Atom−Bond Transition: Transferability of Atomic Length Scales

P. Ganguly*

Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori, Yokohama 226-8503 Japan

Received: May 8, 2000

The expression of equilibrium single-bond interatomic distance, d_{M-X}, of any M−X bond (homonuclear or heteronuclear, ionic, covalent, or metallic) (Ganguly, *J. Am. Chem. Soc.* **1995**, *117*, 2655) in terms of core-atomic lengths is examined in terms of the constraints of an atom−bond transition. These include the following: (i) a description of bonding components of the hydrogen molecule that are applicable to all bonds; (ii) the use of a universal equilibrium chemical potential, $\mu_{\mathrm{univ}} = 0$; (iii) spin-charge conversion and a justification for the choice of valence s electron orbital radius as the core length; (iv) an examination of the atom−bond transition in terms of Thomas−Fermi screening models applied to the insulator−metal transition; (v) bond lengths and direction of polarity; (vi) bond energy of the hydrogen molecule and the maximum excitonic binding energy as the limiting values of the standard heats of formation per X atom in MX_n compound in gas and solid phase. The importance of valence s electron orbital radius, r_s, as a relevant core atomic length in atom−bond transition and in determining ionicity is indicated.

I. Introduction

Transferable atomic lengths[1−4] continue to be used with increasing confidence for estimating interatomic distances as well as obtaining coordination numbers ever since the beginning of the last century when interatomic distances could be measured with some accuracy. Much of our early, eminently successful "chemical intuition", involved in manipulating the properties of molecules and solids, has been indeed based on the interpretation of distances in equilibrium structures in terms of some standard distances of model compounds, real or imagined. An exposition of interatomic bond-distances in terms of simple transferable atomic lengths is eminently desirable, especially if, in doing so, additional insights are obtained on the direction of polarity of a chemical bond as well as its bond order, bond energy, and chemical reactivity. However, there seems to exist a fundamental problem in obtaining information about a chemical bond formed between two atoms, by using core, isolated-atom properties. The atom−bond transition involved in the chemical bonding between two atoms is quintessentially the most fundamental extranuclear quantum phase transition with the creation of an "energy gap" between the atomic and bonding states. Because of this it may not be possible to obtain information on *interatomic* properties by a renormalization of our understanding of *intra-atomic* processes.[5] We venture to report in this communication the conditions under which such a description may be permitted. In doing so, we shall use already available core atomic properties calculated using all of the rigorous paraphernalia available to density-functional/quantum-chemical methods.[6,7] The application of these core atomic properties to describing interatomic bond distances, however, will rely on simple semiclassical concepts derived from early twentieth century Bohr radius[8,9] and Thomas−Fermi methodologies.[10,11]

So far, the theoretical treatment of bonding in model compounds—covalent, ionic, metallic—is based on an energy-*eigenvalue*-based, HΨ = EΨ notion of seeking for every molecule[12] a know-all, complex-space wave function and relying on an energy minimization principle to obtain stationary states. Once the stationary state is obtained, the evaluation of other properties is expected to follow. By this method, the eigenvalues obtained for simple molecules can eventually be so accurate[13a,b] that experiments have to be refined[13d] to match theory sometimes instead of the other way around, as in the case of the hydrogen molecule.[13a,b] Modern refinements of the wave function[13c] of molecular hydrogen aim at removing inaccuracies due to the adiabatic approximation! However, an "uncertainty" principle operates, with the more accurate wave function usually being less general. After all, the greater-than-50-term wave function for molecular hydrogen cannot be transferred to chemical bonds of hydrogen with other elements with equal accuracy. In addition, there is the disconcerting disclosure that the accurate ground-state wave function of the hydrogen molecule has little to do with pure hydrogen 1*s* atomic orbital and requires significantly large contributions from what would be highly excited states.

The inclusion of "ionic" states for the description of "covalent" bonding further complicates any instantaneous real-space understanding of bonding, even if the dynamics of "resonant states" may be assumed to be understood. Such ionic states are notionally important for the understanding of Pauling's persuasive arguments[14] that interatomic distances depend on the nature of the bonding between the atoms. In Pauling's approach, the general wave function, Φ, of a heteronuclear M−X bond is

$$\Phi \equiv p\Psi_{M-X} + q\Psi_{M^+-X^-} + r\Psi_{M-X^+} \qquad (1)$$

with the values of *q*/*p* and *r*/*p* being such that the total energy of the molecule is minimized. Nonzero values of the coefficients *q* and/or *r* imply the introduction of ionicity or "partial ionic character". It is now becoming apparent that there is an inherent difficulty in understanding such "partial" ionic character. Garcia and Cohen[15] have pointed out that *"even if the total charge density were known at every point in the cell, there would be no unique way to decompose it into atomic contributions"*.

---

* On leave from Physical and Materials Chemistry Division, National Chemical Laboratory, Pashan Road, Pune 411008, India. E-mail address: ganguly@rlem.titech.ac.jp or partha_ganguly@hotmail.com.

10.1021/jp001719w CCC: $19.00

Meister and Schwarz[16] have stated, while analyzing the principal components of ionicity, that although there is possibly such a thing as ionicity, *"the projection of charge-density-distribution into atomic point charges is not unique and that it is not possible to define such a term in precise mathematical terms"*. In this case, the understanding of the "ionicity" need not require a wave function for the bonds as in eq 1, but rather may require an understanding of the rudimentary atoms themselves that constitute a bond, in a "child-is-the-parent-of-a-marriage" sense. This seems to be indicated when one considers transferable atomic quantities.

In a break from the conventional description of interatomic distances, Ganguly[17] finds empirically that all (covalent, ionic, metallic) interatomic single bond distances, $d_{\mathrm{M-X}}$, at standard conditions (atmospheric pressure and room temperature) are given by the sum of two lengths CR^{+} and CR^{-}, associated with states arising from the charge-transfer of a hole and electron, respectively. CR^{+} and CR^{-} are given by universal functions of a single, core, atom-specific length-scale, r_{core}. Thus

$$d_{\mathrm{M-X}} = CR^{+} + CR^{-} \tag{2a}$$

$$CR^{\pm} = \mathrm{C}^{\pm}\, r_{\mathrm{core}} + D^{\pm} \qquad C^{+} < C^{-} \tag{2b}$$

with $C^{\pm}$ and $D^{\pm}$ being universal constants (or nearly so), for standard conditions. In this case, $d_{\mathrm{M-X}}$ is thus a sum of atom-specific length derived from the core of an isolated atom and an atom-independent bond-length of the hydrogen molecule in a manner resembling closely the classical chemists' "ball" and "stick" model. The atom-independent bonding part, arising from $D^{\pm}$, is the "stick" and $C^{\pm}$ r_{core} is the atom-specific "ball" component. Such a development is important in understanding the atom−bond transition, since it will be convenient if the actual part of the interaction that contributes to interatomic bonding, the "stick", is universal and atom-independent, being that in the hydrogen molecule. This is implied in eq 2. It will then only remain to renormalize all atom-specific bonding processes in terms of core atomic properties or lengths, r_{core}. One could then anticipate the universality of the quantities, $C^{\pm}$, as well as the inequality, $C^{+} < C^{-}$, since these may not depend on the details of the bond formation. This simple approach is desirable to facilitate an ab initio understanding of large systems, which have their own computational-time paradoxes[18,19] employing the present quantum-computational methods.

In our efforts to obtain such an understanding, we make some new proposals regarding interatomic interactions, which are seemingly counterintuitive, at first. The more important of these in the context of universality are (i) the description of the interatomic distance of the hydrogen molecule using a simple Bohr radius approach to charged states. (ii) the proposal of an universal chemical potential, $\mu_{\mathrm{univ}} = 0$, (iii) the conversion of "spin" to "charge" and the consequent importance of purely electrostatic interactions; and (iv) the singular role of core atomic valence s electron lengths alone in determining the dimensions of the "ball".

Our aim is to propose, some simplifications to the approaches of understanding chemical bonding and reactivity in terms of atomic sizes and distances in a way that yields the direction of polarity or the "ionic character" of a bond without requiring an evaluation of the wave function in eq 1. We present physical arguments which give quantifiable support for the model in which the bond distances of elements seem to be describable simply by a Thomas−Fermi-like kernel and the bond in the hydrogen molecule. These arguments are qualitative, concerning themselves with limiting behavior rather than details. They seem to be appearing for the first time in the literature in the context of chemical bonding. Otherwise, they are borrowed from well-known and well-established phenomena in other areas of condensed matter science, even if diverse areas may be involved. We find that the assumptions we make are accurate in principle and not, in any way, incompatible with the "new" Schrödinger equation based quantum mechanical approaches.

II. Interatomic Distance in Hydrogen Molecule

The hydrogen molecule has to be a prototype for the chemical bond since there are no core electrons and we may assume $r_{\mathrm{core}} = 0$ in eq 2. We will then be concerned with understanding the origin of the lengths D^{+} and D^{-} in eq 2, remembering that these length scales are to be transferable for all bonding situations. Atom-specific wave functions will then require to be simplified in order to incorporate such a universality. However, what is true for the description of bonding of hydrogen atoms in the hydrogen molecule will also be required to be true for the other atoms in other bonds. The simplest of these, in the context of eq 2, is to consider the creation of charged states by the transfer of a charge and its hole. We use the simplest model available, the Bohr model, for this purpose. The Bohr model with its planetary orbits is known to have failed for the hydrogen molecule.[9,22] However, our approach is novel since we treat the hydrogen molecule as being made up of two charge-transfer states, each of which may be treated as Bohr-atom-like quasiparticles associated with the transfer of an electron and a hole. We find that a close approximation to the interatomic distance of the hydrogen molecule is obtained thereby.

The Bohr model for the hydrogen atom begins by obtaining a first Bohr radius, a_{H}, which is then crucial in obtaining the energies.[12,20] Yet a_{H}, a "size eigenvalue", has little application to the explanation of observables involving isolated hydrogen atom itself, even if it remains crucial in defining length scales in dielectric medium.[21] On the other hand, the concept of a Bohr radius is expected to be useful in the context of interatomic distances. The critical aspect of the Bohr model is not the actual existence of circular planetary orbitals, but the quantization of momentum as, $p = \hbar k = \hbar/r$, the law of conservation of energy, $E = T + V$, and the steady-state virial theorem, $E = -T = V/2$. The model is therefore directly applicable to any Bohr-atom-like situation built up of charges and in a steady state, and in which one requires the mass, m, of the particle for calculating the kinetic energy term, $p^{2}/2m$, as well as the charge on the particle for obtaining the electrostatic Coulomb interaction term.

We consider two hydrogen atoms, $\mathrm{H_A}^{\bullet}$ and $\mathrm{H_B}^{\bullet}$ ($\mathrm{H_A}$ and $\mathrm{H_B}$ being the positively charged nucleii) in the field of each other such that there is a charge transfer[23] (virtual or otherwise) of an electron, e^{-}, or a hole, h^{+}. We postulate the formation of quasiparticle charge-transfer states, $\mathrm{H_A}[^{\bullet}(h^{+})]$ and $\mathrm{H_B}[^{\bullet}(e^{-})]$

$$\mathrm{H_A}^{\bullet} + \mathrm{H_B}^{\bullet} \Leftrightarrow \mathrm{H_A}[^{\bullet}(h^{+})] + \mathrm{H_B}[^{\bullet}(e^{-})] \equiv \mathrm{H_A}[(e^{\mathrm{o}}h^{+})] + \mathrm{H_B}[(e^{\mathrm{o}}e)^{-}] \tag{3}$$

with conservation of total energy, mass and charge. Such charge-transfer states are precursors to bond formation. The interactions of the atom, $\mathrm{H}^{\bullet}$, with external charges take place in such a way that the valence electron, $^{\bullet}$, of the neutral atom is treated as being effectively a charge-compensated neutral electron,[24,25] e^{o}, with a mass, m_{o}. The assumption of a "neutral" electron, e^{o}, in eq 3 simply implies that all of the three-body interactions involving a nucleus, its electron, and the external charge have been effectively renormalized such that we are left with only the interactions between a single extranuclear charge and that of the nucleus. In $H_A[(e^oh^+)]$, a positively charged hole is similarly coupled to another "neutral" electron to form a spinless, singly positively charged electron−hole pair $(e^oh)^+$. In $H_B[(e^oe^-)]$, the transferred electron, e^-, is coupled to another "neutral" electron, e^o, to form a spinless, singly negatively charged electron pair, $(e^oe)^-$. Here, $(e^oe)^-$ and $(e^oh)^+$ of eq 3 constitute the new Bohr-atom-like quasiparticles in the field of positively charged nucleii, H_B and H_A, respectively, to form Bohr orbits. The quasiparticle states $(e^oe)^-$ and $(e^oh)^+$ are then treated in the Bohr model with masses, m_{ee} and m_{eh}, Bohr radii, $a^{ee}{}_H$ and $a^{eh}{}_H$, and energies, $E^{ee}{}_{tot}$ and $E^{eh}{}_{tot}$, respectively.

