A new scale of atomic static dipole polarizability invoking other periodic descriptors

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Abstract

Knowledge of the nature of a chemical reactivity descriptor holds immense value to theoretical scientists. An appreciable number of works have been carried out in this realm. Polarizability (α) is one amongst such constructs. Fundamentally, it is a linear response of a systems electron cloud to an external applied electric field. The concept of polarizability is being widely adopted in the contemporary world of chemistry; however a suitable scale of measurement of atomic polarizability is still to be designed. In this work, an ansatz to compute atomic static dipole polarizability is proposed considering the conjoint action of absolute radius (r) and electronegativity (χ) for 103 elements of periodic table. We have evaluated the data invoking regression analysis. The computed data mirrors the periodicity remarkably satisfying all the *sine qua non* of a standard scale of polarizability. It presents an excellent quantitative correlation with ionization energy. Further, molecular polarizability (α_m) is determined conceptualizing the property of additivity. A superior correlation between theoretical *vis-à-vis* existing molecular polarizabilities is observed.

Keywords Conceptual density functional theory (CDFT) · Periodicity · Electronegativity · Ionization energy · Minimum polarizability principle · Molecular polarizability

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1 Introduction

The linear response of an electronic charge distribution of an atom or a molecule with respect to an external applied electric field is described as electric dipole polarizability [1, 2]. This quantity is of fundamental importance in understanding covalent as well as non-covalent interactions. Atomic and molecular polarizabilities are key elements in numerous applications such as blackbody radiation shifts, quantum information, inter-atomic interactions, atoms in optical lattices, atomic scattering, quantum information, polarisable force-field calculations and optical phenomena [2, 3]. Thus, the information of precise values of dipole polarizability is of paramount importance to atomic and molecular physics [4]. Nevertheless, in spite of its significance in numerous domains, precise atomic dipole polarizabilities values are not so readily accessible for many elements of the periodic table, particularly for systems with an open-shell [5]. Electric dipole polarizability is a physical observable. It is a tensor quantity which measures the influence of an external electric field on a charge distribution [2, 6]. The dipole moment (μ) induced in the presence of an external electric field (ε) is given by,

$$\mu = \alpha \cdot \varepsilon \tag{1}$$

where α represents the polarizability of the system. In a static uniform electric field, the quadratic Stark effect describes the dipole polarizability tensor of the electronic ground state [7]. The average or scalar polarizability is obtained through diagonalizing the 3×3 Cartesian tensor matrix and can be represented as,

$$\alpha = \langle \alpha \rangle = \frac{1}{3} \left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz} \right) \tag{2}$$

Polarizability is an important Conceptual Density Functional Theory (CDFT) descriptor that has been known to measure the response of a system, consisting of a fixed number of electrons, with changes in external potential when a weak electric field is the source of the external potential besides that stemming from a set of nuclei. Pearson [8], in 1963, introduced the concept of Lewis acid and base in terms of hardness using the notion of polarizability. His theory is an empirical approach of accounting a plethora of known reactive behaviours [8, 9]. According to him, polarizability is the ease of valence electron cloud deformation of a chemical species.

Based on this idea, he suggested hardness and softness to be associated with low and high polarizability, respectively. In 1967, Jorgensen et al. [10] suggested that polarizability is "a far more physical than chemical quantity". In the mid-1960s, Huheey [11, 12] developed the concept of charge capacity. By definition, it is a measure of change in an atom's electronegativity when it acquires or loses electronic charge at the time of molecule formation [11, 12]. The charge capacity indicates how efficiently an atom becomes accustomed to acquiring or losing electronic charge which in turn signifies its polarizability. Several relationships have been established which correlate polarizability with hardness, softness and charge capacity [13–18]. Ghanty and Ghosh [16] have empirically shown that softness ($1/\eta$) is linearly associated with the cube root of polarizability ($\alpha^{1/3}$) for a number of

