



CORRELATIONS AMONG ATOMIC PROPERTIES AND ESTIMATES ON EXOTIC ATOMS

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ABSTRACT

In this paper we first examine and propose the relationships between the first ionization energy (I_0), polarizability (α_0) and orbital radius specifically for inert gas-atoms. These are known in general over a range of atomic number Z . This paper reports linear relation between I_0 and α_0 especially for the inert gas atoms and predicts the properties of super- heavy inert gas atom $Z = 118$. The correlation study is extended to lesser known regime of ions on one hand and meta-stable atomic species on the other.

INTRODUCTION

First ionization energy (I_0) of atoms is one of the most well known experimental as well as theoretical quantity. This property is known to correlate strongly with another important atomic property i. e., electric dipole polarizability α_0 and this was shown for selected atomic species by Fricke [1]. The quantity α_0 is a measure for the response of an atomic system to an external electric field. While I_0 corresponds to transitions in continuum, α_0 corresponds to virtual excitations. Correlation between α_0 and I_0 , as well as α_0 and the average atomic radius $\langle r \rangle$ were discussed by Dimitrieva & Plindov [2]. Hatti & Dutta [3] have also reported the same correlation using a semi-empirical approach. In earlier studies [4, 5] a relationship between α_0 and atomic volume was also established. Politzer et al [6] also showed relation between local ionization energy and polarizability in his recent publication. Considerable work has been reported in this field till date for atoms in their usual ground state. A number of empirical correlations between polarizabilities and volumes have also been reported [7- 9]. In this paper, we bring out a relationship between the quantities I_0 and α_0 by equations which are exact for 1 electron atoms. We feel that for many - electron atoms it is more appropriate to make this type of generalization on the basis of periodic table groups, and this has been attempted in the present work. Thus we propose semiempirical equations for the important properties of the inert gas atoms. Comparisons of our generated or estimated values are made with available experimental data.

As an outcome of the correlations studied it has been possible to estimate or predict microscopic properties of exotic species like a super-heavy atom on one hand and meta-stable atoms on the other. The importance of present study lies in our quantitative conclusion about these special kinds of atoms for which very little knowledge exists at present.

THEORETICAL ASPECTS

It is well known that polarizability and ionization energies have periodic property. Also, it has been established that atomic polarizabilities are dependent on size of the atoms. The graph of first ionization energy and polarizability in log scale for 88 elements was first plotted by Fricke [1]. The linear relationship between ionization energy and polarizability was extrapolated [1] to estimate the polarizability of heavier atom of a periodic group. To understand the reason for such behavior we can start with a prototype example of hydrogen atom.

Since early days of Quantum Mechanics the exact knowledge

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about 1- electron (hydrogenic atoms) exists. The ionization energy (I_0) for hydrogen atom [10] is given as follows.

$$I_0 = \frac{13.6}{n^2} eV = \frac{1}{2n^2} \text{ au} \quad (1)$$

And the corresponding expectation value of s-electron radius is given by

$$\langle r \rangle = 3/2 a_0 \quad (2)$$

Where ground state value corresponds to $n=1$. Under the influence of infinitely massive nucleus the average or expectation value of the hydrogenic radius becomes

$$\langle r \rangle = 3/2 \text{ au} \\ I_0 = 1/\langle r \rangle \text{ or } I_0 = \delta / \langle r \rangle \quad (3)$$

With δ as a constant, this correlates the atomic size i. e., average radius with ionization energy [10]. Now, it can be seen from [4 - 8] that the atomic dipole polarizability α_0 is proportional to $\langle r \rangle^3$, so that

$$\alpha_0 \propto \frac{1}{I_0^3} \text{ or } \alpha_0 = \frac{\beta}{I_0^3} \quad (4)$$

Here β is a constant. A similar relation was reported in other works [2, 3, 6]. Dimitrieva & Plindov [2] have deduced a similar dependence via a statistical model, as follows

$$\alpha_0(N, Z) = (Z - N + 1)^3 I_0^{-3}(N, Z) f(N, Z) \quad (5)$$

These authors [2] used experimental data for 34 neutral atoms to demonstrate that $f(N, Z)$ is slowly varying function of the nuclear charge, the correlation coefficient for fitting these data was 0.97 which is quite good. But, both the ionization energy and the polarizability cannot be expected to correlate strongly in such a general way as in equation (4) for all atoms, because the structure of the valence shell of each atom is different. But systematic variations are expected over a group in the periodic table. Thus it is more reasonable to search for correlations within a group in the periodic table.

In view of the above discussion, we can generalize and propose an equation connecting α_0 and $1/I_0^3$ in the following linear expression

$$\alpha_0 = A/I_0^3 + B \quad (6)$$

Here slope A and intercept B are parameters for a periodic group and their value varies from one group to another group. This means that these values essentially depend on outer electron configuration or number of electrons and other parameters of atoms in the group. Parameters A and B in a group are obtained by the standard linear least square fitting. Thus we find that for the inert gas group, the linear equation becomes

$$\alpha_0 = 7036.01/I_0^3 - 0.1934 \quad (7)$$

The correlation coefficient for this fitting is 0.99593, which is better than that in [2].

