

Atomic sizes and vacuum polarization.

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Abstract. We obtain an atomic size, r_{nZ}^c , in the presence of an interaction (represented by an electron-positron pair, e^-e^+ as in vacuum polarization methods) as a sum of contribution, r_{nv} , from the interaction of n_{val} valence s - and p - electrons and a contribution r_{RG} from inner filled shell electrons with rare-gas configuration. The method is applicable to all elements once the transition metal elements are treated as group II elements. The sizes thus obtained have no adjustable parameters and there is no requirement for relativistic corrections for heavy atoms, in principle.

1. Introduction

In recent years there has been a search (Ayers 2000, 2007, Ganguly 2008) for fundamental non-wave-function-based descriptors, other than the electron density, that enables a full description of the system. In the context of molecular structure and chemical reactivity, it is preferable that such descriptors have a clear interpretation (Ayers 2007). The size of an atom is the most basic property of its electron density. It is empirically found to change with changes due to its interactions with the environment ((Zachariesen 1931, Pauling 1960, Shannon 1976, Etschmann and Maslen 2000). Interaction-dependent atomic sizes are not unambiguously obtained in wave-function-based approaches. One requires in this context an atomic size that changes in a simple manner with the environment such that explicit and identifiable sizes characteristic of the given interaction is obtained. It has been shown earlier (Ganguly 2008) that there exists such a set of atomic sizes, r_{nZ}^c , which may be used in the form of eqn 1 below

$$P = C_p r_{nZ}^c + D_p \quad (1)$$

to obtain atomic properties such as dielectric polarizability radius, first ionization potential, Pauling's electronegativity scale, as well as atomic sizes contributing to interatomic bond distances. These sizes have also been used (Ganguly and Desiraju, 2008) to quantify intermolecular contact distances in crystals of organic molecules. Eqn 1 could account for other empirical sizes which are usually qualified by the nature (ionic, covalent, metallic, van der Waals) of the interatomic contacts. This submission is meant to provide a simple but new theoretical model for obtaining atom-specific sizes r_{nZ}^c without using adjustable parameters.

Theoretical ab initio approaches to atomic sizes are based on the obvious notion that the atomic size has to be an intrinsic property of the atom and may be obtained from considerations of an isolated atom. Thus the Slater sizes (1964) are a measure of the maximum radial density in the charge-distribution of the outermost electron of neutral atoms obtained from the wave-function. In these wave-function-based approaches, the atom is treated in isolation and in the absence of other external interactions. However, even in true vacuum there are always virtual particle-antiparticle pairs which annihilate each other after a short lifetime. Charged electron-positron pairs act as dipoles and there is a self interaction due to the absorption and emission of these charged particles with the Coulomb field of another charged particle such as an electron. This is

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the classical electron self-energy problem of quantum electrodynamics, which is the instantaneous reaction back on the electron due to the vacuum polarization of the virtual photon of the electron-positron pair. We examine at a very simple level how the concept of vacuum polarization may be used to obtain the set of sizes, r_{nZ}^c , for all atoms making the assumption that what is true for vacuum must be true for real space also. The simplicity of our approach should not diminish from its robustness and novelty.

Interactions of the real or virtual kind involve (Hayes 2004, Huang 2007) sometimes an electron-positron pair, e^-e^+ , which, we find, plays a part in defining an atomic size. The concept of an instantaneous reaction in vacuum polarization approaches naturally demands a time-scale defined by a velocity of propagation of the transverse photon across an intrinsic size that is itself defined by the interaction. Given such a size for the given time-scale, the so-called virtual electron and positron pair may be treated as real within this time. One is not necessarily creating real particles or photons out of vacuum within this lifetime or within this size in space. One may, however, examine the consequence by treating the electron and its antiparticle as if they are real and obey the same rules as real particles. According to Schwinger (see Mehra and Rechenberg 1982)

Vacuum polarization is just a handy word for meaning that there are phenomena in which electron-positron pairs are created; it is a catchword to indicate that class of phenomena and you can't get rid of it.

For the purposes of this communication we do not require going beyond this simple definition. The strong implication, however, is that atomic sizes have meaning even in vacuum because of interactions. We simply assume that in the process of obtaining atomic sizes for all elements we have followed a line of argument that could require small changes in our understanding of the position of transition metal elements vis-à-vis the alkaline earth elements in the periodic table.

2. Valence- and inner-shell sizes.

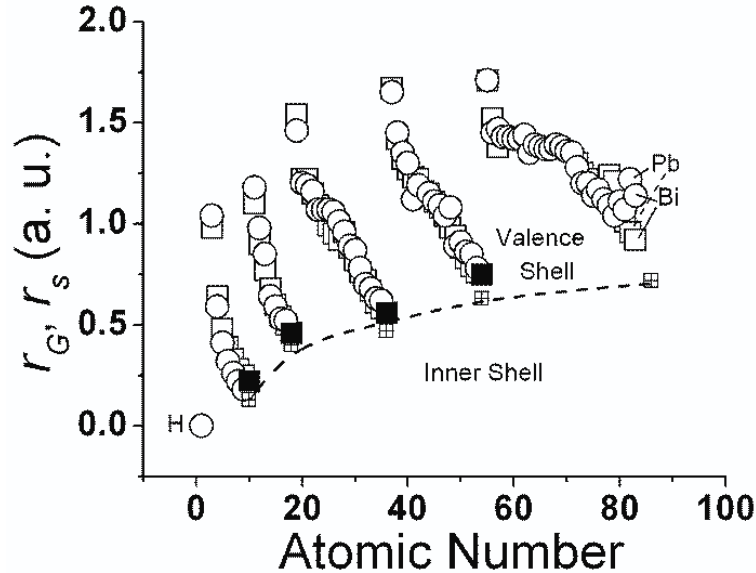


Fig 1. Plots of r_G (open circles, from Ganguly 1995) and r_s (squares, from Zunger, 1980) vs Atomic Number, Z . squares with cross inset: values of $r(\eta_s)$ (see text below). Filled squares are r_s sizes for rare-gas elements. Dotted line is the plot of the best fit of $r_s(\eta) = 0.53 \ln[(Z_{RG}(\eta-1))^{1/3}]$.

We first examine in Fig 1 the relationship of the atomic number, Z , with previously reported Zunger-Cohen valence s -electron orbital radii, r_s (Zunger 1980), and the empirical sizes, r_G (Ganguly 1995) obtained from experimental interatomic distances. We have demarcated—by the dashed line—the contributions from the “valence shell” and the “inner shell” regions (see below). The valence shell size in Fig 1 seems to show a $1/n_{val}$ dependence where n_{val} is the number of s - and p - valence electrons. Further examination of the systematic changes in Fig 1 suggested an additive contribution from the Z_{RG} electrons in the inner shell being logarithmically dependent on Z_{RG} . We thus seem to require that the interaction of the external field with valence electrons is different in nature from that of the “inner shell” electrons. Decompositions of atomic sizes into valence- and inner- size have been used earlier (Poltzer and Parr 1976, Poltzer *et al* 1983, 1985) in a manner very different from that used below.

