Atomic Radii Scale and Related Size Properties from Density Functional Electronegativity Formulation

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Assuming the Mulliken electronegativity density functional theory (DFT) formulation as the primary structural information on atomic systems, we propose a new atomic radii quantitative definition and scale. The radii scale based on DFT first principles is further used to evaluate the atomic diamagnetic susceptibility, polarizability, and chemical hardness. A new chemical hardness expression in terms of atomic radius is also given. The investigated quantities show that periodic trends prove the reliability of the proposed radii definition. Moreover, the proposed method to calculate size of atoms is useful for the theoretical prediction of several size-dependent physicochemical properties.

1. Introduction

The evaluation of periodic properties is a fruitful research field starting from 1869 when Mendeleev proposed the periodic table of elements.[1] One of the most important periodic concepts is, certainly, the atomic size or radius. Indeed, it is very useful in explaining many chemical and physical characteristics of the elements and in predicting their reactivity behavior. The history of atomic radii evaluation is rich and exciting and starts from the beginning of the modern chemistry. Briefly, we are reminded of the pioneering works of Bragg, Goldschmidt, Zachariasen, Pauling, and Slater.[2−6] From an experimental point of view, the atomic radii of some elements can be obtained from X-ray or from spectroscopic measurements, but their reliability is often questionable because of the experimental conditions (e.g., crystal type, allotropic modifications, coordination number, temperature). Because of the importance of the prediction of the internuclear distances into a molecule and between different molecules, many attempts have been made to fix radii values such that a sum of two of them is able to reproduce their distance, no matter the kind of bond existing between the considered atoms. Unfortunately, a plethora of scales has appeared, and a very long series of terms has been introduced to indicate the radius in different environmental conditions. As a consequence, the possibility to estimate theoretically this periodic property is very advantageous because it does not depend on the given physical conditions.

From a theoretical viewpoint, some atomic radii scales have been proposed on the basis of several quantum mechanical tools going from self-consistent field (SCF) to density functional theories (DFT).[7−15] In a very recent work of Ghosh and Biswas, a detailed literature survey on this matter is reported.[16]

With the introduction of DFT of many electrons systems, many useful qualitative chemical concepts (e.g., chemical potential, and chemical hardness and softness) have found a rigorous quantitative definition.[12] In this context, the chemical potential, μ, is defined as the first derivative of the energy with respect to the change of the number of the electrons, *N*, and is ultimately identified with the negative of electronegativity, χ.[17] Because electronegativity measures the tendency of atoms to attract bonding electrons to themselves at their valence shell, it is also related to the outer orbitals and then to the size. Therefore, a definition of electronegativity obtained in the framework of DFT and properly correlated with the atomic radius can provide a quantitatively rigorous atomic radii scale. With the purpose to obtain "constant" atomic radii useful to describe any bonding situation, we propose in this work a new atomic radii scale computed by using the electronegativity formulation based on a new approach, which employs the chemical action concept[18] and the Slater-type orbitals for the considered elements.

2. Method and Computational Details

2.1. Atomic Radii and Electronegativity. The relation between atomic radii and electronegativity is obtained starting from the electronegativity formulation,[18] derived from the first principles of DFT. In this context, we define the atomic radius as the limit until which an electron can be added to an atom from infinity, due to its electronegativity.

In the DFT framework, the analytical expression introduced to evaluate electronegativity is given, according to the work of Garza and Robles,[19] in terms of the local response function, $L(x)$:

$$L(x) = \frac{\nabla \rho(x)}{[-\nabla V(x)]} \tag{1}$$

with *x*, ρ, and *V* being the position vector, electronic density,

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and the external potential, respectively. The final form it assumes is:[18]

$$
\chi_M = \frac{\int L(x)\, V(x)\, dx + N - 1}{2\sqrt{\int L(x)\, dx}} \arctan\left(\frac{N-1}{\sqrt{\int L(x)\, dx}}\right) -
$$

$$
\frac{\int L(x)\, V(x)\, dx + N + 1}{2\sqrt{\int L(x)\, dx}} \arctan\left(\frac{N+1}{\sqrt{\int L(x)\, dx}}\right) +
$$

$$
\frac{\int \rho(x)\, V(x)\, dx - 1}{4} \ln\left[\frac{\int L(x)\, dx + (N-1)^2}{\int L(x)\, dx + (N+1)^2}\right] \quad (2)
$$

with $N = \int \rho(x)\, dx$ being the total number of electrons.

