Atomic Radii based on Effective Nuclear Charge

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Abstract In the present work, a set of atomic radii are provided (from hydrogen to radon). Such values were calculated by using Clementi effective nuclear charges [3,4].The obtained atomic radii were compared with van der Walls atomic radii [1] as well as the Rahm-Hoffmann-Ashcroft values [2]. The obtained results confirm a crossroad position for cerium in the periodic tableas previously proposed [6].

Introduction

As is well known, taking into account the statistical/probabilistic nature of the atomic quantum mechanical model, there is not a definite "cutoff" point for electron density in a given atom, and such fact makes atomic radii a parameter not precisely defined. Nevertheless, such parameter is of paramount importance, since it is widely used in modelling and understanding molecular structure and interactions.

Van der Waals radii are among the most employed values and a complete set of data can be found in CRC Handbook [1]. However, van der Waals radius is defined as half of the distance of the closest approach of two non-bonded atoms, and such definition necessarily implied that there is a significant uncertainty in measure the "size" of an atom by this approach.

Recently, Rahm, Hoffmann and Ashcroft [2] have calculated/proposed a complete set of atomic radii values, employing a density cutoff of 0.001 e Bohr^{-3}. The atomic radii were derived using relativistic all-electron density functional theory calculations.

Ionization energy (IE) is defined as "the minimum energy required to remove an electron from an isolated atom or molecule (in its vibrational ground state) in the gaseous phase".

Since IE values are associated with gas phase isolated atoms, to associate the first IE values (the required energy to remove the outermost electron) with the atomic "size" seems an obvious decision.

Furthermore, I believe that the electrostatic criterion is a more precise and rational one, since it not requires a more or less arbitrary choice of a "boundary" or cutoff point, but a cutoff point is "naturally" establish by the nucleous-outermost electron electrostatic equilibrium distance.

However, IE values can be more precisely associated not with Z (atomic number) values but with Z_{eff} (effective nuclear charge) values.

In the present work, a (I believe) more precise set of atomic radii are provided (from hydrogen to radon). Such values were calculated by using Clementi effective nuclear charges [3,4].

The obtained atomic radii were compared with van der Walls atomic radii [1] as well as the Rahm-Hoffmann-Ashcroft values [2]. A rationalization for trends and exceptions in those correlations is provided

Methodology

Considering the electrostatic interaction between the nucleus and the outermost electron, using the Coulomb´s law and making the suitable algebraic manipulations, the following equation was derived:

$$R = [(1/4\pi)\mu_o Z_{eff} e^2]c^2/nE \qquad (1)$$

where μ_o is the vacuum permeability (1.26×10^{-6} N.A^{-2}), c the light speed (3.0×10^8 ms^{-1}), e is the electron charge (1.602×10^{-19} C), n is the main quantum number of the outermost electron and E is the first ionization energy per atom (J).

In such equation Z_{eff} is the nuclear effective charge and the values employed in the present work are those calculated by Clementi [3,4].

All ionization energy values were taken from Ref. 1, with exception of astatine (not available there), for which the employed value was those obtained by Roth et al [5].

Results and Discussion

The atomic radii calculated by using equation (1), are summarized in Table 1, and are compared with another ones from literature [1,2].

Table 1: Employed auxiliary data (Z_{eff} and IE), atomic radii form literature: van der Waals (vdw) and Rahm, Hoffmann and Ashcroft (rha) values, as well as values calculated by using Equation (1) [5]