3. New model for atomic sizes.

An important demand in the context of eqn 1 is that one requires a transferable atom-specific size, r_{nZ}^c that is not dependent on the specific nature of the interaction that gives the property, P , in eqn 1. Naturally, one seeks a universal feature of all interactions that defines such sizes in a manner specific to the atom. We find all this in a simple but novel variation of a Bohr-like model that has a new non-wave-function-based pre-DFT paradigm for obtaining a set of atomic sizes, r_{nZ}^c (of eqn 1). The resulting expression for the size has no adjustable parameter so that it has the characteristics of an ab initio calculation. There are no large N difficulties either in computational times or in using relativistic corrections for heavy atoms.

As noted earlier, the novelty in our method is to obtain atomic sizes, r_{nZ}^c by considering the interaction of the atom with an external field represented by an electron-positron pair, (e^-e^+), instead of considering the internal mechanics in an isolated atom. We consider specifically the additional interaction of the positron, e^+ , of the electron-positron pair, (e^-e^+), with the extra-nuclear electrons of the atom. This interaction of the positron, e^+ , and the electrons is expected to be absorbed in the final magnitude of the virtual photon energy arising from annihilation of the electron-positron pair, (e^-e^+).

For an atom with atomic in the η^{th} row ($\eta = n + 1$, $n =$ principal quantum number), we write

$$Z(\eta) + (e^-e^+) \equiv [Z]e^+e^- \equiv [n_{val} + Z_{RG(\eta-1)}](e^+e^-) \quad (2)$$

We require the interaction of only the external positron, e^+ , with the n_{val} “valence shell” electrons as well as the $Z_{RG(\eta-1)}$ “inner shell” electrons with the rare-gas configuration. The treatment we adopt is different from usual energetic considerations of positron and positronium atoms (Mitroy *et al* 2002). It is also different, for example, from that of Simons and Bloch (1973), which considers each of the n_{val} valence electron to be in the internal field of a core (“stripped ion”) charge Z^{n^+} ($n^+ \equiv (n_{val})^+$).

In real positron annihilation processes (Surko *et al* 2000) the annihilation rate is dependent on an effective number, Z_{eff} (for small atoms $Z_{eff} \sim Z$) of electrons contributing to the annihilation. Experimentally, it is found (Surko *et al* 2000) that $\ln(Z_{eff}) \sim A(E_i - E_{Ps})^{-1}$ for rare-gas atoms where A is a positive constant, E_i is the ionization energy of the atom and E_{Ps} is the binding energy of a positronium atom. Since E_i^{-1} is deemed to be directly related to core atomic sizes such as the Zunger-Cohen orbital radii (Zunger 1980), one may anticipate a logarithmic relationship between the size, $r_{RG(\eta-1)}$, of the inner shell and the number of “inner shell” electrons, $Z_{RG(\eta-1)}$. Current theories on positron annihilation rates (Laricchia and Wilkin 1997, Gribakin 2000, Igarashi *et al* 2003) consider “direct” annihilation processes in which the positron annihilates with a bound electron. In “indirect” processes annihilation takes place after collision so that there is a finite

lifetime of positronium atoms. The indirect processes require absorption of a positron and *resonance annihilation*. It seems that these real positron annihilation process descriptions to be pertinent for our descriptions of interactions with virtual positrons, e^+ .

Because e^+ is a universal component of the external interaction field represented by the electron-positron pair ($e^- - e^+$), 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. These sizes are thus a simple function of the total number, Z , of electrons when taken as the sum of the number, n_{val} , of valence (s - and p -) electrons and the number, Z_{RG} , of filled shell inner electrons of rare-gas atoms in the previous row of the periodic table. 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 positron). Our methodology gives really a one-dimensional, 1D, size in the direction of the external reaction field.

3. 1. Valence Size.

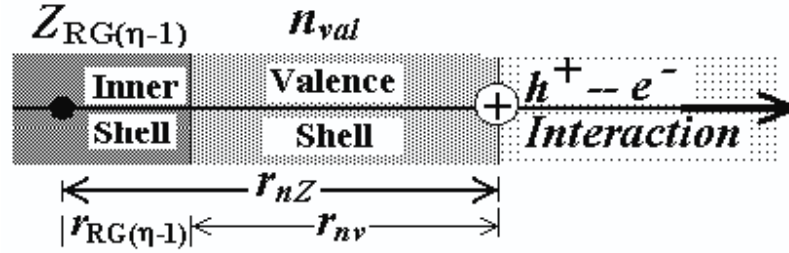


Fig 2. One-dimensional slice through an atom illustrating the sizes of “inner shell” and the “valence core” regions that contribute to $r_{core} \equiv r_{nZ} = (r_{RG(\eta-1)} + r_{nv})$ in the direction of the interaction field, represented by $e^+ - e^-$.

We locate (Fig 2) the external positron, e^+ , at the boundary, r_{nZ} , between the electron-rich “valence shell” of the atom and the external virtual ($e^- - e^+$) pair representing the interaction. The n_{val} electrons of the “valence shell” are treated together as a single unit of negative charge $n_{val}(e^-)$. This negative charge has a heavy mass $M_{nv} \sim Z$ such that $M_{nv} \gg m_h \sim m_o$ where m_h is mass of e^+ and m_o that of the free electron. The interaction of the light external positron (e^+) with the heavy negative charge $n_{val}e^-$ is treated phenomenologically as a charge-inverted hydrogen atom model (see, for example, Van Hooydonk 1985). Using Feynmann’s description (1965) of the interaction energy in the Bohr model we write

$$E_{val}^+ = (\hbar^2/r^2)/2m_o - n_{val}e^2/r \quad (3)$$

It is sufficient to visualize eqn 3 as a one-dimensional equation (see eqn 3. 12 of Spruch 1991 and discussions thereon); in isotropic 2D space the locus of the solutions of the energy minimized state would trace a circular orbit that satisfies eqn 3 with $\hbar/2\pi r$ defining an angular momentum. A 1D first “Bohr size”, r_{nv} , for principal quantum number, $n_{(e^+)} = 1$ of the positron, e^+ , due to its interaction of the n_{val} valence electrons (Fig 2) is obtained as

$$r_{nv} = a_H/n_{val} = 1/n_{val} \text{ (in a.u.)} \quad (4)$$

in terms of the first Bohr size, a_H , of the hydrogen atom. The size, r_{nv} , is thus obtained for a classical stationary state, consistent with a transferability condition, $\mu = 0$ for the chemical potential (Ganguly 2000). This gives a “valence size”, $r_{nv}(\eta)$, for an atom in row number η .

3. 2. Inner Size, $r_{RG(\eta-1)}$.