In an approach that correlates atomic radius with electronegativity, it is of fundamental importance to know the electronic density distribution of a given system, and in this respect a suitable treatment is based on the Slater orbital electronic picture. Therefore, in eqs 1 and 2, the Slater-type orbital expressions have been used and the relative integrals have been performed, resulting in the linear response terms:

$$
a(R_{DFT}) \equiv \int_\infty^R L(x)\, dx|_{R\to 0} =
$$

$$
\frac{2\pi(2n\Gamma[2 + 2n, 2R\xi] - \Gamma[3 + 2n, 2R\xi])}{Z_{eff}\xi(2n)!}\Big|_{R\to 0}
$$

$$
\cong \frac{2\pi}{Z_{eff}\xi(2n)!}\left\{4(R_{DFT}\xi)^{2(1+n)}\left(\frac{2^{1+2n}R_{DFT}\xi}{3 + 2n} - \frac{2^{2n}n}{1+n}\right) + \right.
$$

$$
\left. 2n\Gamma[2 + 2n] - \Gamma[3 + 2n]\right\}, \quad (3)
$$

$$
b(R_{DFT}) \equiv \int_\infty^R L(x)\, V(x)\, dx|_{R\to 0} =
$$

$$
\frac{4\pi(-2n\Gamma[1 + 2n, 2R\xi] + \Gamma[2 + 2n, 2R\xi])}{(2n)!}\Big|_{R\to 0}
$$

$$
\cong \frac{4\pi}{(2n)!}\left\{\frac{(2R_{DFT}\xi)^{1+2n}}{(1+n)(1+2n)}[2n^2 - R_{DFT}\xi + \right.
$$

$$
\left. 2n(1 - R_{DFT}\xi)] - 2n\Gamma[1 + 2n] + \Gamma[2 + 2n]\right\} \quad (4)
$$

and the chemical action index:

$$
C_A(R_{DFT}) \equiv \int_\infty^R 4\pi x^2 \rho_{STO}(x)\, V(x)\, dx|_{R\to 0} =
$$

$$
\frac{8\pi Z_{eff}\xi\Gamma[2n, 2R\xi]}{(2n)!}\Big|_{R\to 0}
$$

$$
\cong \frac{4\pi Z_{eff}\xi[2n\Gamma[2n] - (2R_{DFT}\xi)^{2n}]}{n(2n)!} \quad (5)
$$

with Z_{eff}, n, ξ, and Γ being the nuclear effective charge, the valence principal quantum number, the orbital exponent, and the Gamma Euler function, respectively.

Introducing eqs 3–5 into eq 2 is obtained the equation for the atomic radii:

$$
\chi_M = \frac{b(R_{DFT}) + N - 1}{2\sqrt{a(R_{DFT})}} \arctan\left(\frac{N-1}{\sqrt{a(R_{DFT})}}\right) -
$$

$$
\frac{b(R_{DFT}) + N + 1}{2\sqrt{a(R_{DFT})}} \arctan\left(\frac{N+1}{\sqrt{a(R_{DFT})}}\right) +
$$

$$
\frac{C_A(R_{DFT}) - 1}{4} \ln\left[\frac{a(R_{DFT}) + (N-1)^2}{a(R_{DFT}) + (N+1)^2}\right] \quad (6)
$$

This equation is transcendent in atomic radius and has to be numerically solved for each atomic system once all the other atomic parameters (i.e., total number of electrons, involved quantum valence shell, nuclear effective charge, and orbital exponent) are fixed.