Element	Z	Zeff (ref. 3,4)	1st IE/eV (Ref. 1)	Rvdw/Å (Ref. 1)	Rrha/Å (Ref.2)	R/Å (work; Eq. 1)
H	1	1.00	13.6	1.10	1.54	1.06
He	2	1.69	24.6	1.40	1.34	0.99
Li	3	1.28	5.4	1.82	2.20	1.71
Be	4	1.91	9.3	1.53	2.19	1.48
B	5	2.42	8.3	1.92	2.05	2.10
C	6	3.14	11.3	1.70	1.90	2.00
N	7	3.83	14.5	1.55	1.79	1.90
O	8	4.45	13.6	1.52	1.71	2.36
F	9	5.10	17.4	1.47	1.63	2.11
Ne	10	5.76	21.6	1.54	1.56	1.92
Na	11	2.51	5.1	2.27	2.25	2.36
Mg	12	3.31	7.6	1.73	2.40	2.09
Al	13	4.07	6.0	1.84	2.39	3.26
Si	14	4.29	8.2	2.10	2.32	2.51
P	15	4.89	10.5	1.80	2.23	2.24
S	16	5.48	10.4	1.80	2.14	2.53
Cl	17	6.12	13.0	1.75	2.06	2.26
Ar	18	6.76	15.8	1.88	1.97	2.05
K	19	3.50	4.3	2.75	2.34	2.93
Ca	20	4.40	6.1	2.31	2.70	2.60
Sc	21	4.63	6.6	2.15	2.63	2.53
Ti	22	4.82	6.8	2.11	2.57	2.55
V	23	4.98	6.7	2.07	2.52	2.68
Cr	24	5.13	6.8	2.06	2.33	2.72
Mn	25	5.23	7.4	2.05	2.42	2.55
Fe	26	5.43	7.9	2.04	2.26	2.48
Co	27	5.58	7.9	2.00	2.22	2.54
Ni	28	5.71	7.6	1.97	2.19	2.71
Cu	29	5.84	7.7	1.96	2.17	2.73
Zn	30	5.97	9.4	2.01	2.22	2.29
Ga	31	6.22	6.0	1.87	2.33	3.73
Ge	32	6.78	7.9	2.11	2.34	3.09

As	33	7.45	9.8	1.85	2.31	2.74
Se	34	8.29	9.6	1.90	2.24	3.11
Br	35	9.03	11.8	1.85	2.19	2.76
Kr	36	9.77	14.0	2.02	2.12	2.51
Rb	37	4.98	4.2	3.03	2.40	3.41
Sr	38	6.07	5.7	2.49	2.79	3.07
Y	39	6.26	6.2	2.32	2.74	2.91
Zr	40	6.45	6.6	2.23	2.68	2.81
Nb	41	6.70	6.8	2.39	2.51	2.84
Mo	42	6.98	7.1	2.17	2.44	2.83
Tc	43	7.23	7.3	2.16	2.41	2.85
Ru	44	7.45	7.4	2.13	2.37	2.90
Rh	45	7.64	7.5	2.10	2.33	2.93
Pd	46	7.84	8.3	2.10	2.15	2.72
Ag	47	8.03	7.6	2.11	2.25	3.04
Cd	48	8.19	9.0	2.18	2.38	2.62
In	49	8.47	5.8	1.93	2.46	4.21
Sn	50	9.10	7.3	2.17	2.48	3.59
Sb	51	9.99	8.6	2.06	2.46	3.35
Te	52	10.81	9.0	2.06	2.42	3.46
I	53	11.61	10.5	1.98	2.38	3.18
Xe	54	12.42	12.1	2.16	2.32	2.96
Cs	55	6.36	3.9	3.43	2.49	3.91
Ba	56	7.58	5.2	2.68	2.93	3.50
La	57	9.31	5.6	2.43	2.84	3.99
Ce	58	10.80	5.5	2.42	2.82	4.71
Pr	59	7.75	5.5	2.40	2.86	3.38
Nd	60	9.31	5.5	2.39	2.84	4.06
Pm	61	9.40	5.6	2.38	2.83	4.04
Sm	62	8.01	5.6	2.36	2.80	3.43
Eu	63	8.12	5.7	2.35	2.80	3.42
Gd	64	8.21	6.1	2.34	2.77	3.23
Tb	65	8.30	5.9	2.33	2.76	3.38
Dy	66	8.34	5.9	2.31	2.75	3.39
Ho	67	8.44	6.0	2.30	2.73	3.38
Er	68	8.48	6.1	2.29	2.72	3.34
Tm	69	8.58	6.2	2.27	2.71	3.32
Yb	70	8.59	6.3	2.26	2.77	3.27
Lu	71	8.80	5.4	2.24	2.70	3.91
Hf	72	9.16	6.8	2.23	2.64	3.23
Ta	73	9.53	7.5	2.22	2.58	3.05
W	74	9.85	7.9	2.18	2.53	2.99
Re	75	10.12	7.8	2.16	2.49	3.11
Os	76	10.32	8.4	2.16	2.44	2.95
Ir	77	10.57	8.9	2.13	2.33	2.85
Pt	78	10.75	9.0	2.13	2.30	2.87
Au	79	10.94	9.2	2.14	2.26	2.85
Hg	80	11.15	10.4	2.23	2.29	2.57
Tl	81	12.25	6.1	1.96	2.42	4.80
Pb	82	12.39	7.4	2.02	2.49	4.02
Bi	83	13.34	7.3	2.07	2.50	4.39
Po	84	14.22	8.4	1.97	2.50	4.06
At	85	15.16	9.3*	2.02	2.47	3.91
Rn	86	16.08	10.7	2.20	2.43	3.61

