

Atomic Sizes and Atomic Properties

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Abstract. We examine the dependence of atomic properties on a new atomic size, r_{nZ}^c , that has been rigorously defined by the presence of an interaction without depending on the strength or nature of the interaction. We have thus related the static dielectric polarizability radius, r_α , the inverse of the first ionization potential, I^{-1} , the inverse of Pauling electronegativity scale, χ_P^{-1} , and the size CR of atoms that contribute to interatomic distance involving atoms of the main group elements in the periodic table. There is a linear relationship between a size-dependent atomic property P of the form $P = C_P r_{atom} + D_P$ where r_{atom} is a simple and transparent function of r_{nZ}^c and D_P is simply related to the property of the hydrogen atom, except for $P = I^{-1}$ when D_P is a property of the occupancy of the valence s - and p - electrons. We find a strict criterion for metallicity in elements based on atomic sizes and show how this criterion can be used for accounting for changes in descriptions of interatomic distance for gas-phase MX compounds of metallic elements.

1. Introduction.

Modern demands in chemistry require an understanding from first principles of complex molecular structures involved in the design of, say, molecular electronics, or pharmaceutical compounds or biotechnology. Given the environmental risks arising from a lack of symbiotic understanding of complex natural processes and simplified industry-based ephemeral logic, it is most important that a simple methodology is found that rigorously accounts for complex molecular structures without running into exponential computational time-walls. In recent years there has been a search (Ayers 2000, 2007, De Proft *et al* 2004) for fundamental non wave-function-based descriptors, other than the electron density, that enables a full description of the system with a clear and simple interpretation (Ayers 2007).

We have recently obtained a simple theoretical description of atomic sizes, r_{nZ}^c (Ganguly 2007a), using a classical stationary point. The basic and novel premise of this model is that the external interaction is represented by the absorption or emission of a virtual photon which, in turn, is represented by an electron-hole pair, (e^-h^+) . An atom-specific size, r_{atom} , is obtained by considering the interaction of the outer-electrons with the hole, h^+ , of the electron-hole pair that represents the external interaction. The size r_{nZ}^c is obtained essentially as the equivalent of the "first Bohr size" of the inverted hydrogen atom (negative charges due to outer electrons of the "heavy atom" and light bound hole). Because h^+ is a universal component of the external interaction field, (e^-h^+) , the atomic sizes thus obtained are not dependent on the actual nature of the external interaction. Instead, it is atom-specific, being dependent only on the way the outer electrons are distributed, say, between the valence and inner shells, as well as the way the d - and f - electrons of transition metal elements are treated. Because of this Bohr-model-like formalism, this description predates Schrödinger and Thomas-Fermi (DFT) theory. It avoids being archaic by incorporating important post Schrödinger or DFT insights in several ways. We show in this submission how important atomic properties such as static dielectric polarizability, α , first

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ionization potential, I , electronegativity, χ , and atomic sizes contributing to interatomic distances may be obtained as a linear function of atomic sizes with a clear and simple interpretation.

The core atomic size, r_{nZ}^c of an atom in row η ($= n + 1$, where n is the principal quantum number) of the long periodic table is given by (Ganguly 2007a, part of this treatment appears in appendix of Ganguly and Desiraju, 2008)

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

where r_{nv} is a contribution from n_{val} valence s - and p - electrons (obtained from the position of the atom in the periodic table) and $r_{RG(\square-1)}$ is a contribution from $Z_{RG(\eta-1)}$ core electrons with rare-gas configuration, $RG(\square-1)$. It has been found (Ganguly 2007a) that

$$r_{nZ}^c(\eta) = 1/[n_{val}(-1)^b \ln\{(1 + n_d^\pm + (n_f^+/2))^{1/3}\}] + (\xi a_H/2') [\ln(Z_{RG(\eta-1)}^{1/3})] = r_{core} \quad (2)$$

with $b = 1$ for less than half-filled d orbitals $b = 0$ for more-than half-filled d orbitals; $\xi = 1$ for all elements except Li and Na when $\xi = 1/2$; n_d^\pm is the number of empty (+) or filled (-) d -orbitals and $n_f^+/2 = (14 - n_f)/2$, n_f being the number of f electrons. The first term in eqn 2 is to be regarded as the “valence shell” size, r_{nv}^c of eqn 1 and the second term in eqn 2 as the corresponding “inner shell” size, $r_{RG(\square-1)}$. See Table 1 for some examples of using eqn 2.

Table 1. Examples of various parameters used in eqn 2 for obtaining r_{nZ}^c and $(r_{nZ}^c)^*$ (in a.u.)

Atom	Z	n_{val}	n_d	n_f	Z_{RG}	r_{nZ}^c a.u.	$\{r_{nZ}^c\}^*$ a.u.
Li [@]	3	1	0	0	2	1.06	1.03
Be	4	2	0	0	2	0.62	0.59
F	9	7	0	0	2	0.26	0.23
Mg	12	2	0	0	10	0.88	0.69
S	16	6	0	0	10	0.55	0.36
Ca	20	2	5	0	18	1.19	0.95
Mn	25	2	0	0	18	0.98	0.52
Zn	30	2	5	0	18	0.87	0.53
Ga	31	3	0	0	18	0.81	0.57
Kr	36	8	0	0	18	0.61	0.36
Mo	42	2	1	0	36	1.16	0.63
Sb	51	5	0	0	36	0.80	0.499
Xe	54	8	0	0	36	0.72	0.42
Cs	55	1	0	0	54	1.66	1.33
Ba	56	2	5	0	54	1.54	1.21
La	57	2	4	0	54	1.52	1.00
Sm	62	2	4	5	54	1.46	0.96
Eu	63	2	4	6	54	1.45	0.95
Hg	80	2	5	0	54	1.05	0.61
Pb ^{IV}	82	4	0	0	54	0.91	0.58
Pb ^{II}	82	2	0	0	54	1.16	0.83

@: $\xi = 0.5$ for Li and Na in eqn 2

We seek to show in this communication that a size-dependent atomic property, P , such as the electric polarizability radius, r_α (see Politzer *et al* 2002, Hati and Datta 1994, Nagle 1990; Banerjee and Harbola 1999, Ghanty and Ghosh 1996), the inverse of the first ionization potential, I^{-1} (Fricke 1986, Pearson 1988, Politzer *et al* 1991, Banerjee and Harbola 1999), or atomic sizes CR , contributing to interatomic distances [Ganguly 1995a, Ganguly 2000] may be expressed in terms of a function, $f(r_{nZ}^c)$, of an atomic size, r_{nZ}^c (Ganguly 2007a), as

$$P = C_P f(r_{nZ}^c) + D_P \quad (3)$$

The coefficient C_P is an atom-independent constant for a given property and D_P is the property of a fundamental atom (H or He). The function $f(r_{nZ}^c)$ is not expected to be proportional to r_{nZ}^c for properties that involve an external measuring field (such as r_α or χ_P^{-1}) or changes in the external potential when the chemical potential $\mu \neq 0$.

