Atoms – How Small, and How Large!

K N Joshipura

The spatial extent of a free or an isolated atom can be gauged by defining its *radius*, and there are several different ways in which this quantity can be defined. Four of them are considered in this article. Quantum mechanical wave functions are employed to estimate the most probable and the average radii of atoms. Atomic polarizability radius and van der Waals radius are also considered, and all the four radii are examined across the periodic table. Atomic ions are then briefly dwelt upon, and a big contrast is noted in the sizes of (free) Li^+ ion and the exotic H^- ion, both iso-electronic with helium atom. Brief mention is also made of large exotic species like the metastable atoms and Rydberg atoms. The article seeks to provide a quantitative glimpse of how small or large the atomic systems can be.

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1. Introduction

All things are made of atoms - little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another. In that one sentence ...... there is an enormous amount of (scientific) information about the world.

—Richard Feynman

Famous physicist Feynman's quote highlighting the atomic concept as an important achievement of mankind, has come nearly five decades ago. In the past few decades mankind has successfully ventured into molecules, atoms and also into their constituent particles. This is evident from the excitement generated by the Higgs' boson[1].

Even in today's world, the atom occupies a unique position, since it is a gateway to scientific knowledge about the ultimate structure of matter.

Atoms were born, so to say, nearly 300,000 years after the *big bang,* according to theoretical estimates. The concept of atoms was conceived in the great minds of thinkers like Kanaada in India, and Democritus in Greece, almost in the 5th century BC. Atoms moved from philosophy to science when chemist John Dalton[2] (1808) made a hypothesis of atoms as extremely tiny building blocks of all chemical elements. Later on, in the 19th century, efforts were made to ascertain atomic weights of different elements relative to hydrogen, the lightest atom. Mention must be made here of Lothar Meyer (1864), who attempted to estimate the sizes of atoms, based on molar volumes. He concluded correctly that there were peaks or maxima in the atomic sizes (radii) corresponding to alkali elements Li, Na, K, etc. Eventually the periodic table that was first proposed by Lothar Meyer and Mendeleev (1869) saw many changes and it was put on a firm physical foundation when Moseley (1915) found that, it is the atomic number Z (and not the atomic weight) that determines the position of an element in the periodic table.

Philosophical ideas on atoms are age old. The chemist Dalton brought atom from philosophy to science. How small are atoms actually? Niels Bohr in his atomic model (1913) answered this question by assigning a radius a_0 (= 0.529Å) to the hydrogen atom.

True, atoms are known to be very tiny, but how small are they?! For hydrogen, an answer to this question was found in the Bohr atom model, the birth centenary of which is celebrated in the year 2013. Neils Bohr introduced in his model the quantization (occurrence of discrete values) of angular momentum and energy of electron in the hydrogen atom, and assigned a radius 'a_0' to this atom in its ground (i.e., lowest possible) state. Assuming an infinitely massive proton (nucleus) in H-atom, the so-called Bohr radius a_0 is found to be

$$a_0 = 0.529 \times 10^{-10} m = 0.529 \text{Å}.$$

The symbol Å denotes the Angstrom unit of length.

2. Enter Quantum Mechanics

Quantum mechanics – the basic mechanics of quantum systems – entered the atomic arena in 1926, with Erwin Schrödinger's epoch-making equation $H\Psi = E\Psi$. Here H stands for the Hamiltonian operator and the total energy of the system is E. Let us emphasize that the equation has an exact mathematical solution for hydrogen and in fact, for any one-electron system. Thus the wave function Ψ and energy E are known exactly in this case, as discussed in books on quantum mechanics [1, 2]. The wave function Ψ of a 1-electron atom depends parametrically on principal quantum number n, orbital angular momentum quantum number ℓ and the corresponding projection quantum number m_ℓ. The ground state of H-atom is represented by the wave function (also called the orbital) Ψ_{1s}. A simple diagram of the energy levels of atomic hydrogen, derived by solving the Schrödinger equation, is given in *Figure* 1. The diagram is instructive in many ways; for example, one finds that in the ground state H-atom, the minimum energy needed to just separate out the electron from the proton, called ionization energy I, is 13.6 eV. In the first excited state $(n = 2)$ it is 3.4 eV, and so on.

