

## DFT reactivity indices in confined many-electron atoms

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**Abstract.** The density functional descriptors of chemical reactivity given by electronegativity, global hardness and softness are reported for a representative set of spherically confined atoms of IA, IIA, VA and VIIIA series in the periodic table. The atomic electrons are confined within the impenetrable spherical cavity defined by a given radius of confinement satisfying the Dirichlet boundary condition such that the electron density vanishes at the radius of confinement. With this boundary condition the non-relativistic spin-polarized Kohn–Sham equations were solved. The electronegativity in a confined atom is found to decrease as the radius of confinement is reduced suggesting that relative to the free state the atom loses its capacity to attract electrons under confined conditions. While the global hardness of a confined atom increases as the radius of confinement decreases, due to the accompanying orbital energy level crossing, it does not increase infinitely. At a certain confinement radius, the atomic global hardness is even reduced due to such crossover. General trends of the atomic softness parameter under spherically confined conditions are reported and discussed.

**Keywords.** Density functional descriptors; confined many-electron atoms; chemical reactivity.

### 1. Introduction

The purpose of this paper is to study the Density Functional Theory (DFT) based global descriptors of chemical reactivity for atoms confined within the impenetrable spherical boundary using an accurate and consistent computational DFT model. In this section, we shall first briefly define the reactivity parameters considered in this work followed by an outline of the computational procedure adopted by us.

Density functional theory has been successfully applied to study the electronic structures of a wide variety of chemical systems. The tremendous success of this theory is mainly due to (a) the significantly less computational effort required in carrying out the accurate electronic structure calculations through its practical implementation, (b) the fact that a natural set of indices can be defined within the theory which are useful descriptors of reactivity of chemical systems.

According to the Hohenberg and Kohn (HK) theorems,<sup>1</sup> the ground state energy functional of an  $N$ -electron system with density  $\mathbf{r}(\mathbf{r})$  in an external potential  $\mathbf{u}$ , is given by.

$$E[\mathbf{r}(\mathbf{r})] = F[\mathbf{r}(\mathbf{r})] + \int \mathbf{u}(\mathbf{r})\mathbf{r}(\mathbf{r})d\mathbf{r}, \quad (1)$$

where  $F[\mathbf{r}(\mathbf{r})]$  is called the universal HK-functional containing the contribution of the kinetic energy ( $T$ ) and the electron–electron interaction ( $V_{ee}$ ) of the system. The usual minimization of the energy functional of (1) using the method of Lagrange multipliers subject to the constraint,  $N = \int \mathbf{r}(\mathbf{r})d\mathbf{r}$ , leads to the Euler–Lagrange equation,

$$\mathbf{m} = [dE/d\mathbf{r}]_{\mathbf{u}} = \mathbf{u}(\mathbf{r}) + dF[\mathbf{r}(\mathbf{r})]/d\mathbf{r}(\mathbf{r}), \quad (2)$$

where the constant  $\mathbf{m}$  has been identified, in the grand canonical ensemble at 0 K, as the electronic chemical potential.<sup>2</sup> This quantity arising within the DFT, measures the escaping tendency of an electronic cloud in the ground state system. Being a constant over all space

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for the ground state of an atom or molecule,  $m$  is recognized as a global reactivity index. It has been also shown, that the chemical potential is the slope of the curve  $E$  versus  $N$  at a fixed external potential<sup>3</sup>

$$m = (\partial E / \partial N)_u. \quad (3)$$

Within the finite difference approximation this slope can be written in terms of the ionization potential  $I$ , and the electron affinity  $A$ . In this way, the DFT chemical potential can be associated with the negative of the Mulliken electronegativity ( $c$ ),<sup>3</sup> as

$$m \approx -(I + A) / 2 = -c. \quad (4)$$

The chemical potential can be considered as a function of  $N$  and  $u$ , and describe a change in the system from  $[N, u] \rightarrow [N + dN, u + \partial u]$  according to

$$dm = h dN + \int \partial u(\mathbf{r}) f(\mathbf{r}) d\mathbf{r}. \quad (5)$$

This consideration leads to the definition of another two important indices, which have been used to study chemical reactivity. The global hardness,  $h$ , and the local reactivity index  $f$ , called the Fukui function.<sup>4</sup>