2. Polarizability Radius, r_α .

The static electronic dipole polarizability, α , may be described the linear response of the electron cloud of a chemical species to an external electric field that is less than that needed to ionize the system. For the purpose of this paper it is best characterized by its polarizability radius, $r_\alpha = \alpha^{1/3}$ with the units of polarizability being a volume (Brinck *et al* 1993, Politzer *et al* 2002). The theoretically computed mean valence radius, r_m , introduced by Garcia and Cohen (1993) is a

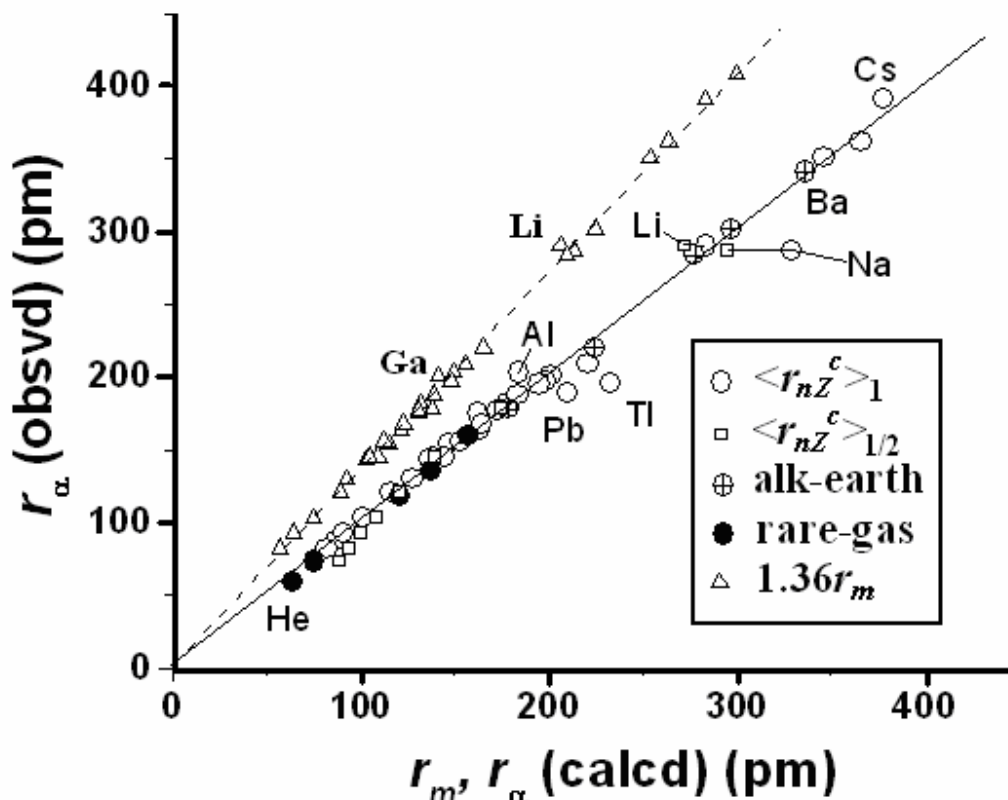


Fig 1. Plot of $r_\alpha(\text{obsvd})$ (from Nagle, 1990) vs the theoretical mean valence radius, r_m (triangles) (r_m from Garcia and Cohen, 1993) and $r_\alpha(\text{calcd}; \text{circles})$ (eqns 4 and 5; $\langle r_{nZ}^c \rangle_1$ and $\langle r_{nZ}^c \rangle_{1/2}$ are values of $\langle r_{nZ}^c \rangle$ calculated with $\xi = 1$ for all elements except Li and Na when $\xi = 1/2$ in eqn 2). Full line: guide to the eye for $r_\alpha = \langle r_{nZ}^c \rangle$; dashed line: $r_\alpha = 1.36r_m$.

measure of atomic size in terms of Gordy's (1946) total valence charge, Z_v , with $r_m = (1/Z_v) \int r \rho_v dV$ where r is the radial coordinate, ρ_v is the spherically symmetric valence charge distribution, the integration extending over all space. From the plot of the polarizability radius, $r_\alpha(\text{obsvd})$ (see Nagle 1990) vs r_m for s - and p -block (Fig 1), we obtain $r_\alpha \approx 1.36r_m$ from the best fit ($R = 0.999$, better than that obtained in Politzer *et al* (1991)). Because of the goodness of the fit the static polarizability radius r_α is likely to be an average property of valence electrons.

The “valence electron” size has already the property of an average valence size, since it is related to $1/n_{\text{val}}$. We now define—modifying eqns 1 and 2— $\langle r_{\text{RG}(\eta-1)} \rangle$ as an average “inner-shell” size, for an average one-dimensional density $\langle N_{1D} \rangle \equiv 0.5[\{(Z_{\text{RG}(\eta-1)})/n_{\text{val}}\}^{1/3}]$ with $\langle r_{\text{RG}(\eta-1)} \rangle = (a_H/2) \ln[\langle N_{1D} \rangle]$. This gives an average size (Ganguly 2007)

$$\langle r_{nZ}^c \rangle = r_{nv}^c + (a_H/2) [\ln\{(Z_{\text{RG}(\eta-1)})/n_{\text{val}}\}^{1/3}] \quad (4)$$

Since r_{nZ}^c for any atom is obtained from a hydrogen-atom-like model (Ganguly 2007a), quantitative insights into the polarizability of atoms in general are expected from an understanding of the polarizability of the hydrogen atom, $\alpha(\text{H})$. The exact quantum mechanical expression (see Purcell 1985, Politzer *et al* 2002) for is obtained as $\alpha(\text{H}) = 4.5a_H^3$ or $r_\alpha(\text{H}) = \{\alpha(\text{H})\}^{1/3} \approx 1.65a_H \approx 87.3$ pm. We may now anticipate from the form of eqn 3 that for hydrogen-like M atoms

$$r_\alpha(\text{obsvd})(\text{M}) \equiv 1.65[A_\alpha(\text{M}) \langle r_{nZ}^c \rangle(\text{M}) + A_\alpha(\text{H})a_H] \quad (5a)$$

The best fit (excluding He and Na for which $\langle r_{nZ}^c \rangle$ may not be unambiguously obtained and Tl and Bi which have more than 5% error in the experimental polarizability) of the plot of $r_\alpha(\text{obsvd})$ vs $\langle r_{nZ}^c \rangle_0$ (in pm) is given in eqn 5b with $A_\alpha(\text{M}) \approx 2$.

$$r_\alpha(\text{obsvd})(\text{M}) = 1.65[1.98\langle r_{nZ}^c \rangle_0(\text{M}) + 1.077a_H] \quad (R > 0.998) \quad (\text{from best fit}) \quad (5b)$$

The size $2\langle r_{nZ}^c \rangle$ correspond to the “Bohr size” for principal quantum number, $n_h = 2$ (first excited state) of the “inverted” Bohr atom just as $\langle r_{nZ}^c \rangle$ is obtained (Ganguly 2007) for $n_h = 1$ (first “Bohr size”). Eqns 5a and 5b are consistent with eqn 3. It suggests that the polarizability radius of an atom may be written as a sum of two contributions—an atom-specific “core” contribution with “ $a_H(\text{core})$ ” = $2\langle r_{nZ}^c \rangle$ —and an atom-independent hydrogen-atom-like contribution from a size $A_\alpha a_H$ ($= 1.077a_H \sim 58$ pm).