The boundary (shown by dashed line in Fig 1) of the “inner shell” region suggests that the contribution of the $Z_{RG(\eta-1)}$ inner shell electrons to size of an atom with row number η is a slow logarithmically growing function of the number of “inner shell” particles in the given (one-) dimension, N_{1D} . For $Z_{RG(\eta-1)}$ inner-shell electrons we expect $N_{1D} = \{Z_{RG(\eta-1)}\}^{1/3}$. The logarithmic dependence is reminiscent of the Beer Lamberts relationship between absorption coefficient and number of particles (photons) absorbed and suggests that the logarithmic term arises from the probability of absorption of the positron, e^+ . We make the simple ansatz that dN_{1D}/N_{1D} is the rate of growth in number in 1D size per particle of “inner shell” due to interactions with e^+ . The total change, ΔN_{1D} , is

$$\Delta N_{1D} = \left[\int_1^{N_{1D}} dN_{1D}/N_{1D} \right] = \ln(N_{1D}) = \ln\{(Z_{inner})^{1/3}\} \quad (5)$$

where Z_{inner} is the appropriate number of “inner” electrons in the given direction. The ΔN_{1D} inner shell electrons occupy in pairs a “Bohr” size, a_{Bohr} ($= a_H/2$ where a_H is the first Bohr radius), such that the size per electron, $r_{inner} = \xi a_{Bohr}$, where $\xi = 1$ in all cases except perhaps for Li and Na for which best results are empirically obtained with $\xi = 1/2$ (see section 3.5). Thus, we may expect for $Z_{inner} = Z_{RG(\eta-1)}$, the “inner shell” contribution (see Fig 2) to be given by

$$r_{RG(\eta-1)} = (r_{inner}) \Delta N_{1D} \equiv \xi(a_H/2)\ln[(Z_{RG(\eta-1)})^{1/3}] \quad (6)$$

A $Z^{1/3}$ leading correction term appears in the Thomas-Fermi theory (see Schwinger 1980). Our approach is different from the Thomas-Fermi theory.

3. 3. Total Core Size, r_{nZ} .

It is to be noted that the valence size, r_{nv} , is measured from the location of the external positron, e^+ , towards the nucleus. The electrons in the valence shell, in this inverted logic therefore are those most proximate to the external positron, e^+ (Fig 2). The inner size, $r_{RG(\eta-1)}$, are due to inner shell electrons which are furthest away from the external positron, e^+ (Fig 2). In this model therefore the strongest effect of an external interaction field involves—as it should—the valence shell electrons which are closest to the external positron, e^+ .

From eqns 4-6 we obtain, to a first approximation ($\xi a_{Bohr} = a_H/2$)

$$r_{nZ} = 1/n_{val} + \xi(a_H/2)[\ln(Z_{RG(\eta-1)})^{1/3}] \quad (7)$$

Eqn 7 for r_{nZ} has no adjustable parameter (when $\xi = 1$), does not depend on the nature (*s*- or *p*-) of the valence electron; is consistent with spherical symmetry of an isolated atom; is simply related to its row number, η , and its atomic number, Z ($= n_{val} + Z_{RG(\eta-1)}$). The plot of r_{nZ} ($\xi = 1$) vs the theoretical valence *s*-electron Zunger-Cohen radii (Zunger 1980), r_s , and the empirical size (Ganguly 1995), r_G , is shown in Fig 3. The fit is fairly satisfactory except primarily for Li, Na and Ca, Sr and Ba. As we discuss below these deviations throw some important insights into the role that *d*- and *f*- orbitals have in determining the sizes. The large deviations of the empirical r_G values of Pb and Bi from the calculated values ($n_{val} = 4$ and 5, respectively) could be due to “lone pair” effects as $n_{val} = 2$ and 3 for Pb and Bi give better fits.

3. 4. Alkaline Earth and Transition Metal Elements.

The calculated values of r_{nZ} of Ca, Sr and Ba from eqn 7 are close to r_s or r_G of elements with half-filled *d* orbitals such as Mn, Tc and Re, respectively. This has prompted us to treat transition metal elements as part of alkaline-earth group of elements with unoccupied *d*- or *f*- orbitals. The following points are important

- i) The *d*- or *f*- electrons are treated as “inner” electrons.
- ii) The nominal number, q , of *d* electrons is obtained from position of element in periodic table—e.g., $q = 0$ for the alkaline earth elements and $q = 5$ for Mn, Tc, Re.
- iii) There is no direct contribution from these *d*- or *f*- electrons to n_{val} . However, there could be changes in q due to promotion of δ electrons to *s-p* manifold to give $(q - \delta)$ *d* electrons (or

acceptance of δ electrons from the s-p manifold to give $(q + \delta)$ d electrons). iv) The actual electronic configuration of these elements is given as $(sp)^{2 \pm \delta} d^{q \mp \delta}$ (the signs on top or below applies, respectively, to elements with $q > 5$ and $q < 5$).

v) We assume $\delta = 0$ for $q = 5$ systems such as Mn, Tc, Re.

vi) The rare-earth f-electron systems are treated as $q < 5$ systems.

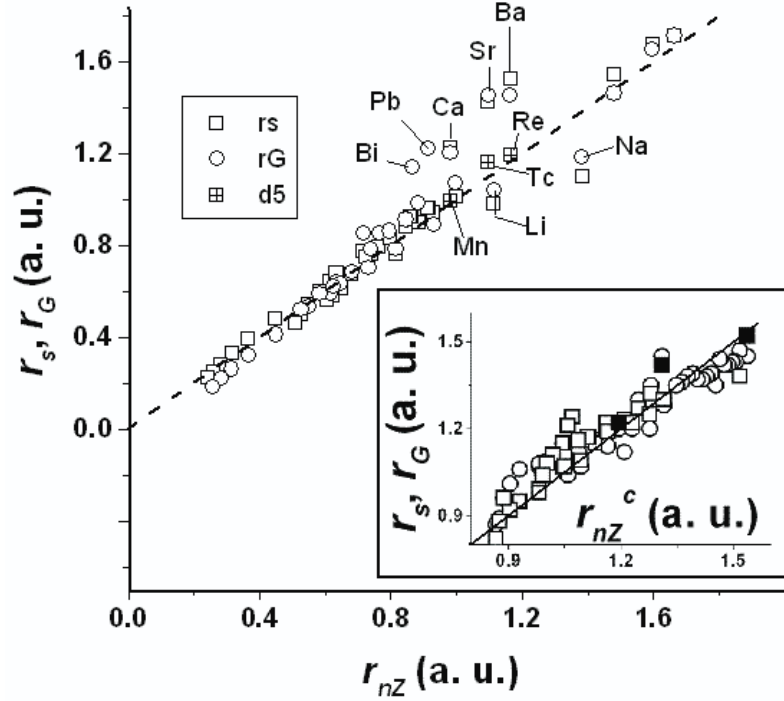


Fig 3. Plot of Zunger-Cohen valence s -electron orbital radius, r_s (squares; from Zunger 1980), and empirically determined core radius, r_G (circles) (from Ganguly 1995) versus the calculated r_{nz} (eqn 7) of main group elements;. Squares with cross inset correspond to r_s values (from Zunger 1980) of Mn, Tc and Re plotted against calculated values of r_{nz} of Ca, Sr and Ba, respectively. The main deviations are indicated. Inset: Plots of r_s and r_G versus calculated values r_{nz}^c (eqn 9) of transition metal elements including r_s of Ca, Sr and Ba shown by filled squares. Lines are meant as a guide to the eye for slope = 1.