Parr and Pearson<sup>5</sup> have defined the former as,

$$h = \frac{1}{2} (\partial^2 E / \partial N^2)_u. \quad (6)$$

The factor 1/2 is arbitrary in the original definition and it is not considered in this paper. From (6),  $h$  is the curvature of the curve  $E$  versus  $N$ , which is always positive.<sup>2</sup> Within the finite difference approximation,

$$h \approx I - A. \quad (7)$$

The inverse of global hardness defines the global softness,<sup>6</sup>

$$S = 1/h = (\partial N / \partial m)_u. \quad (8)$$

Hardness and softness are concepts that have been used to explain chemical reactivity for many years.<sup>7</sup> The hardness can be interpreted as the resistance of a system to the flux of electrons. On another hand, Politzer<sup>8</sup> has shown for atoms that the softness correlates linearly with the polarizability.

Forty years ago, Kohn and Sham (KS)<sup>9</sup> proposed the idea that made DFT calculations feasible, in this theory the energy functional is partitioned as,

$$E[\mathbf{r}(\mathbf{r})] = Ts[\mathbf{r}(\mathbf{r})] + J[\mathbf{r}(\mathbf{r})] + Exc[\mathbf{r}(\mathbf{r})] + \int \mathbf{u}(\mathbf{r}) \mathbf{r}(\mathbf{r}) d\mathbf{r}, \quad (9)$$

and the electron density is written as a function of  $N$  Kohn–Sham orbitals,  $\mathbf{y}_i(\mathbf{r})$ ,

$$\mathbf{r}(\mathbf{r}) = \sum_i^N |\mathbf{y}_i(\mathbf{r})|^2. \quad (10)$$

In (9),  $Ts$  is the kinetic energy functional of the non-interacting reference system,

$$Ts[\mathbf{r}(\mathbf{r})] = \sum_i^N \langle \mathbf{y}_i(\mathbf{r}) | -\frac{1}{2} \nabla^2 | \mathbf{y}_i(\mathbf{r}) \rangle. \quad (11)$$

The  $J$  functional contains the contribution of the Coulombic electron–electron interaction,

$$J[\mathbf{r}(\mathbf{r})] = \frac{1}{2} \iint \frac{\mathbf{r}(\mathbf{r}) \mathbf{r}(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r} d\mathbf{r}', \quad (12)$$

and  $Exc$  is the exchange–correlation functional,

$$Exc[\mathbf{r}(\mathbf{r})] = T[\mathbf{r}(\mathbf{r})] - Ts[\mathbf{r}(\mathbf{r})] + Vee[\mathbf{r}(\mathbf{r})] - J[\mathbf{r}(\mathbf{r})]. \quad (13)$$

The form of the  $Exc$  functional is unknown and it is usually modeled via different approximations.<sup>2</sup>

Minimizing the energy functional of (9), keeping the orbitals to be orthonormal, gives the set of one-electron KS equations

$$\left[ -\frac{1}{2} \nabla^2 + \mathbf{u}(\mathbf{r}) + \int \frac{\mathbf{r}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \mathbf{u}_{XC}(\mathbf{r}) \right] \mathbf{y}_i(\mathbf{r}) = \mathbf{e}_i \mathbf{y}_i(\mathbf{r}). \quad (14)$$

Several codes have been implemented to solve (14) numerically for atoms, molecules and solids. The strategies to solve the equations that emerge in the numerical approach depend on the boundary conditions.

In previous work, the non-relativistic spin-polarized Kohn–Sham equations were solved for atoms subjected to Dirichlet boundary conditions.<sup>10</sup> Under these conditions the electronic density is made to approach zero

at a given arbitrary distance,  $R_c$ , simulating the effect of high pressure on the system. In that report<sup>10</sup> the electronic structure of H, He, Ne and Na was analyzed under extreme confinement conditions, and a complete agreement with the previously reported accurate results were obtained thus providing a suitable reliable method<sup>10</sup> to study atoms under the spherical confinement conditions within the DFT.