From a simple geometrical point of view, the polarizability radius, $r_\alpha(\text{M})$ of an atom M (\neq H or He) is obtained from an atomic volume, $V_\alpha(\text{M})$. From eqn 5b we relate r_α to $V_\alpha(\text{M})$ as

$$V_\alpha^{1/3}(\text{M}) \equiv \alpha(\text{M})^{1/3} \equiv r_\alpha(\text{M}) = 1.024(4\pi/3)^{1/3}[2\langle r_{nZ}^c \rangle(\text{M}) + A_\alpha(\text{H})a_H]. \quad (6)$$

This classical and surprisingly sufficient expression avoids constraints of selection rules required for the exact quantum mechanical formulation involving l and m quantum numbers. It is to be noted from Fig 1 that our method gives fairly accurate values for heavy atoms without requiring relativistic corrections. For example, the polarizability of cesium may be treated as an ideal benchmark for testing theoretical treatments. The relativistic corrections for cesium are believed to reduce polarizability by as much as 14% (Amini and Gould 2003). Our method give $r_\alpha(\text{Cs}) = 384$ pm against the observed (Amini and Gould 2003) value of ~ 390.1 pm.

3. First Ionization Potential, I .

We express I of main-group atoms (Fricke 1986, Pearson 1988, Politzer *et al*, 1991) through its inverse, I^{-1} , as (to be consistent with eqn 3)

$$E_H/I = (B r_{nZ}^c + R_0) \quad (7)$$

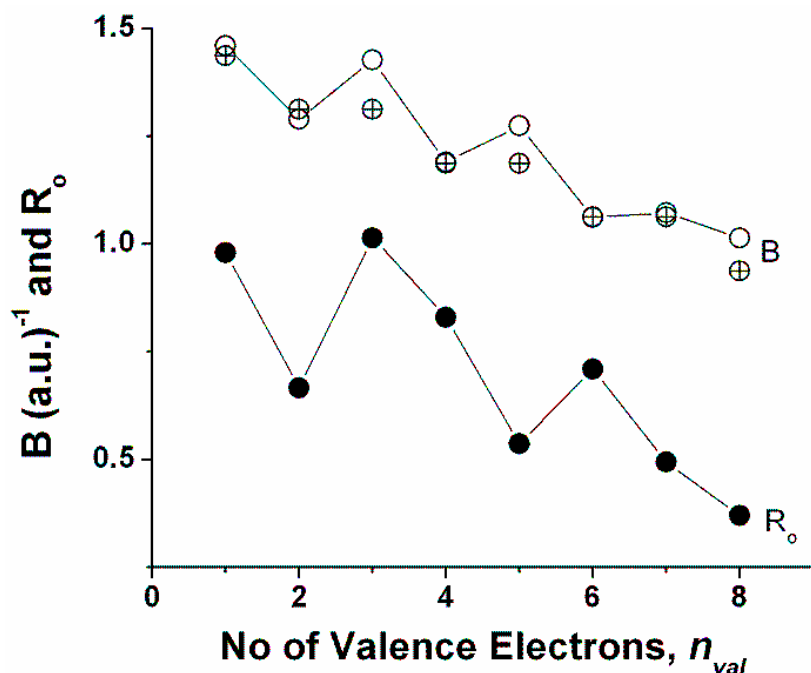


Fig 2. Plots of B (open circle) and R_o (filled circle) obtained from eqn 7 (Table 1) vs n_{val} , the nominal number of valence s - and p - electrons. Circles with cross inset: B calculated from eqn 8.

Table 2. Systematics of Changes in First Ionization Potential, I (from Politzer *et al* 1991), as a function of core Atomic Size, r_{nZ}^c using eqn 7.

Group	B	R^h	R_o^i	$R_o(\text{cal})^j$	Orbital Occupancy
I ^a	1.56	0.989	0.83	1.00	$\langle \uparrow \rangle$
I ^b	1.46	0.997	0.98	1.00	$\langle \uparrow \rangle$
II ^c	1.29	0.998	0.67	0.67	$\langle \uparrow, \downarrow, \text{—} \rangle$
II ^d	1.39	0.998	0.55	0.50	$\langle \uparrow \downarrow \rangle$
I+III ^e	1.38	0.989	1.01	1.00	$\langle \uparrow \rangle$ and $\downarrow \uparrow, \langle \uparrow \rangle$
IV	1.17	0.968	0.83	0.83	$\langle \uparrow \downarrow, \uparrow, \uparrow \rangle$
V	1.26	0.998	0.54	0.50	$\uparrow \uparrow \uparrow \langle \uparrow \downarrow \rangle$
VI	1.06	0.998	0.71	0.75	$\langle \uparrow \downarrow, \uparrow \downarrow, \uparrow, \uparrow \rangle$
VII	1.07	0.998	0.49	0.50	$\uparrow \downarrow, \uparrow \downarrow, \uparrow \langle \uparrow \downarrow \rangle$
VIII ^f	1.01	0.995	0.37	0.40	$\langle \uparrow \downarrow, \uparrow \downarrow, \uparrow \downarrow, \uparrow \downarrow, \text{—} \rangle$
VIII ^g	0.87	0.987	0.46	0.50	$\langle \uparrow \downarrow \rangle$

^a: excluding H as Group I element; ^b: including H as group 1 element; ^c: excluding He as Group II element; ^d: including He as group II element; ^e: from plots of both group I and group III elements; ^f: excluding He as rare-gas element; ^g: including He as rare-gas element; ^h: R factor; ⁱ: from best fits to eqn 7; ^j: calculated from $R_o(\text{cal}) = (\sum R_o) / (\text{number of orbitals in } \langle \rangle \text{ brackets})$

where E_H is the first ionization energy of the hydrogen atom and $(Br_{nZ}^c + R_o)$ is an effective size, such that the ionization energy (expressed in E_H units) increases as the effective size decreases.

The elements do not all fit well into a common linear plot. Instead the fits are rather good when plotted group by group with R greater than 0.995 for Groups I, II, and groups V – VIII. From these fits of experimental first ionization energies in a group of the periodic table to eqn 7 we have obtained values of B and R_o for each group as given in Table 2. The first ionization energies of Group III elements give a bad fit to eqn 7 when plotted separately.