We require, in addition, the number of empty (+) or filled (-) d - or f -orbitals in order to obtain the value of n_{val} as $(sp)^{2 \pm \delta} d^{q \mp \delta}$ for the d - and f - block elements. These are denoted as $n_d^\pm(\eta)$ and $n_f^+(\eta)$. We write $n_f^+ = (14 - n_f)/2$ where n_f is the number of f electrons. For f electron systems the number, n_f^+ , of available f orbitals is added to n_d^\pm . For the alkaline earth and transition metal elements, only the $(sp)^{2 \pm \delta}$ electrons contribute directly to n_{val} in eqn 4 with $n_{val} = (2 - \delta)$, for $q < 5$ and $n_{val} = (2 + \delta)$ for $q > 5$. From arguments similar to that employed in eqn 5 for obtaining the occupation probability in 1D, we equate

$$\delta = \Delta N_{1D}(d, f) = \ln[(1 + n_d^\pm(\eta) + (n_f^+/2)_{(\eta)})^{1/3}] \quad (8)$$

We thus write the refined value of r_{nz} for an element with row η in the long periodic table as

$$r_{nz}^c(\eta) = 1/[n_{val} + (-1)^b \ln\{(1 + n_d^\pm + (n_f^+/2))^{1/3}\}] + \xi(a_H/2)[\ln(Z_{RG(\eta-1)}^{1/3})] = r_{atom} \quad (9)$$

with $b = 1$ when $q < 5$ and $b = 0$ when $q > 5$. In this communication, we use $\xi = 1$ in eqn 9. We note from eqn 9 that the calculated values of r_{nz} (eqn 7) for Ca, Sr and Ba would correspond to

the calculated r_{nZ}^c values (using eqn 9) for Mn, Tc and Re, respectively as indicated in Fig 3. We show in the inset of Fig 3 the plot of r_s and r_G versus r_{nZ}^c (calculated from eqn 9) r_G of all elements from H to Bi with $\xi = 1$ for all transition metal elements including Ca, Sr and Ba. The best linear fit through origin of the plot of r_G versus r_{nZ}^c from eqn 9 ($\xi = 1$) for all elements except Pb, Bi and Na gives $r_G = 1.004(0.006)r_{nZ}^c$ ($R \approx 0.99$, $SD \approx 0.06$).

The calculated values of r_{nZ}^c using eqn 9 and the parameters required for eqns 8 and 9 are given in Table 1 where it compared with the size, r_s , obtained by Zunger (1980) or the empirical size, r_G (Ganguly 1995). Except for Li and Na all other values for other atoms are fairly satisfactory.

3. 5. Alkali Metal Elements

The considerable discrepancy between calculated r_{nZ}^c values for Li and Na (Table 1) could provide important insights. The nature of the deviations in Fig 3 for the alkali metal elements is in the opposite direction to that of the alkaline-earth elements. As discussed in section 3.4 the alkaline earth elements require a reduction in the value of n_{val} from the ideal value of 2. Such a reduction for Ca, Sr, Ba has been attributed to the occupation of empty d -levels by the valence s -electrons. In the case of the alkali metal elements, Li and Na, one could have an increase in n_{val} by the promotion of “inner shell” s - and p - electrons to the “valence shell”. K, Rb, Cs could be different from Li and Na in this case since there are unoccupied “inner shell” d orbitals. The higher value of r_{nZ}^c for Li and Na as compared to r_G or r_s is empirically met by having $\xi = 1/2$. (see Table 1). This could mean that r_{inner} is reduced to $a_H/4$ or the value of ΔN_{ID} in eqn 5 is reduced by half. This aspect requires further exploration.

4. Discussion

An interesting and non-trivial point is that eqn 9 may be used to obtain atomic sizes for all elements without taking relativistic effects into consideration. This is because the value of n_{val} in eqn3 is much less than the fine structure constant, α_c ($8 \leq n_{val} \ll 137 \sim \alpha_c$) so that the interaction energy in eqn 3 never approaches relativistic limits (Spruch 1991). Moreover, the contribution, $r_{RG(\eta-1)}$, from the inner shell electrons has a logarithmic dependence on $Z_{RG(\eta-1)}$ so that relativistic corrections, if any, would be small. It is not surprising, therefore, that there is better agreement with the non-relativistic Zunger-Cohen orbital radii (Zunger 1980) than the relativistic screened orbital radii of Zhang *et al* (1987).

One way to check on the accuracy or usefulness of r_{nZ}^c is to find (Ganguly 2008) a relationship between these sizes and other atomic properties. Of interest is to find how these earlier relationships are extended to the heavier elements such as the actinide or post-actinide elements. We have plotted in Fig 4 a the value of $\{r_{nZ}^c\}^*$ for the various elements. As explained in Ganguly (2008), $\{r_{nZ}^c\}^*$ is the relevant size at the instant of a chemical reaction which may be related to Pauling’s electronegativity scale. The condition $\{r_{nZ}^c\}^* > 0.5$ determines whether an element is metallic or not. According to Fig 4a the halogen, astatine ($Z = 85$) and the elements with rare-gas electron configuration, radon ($Z = 86$) and uuo ($Z = 118$) would be insulating but at the border of the insulator-metal transition. We have also plotted in Fig 4b the plot of the theoretically calculated size ($CR^+(M)/F_S(M)$) (see eqns 13 and 16 of Ganguly 2008) for some of the actinide elements reported versus the empirical sizes tabulated by Shannon (1976) (also see <http://www.webelements.com>, for example). The best fit with slope = unity is shown in Fig 4b. Considering the tentative nature of the empirical sizes because of paucity of experimental results for the actinide elements, the nature of the fit in Fig 4b should be satisfying.

The calculated values [see eqn 6 of Ganguly 2008] of the polarizability radius, r_α , of Po, At and Rn are 187, 178 and 171 pm, respectively, as compared to the reported (see Nagle 1990, for example) values of 189, 182 and 174 pm, respectively. The corresponding calculated values of the r_α for Fr and Ra (398 and 356 pm, respectively) are however, considerably larger than the reported (Nagle 1980) values (365 and 337 pm, respectively). The calculated values of E_H/I (see eqn 8 of ref 6, E_H is the first ionization energy of the hydrogen atom, and I is the first ionization energy) of Po, At, Rn, Fr and Ra (observed values in brackets, from Nagle 1990) are 1.63 (1.56), 1.36 (1.38), 1.14 (1.22), 3.504 (3.34) and 2.87 (2.49), respectively. The lower observed values of r_α and E_H/I for Fr and Ra as compared with the well known reversal of the lowering of binding energy of alkali metal atoms with increasing size. This has been attributed to a lowering of the van der Waals coefficients (Marinescu *et al* 1998), which, in turn, require a lowering of the polarizability of the atoms.