atoms and sodium clusters. Similar conclusions have been drawn by Fuentealba and Reyes [19] as well for a couple of atoms and monoatomic ions. Polarizability has also been equated to R^3 for a conducting sphere [20]. However, owing to the inhomogeneous nature of the electron cloud of an atom, Eq. (3) is found to be more suitable,

$$\alpha = K R^3 \tag{3}$$

Here K is the constant of proportionality. Dmitrieva and Plindov [21] deduced the value of K using a method based on the theory of atomic oscillation. As per their estimation, K is equal to 0.585. A relationship between electronegativity and polarizability was also demonstrated by Nagle [22]. Miller [23] proposed a semiempirical approach to compute the components of molecular polarizability with atomic polarizability components and the dipole tensor. A quantitative relationship was formulated between electric dipole polarizability and hardness by Hati and Datta [17] for atoms and clusters. Dipole moments, molecular static polarizabilities, polarizability anisotropy, first hyperpolarizabilities and second hyperpolarizabilities were calculated by Calaminici et al. [24] in the framework of density functional theory. A study involving computation of polarizabilities for 15 organic molecules suggested that the Time Dependent Density Functional Theory (TD-DFT) and the Direct Reaction Field (DRF) methods are superior to the Restricted Hartree–Fock (RHF) approach in estimating polarizabilities [25]. Polarizability has been known to nicely correlate with volume, $\alpha \sim V$, for both atoms and molecules [20, 21, 26–29]. It is also inversely associated to the first ionization energy for atoms [21, 30–32]. The electrons that are highly affected by the electric field, that is, are polarized, are the ones which are most loosely-held [33, 34]. Numerous reviews as well as tabulations of atomic static dipole polarizabilities have been presented over the past 50 years [3, 5, 35–43]. Recently, there has been an upsurge of interest in density functional theory (DFT) programs to facilitate the calculation of static polarizabilities and hyperpolarizabilities [44–53].

A minimum polarizability principle (MPP) has also been proposed which is rooted on the inverse relation between polarizability and hardness [9, 16, 19]. The principle states that "the natural direction of evolution of any system is towards a state of minimum polarizability" [54–58]. Soundness of the principle has been assessed in diverse physicochemical processes [54–70]. It has been noted for a number of chemical reactions that the reaction progresses in the direction that forms species with the lowest polarizability [59–66].

Thus, it is clear from the above discussion that the knowledge of accurate atomic dipole polarizabilities for all elements has still not been possible despite a number of efforts. In the view of this fact, we are suggesting a model for the computation of CDFT-based descriptor static atomic dipole polarizability by correlating one periodic descriptor with other two fundamental quantities. The computation is carried out by taking proper care of dimensions and including relativistic effects. We have also presented a theoretical justification of the model by assessing the computed data with the available experimental values. A correlation between atomic polarizability and atomic ionization energy has also been presented. Further, molecular polarizability is computed invoking the property of additivity [43].

2 Method of computation

As evident from the literature, polarizability (α) and electronegativity (χ) both are imperative periodic descriptors of reactivity [71–74]. While electronegativity represents the electron attracting power of an atom, polarizability corresponds to the ease of distortion of an electron cloud of an atom resulting in loosely bound electrons [8, 75, 76]. Thus, it implies that polarizability is an electron loosening (or releasing) power of an atom.

As proposed by Szarek and Grochala [77], atomic radius is equal to the square root of the product of polarizability and hardness as presented by the Eq. (4),

$$r = \sqrt{\alpha\eta} \tag{4}$$

Accordingly, the equation can also be written as,

$$\alpha = \frac{r^2}{\eta} \tag{5}$$

We also know that hardness is proportional as well as equal to electronegativity [78, 79],

$$\eta \propto \chi \tag{6}$$

and

$$\eta = \chi \tag{7}$$

Since absolute radius is the true size descriptor of atoms and incorporates relativistic effects as well [80], we are using absolute radius in place of atomic radius in our work. Relying upon these ideas, we suggest that polarizability presents a direct relationship with the square of absolute radius and is inversely proportional to electronegativity. In the present effort, we have computed polarizability in terms of absolute radius and electronegativity.