Quantum mechanics gives exact simple expressions for wave functions and energy levels of one-electron atoms, like hydrogen. The H-atom energy level diagram is instructive in many ways.
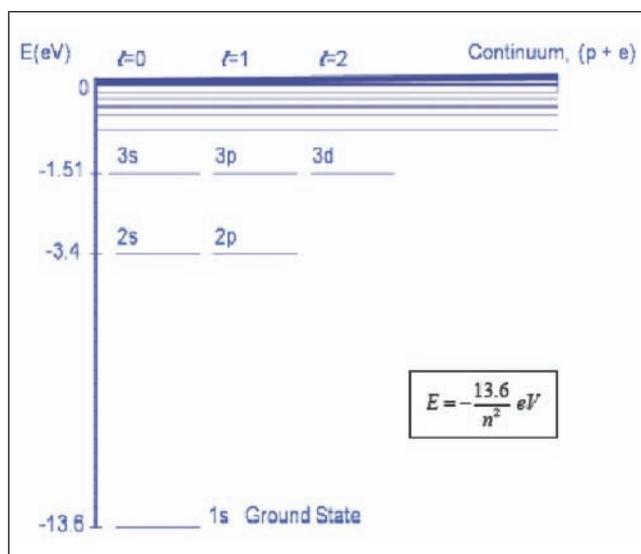

Figure 1. Energy level diagram for hydrogen atom, along with a simple formula to generate the levels.

For atoms with number of electrons $N \geq 2$, we have to specify as well the spin projection quantum number $m_s = \pm\, 1/2$. The electrons in the atom get themselves arranged in a self-disciplined manner, as per the Pauli exclusion principle.

The wave function Ψ bestows upon the electron a smeared out existence, and leads to the position probability density (i.e., probability per unit volume) at a point $\boldsymbol{r}$, through its absolute square $|\Psi(\boldsymbol{r})|^2$. The electron(s) is (are) just somewhere in the vicinity of the nucleus and the atom is no more an object with a sharp boundary. Rather, it is a tiny fuzzy ball with electrons forming negatively charged cloud surrounding the positively charged nucleus. Further it so turns out that the radial probability density $r^2|\Psi|^2$ of atomic hydrogen plotted against distance r from its nucleus exhibits peak or maximum [1,2] at a particular distance $r = a_0$. How nice...! The Bohr radius a_0 mentioned earlier now becomes the most probable radius 'r_{p}'($= 0.529$ Å) of the hydrogen atom in its ground state. The diameter of a free or isolated H-atom is of the order of 1 Å $= 10^{-10}$ m. The quantity a_0 is quite fundamental and it serves as a unit of length in the atomic–molecular physics. The quantity r_{p} may also be termed as the peak radius or the orbital radius.

Now, since probability rules the quantum world, we have two more options for defining the size or dimension (actually radius) of an atom. With the electron position probability in H-atom given by $|\Psi_{1s}|^2$ we define the average radius $\langle r \rangle$, called the expectation value in quantum mechanical jargon, as

$$\langle r \rangle = \frac{\int \Psi_{1s}^* \, r \, \Psi_{1s} \mathrm{d}\tau}{\int \Psi_{1s}^* \, \Psi_{1s} \mathrm{d}\tau}.$$

One more option is to define the root-mean-square (rms) radius given by $\sqrt{(\langle r^2 \rangle)}$, which can also be calculated along the above lines. For ground state hydrogen atom

the average radius $\langle r \rangle$ is $(3/2)\, a_0$ which amounts to 0.79 Å, while the rms radius 0.92 Å is somewhat larger. In the present discussion we focus on r_{p} and $\langle r \rangle$ only.

The definitions indicating averages, like those stated above are also found elsewhere in physics. Readers might recall the speed distribution of atoms/molecules in a gas as given by the Maxwell–Boltzmann (or classical) statistics, where one defines most probable speed v_{p}, average speed denoted by $\langle v \rangle$ and the rms speed v_{rms} at a certain temperature. However, there are basic differences in which probability manifests there and in the present context.

3. Atomic Sizes and the Periodic Table

Hydrogen atom is unique in that it offers an exactly solvable problem. That is not the case with atoms (/molecules/ions)having two or more electrons. Soon after the advent of quantum mechanics, physicists succeeded in finding approximate solutions in such cases. Exactly solvable problems are only a few, and approximation is quite often a practice in quantum mechanics.