With the aim to compare our results with another "absolute environmental-independent" scale, we report the radii scale recently obtained by Ghosh and Biswas (GB) using the condition of the maximum radial charge density distribution function of the topmost electrons of the atoms.[16]

2.2. Size-Dependent Atomic Properties: Diamagnetic Susceptibility, Polarizability, and Chemical Hardness. An electronic system in the presence of an external field (nuclear, magnetic, electric) gives different responses according to the nature of the action. Correspondingly, specific sensitivity parameters can be introduced: diamagnetic susceptibility as the response to an applied magnetic field, static dipole polarizability that accounts for the electronic cloud deformation under an applied electric perturbation, and chemical hardness associated with the resistance of an electronic cloud to deformation induced by applied electrostatic perturbations at constant nuclear potential. Because all these properties are size dependent, their theoretical computation and comparison with available experimental counterparts can give a measure of the reliability of the proposed radii scales.

This diamagnetic effect can be quantified through the diamagnetic susceptibility formula:[20]

$$
\chi_{dia} = -N_{outer}R^2[0.56 \times 10^{-28}\,cm^3/mol] \quad (7)
$$

In this equation, the valence electrons are taken explicitly into account, while the core ones are included in the atomic radius computation.

To obtain the expression for the atomic static dipole polarizability, the electronic response to an applied electrical field is considered not so strong as to cause the first ionization. The final expression[19]

$$
\alpha = \frac{2}{Z_{eff}}R^3[10^{-24}\,cm^3] \quad (8)
$$

is dependent on the cube of atomic radius, R^3, and the nuclear effective charge, Z_{eff}. From the dependence of atomic polarizability on the cube of atomic radius, the dependence on the atomic volume also rises immediately. Therefore, the atomic polarizability values have to closely follow the periodicity of atomic volumes as prescribed by the Lother Meyer's periodic curve.

The last-examined index that quantifies the electronic cloud response to an external perturbation is the chemical hardness. Usually, the chemical hardness is associated with the inverse of polarizability because it accounts for the inertia of the electronic cloud to deformation. However, the relation of inverse proportionality between hardness and polarizability deserves
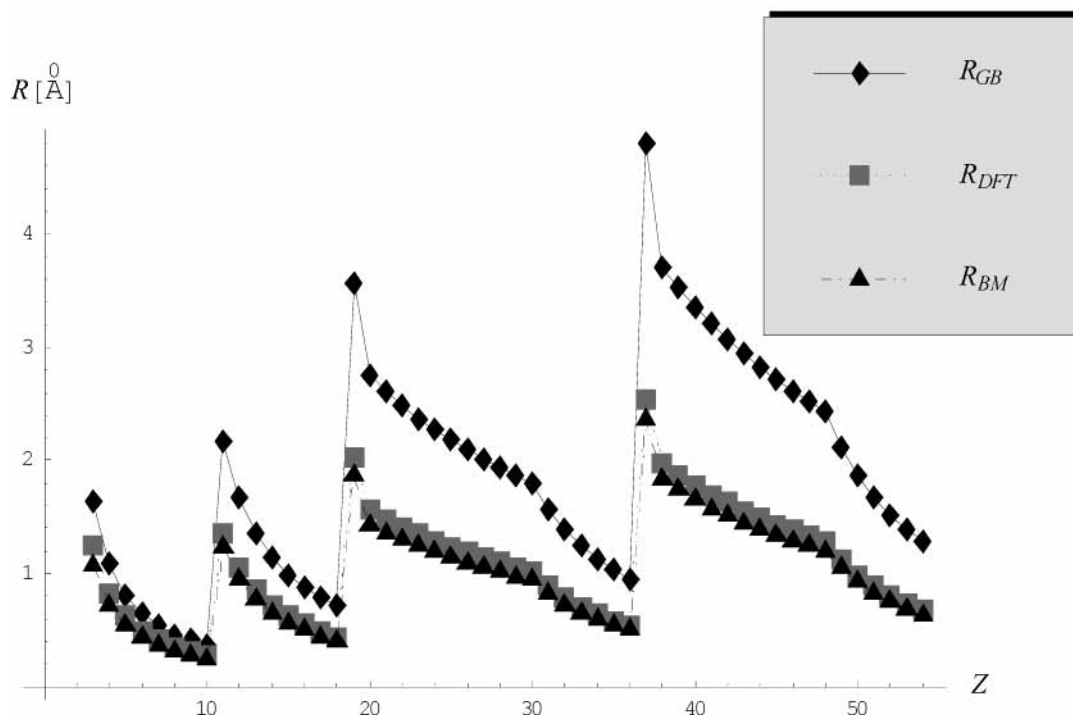
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Figure 1. The plot of atomic radii scales from Ghosh−Biswas (GB), actual (DFT), and Boyd−Markus (BM) formulations.