The study of confined quantum systems is very interesting due to its utility as a model in the wide variety of applications covering a range of novel experimental conditions, for example, atoms and molecules under high pressures,<sup>11–41</sup> atoms and molecules in cavities,<sup>41</sup> electrons in quantum wells and quantum dots,<sup>42–45</sup> among others. We refer to the published reviews<sup>46–47</sup> on confined atomic and molecular electronic structure calculations for a comprehensive account of the various interesting applications.

Different proposals have been used to study many-electron confined atoms. As compared to the confined atomic calculations using the Dirichlet boundary conditions, the results derived from other arbitrary prescriptions to meet the corresponding boundary condition do not usually satisfy the rigorous theoretical requirements of the cavity model. However, there is set of common and useful conclusions, which can be derived from all such calculations. The core orbitals are generally found to be less sensitive to the effects due to the confinement than the valence orbitals.<sup>10,34,40</sup> A large number of the confined atoms studied<sup>10,37,38</sup> exhibit a well defined  $s$ - $d$  orbital energy level crossing. It has also been suggested that the chemical reactivity<sup>34</sup> of atoms under compression undergoes significant modifications.

Recently, Chattaraj and Sarkar<sup>48</sup> have analyzed, in the context of DFT reactivity indices, the ionization energy, softness and polarizability among other properties of some confined atoms and atomic ions. These authors used the method proposed by Boeyens,<sup>34</sup> where a cutoff function is employed to incorporate confining condition. Such a procedure, clearly, does not satisfy the Dirichlet boundary condition as considered in the previous work.<sup>10</sup> As a consequence several exact theoretical requirements of the spherical cavity model are not met when arbitrary cutoff functions are employed. For example, the spherical cavity model requires that the  $1s$  state of the spherically confined hydrogen atom at  $R_c = 2.0$  au is expected to correspond to the energy value of  $-0.125$  au corresponding to the  $2s$  state of the free hydrogen atom. While this condition is exactly followed within the Dirichlet boundary

condition calculations the cutoff function methods produce energies that are significantly higher by a factor of 3–4 depending upon the choice of cutoff function. Similar discrepancies are also observed for the other degeneracy conditions for example the simultaneous degeneracy of the  $2s$  and  $3d$  states at  $R_c = 6.0$  au. It is therefore important to examine the DFT descriptors of chemical reactivity in the light of more accurate confined atom calculations.

In this paper we use the confinement approach proposed in Ref. [10] to study DFT reactivity indices such as electronegativity, hardness and softness. We have evaluated these quantities via the finite difference approximation according to (4) and (7). Thus,  $I$  and  $A$  are also evaluated for atoms of the families IA, IIA, VA and VIIIA of the periodic table.

## 2. Methodology

The non-relativistic spin-polarized Kohn–Sham equations,<sup>2</sup> were solved with the numerical code described earlier.<sup>10</sup> The local Perdew–Wang exchange–correlation potential<sup>49</sup> was used as approximation to  $\mathbf{u}_{xc}$  in (14). For all atoms studied in this work the confinement radii were moved from 1 to 7 au with a step of 0.1 a.u. Furthermore, in this report the reactivity indices  $m$ ,  $h$  and  $S$  are in terms of  $I$  and  $A$ , such that this procedure demands the computation of the neutral, anion and cation systems for each atom. In order to avoid holes in the electron configuration, and in this way satisfy the requirement of the ground state in the Kohn–Sham method, we found for each atom the electron configuration associated to the minimal energy for each confinement radius. For example, for the Kr atom at 1 au the confined neutral system has an electron configuration  $[\text{Ar}]3d^{10}4f^8$ , but at 1.1 a.u. the respective electron configuration is  $[\text{Ar}]4s^23d^{10}4f^6$ . Thus, for each confinement radius we searched for the most stable electron configuration for neutral, cation and anion for each confined species following Hund's maximum multiplicity rule.