Hence, on the basis of above relations, we put forward a new model for the computation of polarizability (α) considering the conjoint action of absolute radius (r) and electronegativity (χ) as

$$\alpha \propto \frac{r^2}{\chi} \tag{8}$$

The computation is carried out for 103 elements of the periodic table to assess polarizability invoking regression analysis using Eq. (8). All the quantities adopted for the computation have been taken in atomic unit. In the study, polarizability is regarded as a dependent variable while absolute radius and electronegativity are taken as independent variables whose values are taken from the work of Schwerdtfeger and Nagle [40], Chakraborty et al. [80] and Ghosh and Chakraborty [81] respectively.

An attempt is made to reveal the effectiveness of our data by comparing it with the polarizability values tabulated by Schwerdtfeger and Nagle [40] for 103 elements of the periodic table. Numerous efforts have been made in the past to establish a relationship between atomic polarizability and atomic ionization energy trends for elements of the periodic table [21, 30–32, 40, 82–85]. We have tried to correlate our computed polarizabilities with ionisation energies according to empirical power relationship for every period as well as group of the periodic table [86].

Molecular polarizabilities can be predicted using the property of additivity [43, 87, 88]. The summation of the polarizabilities of all the isolated atoms present in a system gives an approximate value of the static molecular polarizability (α_m).

$$\alpha_m \approx \sum_i \alpha_i \tag{9}$$

Based on this concept, we have determined molecular polarizabilities for varied sets of molecules, viz. alkanes, halomethanes, alkenes, alcohols, carbonyls, amides, cyanides, sulphurs, diatomics, transition metal molecules and some others, and compared them with the available theoretical data of van Duijnen and Swart [89] and Labello et al. [90] for the same set of molecules to test the suitability of our computed scale.

3 Results and discussion

In this endeavour, we have computed atomic static dipole polarizability, one of the crucial CDFT descriptors, in terms of absolute radius and electronegativity invoking empirical approach for 103 elements of the periodic table. The calculated data is illustrated in Table 1 which transpires periodicity. Atomic polarizability is plotted as a function of atomic number in Fig. 1. It is exciting to note that the alkali metal possesses highest polarizability and the noble gas the least in any period which is in accordance with the minimum polarizability principle (MPP) [9, 16, 19]. On moving from left to right across a period, a decreasing trend of polarizability is noticeable which is accounted by an increase in effective nuclear charge and decrease in atomic size. However, a general increase in the polarizability values is evident on moving from top to bottom within a group. A brief discussion of the periodic trends of each block is presented in this section.

3.1 *s*-Block elements

Alkali and alkaline earth metals, collectively known as *s*-block elements, exactly follow the periodic trend excluding Fr which has a lower value than Cs. The decrease in its polarizability is an outcome of large direct relativistic contraction and stabilization of the 7 *s* orbital [40]. As compared to the other members of the block, the increase in polarizability of Na is not very consistent due to greater effective nuclear charge that arises out of its filled $2p^6$ sub-shell [40].

Table 1 Periodic chart of the computed polarizability values of 103 elements (approximated to 2nd decimal place)