The mass, m_{ee}, of $(e^oe)^-$ (or $[^\bullet(e^-)]$) is assumed to be given by $1/m_{ee} = (1/m_o + 1/m_o)$ or $m_{ee} = m_o/2$, neglecting contributions from the nucleus. The "Bohr radius", $a^{ee}{}_H$, of $(e^oe)^-$ is given by[12,20]

$$a^{ee}{}_H = \hbar^2/m_{ee}\, e^2 = 2\hbar^2/m_o e^2 = 2a_H = 1.06 \text{ Å} \tag{4}$$

when $\epsilon = 1$. The Bohr radius, $a^{ee}{}_H$, is expected to be a characteristic radius of the H atom in the presence of a negative charge. Because of the repulsive Coulomb interaction between the positively charged $(e^oh)^+$ and the nucleus, the energy for the electron−hole pair, $(e^oh)^+$, at a distance, r^{eh}, from the nucleus is given by

$$E^{eh}{}_{tot} = (\hbar/r^{eh})^2/2m_{eh} + e^2/r^{eh} \tag{5}$$

From energy minimization[8] at equilibrium we have the equivalent for the Bohr radius, $a^{eh}{}_H$, of $(e^oh)^+$ given by

$$a^{eh}{}_H = -\hbar^2/m_{eh}e^2 \tag{6}$$

The negative sign of the Bohr radius is obtained from the Bohr model for a repulsive sign of the Coulomb interaction and a positive mass, m_{eh}. It emphasizes the positively charged hole-like nature of $(e^oh)^+$ with a potential for contracting or "puncturing" the electron cloud of the partner. Negative values are routinely used from the Shannon Tables[3] for the size of protons.

The total energy, $E^{\pm}{}_{tot}$ of each of the charge-transfer particles $(e^oe)^-$ and $(e^oh)^+$ can be similarly calculated from the Bohr model.[20] We then obtain

$$E^{ee}{}_{tot} = -m_{ee}e^4/2\hbar^2 = -m_o e^4/4\hbar^2 \tag{7}$$

From energy conservation in eq 3, we require[5] $E^{ee}{}_{tot} + E^{eh}{}_{tot} = 2E^H{}_{tot} = -m_oe^4/\hbar^2$, or

$$E^{eh}{}_{tot} = -3m_oe^4/4\,\hbar^2 = -m_{eh}e^4/2\hbar^2 \text{ (8)} \tag{8}$$

such that

$$m_{eh} = 3m_o/2 \tag{9}$$

$$a^{eh}{}_H = -2a_H/3 = -0.35 \text{ Å} \tag{10}$$

The important feature of these quasiparticles is that the sum $a^{ee}{}_H + a^{eh}{}_H = 1.064$ Å − 0.355 Å ∼ 0.71 Å gives the interatomic distance,[26] d_{H-H}, of the hydrogen molecule in terms of fundamental constants to within 5% of the room-temperature experimental value[27] of ∼0.74 Å. From our novel application of the Bohr model to the charge-transfer components constituting the hydrogen molecule, we may now identify $a^{eh}{}_H$ with D^+ and $a^{ee}{}_H$ with D^-. Now D^+ and D^- may be treated as fundamental transferable length scales of states derived from the hydrogen atom and involving charge-transfer of electron or hole (see Figure 1). The important point that will be addressed later is that these charge-transfer states, which are precursors to bond formation, seem to define length scales—the "stick"—even after bond formation. They are also involved in defining the lengths, d_{M-X}, between M and X atoms (M may or may not be the same as X) with a core length of the atom (the dimensions of the "ball") being added (Figure 2).

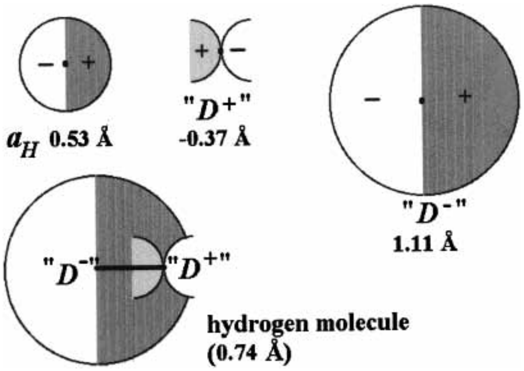

Figure 1. Diagram illustrative of the lengths associated with charge-transfer components, D^- and D^+. Negative size of D^+ relative to position of nucleus is schematically (and hopefully) shown by change in sign of coordinates relative to that of D^-, as well as by the splitting of the circle in the manner shown. The transferable size, $(D^+ + D^-) =$ 0.74 Å is shown.

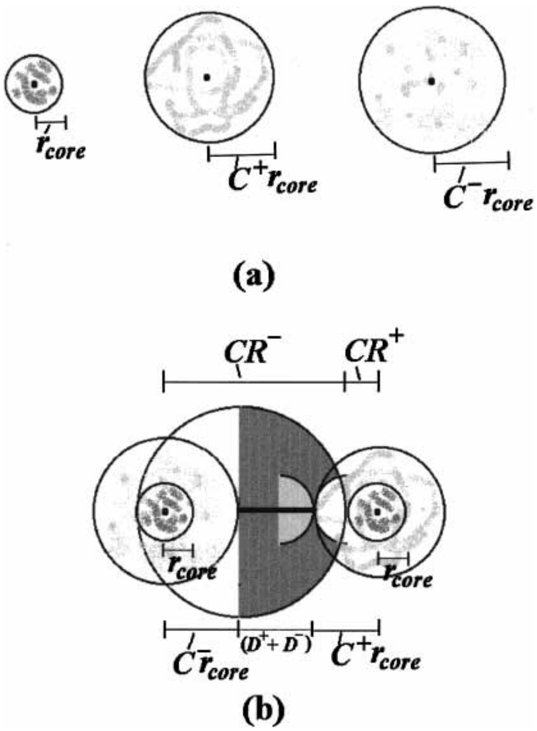

Figure 2. (a) Change of core length, r_{core}, to C^+r_{core} and C^-r_{core} associated with positive and negative charges, respectively. (b) Illustrating the interatomic distance, d_{M-X}, of an M−X bond (M = X in this example) as a sum of two of two lengths, CR^+ and CR^-, which are themselves obtained from eq 2 (see text) as $CR^{\pm} = C^{\pm}\, r_{core} + D^{\pm}$.

III. Universal Chemical Potential, $\mu_{univ} = 0$

The chemical potential or electronegativity is constant throughout an atom or molecule[28−30] at equilbrium. If we consider an assembly consisting of a large number of systems in equilibrium, we could then expect that the equilibrium chemical potential of the entire assembly is likely to have a universal value, μ_{univ}. = constant. Chemical reaction between molecules or atoms then take place when the reactants are taken out of equilibrium due to fluctuations or otherwise and have the electronegativity-generating chemical potential condition, $\mu \neq \mu_{\text{univ}}$; they take place to restore the μ_{univ} = constant equilibrium condition. The magnitude of this universal constant at equilibrium has yet to be determined.

Some insights may be obtained from the density functional formalisms. If we use the arguments of Komorowski,[31] regarding a neutral atom in equilbrium with a surface, then in the Thomas–Fermi (TF) model[10,32] one could expect $\mu_{\text{univ}} = \mu\text{-}(TF) = 0$. In density functional theory, the energy, $\mathrm{E}\upsilon$ (for the given one-particle external potential, υ) and the density, ρ', with $\rho' \geq \rho$, the true density, is obtained from the relation $d\mathrm{E} = \mu d\mathrm{N} + \int \rho d\upsilon d\tau$, and the stationary principle $\delta\{E_{\mathrm{v}}[\rho'] - \mu N[\rho']\} = 0$. The chemical potential is then given by[30,33]

$$\mu = [(\partial E[\rho]/\partial \rho)_{\upsilon}]_{\rho\, =\, \rho(\upsilon)} \tag{11}$$

with the density, ρ, being used instead of N, the number of electrons. In the case of a chemical bond between two atoms at equilibrium separation, r_{eq}, in the stationary steady state, We may write[34]

$$(\partial E/\partial \rho(\mathbf{r}))_{\upsilon} = (\partial E/\partial \rho(\mathbf{r}))_{\mathrm{r}(eq)} + (\partial E/\partial\, r)_{\rho(eq)}/(\partial \rho(\mathbf{r})/\partial r)_{\upsilon} \tag{12}$$

The energy of a chemical bond at equilibrium is a minimum for a given charge at the given internuclear separation so that we obtain $(\partial E/\partial r)_{\rho(\text{eq})} = 0$ for the correct equilibrium density, ρ(eq). Because of the variational principle in the Hohenberg–Kohn formalism,[35] which requires the density $\rho(\mathbf{r})$ at the correct equilibrium separation r(eq) to be such that the energy is minimum, we have $(\partial E/\partial \rho(\mathbf{r}))_{\mathrm{r(eq)}} = 0$. We would then obtain

$$\mu = (\partial E/\partial \rho(\mathbf{r}))_{\upsilon} = 0\, \mu_{\text{univ}} \tag{13}$$

provided

$$(\partial \rho(\mathbf{r})/\partial r)_{\upsilon} \neq 0 \tag{14}$$

at equilibrium. The density is expected to change with r validating eq 13. This need not be a surprise since the stationary principle in the Hohenberg–Kohn model is derived using Thomas-Fermi equations.

Komorowski[31] (based on the radial extension of the wave function of an atom to infinity) and Ganguly[17] (based on the transferability of lengths) have suggested $\mu_{\text{univ}} = 0$. The important impact of a model with an universal, $\mu_{\text{univ}} = 0$, Thomas–Fermi-like chemical potential[10,32] is that one can retain without undue alacrity the concept of the atom-in-molecule[36] for the ground equilibrium state. An important consequence of a ground state with $\mu = \mu_{\text{univ}} = 0$, is that each chemical bond formation takes place to restore the initial, $\mu_{\text{univ}} = 0$, condition. Bonding is imposed only when the atoms constituting the bond at equilibrium are to be separated. The energy of bond formation is a measure of this "ultraviolet freedom, infrared slavery".

In our interpretation, the electronegativity scale is a measure of the enhancement of the chemical potential prior to reaction. Mulliken's electronegativity,[37,38]

$$\chi_{\mathrm{M}} = (I + A)/2 = -\mu \tag{15}$$

is a finite difference approximation of the chemical potential, I and A being the ionization energy and electron affinity, respectively. The electronegativity of atoms is empirically known to be different from each other. As pointed out by Komorowski,[39] while the differential electronegativity of an interacting atom in a molecular system requires the electronegativities of the atoms in the molecules to be equal, this is not required for, say, Mulliken's electronegativity scale.

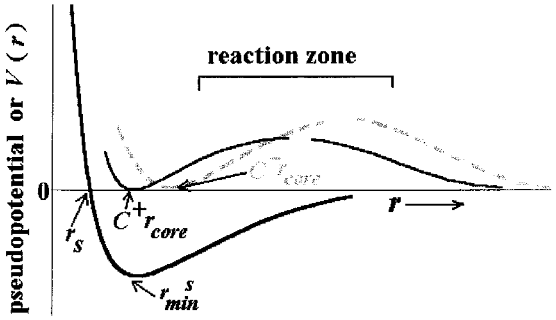

Figure 3. Schematic diagram for the variation with distance of pseudopotential of an isolated atom with distance for the valence s electron (dark thick line; after ref 6). The orbital radii, r_{s}, and the minimum point, $r_{\text{min}}{}^{\mathrm{s}}$, are indicated. Possible changes in electrostatic potential, $V(r)$, of an M atom in the presence of an external more electronegative X atom (dark gray dashed line), and of an X atom in the presence of an external less electronegative M atom (thin black full line) showing minima corresponding to $\mu_{\text{univ}} = 0 = V(r)$, at $C^{+}r_{\text{core}}$ and $C^{-}\ r_{\text{core}}$, respectively (see refs 40). The "reaction zone" is signaled by a higher effective electrostatic potential relative to the equilbrium value.