The interpretation for the changes to B and R_o (Table 2 and Fig 2) as a function of the number of valence electrons are not straightforward in the context of our model. We shall discuss the well known Koopmans' results (1938) later as they have been discussed in different post-Schrödinger formalisms. The ionization energy of hydrogen ($r_{nZ}^c = 0$) requires $R_o = 1$ in the Bohr model. The hydrogen-like alkali metal group I elements also give $R_o = 1$ from the best fits to eqn 7 (Table 1) which must be satisfying to begin with. Thereafter, the actual changes in R_o seem at first to be rather arbitrary. A decrease in R_o indicates an increase in ionization energy for a fixed B in eqn 7. We now assume that the ionization energy from a spin-paired state is higher than that of the hydrogen atom and then try to find a relation between the observed value of R_o^{ob} and the average number, R_o^{av} , of electrons per orbital. We give below what we consider to be a **possible** model.

We take $R_o = 1$ for singly occupied orbitals (as in hydrogen atom) and $R_o = 1/2$ for doubly occupied orbitals (as in He) and obtain a value $R_o(cal) = (\Sigma R_o)/(number\ of\ orbitals\ as\ indicated\ in\ Table\ 2)$. Such a procedure pre-supposes that the orbitals thus considered are degenerate. The possible occupation of the electrons in various orbitals and the calculated values $R_o(cal)$ for such an occupation are given in Table 2. For example, for group IV elements with $s^2p^1p^1$ configuration (Table 2) there are three occupied orbitals with $\Sigma R_o = 2.5$ so that $R_o(cal) = 2.5/3 = 0.833$. For group V elements, an $s^2p^1p^1p^1$ configuration would give $R_o(cal) = 0.875$. The observed value of $R_o \sim 0.50$ or group V elements would indicate in this representation that one needs to consider only the s^2 orbital and that the $p^1p^1p^1$ electrons are at a lower (more stable energy) probably

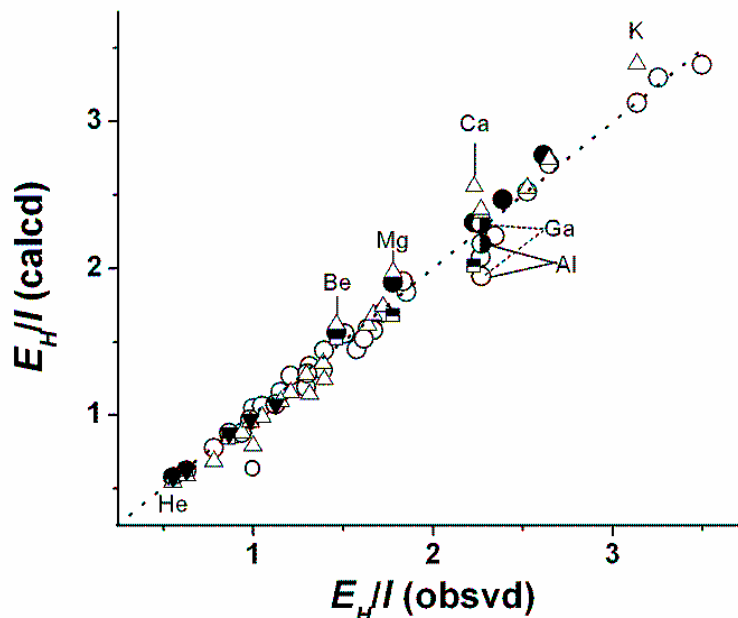


Fig 3. Plots of calculated values of E_H/I (I = first ionization potential; $E_H = 13.6$ eV = ionization energy of H atom) versus $E_H/I(obsvd)$ (Pearson 1988, Politzer *et al* 1991). circles: calculated from eqn 8 with $R_o(cal)$ taken from Table 1; filled circle: alkaline earth elements including He; Circle with filled inverted triangle: rare-gas elements including He. Right-half-filled circles: Ga and Al with r_{nZ} calculated using $n_{val} = 2$ in eqn 2. Open triangles: Koopman's energies as tabulated in Politzer *et al* (1991). Squares : from Banerjee and Harbola (1999).

because of half-filling. We have shown the possible orbital occupancies in Table 2 with the configuration between $\langle \rangle$ brackets being the electron configurations to consider, $\uparrow\downarrow$ indicating double occupancy in a orbital with $R_o = 1/2$, \downarrow (or \downarrow) indicating single occupancy with $R_o = 1$, and — indicating empty orbitals. The occupancies in Table 2 have been chosen so that there is a satisfactory agreement between observed values of R_o and calculated value $R_o(\text{cal})$.

From the fits in Table 2, we calculate E_H/I for main group elements using a formula

$$E_H/I (\text{calcd}) = [\{1.5 - b/16\} - n_{\text{val}}/16]r_{nZ}^c + R_o(\text{cal}) \quad (8)$$

where $R_o(\text{cal})$ is taken from Table 1 and n_{val} is obtained from the nominal position of the element in the periodic table and $b = 0$ or 1 for $n_{\text{val}} = \text{odd}$ or even , respectively. The value of $BE_H/I = 1.5$ for alkali metal elements has been biased (at least numerologically) by the possible influence of a fractional $1/3$ “core” charge on the ionizing electron (see Ganguly 2001) and the term $1/16$ being related to a probability of occupation of valence s - and p -orbitals.

The plots of $E_H/I(\text{obsvd})$ vs $E_H/I(\text{calcd})$ using eqn 8 are given in Fig 3 using r_{nZ}^c values from eqn 2 and compared with Koopman’s results (Politzer *et al* 1991, Koopmans 1938). We are not aware of a comparable fit of I to an atomic size elsewhere in the literature. Our results are also compared with those from recent density functional calculations (Banerjee and Harbola 1999). The nature of eqn 8 (empirical at present) suggests that the oscillatory nature of I across a row in the main group elements is mainly due to the presence of filled (He-like) and half-filled (hydrogen-like) orbitals.