As can be verified from Table 1 data, as a general trend, there is a good (sometimes very good) agreement between the atomic radii calculated in the present work, based only in a electrostatic (Coulombic) approach and the van der Waals radii derived from crystal structures [1], as well as with the Rahm-Hoffmann-Ashcroft values [2] using relativistic all-electron density functional theory calculations.

However, also as a general trend, it is verified that the electrostatic approach provides atomic radii larger than that provided by the Rahm-Hoffmann-Ashcroft approach, and such approach, by its turn, provides atomic radii larger than the van der Walls values.

By the considerations make in the introduction, I believe that the electrostatic approach provides more precise values.

Some specific results must be discussed:

(a) From lanthanum to cerium, both, van der Walls and Rahm-Hoffmann-Ashcroft radius suffers negligible variations: from 2.43 to 2.42 and from 2.84 to 2.82, respectively. However, the electrostatic values for La and Ce, are, respectively 3.99 and 4.71. Such significant increase (18%) can be associated with the filling of an f subshell, which begins with cerium: La [Xe] $5d^1 6s^2$; Ce [Xe] $4f^1 5d^1 6s^2$. Hence, cerium exhibits the larger atomic radii among the lanthanides. That is, the electrostatic approach is "sensitive" enough to account for such radii variation due to a change in the electron configuration, and both, the van der Walls and Rahm-Hoffmann-Ashcroft approach, are not;

(b) In agreement with the previous considerations, it is well known that at high pressure, cerium suffers an isostructural volume collapse (γ phase to α phase). A study of this fundamental characteristic of the cerium volume was made and it was proposed that the localized $\leftrightarrow$ delocalized 4f electron picture provides an adequate description of this behaviour. Based on this result, a crossroad position for cerium in the periodic table was proposed [6]. Such crossroad position is illustrated/confirmed in the present work, with a significant variation in the atomic radii that only the electrostatic approach has depicted;

(c) It is worth noting here that previously, Ghosh [7] adopting another effective nuclear charge approach, have calculated an atomic radii for cerium of 3.21 Å and a larger radii for lanthanum: 3.81Å;

(d) From cadmium to indium, it is verified a decrease in van der Walls radius (2.18 to 1.93). On the other hand, in the Rahm-Hoffmann-Ashcroft values a discrete increase is verified (2.38 to 2.46). In the electrostatic values, a large increase (2.62 to 4.21) of 61% is verified. Such large increase is in agreement with the decrease in melting point (^{o}C) (321 to 257) and density (gcm^{-3}) (8.7 to 7.3) from cadmium to indium;

(e) The previous considerations are valid also for the pair mercury-thallium, with the difference that the remarkable relativistic contributions to mercury properties makes the radii/properties correlations not so straight forward;