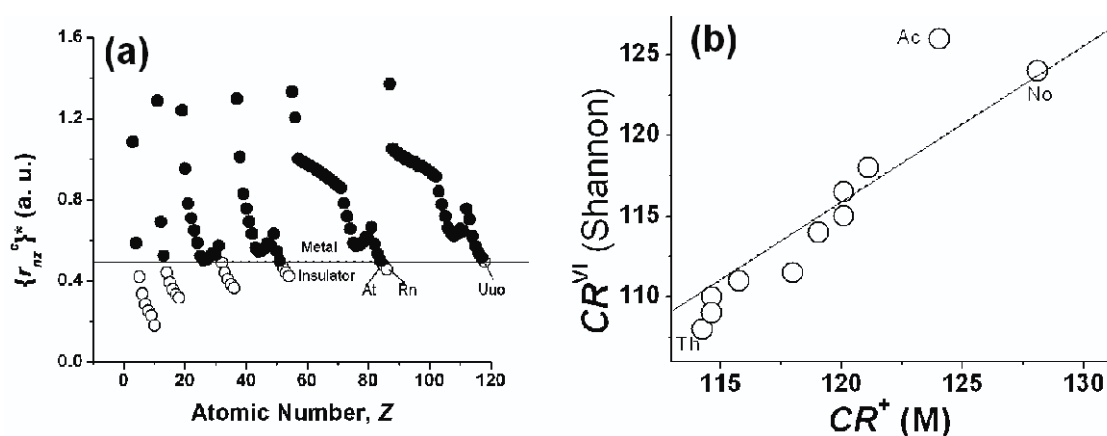


Fig 4. (a) Plot of the value of $\{r_{nZ}^c\}^*$ of the elements (see Ganguly 2008, eqn 9) vs atomic number, Z ; filled circles: elements which are expected to be metallic ($\{r_{nZ}^c\}^* > 0.5$); open circles: elements which are expected to be insulating metallic ($\{r_{nZ}^c\}^* < 0.5$). (b) Plot of calculated (see eqns 13 and 16 of Ganguly 2008) values of $CR^+(M)/F_S(M)$ ($F_S(M) = 1.184$, $n_v = 1$ for all trivalent elements of actinide elements, except tetravalent Th ($F_S = 1.26$; $n_v = 2$) and divalent No ($F_S = 1$, $n_v = 0$) vs the empirical ionic Shannon size (Shannon 1976) in octahedral coordination: Dashed line: best linear fit with zero intercept; slope = 0.97 SD = 2 pm.

As mentioned earlier, we require discounting the importance of relativistic effects in the way we calculate (Ganguly 2008) the polarizability from r_{nZ}^c . This absence of relativistic effects in our methodology is also evident since we obtain fairly accurate values of Po, At, Rn which are only marginally lighter than Fr or Ra. The trends in Fig 4 also point to a reliable prediction of atomic sizes for actinide for even post-actinide elements. The decrease in the observed polarizability radius, r_α , of francium compared to the calculated values using eqn 6 of ref 6, suggests that, for large Z , there could be other factors that are not taken into account in the way r_{nZ}^c is calculated from eqns 7 or 9. In order to check this aspect we see if there is an internal consistency in the way we may calculate r_{nZ}^c from observed experimental values. For example, $r_\alpha(\text{Fr}) = 365$ pm would require $r_{nZ}^c(\text{Fr}) \approx 1.55$ a.u. or $n_{val} \approx 1.15$. The observed (Marinescu *et al* 1998) value of $E_H/I(\text{Fr}) = 3.34$ is obtained when we take $r_{nZ}^c(\text{Fr}) = 1.63$ a.u. as calculated from eqn 8 of Ganguly (2008). Similarly, $r_\alpha(\text{Ra}) = 337$ pm would require $r_{nZ}^c(\text{Ra}) \approx 1.39$ a.u. while $E_H/I(\text{Ra}) = 2.49$ is obtained when $r_{nZ}^c(\text{Ra}) = 1.33$ a.u. from eqn 8 of Ganguly (2008). The first report of experimental ionization energy for Radium of 5.25 eV by Russell (1934) would require $r_{nZ}^c(\text{Ra}) = 1.418$ a.u. The values of r_{nZ}^c calculated from experimental values of the polarizability radius, r_α , or the first

ionization potential, I , using the methodology of Ganguly (2008) are internally self-consistent to within 2-4% accuracy.

5. Conclusions.

We have obtained atomic sizes for all elements (atomic numbers 3 - 118) from conditions of a classical stationary point. This is an important condition since it is consistent with a $\mu = 0$ condition (Ganguly 2000) or the chemical potential that is valid for an energy-minimized density optimized state (see also Politzer *et al* 2002, 2007). It is also a condition for transferability of sizes (Ganguly 1995, 2000, 2006). The basic mathematics used for obtaining atomic sizes in this study is pre-Schrödinger and “before DFT” (see Ayers 2007) and is eminently simple, even if it required many post Schrödinger formalisms and insights to attempts such a description. The descriptor for atomic sizes in this model has no adjustable parameter and represents a robust model—even if at the most primitive/fundamental level—for the influence of vacuum polarization in defining atomic sizes.

The novel aspect of this study is the sizes are obtained simply by considering the interaction of the electrons of an atom with the positron, e^+ , of an electron-positron pair, (e^-e^+), that represents an external interaction. This atomic size is obtained as the sum of contributions from core and valence regions in a manner that is quite different from those of earlier studies (Slater 1964, Politzer and Parr 1976, Simons and Bloch 1973). We obtain our sizes in a manner that is consistent with results from positron annihilation studies (Surko *et al* 2000, Gribakin 2000). In another communication, we will detail the way the size r_{nZ}^c may be used to obtain ionization potentials, dielectric polarizability, and electronegativity of atoms as well as atomic sizes that contribute to interatomic distances. The possibility that this can be done using eqn 1 has already been demonstrated with the empirical sizes, r_G , in earlier communications (Ganguly 1995, 2000, 2006).

Our method caters to the basic and simplifying premise that all atoms may be treated as being hydrogen-atom-like. We do this without Schrödinger- or DFT-formalisms or relativistic corrections for very heavy atoms, and using only the most rudimentary aspects of concepts of vacuum polarization. This “non-erudition” does not seem to be a disadvantage as otherwise the method has no adjustable parameter and has the advantage of obtaining an interpretation of atomic sizes that have been used for obtaining atomic properties (Ganguly 2008). In a way, it also justifies in the simplest manner, Bohr’s statement (see D.M. Harrison in , [http://www.upscale.utoronto.ca/GeneralInterest/Harrison/Bohr Model/- BohrModel.html](http://www.upscale.utoronto.ca/GeneralInterest/Harrison/Bohr%20Model/-BohrModel.html))

“We are tracing the description of natural phenomena back to combinations of pure numbers which far transcends the boldest dreams of the Pythagoreans.”

The arguments presented in this paper represent a complete break from ab initio Schrödinger-wave-function-based quantum methods with its computational-time limitations for large systems (Kohn 1999). It also represents a break from DFT approximants, which are now the “major computational workshop”, have difficulties from a “purist’s theoretical viewpoint” (Koch and Holthausen 2001) because of the use of empirical parameters. Our method is simple but accurate. The sizes, r_{nZ}^c , are appropriate in vacuum and are changed by eqn 1 when an appropriate property is required (Ganguly 2008)

Acknowledgment.