A universal condition helps to set a reference point for all atoms in equilibrium, and all properties associated with the atom may then be scaled in terms of that point. It has the following consequences that are important from the point of view of this communication: (i) It will now be possible to decompose the bond into the "ball" and "stick" components, as long as each component has $\mu = \mu_{\text{univ}} = 0$. (ii) It will also be sufficient for each chemical bonding interaction of a multivalent atom to be carried out single-bond-by-single-bond, in a univalent single-bond manner, in the direction of chemical bonding. (iii) Once a bond is formed in one direction and the system "adjusts" itself to restore the initial atom-like condition, $\mu_{\text{univ}} = 0$, a new bond may be formed in another direction as if it is a neutral atom. This will allow us to consider only the valence s-electron length for each bond, even for a multivalent atom, as far as determining lengths of each bond are concerned. (iv) A ground-state value of $\mu = \mu_{\text{univ}} = 0$ also legitimizes the use of the lengths, $a^{\mathrm{ee}}{}_{\mathrm{H}}$ and $a^{\mathrm{eh}}{}_{\mathrm{H}}$, of precursor states $(e^{\mathrm{o}}e)^{-}$ and $(e^{\mathrm{o}}h)^{+}$, respectively, in understanding the ground-state bond-distances. From eqs 7 and 8 and eq 15, the chemical potential of the bond in the hydrogen molecule is zero if we consider $E^{\mathrm{ee}}{}_{\text{tot}}$ and $E^{\mathrm{eh}}{}_{\text{tot}}$ to be the quantities corresponding, respectively, to the electron affinity, A, and the ionization energy, I, for the hydrogen atoms in the bond of the hydrogen molecule at equilbrium.

IV. Choice of Valence Orbital

The orbital angular momentum, l, dependent orbital radii, r_l, defined[4,6] by the classical turning point (at which the attractive and repulsive terms cancel each other exactly), may have the property of being a core length which coincides with a point[40] at which $\mu = 0$ or the origin of an hydrogen-atom-like wave function or both (Figure 3). The pseudopotential at this turning point, r_l, from the nucleus is identically zero. In this sense it is equivalent to the chemical potential of an isolated atom,[40,41] $\mu = 0$ in the Thomas–Fermi model. The orbital radius, r_l, thus has the desired core property[6,41] of being the classical quantity which can be transferred, for the given background chemical potential, $\mu_{univ} = 0$.

a. Noninclusion of p or d Orbitals. Ganguly[17] finds that the valence s electron orbital radius, r_s, is closest to the fitted values of $r_{\mathrm{core}}(= r_G$ in ref 17). Zhang et al.[7] have also shown empirically that the interatomic distances of heteronuclear bonds may be described solely in terms of the s electron orbital radii, r_s, although their expression requires an additional term that depends on the electronegativity. This neglect of p or d orbitals is (even if it is convenient), of course, chemically counterintuitive in the context of present understanding of chemical bonding, with its emphasis on sp^n hybridization, for example. On the other hand, the requirement of spherical symmetry has been noted in spin-density functional formalisms. The exchange correlation energy depends only on the spherical average of n_{xc} although the exact hole in general may be "strongly aspherical", since the nonspherical components contribute nothing to the energy.[42,43] In the spin density functional formalisms, the averaging is carried out after switching on the interatomic interactions, so that contributions from p and other orbitals may exist after the averaging. This may not account for the universal value of the coefficients, $C^{\pm}$.

It is preferable to look for arguments in which an averaging exists that eliminate the choice of $l \neq 0$ orbitals before the relevant interatomic interactions occur. This may be related to the existence of spin−orbit interactions in such orbitals. The formation of the chemical bond from two neutral atoms may be initiated by the formation of a singlet from two radicals

$$2(^{\bullet})\ \text{“biradical”} \rightarrow [e^{\mathrm{o}}(\uparrow)_{\mathrm{A}} + e^{\mathrm{o}}\,(\downarrow)_{\mathrm{B}}]_{\mathrm{S}=0} \tag{16}$$

due to what has been termed as exchange interactions resulting in a mutual exchange field between the two atoms, $H^{\mathrm{ex}}{}_{\mathrm{AB}}$. Chemical bonding is then obtained, in our approach, by the subsequent conversion to charged states[44] by a spin-conserving charge transfer of an electron from nucleus B to A, written as[45a]

$$[e^{\mathrm{o}}(\uparrow)_{\mathrm{A}} + e^{\mathrm{o}}\,(\downarrow)_{\mathrm{B}}]_{\mathrm{S}=0} \rightarrow [(e^{\mathrm{o}}e)_{\mathrm{A}} - (\uparrow\downarrow)\,h^{+}{}_{\mathrm{B}}]_{\mathrm{S}=0} \leftrightarrow [(e^{\mathrm{o}}e)_{\mathrm{B}} - (\uparrow\downarrow)\,h^{+}{}_{\mathrm{A}}]_{\mathrm{S}=0} \tag{17}$$

A mixing of moments by spin−orbit coupling may compete with the spin-pairing processes.[45b] Spin−orbit interactions control the direction of the spin momenta, and, in the presence of strong spin−orbit coupling (as in isolated atoms), the spin moments may be strongly affected by this coupling.[46] Moreover, the time scale for the intra-atomic spin−orbit interaction (timescale of an orbital motion) is expected to be small compared to the time scale of the interatomic spin-pairing interaction with an external electron/hole (of the order of a Larmor precession period of a Bohr magneton for the corresponding exchange field). In this case, the strict conservation of spin in eq 17 is best satisfied when $l = 0$. We also know, for example, that in the classical Stern−Gerlach experiments[47] the known spin separations are obtained for electrons in ground state $L = 0$ orbitals of the gas-phase atoms.

The above arguments justify the choice of atomic core length, r_{core}, derived solely from valence s electron lengths. Because of this, and even from an empirical point of view, we shall not consider atomic lengths derived from all electrons, such as the r_μ values (the value at which the chemical potential equals the negative of the electrostatic potential) of Politzer et al,[48] which correlate well with the Wigner−Seitz and covalent radius, or the radius, r_{m}, for negatively charged ions of Sen and Politzer[49] (at which the electrostatic potential of a mononegative ion reaches a minimum), or the radius, r_{D}, of Deb et al.[50] obtained from the radius where the electron density aquires the universal value of 0.00871, or the mean valence radius of Garcia and Cohen[15] even if this calculated radius bears a surprisingly linear relationship with the experimental polarizability radius, r_α, as tabulated by Nagle.[51]

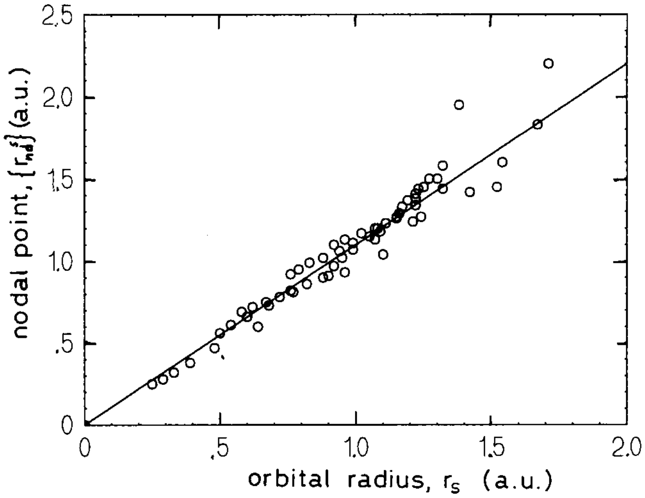

Figure 4. Plot of the orbital radius, r_s, vs the outermost nodal point, $\{r_{\mathrm{nd}}{}^{\mathrm{s}}\}$ of the elements (data from ref 6 and 54). The straight line is obtained from the best fit of the points to a straight line with 0 intercept, yielding $\{r_{\mathrm{nd}}{}^{\mathrm{s}}\} = 1.09r_{\mathrm{s}}$.

b. Valence s Electron Core Lengths. Besides the orbital radii, r_s, there are other valence s electron lengths which have a universal characteristic and which are linearly related to r_s. Thus, at larger values of r, the pseudopotential[6] goes through a minimum at $r_l{}^{\min}$ (Figure 3). This is also a suitable reference point as $\mathrm{d}v_{\mathrm{eff}}(r)/\mathrm{d}r = 0$ at this point. For valence s electrons $r_{\mathrm{s}}{}^{\min} \approx 1.5r_{\mathrm{s}}$. At the same time the nodal point itself has a universal characteristic. As pointed out first by Zunger,[52] there is a nearly linear relation between the valence s electron orbital radius, $r_{\mathrm{s},}$ and the outermost node of the s valence electron-$\{r_{\mathrm{nd}}{}^{\mathrm{s}}\}$. There is also a scaling relation[52,53] between the valence s electron orbital radius, r_s, and the minimum in the radial density function as well as the total electron density. It is important, therefore, to distinguish between these lengths in order to interpret the magnitudes of the coefficients, $C^{\pm}$ in eqs 2 and 18 (see later).

The definition of the orbital radius, r_l, by a turning point requires a finite density of electrons at the point so that attractive and repulsive terms acting on the electrons cancel each other, rendering the pseudopotential to be zero. On the other hand, the total potential will also be identically zero if there was no electron at the point. The nodal point may be taken as an "alternative description of the orbital radii".[54] The nodal point serves the purpose of locating the fixed effective positive charge. From this outermost nodal point, the valence electron, being nodeless, behaves effectively as that in an hydrogen-like atom. We may seek to distinguish between the orbital radii, r_{s} and $\{r_{\mathrm{nd}}\mathrm{s}\}$.

The interatomic distance, $d_{\mathrm{M-M}}$, may be obtained from eq 2 as

$$d_{\mathrm{M-M}} = CR^{+} + CR^{-} = (C^{+} + C^{-})\,r_{\mathrm{core}} + (D^{+} + D^{-}) \tag{18}$$

In the earlier communication[17] it was found that $C^{+} = 2.24$ and $C^{-} = 2.49$ when $r_{\mathrm{core}} = r_G \approx 1.01r_{\mathrm{s}}$. We have shown in Figure 4 the plot of $\{r_{\mathrm{nd}}{}^{\mathrm{s}}\}$ vs r_{s} as tabulated by Zhang et al.[54] for all of the elements. Assuming a linear relationship, the slope yields $\{r_{\mathrm{nd}}{}^{\mathrm{s}}\} \approx 1.10r_{\mathrm{s}}$. The coefficients C^{-} and C^{+} become 2.28

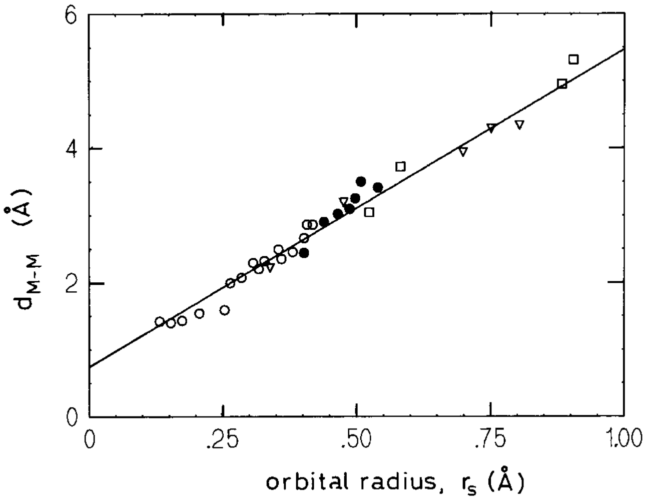

Figure 5. Plot of the homonuclear interatomic single-bond distance, d_{M-M}, (from ref 55) of non transition metal elements vs the orbital radius, r_s (ref 6, 54); alkali metals (squares), alkaline-earth elements (triangles), elements with low melting point (filled circles) and other nontransition metal elements (circles). The straight line shows the best fit to the equation $d_{M-M} = Ar_s + 0.74$ (in Å), with A = 4.79.

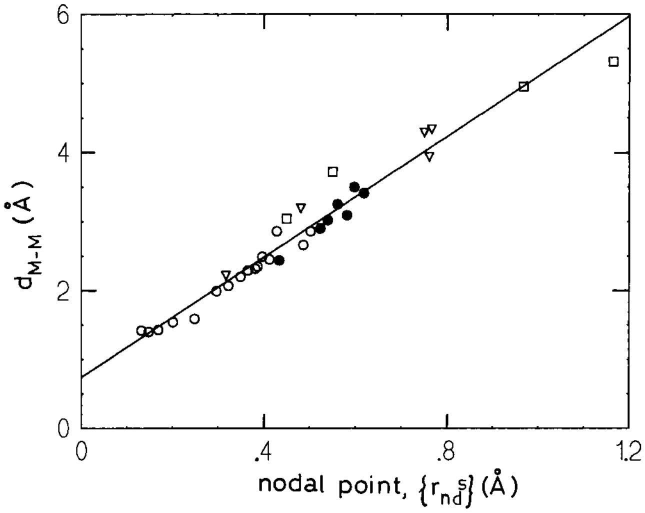

Figure 6. Plot of the homonuclear interatomic single-bond distance, d_{M-M}, (from ref 55) of non transition metal elements vs the outermost nodal point, $\{r_{nd}^{s}\}$, of valence s electron (from ref 54); alkali metals (squares), alkaline-earth elements (triangles), elements with low melting point (filled circles) and other nontransition metal elements (circles). The straight line show the best fit to the equation $d_{M-M} = A\{r_{nd}^{s}\} + 0.74$ (in Å), with A = 4.35.

and 2.06, respectively, when $r_{core} \equiv \{r_{nd}^{s}\} \approx 1.09 r_G$ in eq 18. We may thus write

$$d_{M-M} \approx 4.73\, r_s + 0.74 \text{ (in Å)} \approx 4.34\{r_{nd}^{s}\} + 0.74 \text{ (in Å)} \quad (19)$$

We show in Figures 5 and 6, the plots of the interatomic distances[55] of homonuclear bonds to core lengths for r_s and $\{r_{nd}^{s}\}$, respectively. We obtain a marginally better fit with the orbital radius r_s as compared to that with the nodal point, $\{r_{nd}^{s}\}$.