Other features of interest are the following:-

- a) The hydrogen atom may be treated as an alkali metal atom because of the common value $R_o = 1$.
- b) It has to be noted that the orbital occupancy given for group VIII elements (last column in Table 2) is not applicable to He. It would seem from Table 2 that the He atom with its s^2 valence-shell is actually better treated as an alkaline-earth atom than as a rare-gas element. When $R_o(\text{He}) = 0.5$ in eqn 7, one requires $r_{nZ}^c(\text{He}) \sim 0.04$ a.u. in order to obtain the experimental ionization energy. The value of $r_{\text{RG}(\eta-1)}$ ($= 0.058$ a. u.) when $Z_{\text{RG}(\eta-1)} = 2$ and $\xi = 1/2$ in eqn 2 ($r_{nv} = 0$)
- c) The values of R_o for various groups (Table 2) may be considered to be derived from He-like (filled orbitals) and H-like (half-filled orbitals) consistent with eqn 3.
- d) There is a large discrepancy between the observed and calculated values of ionization energies for Al and Ga from eqn 8 and r_{nZ}^c values calculated from eqn 2 with $n_{\text{val}} = 3$ ($r_{nZ}^c = 0.72$ a. u. and 0.82 a. u. for Al and Ga, respectively) as indicated in Fig 3. This discrepancy is much reduced when r_{nZ}^c calculated from eqn 2 with $n_{\text{val}} = 2$ ($r_{nZ}^c = 0.88$ a. u. and 0.98 a. u. for Al and Ga, respectively) as indicated by half-filled circles in Fig 3.
- e) The calculated values using eqn 8 gives a better fit than that obtained using Koopmans’ results (Koopmans 1938, Politzer *et al* 1991) especially for alkaline earth elements and oxygen as indicated in Fig 3.
- f) Our values calculated from eqn 8 agree better with experiments than the DFT calculations (Banerjee and Harbola 1999) for some elements.

4. Electronegativity and Metallization

The problem of metallization has to be regarded first as a problem associated with overcoming barriers to double occupancy. Because of this the electronegativity of an element must throw some insights into the problem of metallization because of its definition as the “... *power of an atom in a molecule to attract an electron to itself...*”. From this definition there must be two

consequences. The first of these is that from a proper understanding of electronegativity one should be able to find an electronegativity scale that separates metallic elements from insulating ones. Secondly the electronegativity is a property that can be defined only in the context of the presence of another atom in a molecule. We shall find in the next section that such an understanding becomes critically important in obtaining gas-phase interatomic distances from atomic sizes.

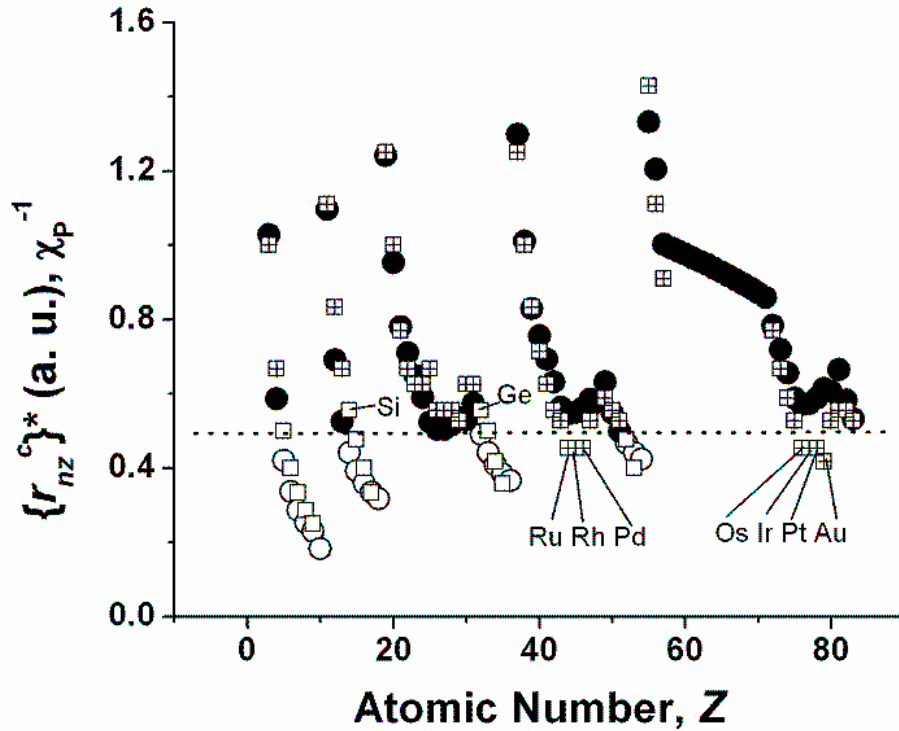


Fig 4. Plots of $\{r_{nZ}^c\}^*$ (circles) (eqn 9) and inverse of Pauling's electronegativity scale, χ_p^{-1} (squares), vs atomic number, Z , of elements. Filled symbols are those of metallic elements at NTP. The horizontal line indicates the value of $\{r_{nZ}^c\}^* = 0.5$ a. u..

The density functional expression for Mulliken electronegativity, χ , has been associated with the chemical potential as $\mu = \partial E / \partial \rho(\mathbf{r}) \big|_{\nu} = -\chi$ for some external fixed potential, ν , and electron density, $\rho(\mathbf{r})$. The density functional definition (Parr *et al* 1978) of the chemical potential as $\mu = [(\partial E[\rho] / \partial \rho)_{\nu}]_{\rho = \rho(\nu)}$ has been expanded (Ganguly 2000) in terms of partial derivatives for a given external potential, ν , as

$$(\partial E / \partial \rho(\mathbf{r}))_{\nu} = (\partial E / \partial \rho(\mathbf{r}))_{r(\text{eq})} + (\partial E / \partial r)_{\rho(\text{eq})} / (\partial \rho(\mathbf{r}) / \partial r)_{\nu}$$

where $r(\text{eq})$ and $\rho(\text{eq})$ are, respectively, the equilibrium or stationary state separation and density. This gives $\mu = 0$ for a stationary state when $(\partial E / \partial \rho(\mathbf{r}))_{r(\text{eq})} = 0 = (\partial E / \partial r)_{\rho(\text{eq})}$ as long as $(\partial \rho(\mathbf{r}) / \partial r)_{\nu} \neq 0$. This classical condition should permit a classical description of atomic properties in an energy-minimized density optimized stationary state. The concept of a stationary state was introduced by Bohr (1913) as “states of the system in which there is no radiation of energy, states which consequently will be stationary as long as the system is not disturbed from outside.” Such a state which does not radiate or absorb energy in the absence of an external perturbation is consistent with a model which is described by the classical or Thomas-Fermi condition of $\mu = 0$. For such an expression we should expect $\chi = 0$ which must be a paradox in the same context as the non-locality paradox discussed by Ayers (2007b).

Properties of an atom, such as electronegativity, which are dependent on its interaction potential with another atom is necessarily a property that requires the chemical potential condition, $\mu \neq 0$. The finite experimental or thermochemical values of the electronegativity, χ_P , of an atom as tabulated, say, by Pauling may be taken as a measure of its chemical potential at the instant of reaction. The sizes r_{nZ}^c , being obtained from a classical stationary point is a transferable quantity for the $\mu = 0$ condition for the chemical potential (Ganguly 2000; see also Politzer 1984 for a first description of the $\mu = 0$ condition). One requires an atomic size that gives electronegativity as a property of valence electron at an instant of reaction.