## 3. Results

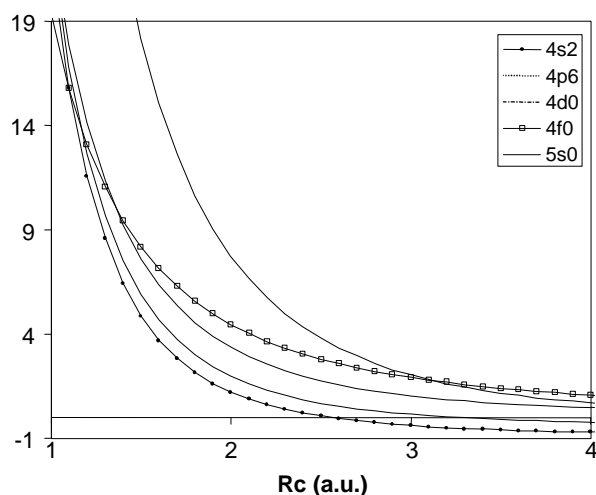
### 3.1 Orbital energies

From the initial stages of the theoretical studies of confined atoms, it has been recognized that when the confinement is increased in an atom its orbital energies cross over. In figure 1 we depict some orbital energies for the Kr atom with configuration  $[\text{Ar}]4s^23d^{10}4p^6$ . It

is clear that at 1 au the unoccupied  $4f$  orbital is most stable than the  $4s$  orbital, this behavior suggests the ground state configuration  $[\text{Ar}]3d^{10}4f^8$ . The relevant result from this observation is the change in the multiplicity, since with this transition the multiplicity changes from 1 to 7, and the atom goes from a closed to an open shell system.

### 3.2 Ionization potential and electron affinity

In table 1 we have compared the total electronic energy  $E$  for a confined He atom as a function of the radius of confinement with those derived respectively from the confined variational Hartree–Fock method and the confined cutoff method. The presently calculated



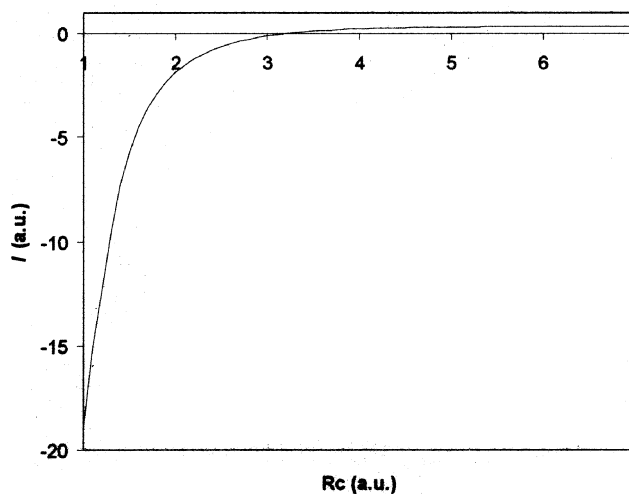
**Figure 1.** Orbital energies for the Kr atom confined with  $R_c = 1\text{--}7$  a.u. The orbital energies are in hartrees.

**Table 1.** A exchange-only comparison of the presently calculated total electronic energy, with the self-interaction correction, for confined He atom with the confined variational Hartree–Fock<sup>31</sup> and the confined cutoff methods.<sup>34,48</sup> All values are in atomic units.

$R_c$	$-E$ (present)	$-E$ (HF <sup>31</sup> )	$-E$ (cutoff <sup>48</sup> )
10	2.8617	2.8616	2.906
6	2.8616	2.8614	2.906
5	2.8614	2.8613	2.9059
4	2.8586	2.8585	2.9054
3	2.8311	2.8038	2.9052
2.5	2.7666	2.7664	2.8857
2	2.5626	2.5625	2.847
1.5	1.8642	1.8642	2.6795
1	1.0612	1.0612	1.966
0.5	-22.791	-22.791	-4.952