1 H 4.50																	2 He 1.38
3 Li 102.20	4 Be 26.53			**Legend** Atomic Number Symbol of Element Polarizability (Atomic Unit)								5 B 29.65	6 C 13.06	7 N 6.64	8 O 6.53	9 F 3.71	10 Ne 2.48
11 Na 122.39	12 Mg 51.72											13 Al 70.57	14 Si 36.90	15 P 23.68	16 S 22.18	17 Cl 16.87	18 Ar 14.32
19 K 281.56	20 Ca 123.25	21 Sc 103.64	22 Ti 92.33	23 V 93.14	24 Cr 90.58	25 Mn 70.94	26 Fe 60.57	27 Co 59.13	28 Ni 62.34	29 Cu 59.20	30 Zn 35.28	31 Ga 94.24	32 Ge 43.80	33 As 21.75	34 Se 19.40	35 Br 8.86	36 Kr 3.07
37 Rb 323.53	38 Sr 156.28	39 Y 119.03	40 Zr 99.94	41 Nb 97.39	42 Mo 89.24	43 Tc 82.87	44 Ru 79.31	45 Rh 75.87	46 Pd 56.66	47 Ag 70.79	48 Cd 45.12	49 In 121.60	50 Sn 63.82	51 Sb 38.52	52 Te 31.14	53 I 17.95	54 Xe 9.11
55 Cs 391.45	56 Ba 207.96	57-71	72 Hf 87.06	73 Ta 56.10	74 W 52.70	75 Re 52.46	76 Os 39.30	77 Ir 33.74	78 Pt 33.22	79 Au 30.10	80 Hg 20.25	81 Tl 143.53	82 Pb 90.67	83 Bi 92.97	84 Po 64.71	85 At 45.17	86 Rn 33.04
87 Fr 317.71	88 Ra 245.93	89-103															

57 La 203.84	58 Ce 210.94	59 Pr 212.66	60 Nd 205.53	61 Pm 198.48	62 Sm 190.62	63 Eu 185.37	64 Gd 157.18	65 Tb 168.38	66 Dy 161.18	67 Ho 153.51	68 Er 146.53	69 Tm 139.85	70 Yb 133.96	71 Lu 168.48
89 Ac 209.15	90 Th 167.27	91 Pa 167.24	92 U 153.08	93 Np 146.43	94 Pu 143.77	95 Am 140.84	96 Cm 139.02	97 Bk 126.88	98 Cf 121.84	99 Es 116.46	100 Fm 112.23	101 Md 108.41	102 No 105.08	103 Lr 145.57
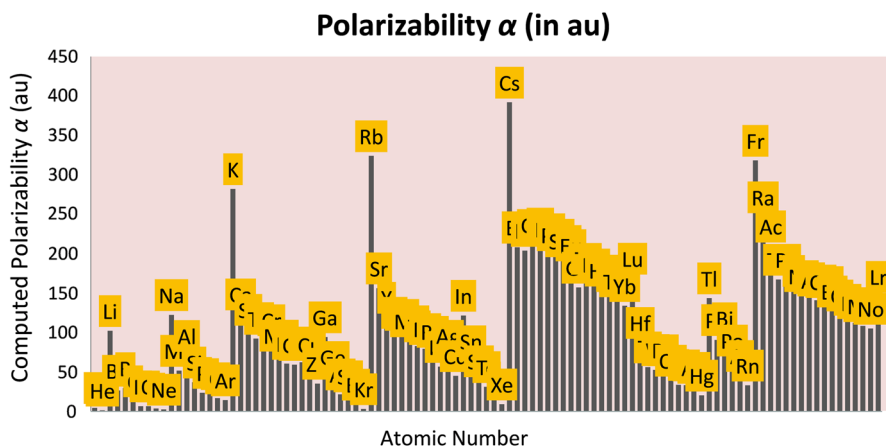
Fig. 1 Plot of polarizability (α) as a function of atomic number (in au)