V. Core Lengths and the Atom−Bond Transition

a. Thomas−Fermi Screening and Atom−Bond Transition. The essential feature for the formation of a chemical bond involves the transfer of an electron from the atom to which it is originally bound to its bonding partner. One expects a change in the core-lengths due to interactions in the presence of an external particle or hole in the case of bond formation even if it only involves two atoms.[56] In a sense, this is equivalent to the delocalization of the electron away from its original localizing potential as in the insulator−metal transition. The relevant model for the insulator−metal transition corresponds to bound excitons (electrons bound to its hole) in an insulator being progressively screened to yield a metal. Mott first examined[56] this aspect of the MI transition in the Thomas−Fermi model[57,58] of screening. The electrons are treated as a gas of free particles, neglecting exchange and correlation.[40,41,44] The electron is always bound to its hole in the potential $-e^2/\epsilon r$, where ϵ is the dielectric constant, especially for large r, and in the absence of another external particle or field. In the presence of another external electron or charge carrier, this is not the case, as there is now a screening of the bound particle by the other particle(s). Thus, when a point charge is introduced in the electron gas with an impurity potential $V_o(r) = \pm Z/r$, the charge density rearranges to screen V_o. The potential becomes the screening potential, V_P, given by $V_P = Z\alpha/r\ \exp(-qr)$, at which there is not a bound state (see Figure 2). For a certain critical concentration or a separation between the charge carriers, the potential is reduced to a negligible size by the exponential damping term and there is no bound state. For Bohr-atom-like dopants in semiconductors, Edward and Sienko[59] showed from a compilation of the experimental results that the critical concentration, n_c, at which there is an insulator−metal transition of doped materials (obtained in the high-temperature limit by a change in sign of the slope of the resistivity vs temperature plot) is given by

$$n_c^{1/3}\, a_H^* \sim 0.26 \pm 0.06 \quad (20)$$

where a_H^* is obtained in most cases from experimental measurements as compared to Mott's prediction[60] of $n_c^{1/3} a_H = 0.25$. We may consider this experimental criterion of Edwards and Sienko[59] (eq 20) as an unprejudiced and a "model-unbiased" estimate for the critical concentration at which the screening is effective such that there is no bound state so that delocalization of charge from one site to another becomes possible.

b. Scaling of Lengths. The volume occupied by the Bohr atoms with radius a_H^* is $4n_c\pi(a_H^*)^3/3 = 0.074$ from eq 20, which is nearly one tenth of the close-packed volume. The effect of screening is thus to effectively scale the Bohr radius, a^*_H, at the insulator−metal transition to a_{eff} by a factor C_{TF} such that $C_{TF}a_H = a_{eff}$ with a volume, V_{eff}. The definition of V_{eff} has its own problems. Thus we may have $V_{eff} = 1$ if all space is included or $V_{eff} = 0.74$, the close-packed volume fraction.[61] At the critical concentration, n_c, we then have

$$C_{TF} = a_{eff}/a_H^* \approx (0.74/0.074)^{1/3} \approx 2.16 \pm 0.6 \text{ when } V_{eff} = 0.74 \quad (21a)$$

$$C_{TF} = a_{eff}/a_H^* \approx (1/0.074)^{1/3} \approx 2.38 \pm 0.6 \text{ when } V_{eff} = 1 \quad (21b)$$

The value of C_{TF} in eq 21 may be taken as an experimental estimate of the critical extension of the Bohr radius of an excitonic atom at the point of the insulator−metal transition. These values of C_{TF} are close to those obtained for the coefficients $C^{\pm}$ of r_{core} in eq 19, suggesting that the analogy between atom−bond transition and the insulator−metal transition may be valid. An exact one-to-one correspondence is not demonstrated.

The difference between an isolated atom and an atom in a bond is that there is an influence of an external charge. Its effect is then to increase an atomic length r_{atom} to a screened length, r_{screen}, given by

$$r_{\mathrm{screen}} = C_{\mathrm{TF}} r_{\mathrm{atom}} \tag{22}$$

where we use the same scaling constant, C_{TF}. The uncertainties involved in the theoretical models preclude the use of such models to distinguish between the theoretically calculated values of, say, r_{s} and $\{r_{\mathrm{nd}}{}^{\mathrm{s}}\}$ by examining the values of their respective coefficients, $C^{\pm}$. The values of the coefficients $C^{\pm}$ (eq 19) of the nodal-point-distance, $\{r_{\mathrm{nd}}{}^{\mathrm{s}}\}$, are close to C_{TF} obtained from the experimental condition for metallisation (eq 21) when $V_{eff} = 0.74$; the coefficients $C^{\pm}$ (eq 19) of the orbital radius, r_{s}, obtained from the turning point are closer to C_{TF} when we use $V_{\mathrm{eff}} = 1$ (eq 21b).

c. Core and Valence Regions. The separation of an atom into a core and valence regions has been the subject of several earlier studies and the basis of several approximate methods,[6] including the pseudopotential method in which the valence wave function is constructed as a smooth nodeless hydrogen 1s-like wave function. Politzer[64] has shown that, in the core region, the relation between the electrostatic potential and the electron density is that given by the Thomas–Fermi model involving independent particles. In this approach, the Thomas–Fermi model is not applicable[64] in the valence region of an atom. In our model, the condition of a universal equilibrium chemical potential, $\mu_{\mathrm{univ}} = 0$, for the ground state of the chemical bond, ensures that the semiclassical description is extended to the bonding pair of electrons as well. Such an $\mu_{\mathrm{univ}} = 0$ condition allows the transferability of the atom-specific as well as atom-independent lengths of eq 2 to all bond distances at equilibrium. If we impose the Thomas–Fermi condition that $V(r) = \mu = 0$ at equilibrium, one requires the electrostatic potential to be zero at the equilibrium distance. A possible plot of the electrostatic potential of a valence electron in the presence of another reacting atom vs the distance from the nucelus is shown in Figure 3. In this plot, we have assumed $\mu = 0 = V(r)$ at equilibrium. The modified orbital radius ($\sim C^{\pm} r_{\mathrm{s}}$) at which $V(r) = 0$, coincides with the minimum in the potential energy curve.

In the context of bonding between atoms, we may now decompose the atom into core and valence regions such that $r_{\mathrm{atom}} = r_{\mathrm{core}} + r_{\mathrm{val}}$, where r_{core} is the atom-specific core length of eqs 2 and 18, and r_{val} is the valence lengths, $D^{\pm}$ which are are unchanged relative to hydrogen

$$C_{\mathrm{TF}} r_{\mathrm{core}} = C_{\mathrm{TF}}(r_{\mathrm{core}} + r_{\mathrm{val}}) \tag{23}$$

The valence region in the chemical bond (the "stick" ($\equiv D^{+} + D^{-}$)) is seemingly un-"screened", continuing to exist as a bound electron pair[62] as in the hydrogen molecule. Such a picture is consistent with some of the modern approaches perhaps initiated by Julg and Julg,[63] who first proposed to identify chemical bonds with the regions of the low fluctuation of the electron pair.

d. Orbital Radius or Nodal Point? We have used another approach for examining the validity of the core lengths, r_{s} or $\{r_{\mathrm{nd}}{}^{\mathrm{s}}\}$. This is to search for a length that separates the insulating elements from the metallic elements[59b] at atmospheric pressure and room temperature. We show in Figures 7 and 8, the plots of the orbital radius, r_{s}, and the outermost nodal point, $\{r_{\mathrm{nd}}{}^{\mathrm{s}}\}$, vs the atomic number of the element. Most of the insulators, except notably, Te and I, are in the region r_{s} or $\{r_{\mathrm{nd}}{}^{\mathrm{s}}\} < |D^{+}| \approx 0.37$ Å. All of the metals, except Be, have r_{s} or $\{r_{\mathrm{nd}}{}^{\mathrm{s}}\} > |D^{+}| \approx 0.37$ Å. The better separation, as measured by the position of the exceptions from the separating line, is obtained with r_{s} rather than with $\{r_{\mathrm{nd}}{}^{\mathrm{s}}\}$.

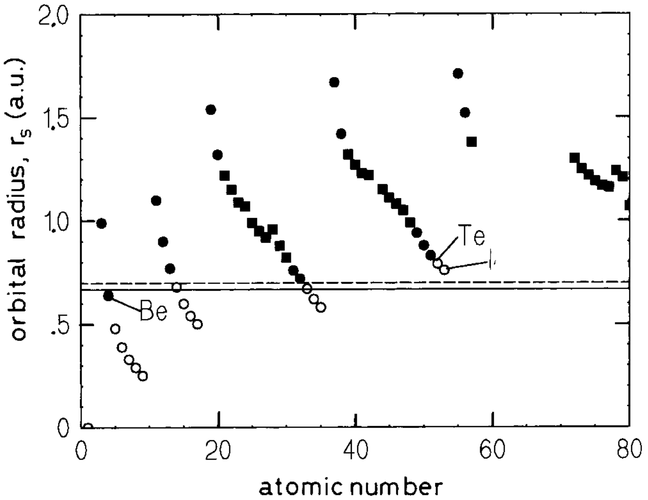

Figure 7. Plot of the orbital radius, r_{s} (from refs 6 and 54) vs atomic number of the elements: open circles, insulators at room tempertaure and atmospheric pressure; filled circles, nontransition elements and filled squares: transition metal elements which are metallic at room temperature and atomospheric pressure. The horizontal full line corresponds to 0.353 Å (see text) and the dashed line corresponds to 0.37 Å.

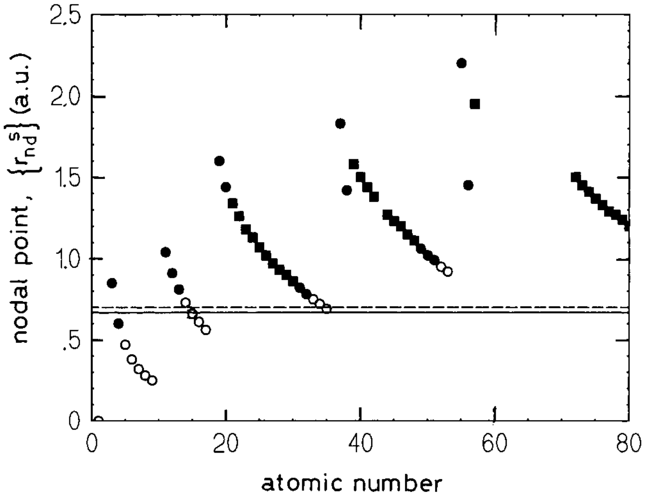

Figure 8. Plot of the outermost nodal point of valence s electron, $\{r_{\mathrm{nd}}{}^{\mathrm{s}}\}$ (from ref 54) vs atomic number of the elements: open circles, insulators at room tempertaure and atmospheric pressure; filled circles, nontransition elements and filled squares: transition metal elements which are metallic at room temperature and atomospheric pressure.

The above discrimination between metallic and insulating elements seems to us to be a strong case in favor of the validity of the core lengths such as r_{s} or $\{r_{\mathrm{nd}}{}^{\mathrm{s}}\}$as a significant radius. This is schematically shown in Figure 9. Since D^{+} is negative, any element, M, in an M–X bond with X being negatively charged (X may be the same as M) such that r_{core} (M) $< |D^{+}|$ would have (r_{core}(M) + D^{+}) < 0. We may interpret this to indicate that the nucleus of the concerned element, *M*, is exposed to the electron cloud of the element X such that strongly bound states are formed which cause localization. When r_{core}(M) $>$ $|D^{+}|$, such bound states are not formed with the core electron cloud serving to screen the nuclear charge and prevent the formation of strongly bound states. The magnitudes of D^{+} as well as r_{core} are expected to change with boundary conditions[65] such as external pressure or polarizability and a true single-atom criterion for metallization may finally still be derived from

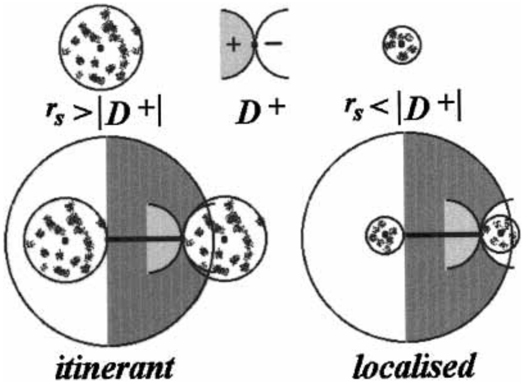

Figure 9. Schematic diagrams of homonuclear bonds illustrating (see Figure 1) (a) the exposure of the nucleus directly to the electron cloud of the bonding partner (the nucleus is inside the larger radius of (D^-) when $r_s < |D^+|$ since (b) when $r_s > |D^+|$, the nucleus is outside the larger radius of D^-, so that the nucleus is not directly exposed to the electron cloud of the bonding partner. Thomas−Fermi screening due to the presence of the bonding atom acts such that the dimensions of the core length scale are changed as in Figure 2.

considerations of dielectric function, such as the Herzfeld criterion.[59b,66]

We conclude from the above discussions that it is difficult to distinguish between the theoretically calculated values of the orbital radius, r_s, and the nodal point, $\{r_{nd}{}^s\}$ as the core valence s electron radius that may be associated with r_{core} in eqs 2, 18, and 19. If at all, there seems to be a better agreement with the orbital radius, r_s.