Let us also consider the cations Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ and Fr^+ which are respectively isoelectronic with the nearby inert gas atom. Therefore, the relation between α_0 & I_0 is expected to be as per equation (6) with a different set of A and B. We have also attempted here a similar correlation between α_0 & I_0 for the metastable atoms $\text{He}^*(2^3S_1)$, $\text{Ne}^*(^3P_2)$, $\text{Ar}^*(^3P_2)$, $\text{Kr}^*(^3P_2)$, $\text{Xe}^*(^3P_2)$. The parameters A and B in each of the above three categories of atomic systems are exhibited in table 1.

Table- 1 Linear fitting parameters A and B for equation (6)

Group of atoms	A	B	Correlation coefficient
Noble gases (ground state)	7036.01	-0.193	0.995
Group IA (cations)	33720.75	-0.172	0.994
Noble gas (Metastable states)	3434.99	1.5123	0.991

RESULT AND DISCUSSION

In the present theoretical study, we have proposed a linear relation between α_0 and $1/I_0^3$ as given in equation (6), for three different atomic systems, viz., noble gases, noble-gas like positive ions and meta-stable atomic states. These are discussed separately below.

Noble gas atoms

We find that there is excellent correlation over the inert gas group. Let us (Fig. 1) take the advantage of the excellent correlation of 99% and extrapolate the graph in figure 1 to super-heavy inert gas atom of $Z = 118$, called EKARADON, Uuo. For this purpose the first ionization potential for this exotic super-heavy atom is taken from [11]. The value of I_0 is 8.92 eV, when supplied to equation (7) brings out the value of polarizability to be 9.72 \AA^3 . However some physical insight also can be made by using semi-quantum mechanical arguments.

The radius of a particular electronic shell is defined as the distance at which the electron charge density $e|\Psi|^2$ is maximum. Denoting this by R_{max} we find from Hirshfelder et al [7] and also from Bransden and Joachain [10] that,

$$R_{\text{max}} = \frac{n^{*2}}{Z-s} \quad (8)$$

Where n^* is effective principal quantum number and $(Z-s)$ is effective nuclear charge, which can be calculated using the Slater rules as stated in Hirschfelder [7].

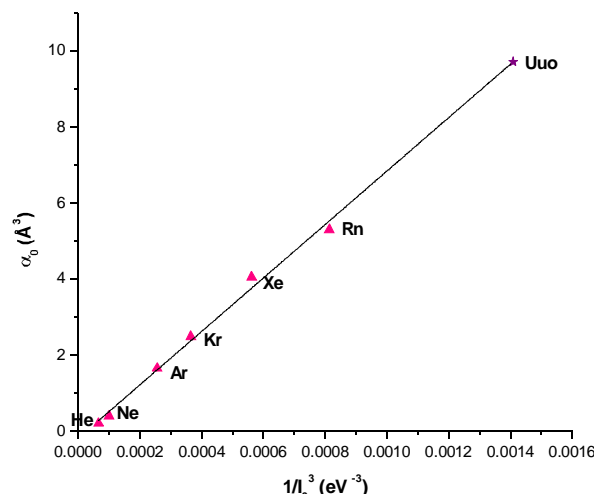


Fig. 1 Fitting of $\alpha_0 \rightarrow 1/I_0^3$ for ground state noble gas atoms.

Thus, the ionization energy corresponding to n^* may be considered as,

$$I_0 \propto \frac{1}{n^{*2}} \quad (9)$$

We first calculate R_{max} for $Z=118$ using equation (8), while $(Z-s)$ is calculated using Slater's rules. The value of R_{max} obtained in this case is $2.35 a_0$. From this we find that the ionization potential is 9.83 eV. Now, again from this I_0 and equation (7), we obtain the value of polarizability to be 7.21 \AA^3 , which is comparable to 9.72 \AA^3 as reported earlier in this section.

Noble Gases and respective iso-electronic ions

Consider now a set of singly charged alkali positive ions Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ and Fr^+ having electronic configuration of the respective (iso-electronic) noble gas atoms. Studying the correlation between α_0 and I_0 for these cations, we find excellent correlation coefficient for the fitting equation (6). The values of A and B of this atomic system are different from that of noble gases. This is due to the nature of the tightly bound cations, resulting into high I_0 and small $\langle r \rangle$ as well as α_0 .