At any instant of reaction, the spin of the frontier valence electron participating in the reaction is polarized by the requirements—say, spin-pairing—of the external reacting atom. When this spin-polarization results in a polarization of the electrons in the inner shell (see Buchachenko 2001) the effective size of the inner shell is expected to be reduced. We assume that the effective size, $r_{RG(\eta-1)}^{spin}$, of the “inner shell” due to the spin-polarization is given by $r_{RG(\eta-1)}^{spin} = 0.5r_{RG(\eta-1)}$. An atomic size, $\{r_{nZ}^c(\eta)\}^*$, for the instant of reaction may be obtained as

$$\{r_{nZ}^c(\eta)\}^* = r_{nv} + 0.5r_{RG(\eta-1)} \quad (9)$$

There is a good correlation between the inverse of the Pauling electronegativity (see Nagle 1990 and references therein), χ_P^{-1} , and $(r_{nZ}^c)^*$ with $\chi_P^{-1} = 1.021(0.016)(r_{nZ}^c)^*$ ($R > 0.98$, $SD = 0.06$) for *s*- and *p*-block main group elements. There is a rough correlation with $\chi_P^{-1} > 0.5$ and metallization in elements. Antimony, $(r_{nZ}^c)^* = 0.499$ (Table 1), is strictly the only exception. The values of χ_P^{-1} of insulating elements which are proximate to a metallic element in the same row are: -B 0.5, Si 0.55, Ge 0.55 and Te 0.48 for the main block elements (see Nagle 1990, Asokamani and Manjula, 1989).

We find that $\{r_{nZ}^c\}^* = 0.5$ (a. u.) neatly separates the insulating elements from the metallic elements (Fig 4). Since an atom of an element cannot be metallic by itself, the implication of the condition $(r_{nZ}^c)^* \geq 0.50$ a.u. for an atom of a metallic element (Fig 4), is that the condition for metallization of an M-X bond is

$$(r_{nZ}^c)^*(M) + (r_{nZ}^c)^*(X) \geq a_H \quad (10)$$

Further discussion on this aspect will be presented in another communication. We find below that eqn 10 is a useful criterion, especially in the context of changes in bond lengths of gas-phase and solids of compounds of metallic elements.

5. Interatomic Bonded Distances.

5. 1. “Charge-Transfer” Expressions for Interatomic Distances.

In the case of interatomic distances, d_{M-X} of an M-X bond, it is found (Ganguly 1993, 1995a) that the interatomic “single bond” distances in gas-phase compounds between atoms of insulating elements or in solids may be expressed (Ganguly 1995a) as

$$d_{M-X} = CR^+(M) + CR^-(X) \quad (11)$$

where

$$CR^\pm = C^\pm r_G + D^\pm \quad (12)$$

which is of the form of eqn 3 with r_G being an atomic size ($r_G \sim r_{nZ}^c$, Ganguly 2007a) obtained empirically (Ganguly 1995a). In the general case including multiple bonds the interatomic distances can be expressed as

$$d_{MX}^\pm = CR^+(M)/F_S(M) + CR^-(X)/F_S(X) \quad (13)$$

The term F_S takes into account (Ganguly 1995a, 1995b) the shortening of bond distances due to the presence of n_v “unsaturated” (or what we henceforth term as “extrabonding”) electrons. F_S is empirically found (Ganguly 1995b) to be $F_S = 1.18, 1.26, 1.32, 1.38$ and 1.42 for $n_v = 1, 2, 3, 4$

and 5, respectively. Writing n_v in terms of a spin $S_v (= n_v/2)$ valence electrons that contribute to bond order ($= n_v + 1$) we may write $F_S \approx [1 + (2/\pi)^2 \{S_v(S_v+1)\}]^{1/3}$ (see web article by Ganguly 2005). We will take the values of F_S as an empirical quantity for the present.

From fitting interatomic distances to eqn 13 it has been found (Ganguly 1995a) that

$$d_{MX} = 2.24r_G(\text{M})/F_S(\text{M}) + 2.49r_G(\text{X})/F_S(\text{X}) + d_{H-H} \quad (14)$$

where d_{H-H} is the “ordinary” bond length (~ 74.2 pm) of the hydrogen molecule. It has been shown from a simple model (Ganguly 2000) that

$$d_{H-H} = \epsilon_{\text{eff}}(D_1^+ + D_1^-) = \epsilon_{\text{eff}}(4a_H/3) \quad (15)$$

with $\epsilon_{\text{eff}} \approx 1.05$ and where $D_1^+ (= -2a_H/3)$ and $D_1^- (= 2a_H)$ are the values of D^+ and D^- for and $\epsilon_{\text{eff}} \approx 1.00$ (Ganguly 2000). Since $r_G \sim r_{nZ}^c$ (Ganguly 2007a) we express eqns 12-15 in terms of r_{nZ}^c as

$$d_{MX}^\pm = \epsilon_{\text{eff}}[\{C_1^+ r_{nZ}^c(\text{M})/F_S(\text{M}) + C_1^- r_{nZ}^c(\text{X})/F_S(\text{X})\}^{\text{“ball”}} + \{2a_H/F_S(\text{X}) - 2a_H/3F_S(\text{M})\}^{\text{“stick”}}] \quad (16)$$

From eqns 14 and 16 and $\epsilon_{\text{eff}} = 1.05$, one expect that C_1^+ and C_1^- to have value close to 2.13 and 2.37, respectively. From purely geometrical arguments (Ganguly 2007b) it has been suggested that $C_1^+ = \pi^{2/3} \sim 2.144$ and $C_1^- = \pi^{4/3}/2 \sim 2.300$.

Another critically important factor is the way one evaluates *a priori* the term ϵ_{eff} , preferably from atomic sizes alone. In such charge-transfer models one may assume that the main contributions to dielectric properties may be associated with (probably) the more polarizable X atom since it is associated with a negative charge. For illustrative purposes and to simplify matters for the present we define a dielectric constant, ϵ_{X^-} ($\equiv \epsilon_{\text{eff}}$) as

$$\epsilon_{X^-} = 1 + 2.2 \times 10^{-6} [\{C_1^- r_{nZ}^c(\text{X}) + 2a_H\}^2] \quad (17)$$

where all atomic sizes are in pm and the term 2.2×10^{-6} has been obtained by fitting. For example, for the hydrogen atom ($r_{nZ}^c = 0$) $\epsilon_{H^-} \approx 1.025$; for the Cs atom $\epsilon_{Cs^-} \approx 1.082$

5. 2. Metallization and Gas-Phase MX Compounds.