(f) From gallium to germanium, an increase in the atomic van der Waals radii is observed (1.87 to 2.11). The Rahm-Hoffmann-Ashcroft is practically the same for both elements (2.33 and 2.34, respectively). However, using the electrostatic/Z_{eff} radii approach, a decrease from gallium to germanium is observed: 3.73 to 3.09. Such decrease is in agreement with a general trend of decrease of atomic radii form left to right along a period;

(g) From hydrogen to helium, van der Walls radius increases (1.10 to 1.40), whereas Rahm-Hoffmann-Ashcroft (1.54 to 1.34) and electrostatic/Z_{eff} radius (1.06 to 0.99) decreases. Such decrease is a reasonable achievement, taking into account that from H to He, the number of proton is the nucleus is doubled and that the "extra" electron will be located in the same energy level of the previous one;

(h) For the pair Ag and Au, the electrostatic/Z_{eff} is the only one that provides sound results: the van der Waals radius increases form Ag to Au (2.11 to 2.14), and the same is verified for the Rahm-Hoffmann-Ashcroft values (2.25 to 2.26). However, a decrease in the electrostatic/Z_{eff} radius is verified (3.04 to 2.85). As is well known, gold, as well as another heavy and superheavy elements, have their properties largely influenced by relativistic contributions and gold is, indeed (proportionally) the element of the periodic table with the large percentage relativistic contraction, with a remarkable effect on its atomic energy levels and

properties, including its magnetism [8]. In fact, due to a relativistic contraction, a minor atomic radii (compared with silver), for gold, must be expected.

