J., Dobado, J.A., Heard, G. L., Bader, R.F. W., Sundberg, M. R., *Theor. Chem. Acc.*, **2001**, *105*, 365-373 and references therein
71. Usually the magnetic length,  $\ell$ , is given as the cyclotron radius with  $\ell = |h/2\pi eB|^{1/2}$ . When one quantum of magnetic flux is present in the first Bohr orbit,  $B_{Bohr}^1$ , the magnetic field is  $m_e^2 e^3 (h/2\pi)^{-3} \approx 2.4 \times 10^5$  T. (see Lieb, E. H., Solovej, J. P., Yngvason, J., *Phys. Rev. Lett.*, **1992**, *69*, 749). For a magnetic field  $\approx (137 \times B_{Bohr}^1)^2 \approx 5 \times 10^9$  T one would expect the magnetic length,  $\lambda_{137} = a_H/137$ , where the fine structure constant,  $\alpha = e^2/\hbar \approx 1/137$ .
72. Since the magnetic force is always perpendicular to the velocity,  $v$ , the centripetal force acting on a charge,  $e$ , due to the magnetic field,  $B$ , will result in a circular path with velocity perpendicular to it. The classical expression for the radius of this circle is given

by  $r = mv/eB$ . For a Bohr orbit the momentum from the uncertainty principle is  $\hbar/r$  from which we obtain the magnetic length  $r = (\hbar/eB)^{1/2}$ .

**Table 1.** Observed and Calculated<sup>#,\*</sup> M-M bond distances between atoms of insulating elements in gas-phase MM' compounds.

M-M'	$d_{MM'}^{nn'}_{\epsilon}^{\#}$ (pm)	$r_G(M)$ (a.u.)	$r_G(M')$ (a.u.)	M-M'	$d_{MM'}^{nn'}_{\epsilon}^{\#}$ (pm)	$r_G(M)$ (a.u.)	$r_G(M')$ (a.u.)
BrBr	228.1 <sup>00</sup> <sub>1.05</sub>	0.62	0.62	PP	189.3 <sup>11</sup> <sub>1.06</sub>	0.59	0.59
C-C	124.2 <sup>22</sup> <sub>1.06</sub>	0.32	0.32	P <sub>4</sub>	221.1 <sup>00</sup> <sub>1.05</sub>	0.59	0.59
C-P	156.2 <sup>11</sup> <sub>1.04</sub>	0.59	0.32	SO	148.1 <sup>11</sup> <sub>1.08</sub>	0.53	0.26
Cl-Cl	198.8 <sup>00</sup> <sub>1.02</sub>	0.52	0.52	SS	188.9 <sup>20</sup> <sub>0.98</sub>	0.53	0.53
F-F	141.9 <sup>00</sup> <sub>1.25</sub>	0.18	0.18	S <sub>6</sub>	207.0 <sup>00</sup> <sub>1.05</sub>	0.53	0.53
F-F*	141.9 <sup>00</sup> <sub>1.03</sub>	0.18	0.18	SeSe	216.6 <sup>20</sup> <sub>1.02</sub>	0.63	0.63
H-H	74.1 <sup>00</sup> <sub>1.05</sub>	0.00	0.00	SiN	157.2 <sup>02</sup> <sub>1.07</sub>	0.64	0.26
I-I	266.6 <sup>00</sup> <sub>1.04</sub>	0.78	0.78	SiO	150.1 <sup>11</sup> <sub>1.04</sub>	0.64	0.22
N-N	109.8 <sup>22</sup> <sub>1.04</sub>	0.26	0.26	SiS	192.9 <sup>01</sup> <sub>1.06</sub>	0.64	0.53
O-O	120.7 <sup>11</sup> <sub>1.16</sub>	0.22	0.22	SiSe	205.8 <sup>01</sup> <sub>1.07</sub>	0.64	0.63
O-O	120.7 <sup>00</sup> <sub>0.98</sub>	0.22	0.22	SiSi	224.6 <sup>00</sup> <sub>1.01</sub>	0.64	0.64
O-O*	127.2 <sup>11</sup> <sub>1.04</sub>	0.22	0.22	TeTe	255.7 <sup>01</sup> <sub>1.06</sub>	0.85	0.85
PN	149.1 <sup>11</sup> <sub>1.04</sub>	0.59	0.26	S-S <sup>\$</sup>	184.2 <sup>01</sup> <sub>1.08</sub>	0.53	0.53
				I-I <sup>\$</sup>	260.3 <sup>00</sup> <sub>1.01</sub>	0.78	0.78