It has recently been realized (see Robinson and Gillespie 2003, Gillespie and Robinson 2005, Ganguly 2006a, Ganguly 2006b) that in gas-phase MX_n compounds, the 1,3-XX distance is the least variable with environment distance and that the 1,2- MX distances are relatively more variable in order to maintain the 1,3- invariance. Consequently, one may consider, the M-X

Table 3. Values of number, n_v , of “extrabonding” valence electrons used to calculate d_{MX}^\pm in eqn 16

MX	n_v	MX	n_v	MX	n_v
M X		M X		M X	
AgBr	1 1	C2	2 2	PO	2 1
AgCl	1 1	NO	1 1	PP	1 1
AgF	1 1	SN	1 1	SF	1 0
AgO	1 1	NN	2 2	SO	1 1
BN	2 2	SN	1 1	SeF	1 0
B-O	1 1	PO	2 1	SeO	1 1
B-S	1 1	NN	2 2	SeSe	1 0
CN	3 1	OF	1 0	SiN	1 1
CO	2 1	O2	1 1	SiO	1 1
PC	2 2	PF	2 0	SiS	1 1
SC	1 1	PN	2 2	SiSe	1 1

distance in gas-phase MX compounds to be the most suitable as model systems for the study of M-X distances because of the lack of constraints from fixing 1,3- distances. Fig 5 gives a plot of the gas-phase MX distances in all (~ 160) MX compounds listed in the CRC Handbook (Lide 2007) versus the calculated distance d_{MX}^{\pm} using eqns 16 and 17 and n_v values listed in Table 3 ($n_v = 0$ in other compounds).

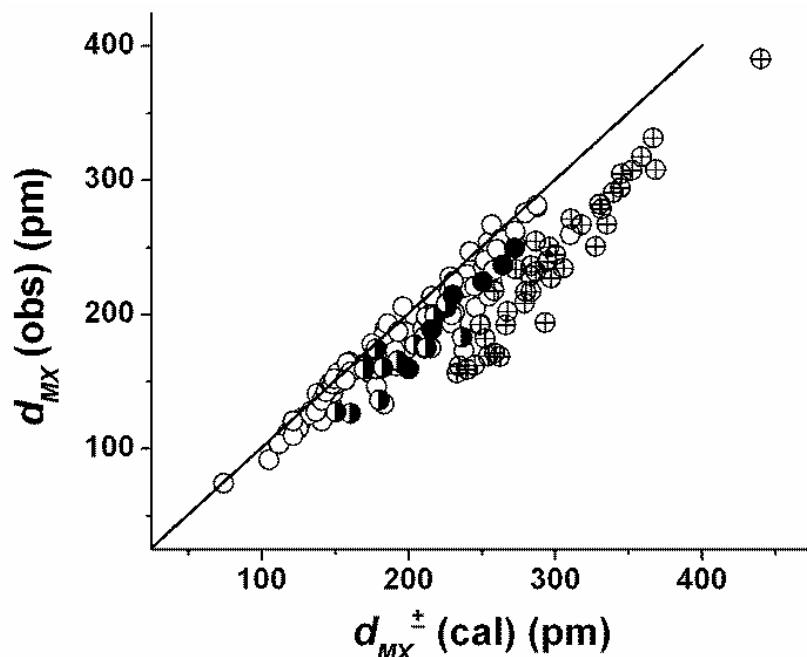


Fig 5. Plots of observed M-X distance in 160 gas-phase MX compounds (from CRC 1980) versus calculated “charge-transfer” M-X distance, d_{MX}^{\pm} (eqn 16) and using $\epsilon_{cf} = \epsilon_X$ (eqn 17). The values of n_v ($\neq 0$ for both M and X) are taken from Table 3. Open circles and half-filled circles: “insulating”, eqn 10 not satisfied; half-filled circles : X = F; filled circles and circles with cross inset: “metallic”, eqn 10 is satisfied; filled circles: HX = H. Straight line: Meant as a guide to the eye for $d_{MX}(\text{obsvd}) = d_{MX}^{\pm}(\text{cal})$.

There are many features in Fig 5 which deserve separate discussion and will be attended to in another communication. Of particular interest to us in this submission is the applicability of the “charge-transfer” description of bond distances (eqn 16) in terms of the “insulating” or “metallic” character of the MX system as described by eqn 10. It is clear from Fig 5 that for isolated M-X bonds, the charge-transfer description (eqn 16) is applicable only when the bond is “insulating”. Eqn 16 does not correctly describe gas phase “metallic” M-X bond distances which satisfy eqn 10. The insights obtained from eqn 10 and its application to the understanding of gas-phase interatomic distances is a more general aspect. It includes the classical problem (Born and Heisenberg 1924) of the “expansion” of M-X distance in alkali metal halides when condensed into a solid as compared to that in the gas-phase. It is apparent that such an expansion is not necessarily related to the importance of repulsive terms in solids (see Törring *et al* 1996 and references therein). We have shown in Fig 6 the plot of observed M-X distance of alkali metal halides vs the calculated distance d_{MX}^{\pm} using eqns 16 and 17. The observed distance in solids agrees well with that calculated ($d_{MX}(\text{obs}) \sim 0.99d_{MX}^{\pm}(\text{cal})$; R factor = 0.99). This indicates that one may consider the gas-phase distance to “contract” relative to that in crystals (in the particular case of alkali metal halides the best fit gives $d_{MX}(\text{obs})(\text{cryst}) \sim d_{MX}(\text{obs})(\text{gas}) + a_H$ with R factor \sim

0.99). This “contraction” seems to us to be due to the “metallization” as per eqn 10. The difference between “bond” states in the gas-phase and “band” states in solids is an aspect that will be considered separately.

This difference between “metallic” and “insulating” bonds seems to us to be important for obtaining insights into the environment-dependent variability of atomic sizes as expressed in the Shannon-Prewitt radii (Shannon Prewitt 1969; Shannon 1976) or in the demonstration of bond-stretch isomerism (see Rohmer and Bénard 2001). This aspect will be discussed in another communication (Ganguly 2007b).