VI. Bond Lengths and Bond Polarity

The expressions for C^+ and C^- (eqs 2 and 18) show electron−hole asymmetry. This inequality is essential to account for the direction of polarity of heteronuclear bonds in terms of a principal of maximum mechanical hardness[67] (PMMH), postulated by Ganguly.[17] PMMH requires that in heteronuclear M−X bonds, the ground-state equilibrium interatomic separation, d_{M-X}, given by

$$d_{M-X} = CR^+(M) + CR^-(X) \tag{24}$$

is the shortest possible distance, which in turn requires (from the inequality $C^+ < C^-$ in eqs 2 and 18) that the element with the smaller value of r_{core} is the more electronegative element,[68] X. The PMMH principle is also consistent with some of the findings in the models of Pearson and Parr[69] for the hard and soft acid base (HSAB) principle. Indeed, as far back as 1884 or earlier, Muller-Erzbach[70,71] expressed the law that "in any chemical reaction the elements tend to arrange themselves in those forms of combination which occupy the smallest volume or that greater condensation is correlated with greater affinity".

The inequality $C^+ < C^-$ is expected to arise from the asymmetry of the electron and the hole, with respect to a positively charged nucleus. A simple qualitative argument is that the inequality, $C^+ < C^-$ may appear as a consequence of changes in the core length scale due to the field of an external positive or negative charge. An external positive charge would add to the attractive terms and postpone the classical turning point to smaller distances, thereby decreasing r_s, while an external negative charge would add to the repulsive terms and increase, r_s. The core length scale, r_s, is then changed to $r_s{}^+$ and $r_s{}^-$ due to the external positive and negative charge, respectively, with $r_s{}^+ < r_s < r_s{}^-$.

The electron hole asymmetry also appears in the Thomas−Fermi model.[57] When a point-charge impurity potential $V \pm Z/r$ is introduced into the electron gas of a Thomas−Fermi atom with Fermi energy, k_F, one requires the adjusted Fermi energy k_{max} to be given by[57] ($\hbar = 1$)

$$(1/2)k_{max}{}^2 + V_P = (1/2)k_F{}^2 \tag{25}$$

Electrons are allowed to have higher kinetic energy when the potential energy is lowered (attractive potential) and vice versa. When V_P is repulsive (in the case of holes in the field of a positive charge), the conservation of energy requires $k_{max}{}^2$ to decrease with an increase in the magnitude of V_P, until at very small values of r, $k_{max}{}^2$ takes negative values. This is not the case when V_P is an attractive potential (in the case of electrons in the field of a positive charge). In this case, k_{max} may be allowed to increase continuously with decreasing r. One may anticipate, therefore, an asymmetry in the magnitude of the screening constants $C_{TF}{}^+$ and $C_{TF}{}^-$ for electrons and holes, respectively. The condition

$$C_{TF}{}^+ < C_{TF} < C_{TF}{}^- \tag{26}$$

and, perhaps,

$$C_{TF}{}^+ + C_{TF}{}^- \approx 2C_{TF} \tag{27}$$

may follow from a conservation of energy such that there is a transfer of the forbidden kinetic energy of the hole (in the negative kinetic energy region) to the electron. Equation 26 is consistent with the empirical observations of Ganguly,[17] if we relate $C_{TF}{}^+$ to C^+ and $C_{TF}{}^-$ to C^- in eqs 2 and 18, respectively. The universality condition is maintained when $r_s{}^{\pm}/r_s = C^{\pm}/C_{TF}$. One expects a minimum in the screened potential as shown in Figure 3. This aspect has not been investigated in the literature.

The inequality $C^+ < C^-$ is crucial to the understanding of polarity of a bond by PMMH,[17] which asserts that there is only one ground-state configuration corresponding to the charge-transfer state, $M^+{-}X^-$. In this sense, it implies that the coefficients, p and r of eq 1, are zero in the ground state. The distance (eq 26) corresponding to $M^+{-}X^-$ is always less than that corresponding to $M^-{-}X^+$ since $C^+ < C^-$, of which $d_{M-X} < (d_{M-M} + d_{X-X})/2$ for single bonds. Such a contraction in the heteronuclear bond distance relative to that of homonuclear bonds had been noticed quite early by Schömaker and Stevenson,[72] who found that "the lengths of bonds are significantly affected by even quite small amounts of ionic character". These authors have related the contraction δd_{M-X} of heteronuclear bond distance over that of homonuclear bond distances by

$$\delta d_{M-X} = (r_{cov}(M) + r_{cov}(X)) - d_{M-X} \tag{28}$$

δd_{M-X} is in turn related to the difference in Pauling's electronegativity[73] scale by

$$|\chi_M - \chi_X| = \delta d_{M-X}/c_{SS} \tag{29}$$

where χ_M and χ_X are the electronegativity in Pauling's scale and the Schömaker−Stevenson coefficient c_{SS} depends on the row to which the elements belong. The important point is that the Schömaker−Stevenson contraction, $\delta d_{M-X,}$ follows naturally from PMMH and is given from eqs 2, 18, 19, and 28 by

$$\begin{aligned}\delta d_{M-X} = r_{cov}(M) + r_{cov}(X) - \{CR^+(M) + CR^-(X)\} = \\ 0.125\{r_s(M) - r_s(X)\}\end{aligned} \tag{30}$$

A relation between atomic lengths and electronegativity is expected to follow once the extent of contraction is related to changes in thermochemical quantities.

VII. Bond Energies

In homonuclear M−M bonds the charge-transfer states are degenerate. Because of this there is likely to be a rapid fluctuation between the two possible configurations.

$$CR^{+}(\mathrm{M}_a) + CR^{-}(\mathrm{M}_b) \Leftrightarrow CR^{-}(\mathrm{M}_a) + CR^{+}(\mathrm{M}_b) \quad (31)$$

where M_a and M_b correspond to different nucleii of the same species. As long as the fluctuation time is fast compared to the measurement time, the charge-difference on the two atoms will average out to zero. This is the situation discussed in terms of the homogeneous mixed valence systems in condensed matter studies.[23] In writing such a valence fluctuation, we are really exchanging the bonding pair of electrons. Because of the rapid fluctuations we may define a covalent radius

$$r_{\mathrm{cov}}(\mathrm{M}) = (C^{+} + C^{-})r_{\mathrm{core}}(\mathrm{M})/2 + 0.37\ \text{Å} \quad (32)$$

such that $2r_{\mathrm{cov}} = 2d_{\mathrm{M-M}}$ and where the term 0.37 Å is an expression of sharing of the bonding lengths of the hydrogen molecule, $d_{\mathrm{H-H}}$ (= 0.74 Å).

For heteronuclear bonds, we may consider thermochemical quantities via the electronegativity scale in terms of (what we will term) the Schömaker−Stevenson contraction, $\delta d_{\mathrm{M-X}}$, of eqs 29 and 30. In our approach, $\delta d_{\mathrm{M-X}}$ is a measure of the contraction of ground-state bond distances, with universal chemical potential, $\mu_{\mathrm{univ}} = 0$. The utility of the electronegativity scale is in specifying the position of an element "in an ordinal listing such that it would be negative with any element listed below it". The thermochemical electronegativity scale[73] of Pauling, where chemical reactivity is really a measure of the changes in the energy from an excited nonequilibrium state, has necessarily to be different from the "spatial" electronegativity scale in which the atoms are "rank-ordered" by their sizes in the ground equilibrium state. This aspect will be dealt with in another communication, especially since we have not yet discussed the observed relation between multiple-bond distances[74] and core lengths.

We may use eqs 29 and 30 as a first approximation[75] to set up a relation between thermochemical quantities such as the standard heat of formation, ΔH_f°, of compounds and a "spatial" electronegativity difference, $\Delta\chi_{\mathrm{r(s)}} = \{-(r_{\mathrm{s}}(\mathrm{X})^{-1} - r_{\mathrm{s}}(\mathrm{M})^{-1})\}$, derived from atomic lengths.[76] We have used the values of the standard heat of formation, $(\Delta H_f^{\circ})^{\mathrm{X}}$(gas) or $(\Delta H_f^{\circ})^{\mathrm{X}}$(solid), of MX_n ($n \geq 1$) compounds per g at X. Here, $(\Delta H_f^{\circ})^{\mathrm{X}}$(gas) is identical to Pauling's extraionic energy term,[73] Δ. We find[75,77] that $\Delta\chi_{\mathrm{r(s)}} = \{-(r_{\mathrm{s}}(\mathrm{X})^{-1} - r_{\mathrm{s}}(\mathrm{M})^{-1})\}$, the difference in the inverse[68] of the valence s electron length, r_{s}, is related to thermochemical quantities[78−80] by the relation (see Figure 10)

$$(\Delta H_f^{\circ})^{\mathrm{X}}(\mathrm{gas}) \sim -104\,[1 - \exp(-\Delta\chi_{\mathrm{r(s)}})] + b_g\exp(\Delta\chi_{\mathrm{r(s)}})\ (\text{in kcal}) \quad (33)$$

$$(\Delta H_f^{\circ})^{\mathrm{X}}(\mathrm{solid}) \sim -160[1 - \exp(-\Delta\chi_{\mathrm{r(s)}})] + b_s\exp(\Delta\chi_{\mathrm{r(s)}})\ (\text{in kcal}) \quad (34)$$

The term due to b (which is small and positive) becomes important[81] in solids at large size differences between M and X. Equation 33 sets an upper limit, $(\Delta H_f^{\circ})^{\mathrm{X}}$(gas), to the standard heat of formation per single bond of ~104 kcal/mol of alkali. $(\Delta H_f^{\circ})^{\mathrm{X}}$(gas) is close to the bond-dissociation energy, D_{H-H}, of the hydrogen molecule. Similarly, eq 34 sets an upper limit for the heat of formation, $(\Delta H_f^{\circ})^{\mathrm{X}}_{\mathrm{max}}$(solid) ~ 160 kcal/mol of the standard heat of formation in the condensed phase.

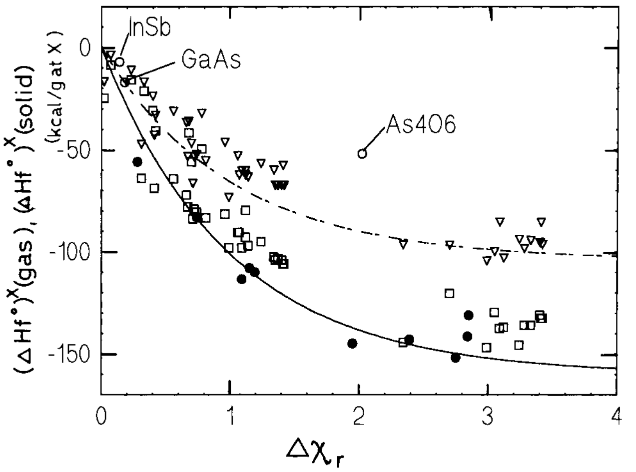

Figure 10. Plot of standard heat of formation $(\Delta H_f^{\circ})^{\mathrm{X}}$(gas) (≡ extraionic energy per bond, Δ^{X} of Pauling), of MX_n compounds in the gas-phase (see ref 78) (triangles) and the standard heat of formation, $(\Delta H_f^{\circ})^{\mathrm{X}}$(solid) of the corresponding solids (squares) vs $\Delta\chi_{\mathrm{r(s)}} = (r_s(X)^{-1} - r_s(M)^{-1})$. The $(\Delta H_f^{\circ})^{\mathrm{X}}$ of some other compounds including alkaline-earth oxides and chalcogenides (filled circles), as well as InSb, GaAs, and $\mathrm{As_4O_6}$ are shown (open circles). The dashed and full lines correspond to eqs 33 and 34 in the text with $b = 0$.