<sup>#</sup> The M-M distance has been calculated using the relationship  
 $d_{M-M'} = \epsilon_{\text{eff}}[\{2.13r_G(M) - 35.3\}/F_S(M) + \{2.37r_G(M') + 105.8\}/F_S(M')]$   
 reported in Ref 17 and Ref 4 (where  $\epsilon_{\text{eff}} = 1.05$ ). The superscripts  $n$  and  $n'$  refer to the values of  $n_v$  associated, respectively with M and M' and the subscripts refer to the values of  $\epsilon_{\text{eff}}$  required to match the observed distance. The respective values of  $F_S$  has then been calculated using eqn 15. The values of  $r_G$  has been taken from Ref 2.

\* The M-M distance has been calculated using the relationship  
 $d_{M-M'} = \epsilon_{\text{eff}}[\{r_G(M) + \{2.37r_G(M') + 105.8\}/F_S(M')]$

**Table 2.**

Comparison of empirically observed changes in Shannon Radius of M and M' atoms due to changes in Valence or Spin State.

M <sup>a</sup>	S(M) <sup>c</sup>	F <sub>S</sub> (M)	r <sub>S</sub> (M) <sup>d</sup> (pm)	M'	S(M')	F <sub>S</sub> (M')	r <sub>S</sub> (M') <sup>d</sup> (pm)	$\frac{F_S(M')}{F_S(M)}$	$\frac{r_S(M)}{r_S(M')}$
<u>Valence State Changes</u>									
Ti <sup>2+</sup>	0	1	100	Ti <sup>4+</sup>	1	1.25	0.745	1.25	1.33
V <sup>2+</sup>	0	1	93	V <sup>5+</sup>	1.5	1.31	0.68	1.31	1.37
Cr <sup>2+</sup> (HS) <sup>b</sup>	0	1	94	Cr <sup>3+</sup>	0.5	1.16	0.755	1.18	1.23
Mn <sup>2+</sup> (HS) <sup>b</sup>	0	1	97	Mn <sup>3+</sup> (HS) <sup>b</sup>	0.5	1.16	0.785	1.18	1.24
Cu <sup>1+</sup>	0	1	91	Cu <sup>2+</sup>	0.5	1.16	0.87	1.18	1.05
<u>Spin-State Changes<sup>e</sup></u>									
Mn <sup>2+</sup> (HS) <sup>b</sup>	0	1	97	Mn <sup>II</sup> (LS) <sup>b</sup>	1	1.25	0.81	1.25	1.20
Fe <sup>2+</sup> (HS) <sup>b</sup>	0	1	92	Fe <sup>II</sup> (LS) <sup>b</sup>	1	1.25	0.75	1.25	1.22
Fe <sup>3+</sup> (HS) <sup>b</sup>	0.5	1.18	78.5	Fe <sup>III</sup> (LS) <sup>b</sup>	1.5	1.31	0.69	1.11	1.14
Co <sup>3+</sup> (HS) <sup>b</sup>	0.5	1.18	75	Co <sup>III</sup> (LS) <sup>b</sup>	1.5	1.31	0.685	1.11	1.10

<sup>a</sup> The choice of the M and M' atoms in this case is based on the decision that these states require to be well above the valence band of the ligand. We have chosen the band level diagrams of Mizushima *et al* (Ref. 36) for this purpose.

<sup>b</sup> HS and LS refers to high-spin and low-spin states, respectively

<sup>c</sup> The divalent state of the transition metal atom has been taken as the  $S = 0$  state except for the case of Cu<sup>1+</sup> where the monovalent state is taken as the  $S = 0$  state

<sup>d</sup> The crystal radius of the Shannon Tables (Ref. 35) are used here since they are close to the values of  $CR_S^+$  calculated (ref 4) from  $r_{core}$ .

<sup>e</sup> The spin state changes considers the number  $n_v$  to be the number of spins that have been flipped in the low-spin state relative to the high-spin state