values derived from an exchange-only potential are found to be in excellent agreement with the HF estimates at all radii. This establishes the high degree of accuracy of the total energy calculations employed in the present work. In order to obtain the hardness, softness and electronegativity in this work we evaluated the  $I$  and  $A$ . In figure 2 we show a typical behavior that we observed for the  $I$  in all analyzed atoms. It is clear in this figure that there is an  $R_c$  value where  $I$  becomes negative, which means that the confined atom prefers the ionized system. Thus the atomic critical radius,  $R_I$ , is defined such that  $I$  is zero on this point. Since we use a step of 0.1 au, for each case, we interpolate the  $I$  with four points, in order to get the  $R_I$ . In table 2 we list the  $R_I$  found for the atoms considered in this work, also the  $R_I$  obtained from other works are included in table 2.<sup>31,34,36</sup> The  $R_I$  reported previously in other works is based on Koopmans' theorem or on the Slater transition-state approximation. Thus our results are more reliable since the  $I$  is evaluated as an energy difference and we are including correlation effects. As discussed previously,<sup>36</sup> the  $R_I$  reported by Boeyens<sup>34</sup> are in disagreement with the other results. This observation along with the incorrect description of the energy degeneracy conditions of the confined atoms resulting from the arbitrary cutoff function method<sup>34</sup> of confined atom calculations, highlights the serious limitations of such methods in comparison to the those employing the direct Dirichlet boundary condition.<sup>10</sup>

The behavior of  $A$  as a function of  $R_c$  for the confined Kr atom is shown in figure 3. Comparing figures 2 and 3 we can see that the behavior of  $A$  is different



**Figure 2.** Ionization potential for the Kr atom estimated by computing the total energy of neutral atom and cation for each confinement radius. All quantities are in atomic units.

with respect to that observed for  $I$ . First, around 1 a.u. of  $R_c$ ,  $A$  is a non-monotonous crescent function since it exhibits a step. Second, although  $A$  is a crescent function it shows deeper values with respect to  $I$ , this observation is important for the following discussion related with hardness in the next section. The main conclusion obtained from figures 2 and 3 is that a confined atom prefers to eject an electron for a critical  $R_c$ .

### 3.3 Electronegativity

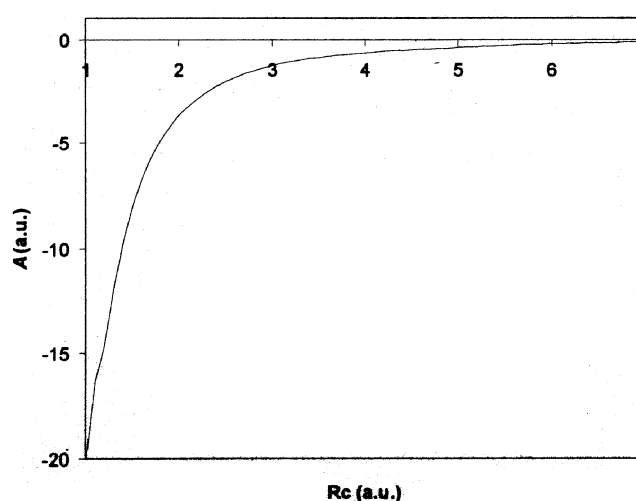
Electronegativity behavior as a function of  $R_c$  for the confined Kr atom is shown in figure 4. According to (4), the electronegativity is obtained from an average between  $I$  and  $A$ . Due to the negative values of  $I$  and  $A$ , downwards from  $R_c$ , the electronegativity attains negative values, as we can see in figure 4. Physically negative values for  $\chi$  represent a tendency to repel

electrons, since  $\chi > 0$  represents the tendency of an atom to attract electrons. From figures 2 and 4, we may say that when an atom is confined, it starts to lose its capacity to attract electrons and, after that, the confined atom ejects an electron since the ionization radius is less than that  $R_c$  where the electronegativity starts to attain negative values. The electronegativity behavior found by us, as a function of  $R_c$ , differs enormously from that presented earlier.<sup>48</sup> Whereas we found negative  $\chi$  for small  $R_c$  values, earlier researchers<sup>46</sup> obtained positive values for this quantity. Evidently in that work,<sup>48</sup> such discrepancy arises due to the way the confinement is imposed.