more attention.[21−23] In the DFT framework, the chemical hardness assumes different general formulations. One of these directly correlates the chemical hardness with the inverse of the global softness, S. The atomic resulting formula, relating hardness with the atomic radius, looks like:[19]

$$\eta_S = \frac{Z_{eff}}{8R}[eV] \qquad (9)$$

Another way to quantify the chemical hardness in DFT is to use its relation with electronegativity:[12]

$$\eta_\chi = -\frac{1}{2}\left(\frac{\partial\chi}{\partial N}\right)_V[eV] \qquad (10)$$

Then, the next step is to use the electronegativity formulation proposed by us, (see eq 2).[18] After partial derivation of both sides of eq 2 with respect to the total number of electrons is performed, the chemical hardness takes the form:

$$\eta_\chi = \Big\{2\sqrt{a}[C_A(1 + a - N^2) + 2N] + [(1 + a)^2 +$$

$$2(a - 1)N^2 + N^4]\Big[\arctan\Big(\frac{N + 1}{\sqrt{a}}\Big) - \arctan\Big(\frac{N - 1}{\sqrt{a}}\Big)\Big]\Big\}\Big/$$

$$\{4\sqrt{a}[a + (N - 1)^2][a + (N + 1)^2]\} \qquad (11)$$

where the following definitions are used:

$$a = \int L(x)\, dx$$

$$C_A = \int \rho(x)\, V(x)\, dx \qquad (12)$$

If an effective nuclear central atomic field is considered and the same approximations involved in the derivation of eq 8 are

used, the final working formula for the atomic chemical hardness becomes:

$$\eta_\chi = \frac{Z_{eff}}{8R}\Bigg\{\frac{4Z_{eff}[2R(N_{outer} - 2) - Z_{eff}]}{16R^2 + 8RZ_{eff} + Z_{eff}^2(N_{outer}^2 - 1)^2} +$$

$$\sqrt{\frac{R}{Z_{eff}}}\Big[\arctan\Big(\frac{1}{2}\sqrt{\frac{Z_{eff}}{R}}\Big) - \arctan\Big(-\frac{1}{2}\sqrt{\frac{Z_{eff}}{R}}\Big)\Big]\Bigg\} \qquad (13)$$

We would like to underline that because the atomic radii are eliminated from both eqs 8 and 13, an expression results which directly links chemical hardness and atomic polarizability but in a more complex manner than the previously proposed inverse relations.[21,22]

3. Results and Discussion

The atomic radii computed by our model (eq 6, R_{DFT}) for 52 elements starting from lithium are collected in Table 1 together with those derived by Ghosh and Biswas (R_{GB}).[16] To better understand the periodic behaviors, the same data are depicted in Figure 1. The analysis of Table 1 and Figure 1 clearly shows that the considered atomic radii scales follow the same trend, whereas the absolute values differ significantly, with the R_{GB} values higher than the corresponding R_{DFT}. This difference can be ascribed to the difference in the approaches used to evaluate the radii based on the gradient and on the integral of the electronic density, respectively. With the aim of comparison, in the same figure the atomic radii scale obtained employing the Boyd−Markus (BM) electronegativity definition[24] was also depicted (R_{BM}). It is worth noting that the proposed DFT procedure fits very well with the Boyd and Marcus scale. Because of the similarity in the BM and DFT formalisms, both based on the integral approaches, the corresponding atomic radii scales show very close trends.