3.2 *p*-Block elements

For the *p*-block elements, a regular increase in polarizabilities is evident with increasing period number, with no exceptions in boron and carbon family. However, pnictogens, chalcogens, halogens and inert gases show decrease in polarizabilities of As, Se, Br and Kr as compared to P, S, Cl and Ar, respectively. This is probably signifying the increase in effective nuclear charge of As, Se, Br and Kr originating out of their
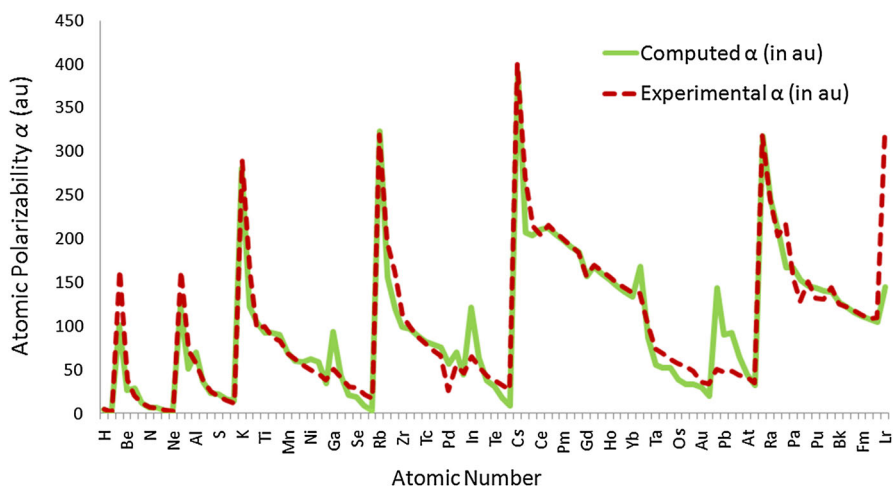
Fig. 2 Comparative plot of computed polarizability values *vis-à-vis* Schwerdtfeger and Nagle's [40] polarizability values (in au)

completely filled 3*d* sub-shell. In addition, half filled stability of shell structure of N can also be addressed in terms of our computed data.

3.3 *d*-Block elements

In case of *d*-block elements, which are also known as transition metals, polarizability of 4*d* series elements is found to be greater than 3*d* and 5*d* series elements in a group with an exception of Group 10 where polarizability of Pd is less than that of Ni which reflects its unique $4d^{10}5s^0$ ground state electronic configuration [40].

3.4 *f*-Block elements

We have noticed that the polarizability of lanthanide elements of present calculation exhibits the expected trend of variation. Moving across the actinides, an abrupt increase in the polarizability is shown by Lr which is likely a result of its unique $5f^{14}6d^07s^27p^1$ ground state electron configuration [40, 91]. For the *f*-block elements, viz. inner transition elements, polarizability of 4*f*-series is persistently higher than 5*f*-series.

In general, our computed scale of polarizability observes all the *sine qua non* of periodic properties, thus, speaking volumes for itself.