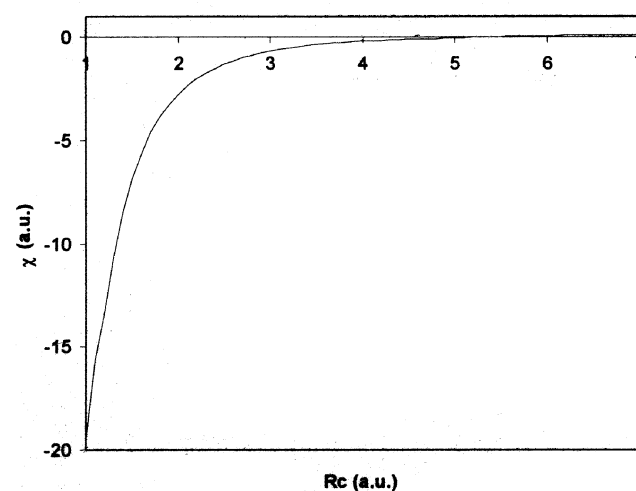
**Table 2.** Atomic ionization radii for all atoms considered in this work. All distances are given in Å.

Atom	Critical radius	
	This work	Other works
Li	2.17	2.26 <sup>a</sup> 1.25 <sup>b</sup> 2.21 <sup>c</sup>
Na	2.26	2.39 <sup>a</sup> 2.73 <sup>b</sup>
K	2.71	2.88 <sup>a</sup> 3.74 <sup>b</sup>
Be	1.70	1.70 <sup>a</sup> 1.09 <sup>b</sup>
Mg	1.98	2.02 <sup>a</sup> 2.36 <sup>b</sup>
Ca	2.54	2.52 <sup>a</sup> 3.26 <sup>b</sup>
N	1.21	1.29 <sup>a</sup> 1.56 <sup>b</sup>
P	1.69	1.79 <sup>a</sup> 2.20 <sup>b</sup>
As	1.77	
Ne	0.97	0.98 <sup>a</sup> 1.20 <sup>b</sup> 0.97 <sup>c</sup>
Ar	1.36	1.38 <sup>a</sup> 1.81 <sup>b</sup>
Kr	1.68	

<sup>a</sup>Ref. 36; <sup>b</sup>Ref. 34; <sup>c</sup>Ref. 31



**Figure 3.** Electron affinity for the Kr atom estimated by computing the total energy of neutral atom and anion for each confinement radius. All quantities are in atomic units.

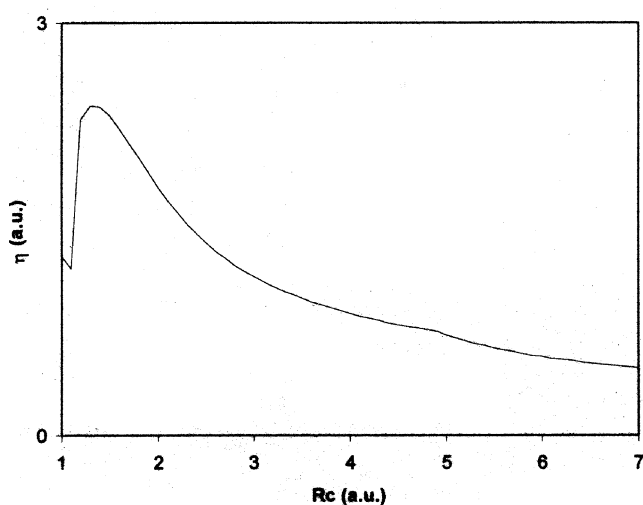


**Figure 4.** Electronegativity as a function of the confinement radius,  $R_c$ , for the Kr atom estimated by the finite difference approximation. All quantities are in atomic units.