The interpolation of the atomic radii data in terms of Z gives a functional dependence ($R_{DFT} = 0.74 + 0.01Z$), which can be used also to directly estimate the ionic radii when the nuclear
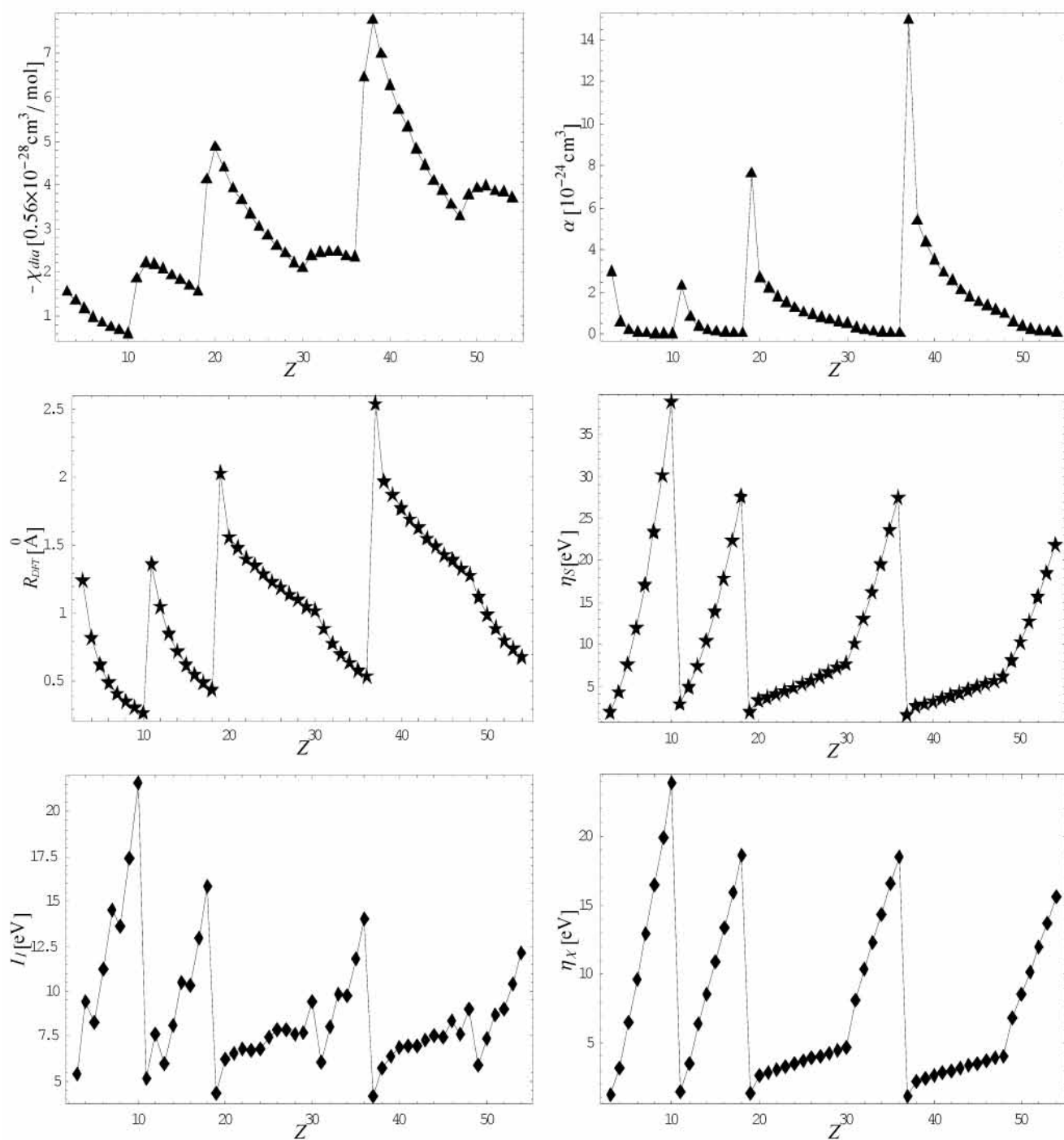
Figure 2. The comparative trend of the atomic DFT radii scale (middle left) with respect to the diamagnetic part of atomic susceptibilities (upper left), the atomic first ionization potential (lower left),[25] the atomic static dipole polarizability (upper right) with respect to the chemical hardness from softness (middle right), and from electronegativity (lower right) formulations, respectively.

charge is replaced by the effective one corresponding to the considered ionic structure.