The limiting values of $(\Delta H_f^{\circ})^{\mathrm{X}}$(gas) and $(\Delta H_f^{\circ})^{\mathrm{X}}_{\mathrm{max}}$(solid) may arise from simple geometric conditions. In the gas phase, the molecules are isolated with considerable edge effects and cannot be treated as a three-dimensional dielectric continuum. The same is true for molecular solids in which the molecules are packed by van der Waals' interactions. The requirement of the conservation of spin during charge transfer (eqs 16 and 17) could impose a constraint on the allowed orbital geometries in isolated bonds such as that in the hydrogen molecule. We treat the spins classically. In an ideal isotropic 3-D continuum medium, every orientation of a spin on an electron (hole) is likely to find a corresponding antiparallel spin on another electron (hole). Because of this, the three-dimensional geometry itself does not impose a constraint on the pairing of electron spins. In the case of the fixed geometry of an isolated bond, the orbit (virtual or real) of the interatomic electron−hole Bohr orbit is confined at any instant to a plane (say, the xy plane) which includes the bonding axis (say, the x axis). The plane of the orbit may be related to the plane of precession of the electron spin oriented along the z-axis, as required from the uncertainty principle. Because of the confinement to a 2-D plane, a degree of freedom is lost, in effect. This leads to a loss of kinetic energy by one-third and, from the virial theorem, the total stabilizing energy is also decreased by one-third.[82]

The universal relationship between $(\Delta H_f^{\circ})^{\mathrm{X}}$(gas) and $(\Delta H_f^{\circ})^{\mathrm{X}}$(solid) suggested by eqs 33 and 34, is satisfying. To a first approximation, the core atomic lengths play an important role in determining not only lengths but also the bond energies in a simple transparent manner, in a manner that is consistent with PMMH.[17] The term $[1/r_{\mathrm{s}}(\mathrm{X}) - 1/r(\mathrm{M})]$ may be taken as a measure of difference in energy between two negatively charged states, X^- and M^-, once $1/r_{\mathrm{s}}$ is related to an energy scale. Zunger[6] has suggested that the theoretical r_{s}^{-1} can be used as an energy scale "much like Mulliken's electronegativity".

There are several issues arising from the observations in eqs 33 and 34. One of these, of immediate relevance to this communication, is that the maximum values of $(\Delta H_f°)^{X}_{max}$(gas) or $(\Delta H_f°)^{X}_{max}$(solid) are independent of the valence, v, of the X atom. The limiting value for the heat of formation, $(\Delta H_f°)^{X}$(solid), in the solid alkali halides is ~159 kcal/mol $\approx E_{exc}$, the maximum excitonic binding energy[83], for $\epsilon = 1$. For example,[78] LiF, MgF_2, and MgO have the same standard heat of formation, $(\Delta H_f°)^{X}$, per anion (−140 ± 7 kcal/X atom) at room temperature. The excess interaction energy due to the ionic character is not related to the formal valence of the anion or the cation. Instead, we may consider the solid medium as a continuum dielectric medium with the strength of the interaction between each heteronuclear bond being limited by the maximum excitonic binding energy,[82] E_{exc}, in an isotropic dielectric medium. Discrete structural details or coordination numbers are seemingly unimportant since BeO with the zinc blende, ZnO structure and MgO, with the rock-salt structure, yield nearly the same heat of formation, $(\Delta H_f°)^{X}$.

One expects a universal relationship between $\Delta\chi_{r*s}$ and $(\Delta H_f°)^{X}/v$ (or Δ^{X}/v), the g equivalent thermochemical quantities. This is the point made by Vijh[84] who found that the standard state heat of formation per equivalent, $-(\Delta H_f°)^{X}/v \approx (E_g\ (\pm 20\%))/2$. Each unpaired electron state of an atom X of valence v is stabilized by $-(\Delta H_f°)^{X}/v$ so that the band gap, E_g, is twice this value. It seems to us that the heat of formation of M−X bonds is better expressed in terms of g of X, because the most elementary excitonic excitation may be considered to be localized on the anion since the anionic X atoms dominate the properties of the valence band of the crystal. This emphasizes the possible role of the smaller X atoms in attracting electrons and initiating single charge separation between the multivalent M and X atoms for each M−X bond (see eq 17). This charge separation has been traditionally related to the electronegativity[2,14] or the "power of an atom in a molecule to attract electrons to itself ". The important consequence then seems to be that bonding between two atoms, M and X, is initiated by the annihilation of spins to create a single negative charge on the more electronegative atom, X.

The maximum heat of formation of a heteronuclear bond in a solid is thus not expected to be greater than the maximum value of $E_{exc} \sim -159$ kcal per X atom and is independent of the formal valence state.

VIII. On the Ionic Character of a Bond

Pauling attributed additional electrostatic stabilization of heteronuclear bonds in the limit of large $\Delta\chi_{r*s}$ to ionic character measured by the contribution of the so-called"ionic resonance energy" to Δ, the extra-ionic stabilization energy.[2] This term was considered by Pauling to come from the inclusion of the ionic terms, $\Psi_{M^+-X^-}$ and $\Psi_{M^--X^+}$ in eq 1. Our model for the homonuclear chemical bond (eqs 2 and 10/18) involves only oppositely (singly) charged species. In heteronuclear bonds the charge fluctuations are slow relative to that of the homonuclear bond. The different charged states may be distinguished during some measurement times as in "heterogeneous" mixed valence system. This additional charge separation contributes to the heat of formation of heteronuclear bonds. Such a charge separation is equivalent to a transfer of lengths associated with the bonding pair of electrons ($= D^+ + D^- = 0.74$ Å) from M to X. We may thus write

$$CR^+(M) = r_{cov}(M) - (C^- - C^+)r_{core}(M)/2 - 0.74 \text{ (in Å)} \tag{35a}$$

and

$$CR^-(X) = r_{cov}(X) + (C^- - C^+)r_{core}(X)/2 + 0.74 \text{ (in Å)} \tag{35b}$$

From PMMH, the ground state is M^+-X^-. At finite temperatures, one may expect an admixture of the M^+-X^- and M^-X^+ states at finite temperatures with the equilibrium

$$M^+ + X^- \Leftrightarrow M^- + X^+ \tag{36}$$

shifted to the left. The extent of admixture of the two states is expected to decrease with an increase in the Schömaker−Stevenson contraction or the spatial mismatch, $(\Delta\chi_{r*s})$, in eqs 35 and 36. The interatomic distance at a finite temperature, $d_{M-X}^{(T)}$, is then changed by the extent of admixture, x, given by

$$\begin{aligned} d_{M-X}^{(T)} &= (1-x)d_{M-X}(M^+-X^-) + x d_{X-M}(M^-X^+) \\ &= (1-2x)d_{M-X}(M^+-X^-) + 2x[r_{cov}(M) + r_{cov}(X)] \end{aligned} \tag{37}$$

In effect, there will be an admixture of "homogeneous mixed valence" states into the "heterogeneous mixed valence" states, with an increase in bond distance. Such an admixture is expected to reduce the heat of formation. The relation $\exp(-[1/r_s(X) - 1/r(M)]/kT)$ is now a measure of the probability of mixing-in of the excited X^+-M^- state into the ground M^+-X^- state. As, what we shall term, spatial electronegativity scale $[1/r_s(X) - 1/r(M)]$ increases, one could expect, the ground state to be purely the M^+-X^- configuration, for large difference in core lengths. In this case, eqs 33 and 34 represent the maximum thermochemical quantities, (when $b = 0$) as indicated, respectively, by the dashed and full lines, in Figure 10. Pauling's interpretation of the heat of formation as an expression of "ionic character" is therefore a valid description of the bonding. However, the number and nature of terms in eq 1 require modification in the light of our interpretation relating changes in the atom−bond transition to changes in core atomic length scales.

IX. Conclusions

The present manuscript deals with the atom−bond transition, concerning itself mainly with expressing the length of the single bond between all M and X atoms and the heat of formation of heteronuclear bonds in terms of universal functions of core atomic lengths. The chemistry of elements seems to be describable simply by a Thomas−Fermi-like kernel and the bond in the hydrogen molecule. One recovers, by our approach, the "ball" and "stick" model of the classical chemist that has been so useful in understanding chemical reactions in real space. The central requirement is the existence of a universal chemical potential, $\mu_{univ} = 0$, at equilibrium. The main conclusions of our model are reminiscent of another early idea of Pauling who introduced[2] the concept of univalent radii, R_1, of atoms, which is the radii that the atoms (even if multivalent) would possess "if they were to retain their electron distribution but to enter into Coulomb interaction as if they were univalent". The approach of this communication has the following new features that rationalizes the early observation[17] wherein all single-bond interatomic (covalent, ionic, or metallic) distances, d_{M-X}, are given by the sum of components[17] associated with positive and negative charges, CR^+(M) and CR^-(X):

(i) The fundamental universal bonding length scales are those of the hydrogen molecule for which the experimental interatomic distance $d_{H-H} = D^+ + D^- \approx 4a_H/3$, where $D^+ \approx -2a_H/3$ and

$D^- = 2a_H$, may be obtained in terms of the Bohr radius of the hydrogen atom, a_H, to a close approximation.

(ii) The lengths CR^+ and CR^- are defined in the context of a universal chemical potential, $\mu_{univ} = 0$, which acts as a fixed point of reference to which every atomic constituent of a system adjusts itself when approaching/realizing equilibrium.

(iii) Arguments based on spin−orbit interaction of electrons in $l \neq 0$ orbitals are presented to show that the transferable "core" length may be derived from valence s electrons alone.

(iv) The core length, r_{core}, is best obtained from the orbital radii defined by the classical turning point, r_s, or the outermost nodal point, $\{r_{nd}{}^s\}$, of the valence s electron. A novel criterion, based on the metallisation of elements, is used to show that the orbital radii, r_s, is preferred.

(v) The formation of a chemical bond involves the delocalization of a charge from one atom to another. The atom-to-bond transition has been examined in the Thomas−Fermi screening model employed for the insulator−metal transition. On the formation of a chemical bond, these core lengths are transformed to C^+r_{core} or C^-r_{core} depending on the direction of charge transfer.

(vi) The electron/hole asymmetry of the transferred charge relative to the positively charged nucleus gives a rationale for the empirically observed feature that $C^+ < C^-$. The principal of maximum mechanical hardness[17](PMMH) that gives a justification for the direction of polarity of a bond is thus rationalized.

(vii) Upper limits to thermochemical quantities such as the "extraionic" energies for gas-phase compounds or the heats of fomation for solid-state compounds have been pointed out. These limits are based on the dissociation energy of the hydrogen molecule and the upper bounds of an excitonic binding energy.

(viii) The concept of an "ionic character" obtained from thermochemical quantities has been rationalized in terms of what has been called a Schömaker−Stevenson contraction[72] of heteronuclear bond distances relative to that obtained from the average of the corresponding homonuclear bond distances. This helps in obtaining a "spatial" electronegativity scale, from which thermochemical quantities may be obtained.

In arriving at our conclusions regarding interatomic distances in this communication, we have circumvented the problems underlying the rigorous approaches of the "new" Schrödinger equation based quantum mechanics. Instead we have relied on application of some semiclassical methods to "new" quantum mechanical results obtained in the atomic limit and a new application of the "old" Bohr model to molecules. The chemistry of elements[85] may finally be understood in terms of their core transferable atomic properties, even if additional theoretical and experimental efforts may be required to define these core lengths more accurately. Hopefully, the "ball" and "stick" model will result in identifying the participation of all chemical elements in a chemical bond as a hydrogen-atom problem. The atom-specific "core" properties of the "ball" is a function of properties of integers and the "stick" is described by the Bohr model for hydrogen-atom-like charge-transfer states. Such an approach could give rise to the much sought after universal density functional that will save on the computational time for biologically important systems. This could pave the way for a better ab initio understanding/exploiting of nature, which, finally/fortunately may be manyfold less exciting than just living with nature.

Acknowledgment. The author thanks Professor Carlo Taliani, Direttore, Istituto Spettroscopia Molecolare, Bologna, Italy, for discussions and suggestions and for providing the hospitality and the facility for finishing this manuscript, at the expense of other more concrete/interesting experiments and manuscripts. A special thanks to Dr. Peter Nozzar for a critical reading of the manuscript and enthusiasm shown for some aspects of the manuscript.

References and Notes

(1) Bragg, W. L. *Philos. Mag.* **1920**, *40*, 169. Bragg, W. L.; West, J. *Proc. R. Soc. A* **1927**, *114*, 450. Goldschmidt, V. M.; Barth, T.; Lunde, G.; Zachariasen, W. H. *Shr. Novske. Vidensk, Akad. 1, Mater.-Nat.* **1926**, *Kl.* No. 2. Zachariesen, W. H. *Z. Kristallogr.* **1931**, *80*, 137.

(2) Pauling, L. *J. Am. Chem. Soc.* **1927**, *49*, 765. Pauling, L. *Proc. R. Soc. London A* **1927**, *114*, 181. See Pauling, L. In *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, New York, 1960, Chapter 13.