Thus, according to them, the capacity to attract electrons in a confined atom increases when  $Rc$  is reduced. In order to check our finite difference results, we numerically evaluated the derivative of the total energy with respect to the number of electrons at a fixed  $Rc$ . We evaluated directional derivatives of the energy, because the discontinuity of the derivative of the total energy with respect to the number of electrons. For the confined Kr atom at  $Rc = 1$  au we moved the number of electrons from 36 to 36.15 and 35.85, each 0.05 electrons. Thus, a four-point interpolation function was used to evaluate the directional derivative. With this procedure we found  $\bar{m}^{\dagger} = 19.63$  a.u. and  $\bar{m}^{-} = 19.82$  or  $c^{\dagger} = -19.63$  a.u. and  $c^{-} = -19.82$ . For this  $Rc$ , using  $I$  and  $A$  values, we calculated the mean  $c^{\dagger} = -19.63$  a.u. Thus, we observed that with numerical derivatives and the finite difference approximation the electronegativity has a negative sign for the confined Kr at  $Rc = 1$  a.u. As we can see, with two different ways to evaluate the electronegativity, this quantity is reduced when an atom is confined, and for  $Rc$  less than a critical radius the electronegativity changes its sign. It is worth noting that for this case the finite difference approximation gives a similar value of  $c$  with respect to the numerical derivatives.

### 3.4 Hardness and softness

In figure 5 we present the hardness as a function of  $Rc$  for the confined Kr atom. We can see the interesting behavior of the hardness for the confined Kr



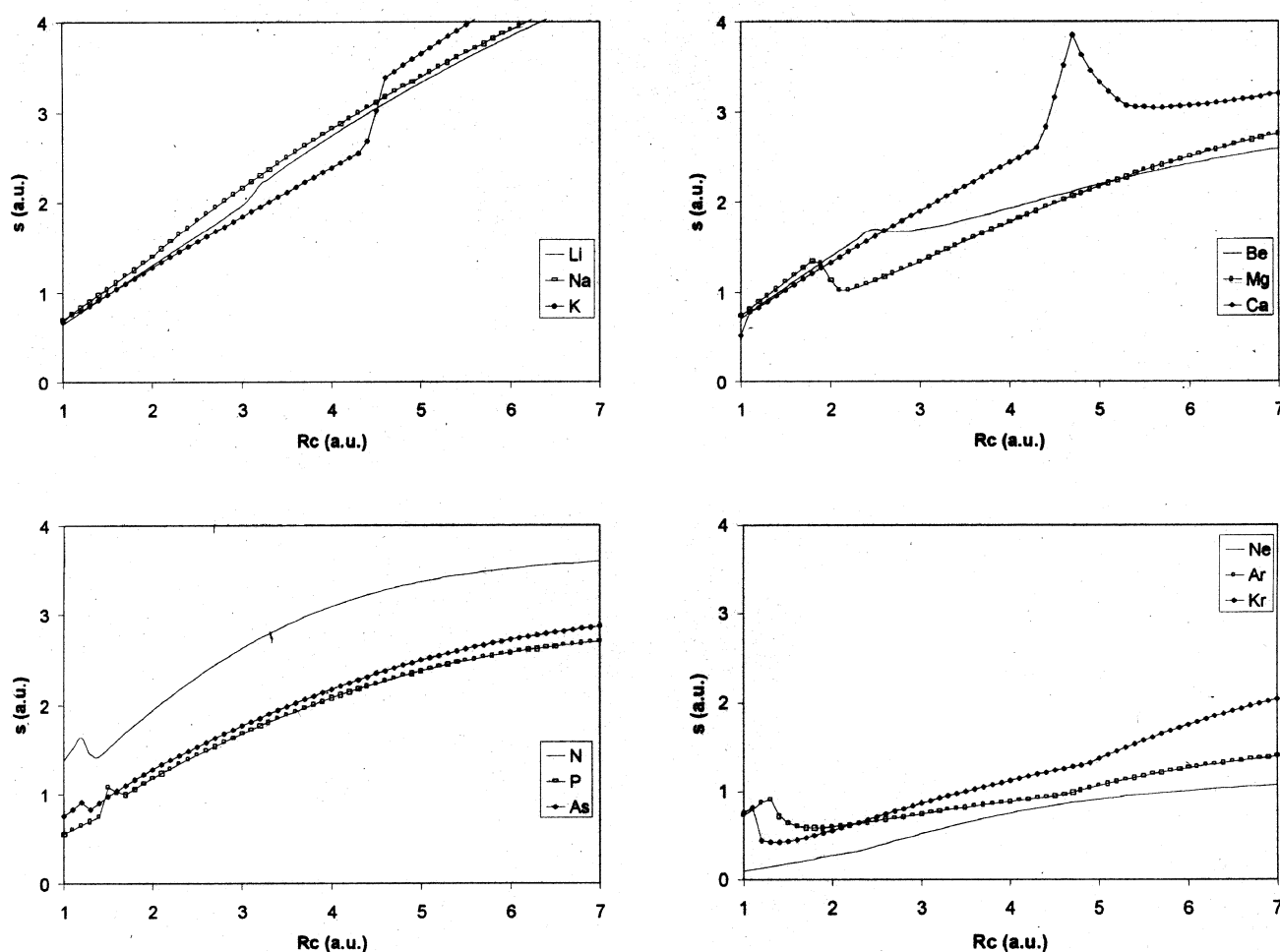
**Figure 5.** Hardness as a function of the confinement radius,  $Rc$ , for the Kr atom estimated by the finite difference approximation. All quantities are in atomic units.