In addition, we have compared our computed polarizability (α) values *vis-à-vis* polarizability data of Schwerdtfeger and Nagle [40] to further substantiate the exactness of our model. A fine trend depicted in Fig. 2 supports the preciseness of our model of polarizability. The inclusion of increasingly important relativistic effects in our computation is evident from the varying values of polarizability in case of some
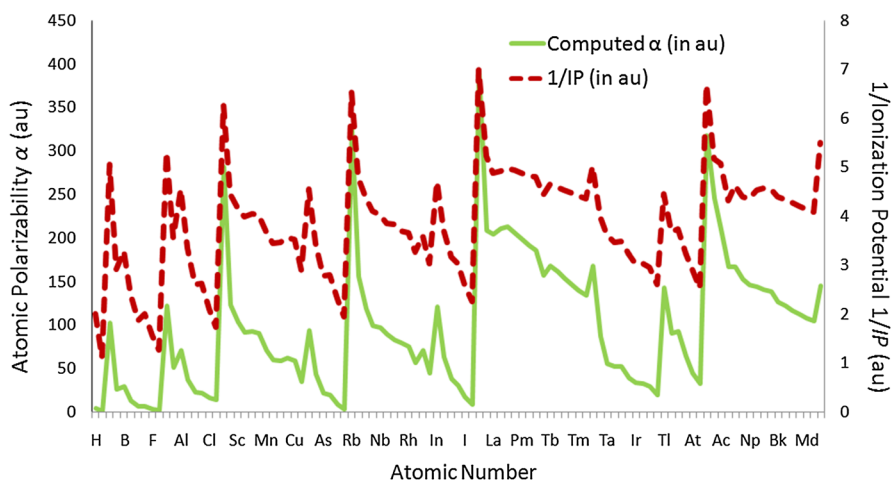
Fig. 3 Comparative plot of computed atomic polarizability values *vis-à-vis* inverse of their ionization energy values [86] (in au)
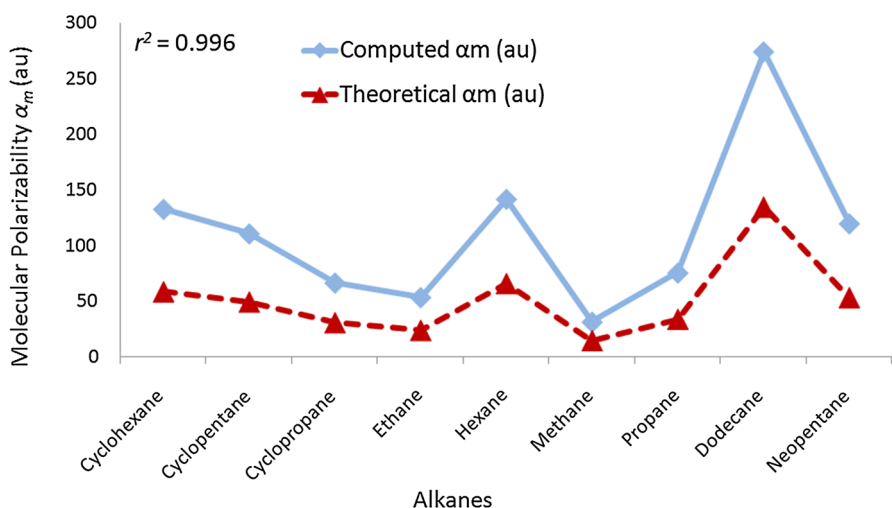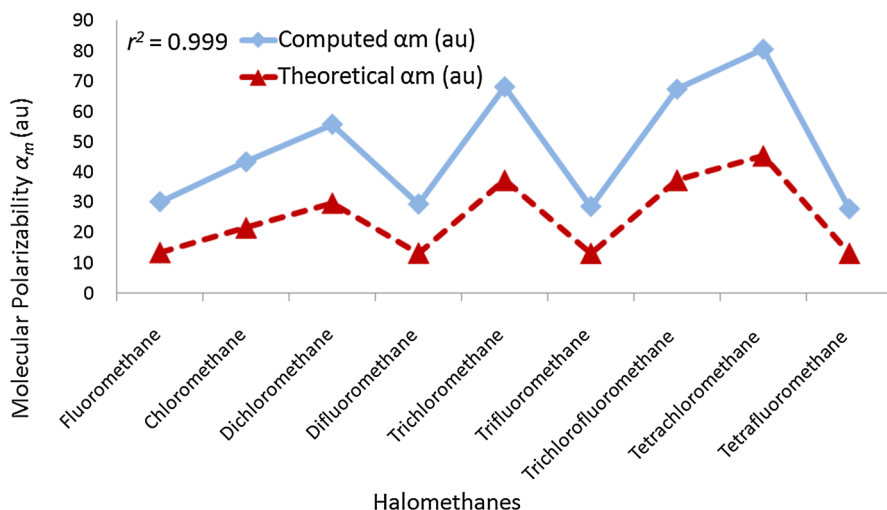

Fig. 4 Comparative plot of computed and theoretical molecular polarizabilities (α_m) [89] of some alkanes (in au)

atoms. The relativistic effects are incorporated in our data by the use of absolute radius [80], a descriptor that considers the relativistic changes.