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Table 1. Atomic Sizes, r_{nZ}^c (in a. u.). Parameters used for their calculation from eqn 9 and comparison with theoretical sizes (in a. u.) r_{s_2} (from Zunger 1980) and empirical sizes, r_G (from Ganguly 1995)

Atom	Z	n_{val}	n_d	n_f	Z_{RG}	r_{nZ}^c	r_s^a	r_G^b
H	1	1	0	0	1			0
He	2	2	0	0	1			
Li	3	1	0	0	2	1.116 (1.06) ^c	0.98	1.04
Be	4	2	0	0	2	0.616	0.64	0.59
B	5	3	0	0	2	0.449	0.48	0.41
C	6	4	0	0	2	0.366	0.39	0.32
N	7	5	0	0	2	0.316	0.33	0.26
O	8	6	0	0	2	0.282	0.28	0.22
F	9	7	0	0	2	0.258	0.25	0.18
Ne	10	8	0	0	2	0.241	0.22	--
Na	11	1	0	0	10	1.384 (1.19) ^c	1.1	1.18
Mg	12	2	0	0	10	0.884	0.9	0.98
Al	13	3	0	0	10	0.717	0.77	0.85
Si	14	4	0	0	10	0.634	0.68	0.64
P	15	5	0	0	10	0.584	0.6	0.59
S	16	6	0	0	10	0.55	0.54	0.53
Cl	17	7	0	0	10	0.527	0.5	0.52
Ar	18	8	0	0	10	0.509	0.46	--
K	19	1	0	0	18	1.482	1.54	1.46
Ca	20	2	5	0	18	1.195	1.22	1.2
Sc	21	2	4	0	18	1.165	1.22	1.19
Ti	22	2	3	0	18	1.132	1.15	1.16
V	23	2	2	0	18	1.094	1.09	1.07
Cr	24	2	1	0	18	1.047	1.07	1.07
Mn	25	2	0	0	18	0.982	0.99	1.07
Fe	26	2	1	0	18	0.93	0.95	1.06
Co	27	2	2	0	18	0.904	0.92	1.01
Ni	28	2	3	0	18	0.888	0.96	0.96
Cu	29	2	4	0	18	0.876	0.88	0.89
Zn	30	2	5	0	18	0.867	0.82	0.87
Ga	31	3	0	0	18	0.815	0.76	0.78
Ge	32	4	0	0	18	0.732	0.72	0.7
As	33	5	0	0	18	0.682	0.67	0.68
Se	34	6	0	0	18	0.648	0.61	0.63
Br	35	7	0	0	18	0.625	0.58	0.62
Kr	36	8	0	0	18	0.607	0.56	--

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(Table 1 contd from previous page)

Atom	Z	n_{val}	n_d	n_f	Z_{RG}	r_{nZ}^c	r_s^a	r_G^b
Rb	37	1	0	0	36	1.597	1.67	1.65
Sr	38	2	5	0	36	1.31	1.42	1.45
Y	39	2	4	0	36	1.28	1.32	1.35
Zr	40	2	3	0	36	1.247	1.27	1.3
Nb	41	2	2	0	36	1.209	1.23	1.12
Mo	42	2	1	0	36	1.162	1.22	1.19
Tc	43	2	0	0	36	1.097	1.16	--
Ru	44	2	1	0	36	1.045	1.15	1.15
Rh	45	2	2	0	36	1.02	1.11	1.11
Pd	46	2	3	0	36	1.003	1.08	1.09
Ag	47	2	4	0	36	0.991	1.04	1.04
Cd	48	2	5	0	36	0.982	0.98	1.08
In	49	3	0	0	36	0.931	0.94	0.89
Sn	50	4	0	0	36	0.847	0.88	0.91
Sb	51	5	0	0	36	0.797	0.83	0.86
Te	52	6	0	0	36	0.764	0.79	0.85
I	53	7	0	0	36	0.74	0.76	0.78
Xe	54	8	0	0	36	0.722	0.75	--
Cs	55	1	0	0	54	1.665	1.71	1.71
Ba	56	2	5	0	54	1.538	1.52	1.45
La	57	2	4	0	54	1.518	1.38	1.47
Ce	58	2	4	1	54	1.508	--	1.43
Pr	59	2	4	2	54	1.498	--	1.43
Nd	60	2	4	3	54	1.487	--	1.42
Pm	61	2	4	4	54	1.476	--	1.42
Sm	62	2	4	5	54	1.465	--	1.44
Eu	63	2	4	6	54	1.454	--	1.35
Gd	64	2	4	7	54	1.442	--	1.39
Tb	65	2	4	8	54	1.43	--	1.38
Dy	66	2	4	9	54	1.418	--	1.37
Ho	67	2	4	10	54	1.405	--	1.37
Er	68	2	4	11	54	1.391	--	1.39
Tm	69	2	4	12	54	1.378	--	1.38
Yb	70	2	4	13	54	1.363	--	1.36
Lu	71	2	4	14	54	1.348	--	1.35
Hf	72	2	3	0	54	1.315	1.3	1.28
Ta	73	2	2	0	54	1.277	1.25	1.2
W	74	2	1	0	54	1.23	1.22	1.2
Re	75	2	0	0	54	1.165	1.19	1.14

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(Table 1 contd from previous page)

Atom	Z	n_{val}	n_d	n_f	Z_{RG}	r_{nZ}^c	r_s^a	r_G^b
Os	76	2	1	0	54	1.113	1.17	1.17
Ir	77	2	2	0	54	1.087	1.16	1.12
Pt	78	2	3	0	54	1.071	1.24	1.09
Au	79	2	4	0	54	1.059	1.21	1.04
Hg	80	2	5	0	54	1.05	1.07	1.11
Tl	81	3	0	0	54	0.998	1.01	1.07
Pb	82	4	0	0	54	0.915	0.96	1.22
Bi	83	5	0	0	54	0.865	0.92	1.14
Pb	--	2	0	0	54	1.165	--	1.22
Bi	--	3	0	0	54	0.998	--	1.14
Po	84	6	0	0	54	0.831	0.88	--
At	85	7	0	0	54	0.808	0.85	--
Rn	86	8	0	0	54	0.79	0.84	--
Fr	87	1	0	0	86	1.742	--	--
Ra	88	2	5	0	86	1.616	--	--
Ac	89	2	4	1	86	1.596	--	--
Th	90	2	4	2	86	1.586	--	--
Pa	91	2	4	3	86	1.575	--	--
U	92	2	4	4	86	1.564	--	--
Np	93	2	4	5	86	1.554	--	--
Pu	94	2	4	6	86	1.543	--	--
Am	95	2	4	7	86	1.543	--	--
Cm	96	2	4	8	86	1.519	--	--
Bk	97	2	4	9	86	1.519	--	--
Cf	98	2	4	10	86	1.507	--	--
Es	99	2	4	11	86	1.495	--	--
Fm	100	2	4	12	86	1.482	--	--
Md	101	2	4	13	86	1.469	--	--
No	102	2	4	14	86	1.455	--	--
Lr	103	2	4	0	86	1.426	--	--
Rf	104	2	3	0	86	1.393	--	--
Db	105	2	2	0	86	1.354	--	--
Sg	106	2	1	0	86	1.308	--	--
Bh	107	2	0	0	86	1.242	--	--
Hs	108	2	1	0	86	1.191	--	--
Mt	109	2	2	0	86	1.165	--	--
Ds	110	2	3	0	86	1.148	--	--
Rg	111	2	4	0	86	1.137	--	--
Uub	112	2	5	0	86	1.127	--	--

^a: From Zunger (1980); ^b: from Ganguly (1995); ^c: $\xi = 1/2$ in eqn 9

Table 1. Atomic Sizes, r_{nZ}^c (in a. u.). Parameters used for their calculation from eqn 9 and comparison with theoretical sizes (in a. u.) r_s (from Zunger 1980) and empirical sizes, r_G (from Ganguly 1995)