atom. If we have the free Kr (large  $Rc$  values) the hardness exhibits asymptotic behavior. However, when we start confining the atom, the hardness still increases but at a different rate. It is clear in this figure that in  $Rc = 4.9$  a.u., the incremental rate of hardness is reduced, precisely at the point where the anion exhibits the electron transition,  $[\text{Ar}]3d^{10}4s^24p^65s^1$  to  $[\text{Ar}]3d^{10}4s^24p^64d^1$ . According to figure 1, the orbital  $5s$  energy increases at a faster rate with respect to that of the  $4d$  orbital, when  $Rc$  is reduced. For the confined Kr atom we found several electron transitions, particularly for small  $Rc$ . These orbital transitions induce the behavior shown for the hardness in figure 5 where we can see a maximum at  $Rc = 1.3$  a.u. Thus when an atom is confined it does not show an infinity hardness, instead of this expected behavior the orbital transitions provoke a reduction in this quantity. It is worth to note that the hardness exhibit positive values for all  $Rc$ . This behavior is presented since according to figures 2 and 3,  $A$  always is less than  $I$  and therefore the difference  $I - A$  is positive.

There are systems, such as neon, where the electron transitions are not manifested in the  $Rc$  interval considered, for these cases the hardness increases rapidly. For that reason we decided to contrast the softness of all studied atoms in the same plot. The softness as a function of  $Rc$  for each family of all confined atoms considered in this work is depicted in figure 6. From this figure, we can obtain several observations. First, at the biggest  $Rc$  used in this study the confined atoms with the biggest softness, as expected, are those that belong to family IA, and the confined atoms with smallest softness are the atoms that belong to family VIIIA. Second, for small  $Rc$  values, all atoms exhibit almost the same values of softness. Third, the confined nitrogen atom exhibits a different behavior with respect to the atoms of other families since in principle it should present a softness less than the phosphorus, but it does not. This behavior can be attributed to the open shell presented in atoms of that family. The most important observation obtained from figure 6 is that the changes in the electronic configuration induce increment in the softness when the atoms are extremely confined.

## 4 Conclusions

For an atom confined within an impenetrable spherical cavity the electronegativity is found to decrease relative to the free atom. If the confinement is increased, the electronegativity changes its sign and after that the



**Figure 6.** Softness as a function of the confinement radius,  $R_c$ , for some atoms of the families IA, IIA, VA and VIIIA of the periodic table. The softness was estimated as the inverse of the hardness. All quantities are in atomic units.

atom prefers to be ionized. On the other hand, while the softness undergoes a reduction under confinement, in some specific atoms different behaviour is attained. In these specific atoms, the energy level crossover as  $R_c$  decreases leads to the changes in electronic configuration as a consequence of which the softness is increased. This observation indicates that a confined atom cannot be infinitely hard – chemical hardness is thus numerically found to be a finite positive quantity.

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