(3) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr.* **1969**, *25B*, 925. Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

(4) Simons, G. *J. Chem. Phys.* **1971**, *55*, 756. Simons, G. *Chem. Phys. Lett.* **1971**, *12*, 404. Topiol, S.; Zunger, A.; Ratner, M. A. *Chem. Phys. Lett.* **1977**, *49*, 367. Zunger, A.; Cohen, M. L. *Phys. Rev. Lett.* **1978**, *41*, 53. Zunger, A.; Cohen, M. L. *Phys. Rev. B* **1979**, *20*, 581, 4082.

(5) See Laughlin, R. B. *Rev. Modern Phys.* **1999**, *71*, 863 and references therein. This point was first driven home to the author in the context of interactions leading to fractional charges and fractional quantum Hall effect. A point that requires clarification (at least to the present author) is whether atomic orbitals can ever be used for the description of molecular states when we cross a phase boundary between atomic and bonding states. Because of this, a formal connection between the present model and existing textbook level theories for chemical bonding such as valence band and molecular orbital descriptions, is not attempted. It is in any case seemingly unnecessary besides being beyond the author's present competence. The density functional approach need not suffer from such a philosophical problem.

(6) See Zunger, A. *Phys. Rev. B* **1980**, *22*, 5839 and references therein.

(7) Zhang, S. B.; Cohen, M. L.; Phillips, J. C. *Phys. Rev. B* **1988**, *38*, 12085. See also Zhang, S. B.; Cohen, M. L. *Phys. Rev. B* **1989**, *39*, 1077.

(8) (a)Bohr, N. *Philos. Mag.* **1913**, *26*, 1. (b) Bohr, N. *Philos. Mag.* **1913**, *26*, 476. (c) Bohr, N. *Philos. Mag.* **1913**, *26*, 856.

(9) For a review of the success and failure of the Bohr model see Berry, S. A. *Contemp. Phys.* **1989**, *30*, 1, and references therein.

(10) See March, N, H. *Self-Consistent Field in Atoms*, Pergamon: Oxford, **1975**.

(11) See March, N. H. *Adv. Phys.* **1954**, *3*, 1; Friedel, J. *Adv. Phys.* **1956**, *6*, 446. Resta, R. *Phys. Rev.* **1977**, *B16*, 2717.

(12) See, for example, Pilar, F. L. *Elementary Quantum Chemistry*; McGraw-Hill: New York, 1968; Chapter I.

(13) See, (a) Kolos, W.; Wolniewicz, L. *J. Chem. Phys.* **1968**, *49*, 404. (b) Kolos, W.; Roothan, C. C. J. *Rev. Modern Phys.* **1960**, *32*, 219. (c) Handy, N. C.; Lee, A. M. *Chem. Phys. Lett.* **1996**, *252*, 425. (d) See Cencek, W.; Kutzelnigg, W. *Chem. Phys. Lett.* **1997**, *266*, 383 and references therein; (e) Herzberg, G. *Phys. Rev. Lett.* **1969**, *23*, 1081.

(14) Pauling, L. *J. Am. Chem. Soc.* **1932**, *54*, 3570. See Pauling, L. In *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press: Ithaca, New York, 1960, Chapter 3.

(15) Garcia, A.; Cohen, M. L. *Phys. Rev. B* **1993**, *47*, 4221.

(16) Meister, J.; Schwarz, W. H. E. *J. Phys. Chem.* **1994**, *98*, 9245.

(17) Ganguly, P. *J. Am. Chem. Soc.* **1995**, *117*, 2655.

(18) Levinthal, C. In *Mössbayer Spectroscopy in Biological Systems*; Debrunner, P., Tsibris, J. C. M., Munck, E., Eds.; University of Illinois Press: Urbana, 1969: pp 22−24. Levinthal, C. *J. Chim. Phys.-Chim. Biol.* **1968**, *65*, 44.

(19) See Zwanzig, R.; Szabo, A.; Bagchi, B. *Proc. Natl. Acad. Sci.*, U.S.A. **1992**, *89*, 20.

(20) 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). The Bohr model for the hydrogen atom yields the total energy, $E^H{}_{tot}$, in terms of contribution from the kinetic energy, E_{kin}, and potential energy, E_{pot}, given by $E^H{}_{tot} = E_{kin} + E_{pot} = (\hbar/r)^2/2m_o - e^2/\epsilon r$, where m_o is the free electron mass and ϵ is the dielectric constant. $E_{kin} = \mathrm{p}^2/2m_o = (\hbar/r)^2/2m_o$ (from the uncertainty relation, Δp, $\Delta r = \hbar$) and $E_{pot} = -e^2/\epsilon\ r$. From the condition for the minimization of energy, one obtains $0 = \mathrm{d}E^H{}_{tot}/\mathrm{d}r = (-\hbar^2/r^3)(1/m_o) + e^2/\epsilon \mathrm{r}^2$. The value of r satisfying this condition is then defined as the Bohr radius, a_H, given by $a_H = \hbar^2 \epsilon/m_o e^2 = 0.53$ au, so that under stationary conditions $E^H{}_{tot} = m_o e^4/2\epsilon^2\hbar^2 - \mathrm{m_o e^4}/\epsilon^2\hbar^2 = -m_o \mathrm{e}^4/2\epsilon^2\ \hbar^2 \sim e^2/2\epsilon a_H \sim -13.6$ eV when $\epsilon = 1$.

(21) See Banyai, L.; Koch, S. W. *Phys. Rev. Lett.* **1986**, *57*, 2722 and references therein.

(22) The classical Bohr approach to the H_2 molecule is to extend the one-nucleus two-electron model for the He atom to the two-nuclei-two-electron hydrogen molecule and end up with singular, nonintegrable, and multidimensional Hamiltonian) See A. López-Castillo, A. *Phys. Rev. Letts.* **1996**, *77*, 4516 and references therein).

(23) In homonuclear M−M bonds, the charge-transfer states are degenerate with respect to the direction of charge transfer. Because of this there is likely to be a rapid fluctuation between the two possible charged configurations of the atoms constituting the bond. As long as the fluctuation time is fast compared to the measurement time, the measured charge-difference on the two atoms will average out to zero. The length scales in the bonding direction remain unaffected, however. Such an averaging in intermediate valence systems is discussed in terms of the homogeneous mixed valence systems in condensed matter studies (For a review see Lawrence, J. M.; Rizeborough, P. S.; Parks, R. D. *Rep. Prog. Phys*. **1981**, *44*, 1. Wohlleben, D. K. In *Valence Fluctuation in Solids*, Falicov, L. M., Hanke, W., Maple, M. B., Eds.; North-Holland: Amsterdam, 1981; pp 1−10. Ramakrishnan, T. V. *J. Magn. Magn. Maters*. **1987**, *63,64*, 529. Nowik, I. *Hyperfine Interact.* **1983**, *13*, 89.

(24) Su, W. P.; Schrieffer, J. R.; Heeger, A. J. *Phys. Rev. B* **1980**, *22*, 2099. Su, W. P.; Schrieffer, J. R. *Phys. Rev. Lett.* **1981**, *46*, 738 and references therein.

(25) Kivelson, S. A.; Rokhsar, D. S.; Sethna, J. P. *Phys. Rev. B* **1987**, *35*, 8865. Anderson, P. W.; Baskaran, G.; Zou, Z.; Hsu, T. *Phys. Rev. Lett.* **1987**, *58*, 2790.

(26) We note in passing that the ratio $2a_H/(a^{ee}{}_H + a^{eh}{}_H) = 1.5$ obtained from the model may be tied to the early Coulson−Fischer observation (Coulson, C. A.; Fischer, I. *Philos. Mag*. **1949**, *40*, 386) that $R/R_{eq} = 1.6$ sets the chemical bond criterion for the breaking of chemical bond (lack of spin-pairing) of the hydrogen molecule, as a function of the internuclear separation, R, with R_{eq} being the calculated value for the equilibrium separation.

(27) This discrepancy is expected if we consider mixing in of higher principal quantum number Bohr states (see ref 12). Such effects may be included by considering the local effective dielectric constant, ϵ_{H-H}, of the bond in the hydrogen molecule, to be greater than unity, and consider only the ground state. In this particular case, we would require the effective dielectric constant, $\epsilon_{H-H} \approx 0.74/0.71 \approx 1.04$, at room temperature.

(28) Sanderson, R. T. *Science* **1951**, *114*, 670.

(29) Politzer, P.; Weinstein, H. *J. Chem. Phys.* **1979**, *71*, 4218.

(30) Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. *J. Chem. Phys.* **1978**, *68*, 3801. Levy, M. *Proc. Natl. Acad. Sci.,* U.S.A. **1979**, *76*, 6062. Levy, M. *Phys. Rev. A* **1982**, *26*, 1200.

(31) Komorowski, L. *Chem. Phys.* **1983**, *76*, 31.

(32) See Alonso, J. A.; Balbas, L. C. *Struct. Bonding* **1987**, *66*, 41.

(33) Icskowski, R. P.; Margrave J. L. *J. Am. Chem. Soc.* **1961**, *83*, 3547.

(34) The constraints for the minimization of energy is here taken in the context of chemical bond and its equilibrium distance, r_{eq}, such that at this equilibrium separation the density is the correct density, ρ(eq).

(35) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *136*, B864.

(36) Bader, R. F. W. *Atoms in Molecules − A Quantum Theory*; Oxford University Press: Oxford, 1990.

(37) Mulliken, R. S. *J. Chem. Phys.* **1934**, *2*, 782. Mulliken, R. S. *J. Chem. Phys.* **1935**, *3*, 573.

(38) See Parr, R. G. *Annu. Rev. Phys. Chem.* **1983**, *34*, 631. Kohn, W.; Becke, A. D.; Parr, R. G. *J. Phys. Chem.* **1996**, *100*, 12974. March, N. H. *Int. J. Quantum Chem.* **1999**, *74*, 163. Kunne, L. *Int. J. Quantum Chem.* **1999**, *74*, 55.

(39) Komorowski, L. *Chem. Phys.* **1987**, *114*, 55. *Chem. Phys. Lett.* **1983**, *103*, 201.

(40) In the density functional theory (March, N. H. *J. Phys. Chem.* **1982**, 2262. Parr, R. G. *Annu. Rev. Phys. Chem.* **1983**, *34*, 631. Spruch, L. *Rev. Modern Phys.* **1991**, *63*, 1351), the chemical potential, μ, for many electron systems is given by $\mu = \delta T/\delta\rho(r) - V(r) + \delta\epsilon_x/\delta\rho(r) + \delta\epsilon_c/\delta\rho(r)$ where $\rho(r)$ is the electron density function, $T[\rho]$, $\epsilon_x[\rho]$, and $\epsilon_c[\rho]$ are, respectively, the kinetic, exchange, and correlation energy functionals and $V(r)$ is the total electrostatic potential. The special case of $\mu_{univ} = 0$ corresponds to the condition when $\delta T/\delta\rho(r) = -(\delta\epsilon_x + \delta\epsilon_c)/\delta\rho(r)$ and $V(r) = 0 = \mu$.

(41) So far, the view has been that the Thomas−Fermi model is not expected to lead to chemical bonding and that exchange terms are necessary (see ref 32 for a discussion). This yield the Thomas−Fermi−Dirac model for the atom with a universal value of the chemical potential, $\mu_{univ}{}^{TFD} = 1/2\pi^2$. In our model, we consider the ground state to define/necessitate/impose an $\mu_{univ} = 0$ condition.

(42) Gunnarsson, O.; Johansson, P. *Int. J. Quantum Chem.* **1976**, *10*, 307. Gunnarsson, O.; Lundqvist, B. I. *Phys. Rev. B* **1976**, *A52*, 751.

(43) It has to be noted that in such spin-density functional formalisms (see ref 42) there is a sum rule arising out of charge conservation that requires the exchange correlation hole to correspond to the removal of one electron charge. The expression of the internuclear distance as a sum of radii associated with two integral charges of opposite sign, is consistent with this picture.

(44) It follows from the notes in ref 40 that when $V(r) = 0 = \mu$, the exchange and correlation are balanced out by the kinetic energy term. The conversion of spin to charge by pairing of electrons results in the residual interactions being only electrostatic in nature, with the cancellation of exchange and correlation terms by the kinetic energy term. This cancellation is reminiscent of the early, and trend-setting, theorem (Phillips, J. C.; Kleinmann, L. *Phys. Rev.* **1958**, *116*, 287. Cohen, M. H.; Heine, V. *Phys. Rev.* **1961**, *122*, 1821) involving cancellation of the potential energy terms of core states by the kinetic energy terms.

(45) See Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Eng.* **1972**, *11*, 92, for example. (a) The distinction between spin-pairing and charge separation is similar to the proposal of covalent and zwitterion formation. (b) It is well known that conservation of angular momentum may be violated when there is spin−orbit coupling. Our argument is the reverse of this, since we claim that spin-charge conversion is not favored because strict angular momentum conservation may be violated.