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H	1	1	0	0	1			0
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Li	3	1	0	0	2	1.116 (1.06) ^c	0.98	1.04
Be	4	2	0	0	2	0.616	0.64	0.59
B	5	3	0	0	2	0.449	0.48	0.41
C	6	4	0	0	2	0.366	0.39	0.32
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Cr	24	2	1	0	18	1.047	1.07	1.07
Mn	25	2	0	0	18	0.982	0.99	1.07
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Co	27	2	2	0	18	0.904	0.92	1.01
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Cu	29	2	4	0	18	0.876	0.88	0.89
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Ga	31	3	0	0	18	0.815	0.76	0.78
Ge	32	4	0	0	18	0.732	0.72	0.7
As	33	5	0	0	18	0.682	0.67	0.68
Se	34	6	0	0	18	0.648	0.61	0.63
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Pd	46	2	3	0	36	1.003	1.08	1.09
Ag	47	2	4	0	36	0.991	1.04	1.04
Cd	48	2	5	0	36	0.982	0.98	1.08
In	49	3	0	0	36	0.931	0.94	0.89
Sn	50	4	0	0	36	0.847	0.88	0.91
Sb	51	5	0	0	36	0.797	0.83	0.86
Te	52	6	0	0	36	0.764	0.79	0.85
I	53	7	0	0	36	0.74	0.76	0.78
Xe	54	8	0	0	36	0.722	0.75	--
Cs	55	1	0	0	54	1.665	1.71	1.71
Ba	56	2	5	0	54	1.538	1.52	1.45
La	57	2	4	0	54	1.518	1.38	1.47
Ce	58	2	4	1	54	1.508	--	1.43
Pr	59	2	4	2	54	1.498	--	1.43
Nd	60	2	4	3	54	1.487	--	1.42
Pm	61	2	4	4	54	1.476	--	1.42
Sm	62	2	4	5	54	1.465	--	1.44
Eu	63	2	4	6	54	1.454	--	1.35
Gd	64	2	4	7	54	1.442	--	1.39
Tb	65	2	4	8	54	1.43	--	1.38
Dy	66	2	4	9	54	1.418	--	1.37
Ho	67	2	4	10	54	1.405	--	1.37
Er	68	2	4	11	54	1.391	--	1.39
Tm	69	2	4	12	54	1.378	--	1.38
Yb	70	2	4	13	54	1.363	--	1.36
Lu	71	2	4	14	54	1.348	--	1.35
Hf	72	2	3	0	54	1.315	1.3	1.28
Ta	73	2	2	0	54	1.277	1.25	1.2
W	74	2	1	0	54	1.23	1.22	1.2
Re	75	2	0	0	54	1.165	1.19	1.14

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(Table 1 contd from previous page)

Atom	Z	n_{val}	n_d	n_f	Z_{RG}	r_{nZ}^c	r_s^a	r_G^b
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Ir	77	2	2	0	54	1.087	1.16	1.12
Pt	78	2	3	0	54	1.071	1.24	1.09
Au	79	2	4	0	54	1.059	1.21	1.04
Hg	80	2	5	0	54	1.05	1.07	1.11
Tl	81	3	0	0	54	0.998	1.01	1.07
Pb	82	4	0	0	54	0.915	0.96	1.22
Bi	83	5	0	0	54	0.865	0.92	1.14
Pb	--	2	0	0	54	1.165	--	1.22
Bi	--	3	0	0	54	0.998	--	1.14
Po	84	6	0	0	54	0.831	0.88	--
At	85	7	0	0	54	0.808	0.85	--
Rn	86	8	0	0	54	0.79	0.84	--
Fr	87	1	0	0	86	1.742	--	--
Ra	88	2	5	0	86	1.616	--	--
Ac	89	2	4	1	86	1.596	--	--
Th	90	2	4	2	86	1.586	--	--
Pa	91	2	4	3	86	1.575	--	--
U	92	2	4	4	86	1.564	--	--
Np	93	2	4	5	86	1.554	--	--
Pu	94	2	4	6	86	1.543	--	--
Am	95	2	4	7	86	1.543	--	--
Cm	96	2	4	8	86	1.519	--	--
Bk	97	2	4	9	86	1.519	--	--
Cf	98	2	4	10	86	1.507	--	--
Es	99	2	4	11	86	1.495	--	--
Fm	100	2	4	12	86	1.482	--	--
Md	101	2	4	13	86	1.469	--	--
No	102	2	4	14	86	1.455	--	--
Lr	103	2	4	0	86	1.426	--	--
Rf	104	2	3	0	86	1.393	--	--
Db	105	2	2	0	86	1.354	--	--
Sg	106	2	1	0	86	1.308	--	--
Bh	107	2	0	0	86	1.242	--	--
Hs	108	2	1	0	86	1.191	--	--
Mt	109	2	2	0	86	1.165	--	--
Ds	110	2	3	0	86	1.148	--	--
Rg	111	2	4	0	86	1.137	--	--
Uub	112	2	5	0	86	1.127	--	--

^a: From Zunger (1980); ^b: from Ganguly (1995); ^c: $\xi = 1/2$ in eqn 9

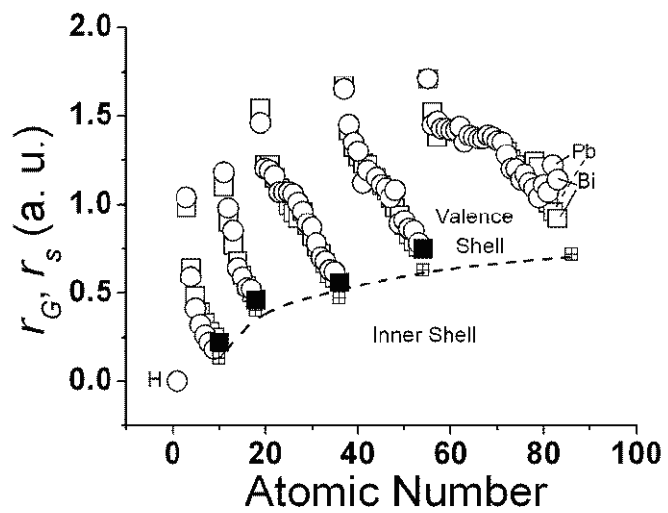


Figure 1 (Fig 1.TIF)

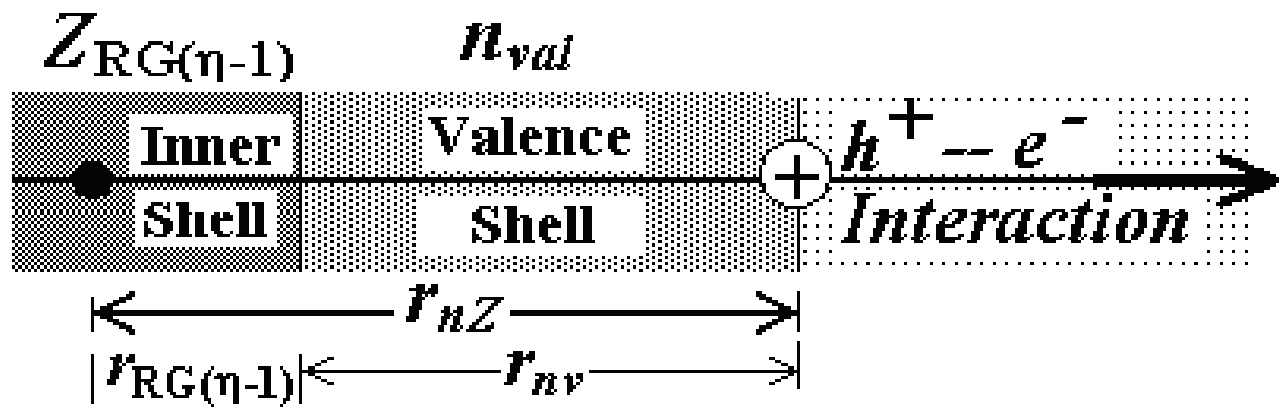


Figure 2 (Fig 2.TIF)