While verifying whether our scale respects the fundamental periodic behaviors, we noted that the atomic size decreases along the rows and increases down the main groups.

The contraction of the atomic size among the transition metals is also well reproduced. Indeed, the d-block radii decreased in going from 1.48 Å for scandium to 1.02 Å for zinc and from 1.87 Å for yttrium to 1.28 Å for cadmium.

As previously mentioned, a first analysis of the reliability of the obtained radii can be performed by using them to compute other size-dependent properties such as chemical hardness, static

polarizability, and diamagnetic susceptibility. The obtained values for these response indices have been sketched in Figure 2 to demonstrate the periodic trends.

As the first ionization potential (I_1) is directly related to the atomic size and is experimentally measured,[25] the comparison between the trends of I_1 and the calculated radii gives a direct measure of the goodness of the proposed scale. From Figure 2 it is evident that I_1 and R_{DFT} profiles, with some deviations, are homomorphic, and that a decrease of R_{DFT} corresponds to an increase of I_1. The natural relationship between these two quantities is obeyed because a more compact atomic volume requires a higher energy for the ionization.

TABLE 1: Atomic Radii Scales Computed from DFT Electronegativity (Upper) and Ghosh−Biswas (Lower) Formulations[a]

Li	Be											B	C	N	O	F	Ne
1.24	0.82											0.62	0.49	0.41	0.35	0.31	0.27
1.63	1.09											0.81	0.65	0.54	0.46	0.41	0.36
Na	Mg											Al	Si	P	S	Cl	Ar
1.36	1.05											0.85	0.72	0.62	0.55	0.49	0.44
2.16	1.67											1.36	1.15	0.99	0.87	0.78	0.71

K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
2.03	1.56	1.48	1.40	1.35	1.29	1.23	1.19	1.14	1.10	1.05	1.02	0.89	0.78	0.70	0.64	0.58	0.54
3.56	2.75	2.61	2.49	2.37	2.27	2.18	2.09	2.01	1.93	1.86	1.8	1.57	1.39	1.24	1.13	1.03	0.95

Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
2.54	1.97	1.87	1.77	1.69	1.63	1.55	1.49	1.43	1.39	1.33	1.28	1.12	0.99	0.89	0.80	0.74	0.68
4.81	3.71	3.53	3.36	3.21	3.07	2.94	2.82	2.71	2.61	2.52	2.43	2.12	1.87	1.68	1.52	1.39	1.28

[a] All radii values are in Å.

The analysis of the periodic trends of the other physical−chemical properties, diamagnetic susceptibility, polarizability, and hardness, obtained using the newly proposed radii values is equally satisfactory. Along a period, as a result of the competition between the quadratic decreasing of the atomic radii and the linear increasing of the valence electrons, the diamagnetic susceptibility follows a profile that is similar to that of R_{DFT} (see Figure 2).

Because the hardness and the polarizability indices are linked through an inverse relationship (see, for instance, eqs 8 and 9), their trends can be simultaneously compared with the atomic size. Their periodicity can be correlated to the maximum hardness and minimum polarizability principles, as recently pointed out by Chattaraj and Maiti.[26] Thus, like the other properties previously discussed, hardness and polarizability follow well-defined periodic trends as a function of the atomic number. Figure 2 shows that when α decreases, η increases along the period. It is also evident that the two hardness scales, computed by using eqs 9 and 10 for their definitions, differ only in their absolute values.

4. Conclusions

In this paper we have reported a new method, based on the electronegativity definition, to obtain quantitative atomic radii in the framework of the density functional theory. The reliability of the computed atomic radii for the first four rows of the periodic table has been checked through a comparison with the directly size-dependent and experimentally measured ionization potential. From the proposed radii values, other response functions (diamagnetic susceptibility, polarizability, global hardness, as well as a new atomic radii dependence) have been derived and their calculated periodic behaviors have been examined. It has been shown that all these properties compare well with the proposed atomic radii periodic trends. Work is in progress to test the reliability of the proposed scale in reproducing other experimental parameters.

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