Turning to helium atom $(Z = 2)$, we learn that its two electrons with opposite spins exist together happily forming a tightly bound atomic system. He-atom is quite compact as its r_{p} value turns out to be 0.31 Å while its average radius $\langle r \rangle = 0.49$ Å. Helium is indeed strongly bound; its first ionization energy I (minimum energy required to release the outermost electron) $= 24.6$ eV is the highest among all members of the periodic table. The next atom lithium $(Z = 3)$ has two 1s electrons tightly bound in the K-shell as in He, with the third one in the 2s orbital. The 2s electron feels the coulomb potential of the nucleus screened by the inner K-electrons, and therefore it tends to be rather away from the nucleus. Li atom is fairly large with $\langle r \rangle = 2.05$ Å while its first ionization energy I is quite small, i.e., about 5.4 eV.

Readers might recall atomic/molecular speed distribution in Maxwell–Boltzman statistics, and definitions like most probable, average and rms speeds. Probability manifests itself differently there and here in quantum mechanics.

We have started journey along the periodic table in exploring atomic sizes. Radii r_p and $\langle r \rangle$ are evaluated from atomic wave functions. Elaborate attempts have been made to find accurate wave functions of atoms from $Z = 2$ to 54, and beyond.

In a way we have started our journey along the periodic table in exploring how small or large a free (or isolated) atom could be. Now, we will not move continuously along the increasing atomic number Z. One of the most important characteristics of the periodic table is the periodicity in the properties of chemical elements. We notice columns or 'groups' of elements having similar properties. Helium along with Ne, Ar, Kr, Xe and Rn forms the group of inert (or noble or rare) gases. The atoms of these gases are relatively compact (and strong), and helium offers the best example. As against this, we have the group of alkali atoms Li, Na, K, Rb, Cs and Fr, which are relatively larger, and each of them has a loosely bound outermost electron. We consider two radius parameters r_p and $\langle r \rangle$ as indications of the atomic size. For many-electron atoms, these radii are calculated for the outermost orbital, as for example, 2s for Li and so on. We shall not go into the details, but suffice it to say that these can be evaluated by using the atomic wave functions.

Elaborate attempts have been made to determine atomic wave functions accurately, as can be seen from relevant literature. Somewhat old but popular in this regard are the Roothan Hartree–Fock wave functions given by Clementi and Roetti [3]. The so-called Clementi tables [3] provide parametrized orbitals for atoms and ions corresponding to Z from 2 to 54, above which these are available from McLean and McLean [4]. Bunge et al [5] have given average atomic radii along with their tables of parametric wave functions for $Z = 2$ to 54. We have employed inputs obtained from [3–5] to determine the quantities r_p and $\langle r \rangle$. The integrals involved in evaluating $\langle r \rangle$ are calculated by using standard computational softwares.

We have plotted in *Figure* 2, the two types of radii, viz., peak position distance r_p and average radius $\langle r \rangle$ as functions of atomic number Z from 1 to 92. The graphical
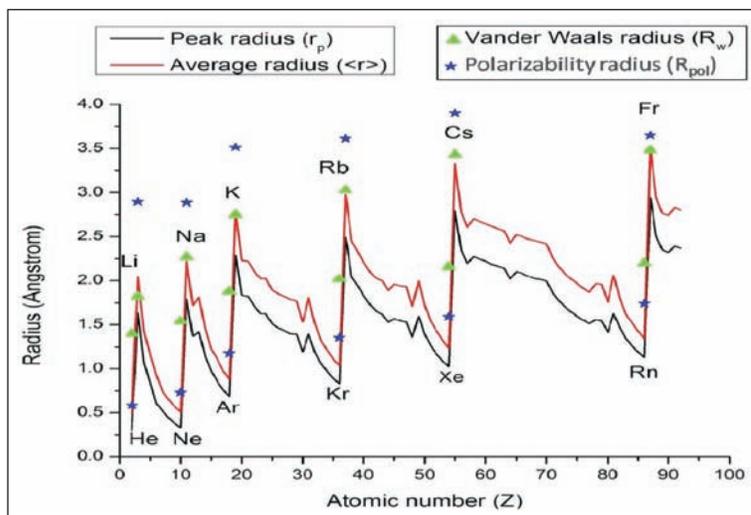
Figure 2. Variation of atomic radii r_p and $\langle r \rangle$ across the periodic table. Also shown are the van der Waals radii R_W and the polarizability radii R_{pol} for inert gases and the alkali atoms.