From Figure 2 we can obtain a fitting relation as predicted by our model with the help of which we can estimate the polarizability of an atom whose ionization energy is known. The fitting parameters along with their respective correlation coefficient are mentioned in Table 3. Whereas Table 2 displays the estimated values of polarizability obtained from the fitting relation. The unphysical negative but small value of α_0 of Li^+ generated by the fitting equation, wide a Table 2, indicates very small polarizability arising out of very tight binding of this

Table 2 ionization potential and polarizability for noble gas-like positive alkali ions

Sr. No	Ion (no. of electrons)	Ionization potential I_0 (eV)	Electric dipole polarizability α_0 (\AA^3)	Calculated α_0 (\AA^3) From (6)
1	Li^+ (2)	75.64	0.03	-0.09
2	Na^+ (10)	47.28	0.14	0.14
3	K^+ (18)	31.63	0.79	0.89
4	Rb^+ (36)	27.28	1.41	1.48
5	Cs^+ (54)	23.15	2.42	2.54
6	Fr^+ (86)	22.40	3.02	2.82

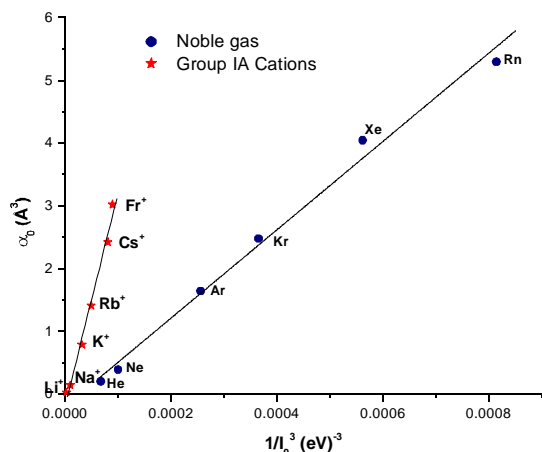


Fig. 2 Fitting of $\alpha_0 \rightarrow 1/I_0^3$ for Alkali metal ions, along with noble gas atoms. The values of ionization energy I_0 and polarizability are taken from References 11 - 14.

One can also think of a similar fitting of $\alpha_0 \rightarrow I_0^{-3}$ for the group VII A negative ions, F, Cl, Br and I whose electron configuration also corresponds to the noble gases. However, preliminary study does not indicate a good linear relation between $\alpha_0 \rightarrow I_0^{-3}$ in this case. The F particularly differs considerably from the other three anions. Therefore, these results are not exhibited here.

Metastable atoms

Metastable states are electronically excited states of atoms or molecules having longer life time in view of the dipole selection rules. Metastable states exhibit characteristics like large size, larger polarizability and lower ionization potentials. Ionization energies of these states can be determined easily, but there is lack of data on polarizability of these species. This is because of difficulties arising in experimental techniques and complicated method of calculating the polarizability tensors. So, we extend the present correlation study to the metastable excited states, where the plot of α_0 as a function of $1/I_0^3$ again gives a linear relation between the two quantities as shown in the Figure 3.

Table 3 ionization potential and polarizability of meta-stable states of noble gas-atoms.

Sr. No	Metastable Atom	Ionization potential I_0 (eV)	Electric dipole Polarizability α_0 (\AA^3)	Calculated α_0 (\AA^3) From eq (6)
1	He*(2^3S_1)	4.77	44.66	33.24
2	Ne*(3P_2)	4.94	27.79	30.01
3	Ar*(3P_2)	4.21	47.89	47.44
4	Kr*(3P_2)	4.09	50.70	51.71
5	Xe*(3P_2)	3.81	63.59	63.43

We note the special behavior of He* with respect to Ne* in the graphical plot of Figure 3. The data values and the generated values of α_0 show a good matching as shown in Table 3.

Conclusions

Thus, this paper presents our semi-empirical studies on the linear relations of α_0 as a function of $1/I_0^3$ in several atomic cases. Searching for general trend and correlations among the physical properties has been a passion with physicists. Several attempts have been done, as highlighted in the Introduction section, to find the equations relating the atomic first ionization threshold

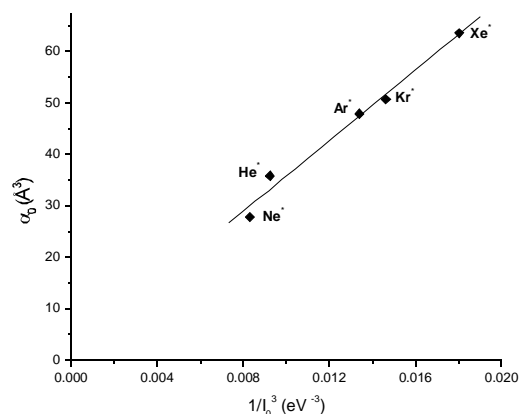


Fig.3 of Fitting $\alpha_0 \rightarrow 1/I_0^3$ for metastable excited states of noble gas atoms. The values of ionization energy I_0 and polarizability are taken from References 15 - 20.

and the polarizability, and the present equation (6) is a yet another effort. We focus on a periodic table group rather than choosing a range of continuous Z values, and this is reasonable. The present study can be extended to other groups as well. Further, interesting correlations can also be found among the static properties I_0 and α_0 , and a dynamic quantity viz., electron impact ionization cross section peak, at a given incident energy. This work is underway. Finally correlations between I_0 and α_0 can also exist for atoms under extreme conditions, say in dense plasma or under high pressure.

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