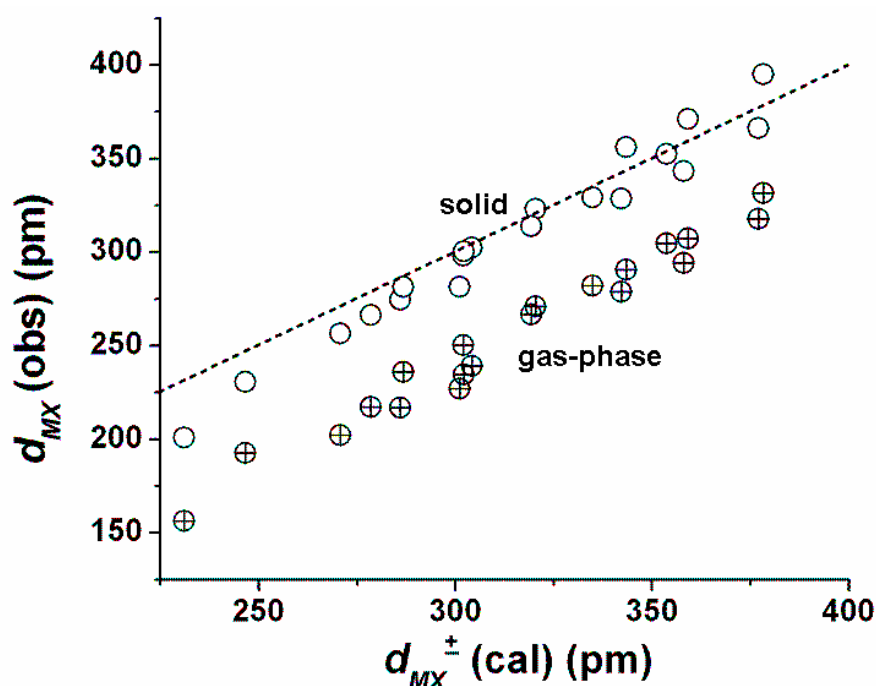


Fig 6. Plots of observed MX distances of alkali metal halides *versus* the calculated distance d_{MX}^{\pm} (eqns 16 and 17). Open circles: solids; Circles with cross inset: gas-phase compounds. Dashed straight line is mean as a guide to the eye for $d_{MX}^{obs} = d_{MX}^{\pm}$ (cal).

6. Conclusions

Our main effort in this communication has been to show the way that atomic sizes, r_{nZ}^c (Ganguly 2007a), obtained by using pre-Schrödinger, pre-Thomas-Fermi methods may also be used to obtain important atomic properties by the same primordial methodology. In this way we satisfy the requirement (Ayers *et al* 2002, Ayers 2007a) that in the context of complex molecular systems one requires replacing the electron density descriptor by another descriptor with “greater simplicity” and “a direct chemical interpretation”.

We have now shown that atomic properties such as static dielectric polarizability, α , the inverse of the first ionization potential, I^1 , Pauling’s electronegativity, metallization in elements, atomic sizes, CR , that contribute to interatomic distance may be obtained as a simple linear function, $f(r_{nZ}^c)$, of the atomic size, r_{nZ}^c , defined in the presence of an interaction but independent of the strength of the interaction. The linear relationship suggests that atomic properties consist of two

terms. One of these is a property dependent on a simple function $f(r_{nZ}^c)$ of an atom-specific size r_{nZ}^c (to first order) and another term which is an atom-independent property that may be related to that of the hydrogen or He atom. Of particular interest to us is the description of electronegativity in terms of $f(r_{nZ}^c)$ itself allows a neat and rigorous characterization of a “metallic” and “insulating” states of the chemical bond (eqn 10). Such a distinction is used to understand changes in description of M-X bond lengths in gas-phase and solid MX compounds of the kind first recognized by Born and Heisenberg (1924) for alkali metal halides.

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Table 1. Examples of various parameters used in eqn 2 for obtaining r_{nZ}^c and $(r_{nZ}^c)^*$ (in a.u.)

Atom	Z	n_{val}	n_d	n_f	Z_{RG}	r_{nZ}^c a.u.	$\{r_{nZ}^c\}^*$ a.u.
Li [@]	3	1	0	0	2	1.06	1.03
Be	4	2	0	0	2	0.62	0.59
F	9	7	0	0	2	0.26	0.23
Mg	12	2	0	0	10	0.88	0.69
S	16	6	0	0	10	0.55	0.36
Ca	20	2	5	0	18	1.19	0.95
Mn	25	2	0	0	18	0.98	0.52
Zn	30	2	5	0	18	0.87	0.53
Ga	31	3	0	0	18	0.81	0.57
Kr	36	8	0	0	18	0.61	0.36
Mo	42	2	1	0	36	1.16	0.63
Sb	51	5	0	0	36	0.80	0.499
Xe	54	8	0	0	36	0.72	0.42
Cs	55	1	0	0	54	1.66	1.33
Ba	56	2	5	0	54	1.54	1.21
La	57	2	4	0	54	1.52	1.00
Sm	62	2	4	5	54	1.46	0.96
Eu	63	2	4	6	54	1.45	0.95
Hg	80	2	5	0	54	1.05	0.61
Pb ^{IV}	82	4	0	0	54	0.91	0.58
Pb ^{II}	82	2	0	0	54	1.16	0.83

[@]: $\xi = 0.5$ for Li and Na in eqn 2

Table 2. Systematics of Changes in First Ionization Potential, I (from Politzer *et al* 1991), as a function of core Atomic Size, r_{nZ}^c using eqn 7.

Group	B	R^h	R_o^i	$R_o(\text{cal})^j$	Orbital Occupancy
I ^a	1.56	0.989	0.83	1.00	$\langle \rangle$
I ^b	1.46	0.997	0.98	1.00	$\langle \rangle$
II ^c	1.29	0.998	0.67	0.67	$\langle , \emptyset, \text{æ} \rangle$
II ^d	1.39	0.998	0.55	0.50	$\langle \emptyset$
I+III ^e	1.38	0.989	1.01	1.00	$\langle \rangle$ and $\emptyset , \langle \rangle$
IV	1.17	0.968	0.83	0.83	$\langle \emptyset , \rangle$
V	1.26	0.998	0.54	0.50	$\langle \emptyset$
VI	1.06	0.998	0.71	0.75	$\langle \emptyset \emptyset , \rangle$
VII	1.07	0.998	0.49	0.50	$\emptyset \emptyset \langle \emptyset$
VIII ^f	1.01	0.995	0.37	0.40	$\langle \emptyset \emptyset \emptyset \emptyset \text{æ} \rangle$
VIII ^g	0.87	0.987	0.46	0.50	$\langle \emptyset$

^a: excluding H as Group I element; ^b: including H as group 1 element; ^c: excluding He as Group II element; ^d: including He as group II element; ^e: from plots of both group I and group III elements; ^f: excluding He as rare-gas element; ^g: including He as rare-gas element; ^h: R factor; ⁱ: from best fits to eqn 7; ^j: calculated from $R_o(\text{cal}) = (SR_o)/(\text{number of orbitals in } \langle \rangle \text{ brackets})$

Table 3. Values of number, n_v , of “extrabonding” valence electrons used to calculate d_{MX^\pm} in eqn 16

MX	n_v	MX	n_v	MX	n_v
	M X		M X		M X
AgBr	1 1	C2	2 2	PO	2 1
AgCl	1 1	NO	1 1	PP	1 1
AgF	1 1	SN	1 1	SF	1 0
AgO	1 1	NN	2 2	SO	1 1
BN	2 2	SN	1 1	SeF	1 0
B-O	1 1	PO	2 1	SeO	1 1
B-S	1 1	NN	2 2	SeSe	1 0
CN	3 1	OF	1 0	SiN	1 1
CO	2 1	O2	1 1	SiO	1 1
PC	2 2	PF	2 0	SiS	1 1
SC	1 1	PN	2 2	SiSe	1 1