plot exhibits hills and valleys in the atomic sizes across the entire stretch. Both types of radii show an increase as one goes down a column in the periodic table and a decrease as one goes from an alkali atom to the inert-gas atom. One can also see small ups and downs, depending on the specific electronic configurations. An important point must be noted here. As Z increases, the inner electrons acquire high kinetic energy. The resulting speeds are such that it becomes necessary to include the special theory of relativity. Omitting details, we simply mention that relativistic wave functions are needed for high Z (typically above 54) atoms.
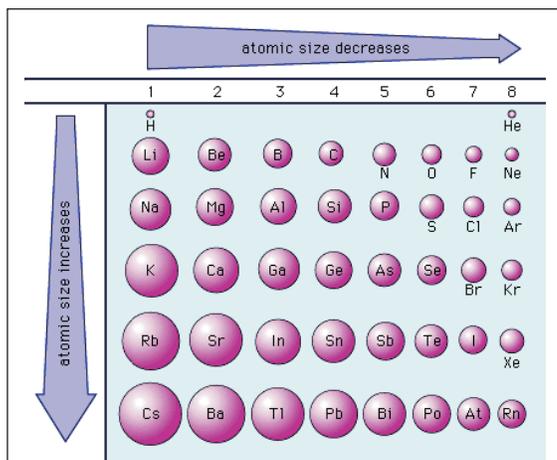
A picture of the periodic table (in part) in terms of relative atomic sizes is highlighted in *Figure* 3, which is self-explanatory.

At this stage let us ask again; how 'large' is an atom? The answer to this question, in terms of the number of electrons, is uranium ($Z = 92$) among the atoms of the natural elements. But one finds from *Figures* 2 and 3 that in terms of spatial extension or size, the largest atom atom is caesium Cs ($Z = 54$), with $\langle r \rangle = 3.33$ Å. Francium (Fr), the last member of the alkali-atom group is extremely rare in occurrence.

Atomic radii plotted versus Z exhibit interesting hills and valleys, depending upon electronic configurations. The largest atom in terms of $\langle r \rangle$ is caesium, ignoring the rare element francium.

4. van der Waals Radius, Polarizability Radius

The question of finite non-zero dimensions of atoms was addressed much earlier from a different point of view by van der Waals[3] in 1873. His interest was in the deviations from ideal gas behaviour observed in different gaseous substances. He attributed this deviation to two factors, viz., interaction (forces) between two colliding atoms (or molecules), and their size, though very small but non-zero. His surmise was correct. Free atoms or molecules exert forces on each other when they are close enough, mainly due to the electric field produced by the charge distribution within the atom/molecule. The potential energy $V(r)$ of an interacting pair of neutral, free, identical atoms can be given by the so-called Lennard–Jones potential shown graphically in *Figure* 4. The distance σ in this figure corresponds to a balance between attractive and repulsive forces between the two free atoms. Half of this distance σ can be taken as a typical size called van der Waals radius R_W [6] of the atomic species.

Readers will recall at this stage Richard Feynman's quote inserted in the beginning of this article. His words elegantly reflect the attraction between atoms at small distances, and repulsion at a close (just touching) distance.

The question of finite non-zero size of atoms was addressed much earlier by van der Waals. He surmised an attractive force between two colliding atoms, each having a finite size. Free atoms/molecules exert short-range forces on each other. The forces turn repulsive at a very close distance, enabling us to define van der Waals radius R_W.
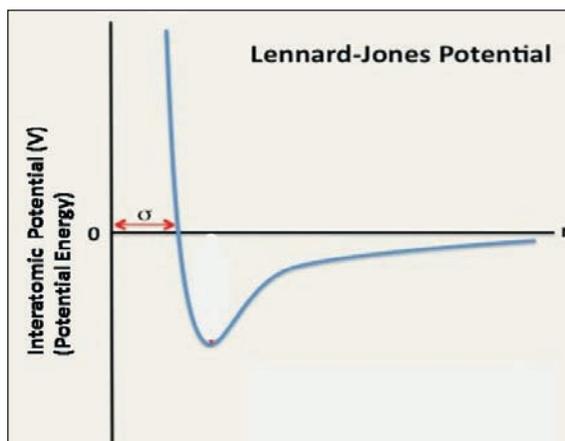
Now, in our attempts to delimit atomic borders, let us consider the response of an atom to an external electric field. Suppose that atoms are immersed in a static electric field of strength E, which induces a temporary electric dipole moment p in the atomic charge distribution. In a simple linear approximation we can assume $|p| \, \alpha \, |E|$, and hence $p = \alpha_d E$. The proportionality constant α_d, called the electric dipole polarizability of the atom, is expressed in terms of volume, i.e., in Å^3. Thus, the quantity $(\alpha_d)^{1/3}$ having length dimensions is yet another measure of atomic size. We therefore define $R_{pol} = (\alpha_d)^{1/3}$ as the polarizability radius [7] of the atom. The quantities R_W and R_{pol} are also included in *Figure* 2, not for all atoms, but for inert gases and alkali atoms, for obvious reasons.