The greater sensitivity of the atomic radius set calculated in the present work can be verified graphically in Figure 1, where the van der Waals (vdw), Rahm, Hoffmann and Ashcroft (rha) values, as well as the values calculated by using Equation (1) are plotted as a function of atomic number (Z). As can be verified, the atomic radius values calculated by using Equation (1) are very "sensitive" to the atomic numbers variations, whereas the Rahm, Hoffmann and Ashcroft (rha) values are very insensitive to such variations, been, by comparison, a most "rough" approach.
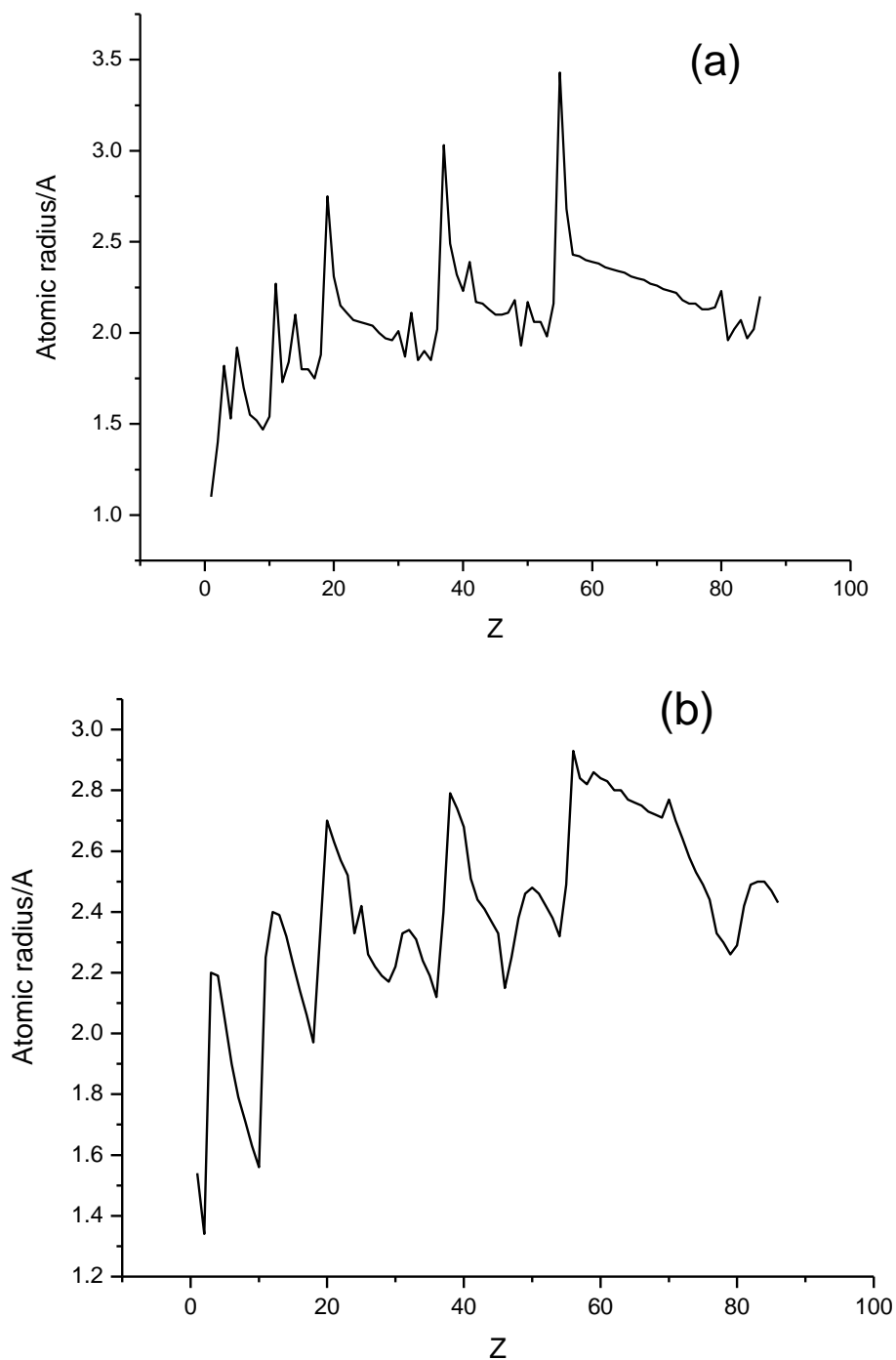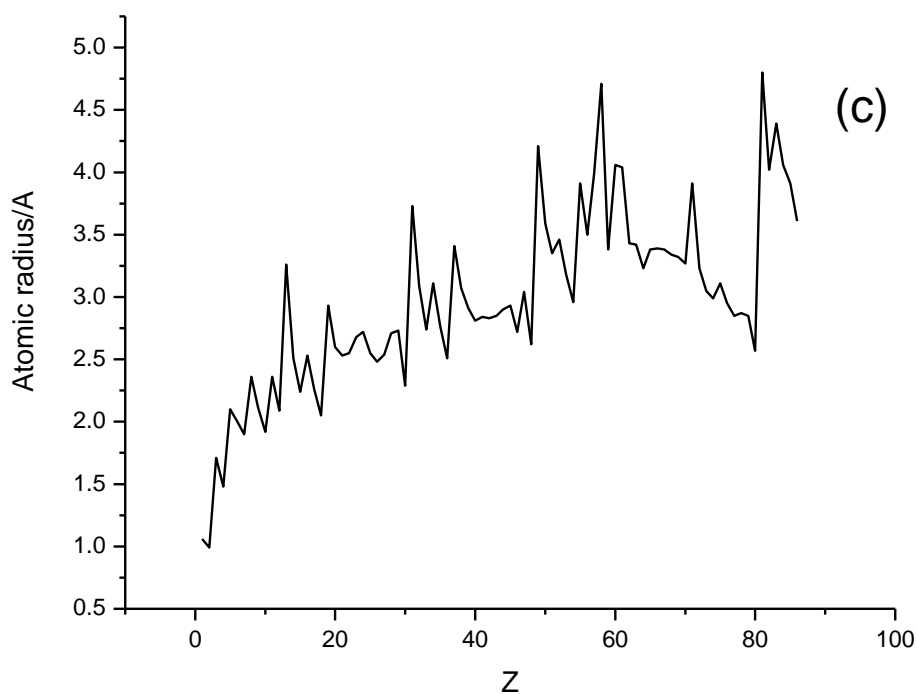
Figure 1: van der Waals (a), Rahm, Hoffmann and Ashcroft (b) and Equation (c) atomic radius as a function of atomic number (Z).

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