A non-linear power regression analysis for each group and period of elements presents a high value of correlation ($r^2 > 0.9$) for polarizability and ionization energy [86]; with Group 4 and 10 as well as actinide series as exceptions. A slightly lower correlation is observed in these cases which may be a result of relativistic effects in case of Hf (Group 4) and a unique electronic configuration for both Pd (Group 10) and Lr (Actinides). To sum up, the analysis transpires valuable quantitative correlations

Fig. 5 Comparative plot of computed and theoretical molecular polarizabilities (α_m) [89] of some halomethanes (in au)
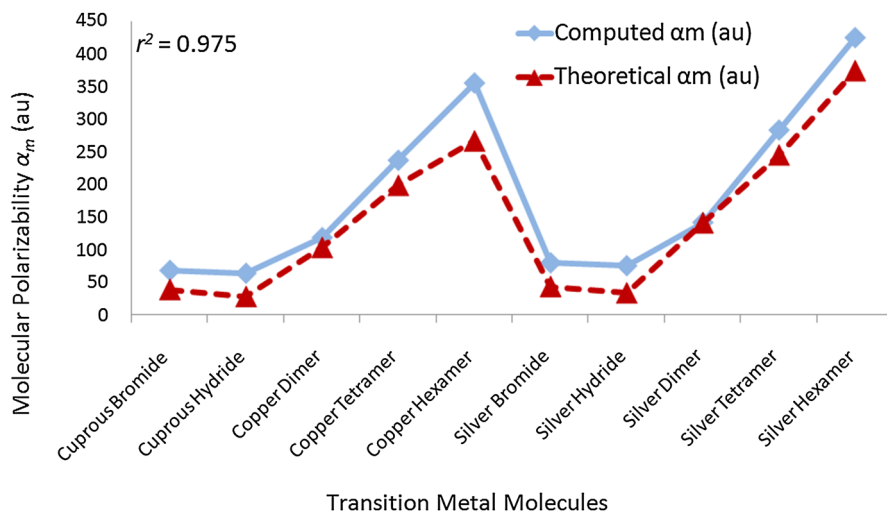
Fig. 6 Comparative plot of computed and theoretical molecular polarizabilities (α_m) [90] of some transition metal molecules (in au)

between ionization energy and polarizability, although including some outliers, viz. Hf, Pd, Tl, Br, Ar, Kr, Lu, Th, Lr. It appears that ionization energy can be possibly used as a measure of polarizability. Figure 3 presents a general comparison of both the properties for 103 elements of the periodic table.

We have applied our computed atomic polarizability to calculate molecular polarizability for bigger systems. The calculation has been made for 72 molecules divided into ten sets (with a not-too-strict nomenclature), viz. alcohols, alkanes, "alkenes",

"carbonyls", amides, cyanides, halogens, "sulphurs", diatomics, "various" and "transition metal molecules" for bigger systems. Working with Eq. (9) we have invoked additive property for computation of molecular polarizability using our newly computed data. All the sets show a suitable correlation between our computed molecular polarizability and the corresponding theoretical data. Comparative plots of the calculated and available theoretical molecular polarizabilities for three sets are presented in Figs. 4, 5 and 6 along with their correlation coefficients (r^2) [89, 90]. The plots reflect a high similarity between both the data. The difference in the theoretical and computed molecular values is again perhaps due to the inclusion of important relativistic effects in the present calculation, as suggested by Labello et al. [90] as well. A superior correlation between the available theoretical data and our result displays the suitability of our model.

4 Conclusions

In summary, atomic static dipole polarizability (α), a fundamental periodic descriptor, is defined in terms of absolute radius and electronegativity for the first time. An ansatz has been proposed to compute polarizability invoking crucial periodic descriptors of atoms, electronegativity and absolute radius. Values of atomic polarizability are determined empirically for 103 elements of the periodic table in atomic units (au). The new scale satisfactorily follows all the *sine qua non* of periodic properties. Additionally, it presents a good correlation with an existing scale further validating its suitability. Useful correlations exist between polarizability and ionization energy as well. Property of additivity is excellently followed by our scale of polarizability giving static molecular polarizability. Thus, it is apparent that our new scale of atomic polarizability is theoretically reasonable.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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