In the present discussion we can include atomic free *ions*, both positive and negative. Let us briefly consider two extreme cases, viz., the lithium Li^+ ion and the exotic hydrogen H^- ion. Both these are helium-like atomic systems; the first ionization threshold of Li^+ is 75.64 eV, while that of H^- is just about 0.75 eV. Nobel Laureate and astronomer S Chandrasekhar had given a simple approximate wave function for the negative hydrogen ion [1, 8]. We have employed this wave function to calculate its average radius and found that $\langle r \rangle = 3.1$ Å for H^-, in

Polarizability α_d expressed in Å^3 measures the response of an atom to external electric field, and so $(\alpha_d)^{1/3}$ defines the polarizability radius R_{pol}.

big contrast to Li$^+$ having $\langle r \rangle = 0.30$ Å, in comparison with $\langle r \rangle = 0.49$ Å for helium atom. The corresponding polarizabilities exhibit order-of-magnitude differences, as expected.

5. Conclusions

The physical world around us can be classified broadly into astro-systems, meso-systems and micro-systems (also called micro-cosm). Atomic dimensions provide a very important reference to judge the size and other properties of a variety of micro-systems that we speak about in science and technology today. In this article we have considered different concepts of assigning radius to an atom. The most probable radius and the average radius are derived from a direct application of quantum mechanics to available atomic wave functions. The other two concepts, viz., the van der Waals radius and the polarizability radius emerge from the response of the atomic charge distribution to external influence, as mentioned. All these radii show (*Figure* 2) a periodic variation from minima at inert-gas atoms to maxima at alkali atoms. The spatial extent of an atom as indicated by radii r_{p} and $\langle r \rangle$ correspond to static charge distribution of atomic electrons, and both these are generally smaller than the 'response' radii R_{W} and R_{pol}.

Nobel Laureate astronomer S Chandrasekhar had given a simple approximate wave function for H$^-$ ion. We have used this to find its $\langle r \rangle$. While H$^-$ ion is much larger, the Li$^+$ ion is much smaller than the iso-electronic He atom.

Now before we conclude, it is tempting to ask a rather strange question – can atoms be unusually bigger!? The answer is yes, and a brief explanation follows. According to the Bohr model for H-atom the atomic radius in the n-th level is $r = a_0 n^2$. Quantum mechanically also, the radius of the excited states increases as n^2. Now it is interesting to note that hydrogen atoms in highly excited states (say $n \sim 100$ or more), called *Rydberg* atoms, are found to exist in certain astrophysical systems. Due to high value of the principal quantum number n, they are endowed with an unusually large size; a Rydberg atom can be as big as a bacterium! Their ionization

thresholds are extremely small, as seen from the energy-level formula given in *Figure* 1.

Apart from the high 'n' situation, consider the hydrogen atom in $n = 2$ level, which means either 2s or 2p state. Normally one would expect the excited atom to return to ground (or a lower) state by quickly emitting a photon of appropriate energy. However, the quantum mechanical (electric dipole) selection rules do not allow the 2s state to de-excite into ground (1s) state. Let us simply say that hydrogen 2s is a *metastable* state with a very large radiative lifetime of about $1/7$ s as against the 2p state having lifetime of $\sim 10^{-8}$ s, and the metastable H atom has a large radius too [9]. Other atoms and molecules can also exist in metastable states, and since their radiative lifetimes are rather large, they act as storage of energy in a medium.

> An atom with a high principal quantum number *n*, called a Rydberg atom, can be as large as a bacterium. Excited metastable atoms are exotic species having a large radiative life-time, and a large average radius. They act as a storage of energy in a medium.

Acknowledgements

Suggested Reading

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