(46) The crystal field of neighboring atom(s) is known to quench orbital moments (See Martin, D. H. *Magnetism in Solids*; London Iliffe Books Ltd., 1967, p 135) of $l \neq 0$ orbitals, to first order. It requires to be examined whether such an averaging also averages out the spin moments because of the vectorial spin−orbit coupling. The exchange field, $H^{ex}{}_{AB}$, experienced by an external B atom spin, S_B, in an $\langle S_A\rangle S_B$ coupling due to the *A*-atom spin, will be vanishingly small when the value (to first order) of spin angular momentum of an A atom, $\langle S_A\rangle$, is averaged to zero, within the time scales of the exchange interaction.

(47) See Feynman, R. P. *The Feynman Lectures on Physics*, Quantum Mechanics, (Indian Edition); Addison-Wesley Publishing Co.: Reading, MA, 1965; Vol. II, pp 35:3; Vol. III. pp 5:1. See also Batelaan, H.; Gay, T. J.; Schwendiman, J. J. *Phys. Rev. Lett*. **1997**, *79*, 4517.

(48) Politzer, P.; Parr, R. G.; Murphy, D. R. *J. Chem. Phys.* **1983**, *79*, 3859. Politzer, P.; Parr, R. G.; Murphy, D. R. *Phys. Rev. B* **1985**, *31*, 6809.

(49) Sen, K. D.; Politzer, P. *J. Chem. Phys.* **1989**, *90*, 4370. Sen, K. D.; Politzer, P. *J. Chem. Phys.* **1989**, *91*, 5123.

(50) Deb, B. M.; Singh, Ranbir; Sukumar, N. *THEOCHEM* **1992**, *91*, 121.

(51) Nagle, J. K. *J. Am. Chem. Soc.* **1990**, *112*, 4741.

(52) Zunger, A. *J. Chem. Phys.* **1981**, *74*, 4209. Zunger, who first noticed the near equality of these two length scales, ignored the significance of $\{r_{nd}{}^s\}$ because the corresponding values of the valence p electrons showed clearly different relationship from those of the p electron orbital radii, r_p.

(53) Politzer, P.; Parr, R. G. *J. Chem. Phys.* **1976**, *64*, 4634. Boyd, R. J. *J. Chem. Phys.* **1977**, *66*, 356.

(54) Zhang, S. B.; Cohen, M. L.; Phillips, J. C. *Phys. Rev. B* **1987**, *36*, 5861.

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

(56) Mott, N. F. *Proc. Cambr. Philos. Soc.* **1936**, *32*, 281. Although Mott addressed himself to the many-body problem of the insulator−metal transition, the arguments involved the effects of screening of a single Bohr atom.

(57) See March, N. H. *Adv. Phys*. **1954**, *3*, 1. Friedel, J. *Adv. Phys.* **1956**, *6*, 446. Resta, R. *Phys. Rev.* **1977**, *B16*, 2717.

(58) Calkin, M. G.; Nicholson, P. J. *Rev. Mod. Phys.* **1967**, *39*, 361.

(59) (a) Edwards, P. P.; Sienko, M. J. *Phys. Rev. B* **1978**, *17*, 2575. (b) See also Edwards, P. P.; Senko, M. J. *Acc. Chem. Res.* **1982**, *15*, 87.

(60) Mott, N. F. *Can. J. Phys.* **1956**, *34*, 1356. Mott predicted that the critical concentration, n_c, at which the insulator−metal transition is observed is given under certain conditions obtained from approximations of the hydrogen atom ($E \sim 0.1\ I$, where E is the electron affinity and I is the ionisation potential) by $n_c a_H{}^{1/3} \sim 0.25$ and that the effective radius, a_{eff}, of the Bohr-atom-like object is given by $a_{eff} = Xa_H$ with $X \sim 2.2$.

(61) The use of a close-packed volume fraction is important as it emphasizes the points of closest contact between two lines. The largest number of such lines, for a given size of the Bohr-like atom, is obtained from a close-packing model.

(62) There is no requirement that the bound electron pair is localized in a particular region in space or is even real. The only requirement is that the expression for the distance is obtained from a description equivalent to a screened metallic core and a bound electron pair, the length scales of the bound pair being described by a Bohr-like model (Section II).

(63) Julg, A.; Julg, P. *Int. J. Quantum Chem.* **1978**, *13*, 483. It was Bader and Stephens (Bader, R. F. W.; Stephens, M. E. *J. Am. Chem. Soc.* **1975**, *97*, 7391. Bader, R. F. W.; Stephens, M. E. *Chem. Phys. Lett.* **1974**, *26*, 445) who first stressed the necessity of analyzing the pair density as the simplest theoretical quantity describing the behavior of an electron pair in microscopic systems.

(64) Politzer, P. *J. Chem. Phys.* **1980**, *72*, 3027.

(65) One expects, for example, $D^{\pm}$ to increase with increasing polarizability or increasing local dielectric constant, ϵ_{H-H}, of the bonding pair of electrons. A similar increase in the dielectric constant could reduce the magnitude of the attractive terms of the core, so that the orbital radius may actually increase with pressure.

(66) Herzfeld, K. F. *Phys. Rev.* **1927**, *29*, 701.

(67) The principle of maximum mechanical hardness, which requires simply that mechanical hardness be related to equilibrium interatomic distances and that the hardness, is related to the extent of shortening of this distance for a given external field. This problem is consistent with the expectation that the stabilization energy will be inversely related to the

interatomic separation. See also Pearson, R. G. *J. Chem. Ed.* **1999**, *76*, 267 and references therein for a discussion on physical hardness.

(68) St. John, J.; Bloch, A. N. *Phys. Rev. Lett.* **1974**, *33*, 1095.

(69) (a) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533. (b) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512. (c) See Pearson, R. G. *Acc. Chem. Res.* **1990**, *23*, 1.

(70) Müller-Erzbach, W. *Annales* Vol. 221, p 125 as cited in *J. Chem. Soc.* **1884**, *46*, 23.

(71) It is also consistent with the philosophy of Pearson's hard-soft-acid-base principle, which, of course, forms a cornerstone of some of the modern approaches in chemistry. There has been some debate (Sebastian, K. L. *Chem. Phys. Lett.* **1994**, *231*, 40. Chattaraj, P. K.; Liu, G. H.; Parr, R. G. *Chem. Phys. Lett.* **1995**, *237*, 171) on the validity of the proof of the principle given by Parr and Chattaraj (Parr, R. G.; Chattaraj, P. K. *J. Am. Chem. Soc.* **1991**, *113*, 1854. Parr, R. G.; Chattaraj, P. *J. Am. Chem. Soc.* **1991**, *113*, 1856. The debate concerns the constancy of the external potential used. In our opinion, the requirement of a universal equilibrium chemical potential, $\mu_{\text{univ}} = 0$, in Section II, satisfies the conditions assumed by Parr and Chattaraj.

(72) Schömaker, V.; Stevenson, D. P. *J. Am. Chem. Soc.* **1941**, *63*, 37.

(73) Pauling's definition (see ref 14) of electronegativity is based on the observation of an extraionic energy term, Δ, which contributes to an additional bond energy of heteronuclear bonds. Δ is given by the difference between the actual bond energy D(M−X) of the heteronuclear bond and the *arithmetic* mean of the bond energies D(M−M) and D(X−X) of the corresponding homonuclear bonds $\Delta = D(\text{M}-\text{X}) - 0.5\{D(\text{M}-\text{M}) + D(\text{X}-\text{X})$. In such a definition, Δ is in the exothermic direction.

(74) Ganguly, P. *J. Am. Chem. Soc.* **1995**, *117*, 1777.

(75) The standard heat of formation is a quantity that relates to changes in energies relative to a standard state. As such it is expected to be a measure of the stability of the ground state. However, Pauling's interpretation of electronegativity is for an isolated atom and the heat of formation concerns the reactivity of these isolated atoms with reactive unpaired electrons, which is a measure of the energy liberated on reaching the standard state, which, in our model, is the charged, $\mu_{\text{univ}} = 0$ state. A quantitative relation between length scales describing ground-state properties and heat of formation is not anticipated.

(76) Yin, M. T.; Cohen, M. L. *Phys. Rev. Lett.* **1980**, *45*, 1004. Chang, K. J.; Cohen, M. L. *Phys. Rev. B* **1984**, *30*, 5376. Cohen, M. L. *Science* **1986**, *234*, 549. Gordy, W. *Phys. Rev.* **1946**, *69*, 604. Nagle, J. K. *J. Am. Chem. Soc.* **1990**, *112*, 4741. Garcia, A.; Cohen, M. L. *Phys. Rev. B* **1993**, *47*, 4221.

(77) Ganguly, P., to be published. These relationships are applicable to binary compounds of multivalent metals when one considers the heat of formation per atom of the more electronegative element X. These equations, in their present form, are obviously not applicable to compounds of hydrogen.

(78) The data for the heat of formation per atom of the more electronegative element, X, of a binary MX*n* compound, in the gas phase, Δ^{X}, and in the crystalline state, Δ_f^{X}, have been taken mainly from; *Lange's Handbook of Chemistry*, 13th ed.; Dean, J. A., Ed.; McGraw-Hill: New York; 1985; Chapter 9. (b) See also Pritchard, H. O.; Skinner, H. A. *Chem. Rev.* **1955**, *55*, 745. (c) Pauling, L. *J. Am. Chem. Soc.* **1932**, *54*, 3570. (d) See Pauling, L. In *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, New York, 1960, Chapter 3. (e) see Ganguly, P.; Venkatraman, T: N.; Pradhan, S.; Rajamohanan, P. R.; Ganapathy S. *J. Phys. Chem.* **1996**, *100*, 5017, in which the maximum value of Δ_f^{X} for solids has been first shown to be approximately −160 kcal/g at X.

(79) The use of eq 33 is somewhat unsatisfactory in many cases such as the C−Cl bond. The Cl atom ($r_G = 0.52$ au) is expected to be more electropositive as compared to C ($r_G = 0.32$ au) which seemingly contradicts the results of Pauling's electronegativity scales. Similarly, the PMMH principle (see ref 17) requires H to be the more electronegative atom in all M−H bonds. This aspect requires further clarification and will be discussed in a separate communication. Equations 33 and 34 are meant for illustrative purposes at the moment.

(80) The relationship 1.5 $(\Delta H_f^{\circ})^{\text{X}}$(gas) ∼ $(\Delta H_f^{\circ})^{\text{X}}$(solid) of eqs 25 and 26 is found to hold for the same MX_n compounds when they are as the alkali metal halides, alkaline-earth halides, halides of the rare-earth elements, Sb, As, Ga, Al, Y besides ScF_3, as well as other compounds such as B_2O_3, CsOH, Ba(OH)_2, etc. The exceptions are generally multinuclear or multi-atomic clusters, and strongly covalent molecules including the more "covalent" compounds such as NbCl_5, IrF_6, MoO_3, or clusters such as As_4O_6, Al_4C_3, $\text{Mn}_2(\text{CO})_{10}$, which show $\Delta^{\text{X}} \sim \Delta H_f^{\text{X}}$.

(81) b becomes important at large values of $\Delta\chi_{\text{r*s}}$, or large values of $r_{\text{s}}(\text{M}) - r_{\text{s}}(\text{X})$. For these large differences, the repulsive interactions between the M atoms may become important. At the same time, the distance between the metal atoms becomes comparable to that in the elements themselves. This could lead to direct M−M interactions, which eventually leads to a reduction in the value of the heat of formation which is referenced to the standard elemental state.

(82) See, for example, Lowe, J. P. *Quantum Chemistry*, 2nd ed.; Academic Press: New York, 1993; p 376.

(83) The ground-state excitonic binding energy $E_{\text{exc}} = \mu e^4/(h^-)^2\epsilon^2 \sim 6.8$ eV ∼ 159 eV (see Kittel, C. *Introduction to Solid State Physics*, 4th ed.; John Wiley & Sons: New York, 1971; pp 612) when $\epsilon = 1$.

(84) Vijh, A. K. *J. Phys. Chem. Solids* **1968**, *29*, 2233. Vijh, A. K. *J. Mater. Sci.* **1970**, *5*, 379.

(85) A major part of chemistry deals with multivalent bonds. A relationship between multiple bond distances and single bond distances has been made earlier (refs 17 and 74). In this treatment, the number of unsaturated valence electrons, n_v, is expressed in terms of a spin S $(= n_v/2)$. The length scales are then reduced by an S-dependent quantity, F_{s} which has been empirically shown to be given by $F_{\text{s}} = 1.18[\text{S}(\text{S} + 1)]^{0.08} \sim \{2\ln 2\text{-}[S(S + 1)]^{1/2\pi}\}^{1/2}$. The explanation of the shortening of multiple bonds as well as rationalizations of electronegativity scales will follow in another communication, once the premises of this communication find some acceptance.