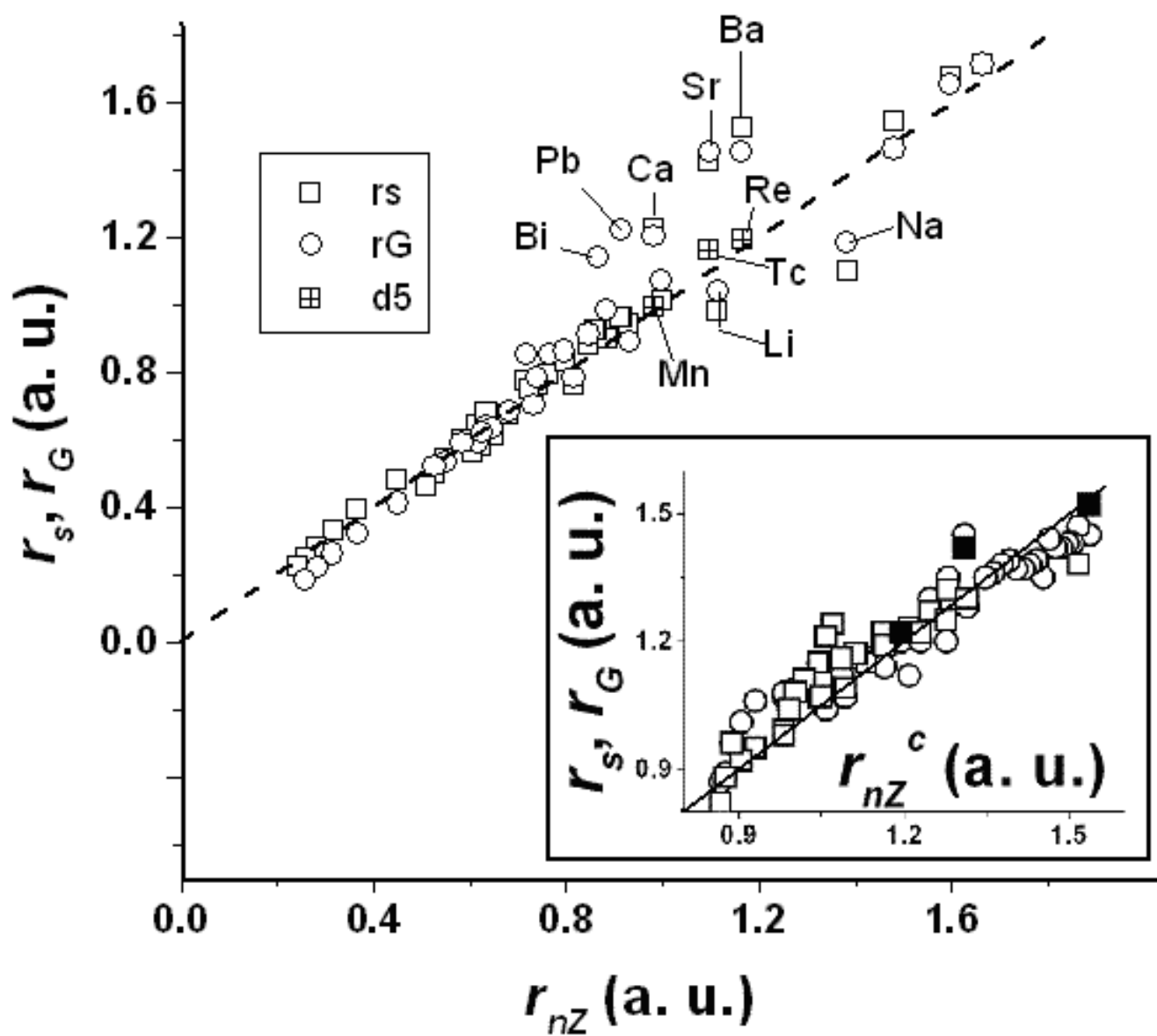


Figure 3 (Fig 3.TIF)

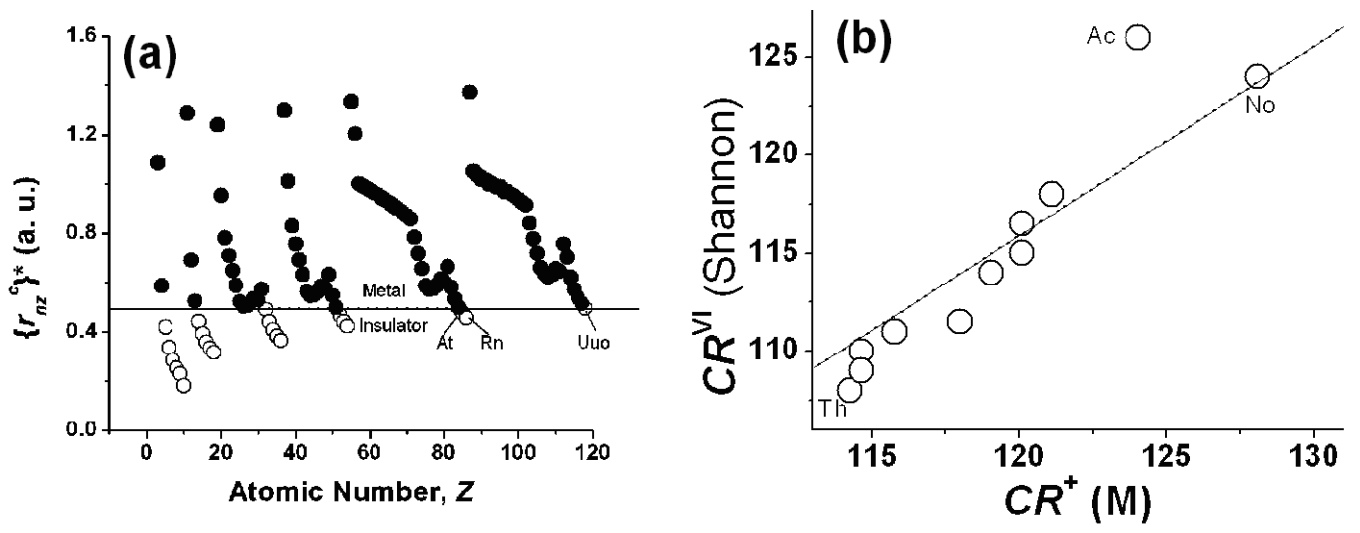


Figure 4 (Fig 4.TIF)