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Atomic softness and the electric dipole polarizability

P. Fuentealba*, O. Reyes

Departamento de Física, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago, Chile

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Abstract

The relations between the atomic softness and the atomic electric dipole polarizability are studied, both in a theoretical and an empirical way. For atoms and ions with one or two valence electrons a remarkably good correlation is found between the atomic electric dipole polarizability and the third power of the softness.

Introduction

The electric dipole polarizability and the softness are important atomic and molecular properties often used in chemistry as a measure of reactivity. The electric dipole polarizability describes the change of the electron cloud due to the presence of an electric field. The concept of softness (introduced by Pearson [1]) is a measure of the ability of a system to change. It plays an important role in connection with the behavior of Lewis acids and bases. The softness is a central part of the hard and soft acids and bases (HSAB) principle: hard acids prefer to coordinate to hard bases and soft acids to soft bases. The relation of the softness to the electric dipole polarizability was recognized very early. A soft base is one with a donor atom of high polarizability and a soft acid should have an acceptor atom with several easily excited outer electrons.

Softness and electric dipole polarizabilities both depend primarily on the valence electrons. It is known that some relation between them exist [2,3] but this is difficult to quantify because softness is difficult to quantify. Some years ago, an important step forward was made by Parr and Pearson [4], in which they demonstrated the relationship of hardness (the inverse of softness) with the second derivative of the energy with respect to the number of electrons. In this way, the chemical concept of softness was introduced into the theoretical framework of the density functional theory [5] exactly as it had been done before with electronegativity [6]. In the context of the density functional theory, and using the finite difference approximation, it is then possible to calculate the softness.

In this paper we correlate the atomic softness and the electric dipole polarizability. In Fig. 1 we present the softness of all atoms vs. the electric dipole polarizability. Although some general correlation appears, some points lie far off. A general correlation for all elements cannot be expected, because the number of valence electrons must play an important role. It is known from the periodic system that the elements are structured in chemical groups of analogous behavior and analogous structures of the valence electrons. A very similar trend has already been observed between electric dipole polarizabilities and the ionization potentials of atoms [7].

In the next section (Theory) we present some theoretical background to justify the relation between softness and polarizabilities. Then

* Corresponding author.

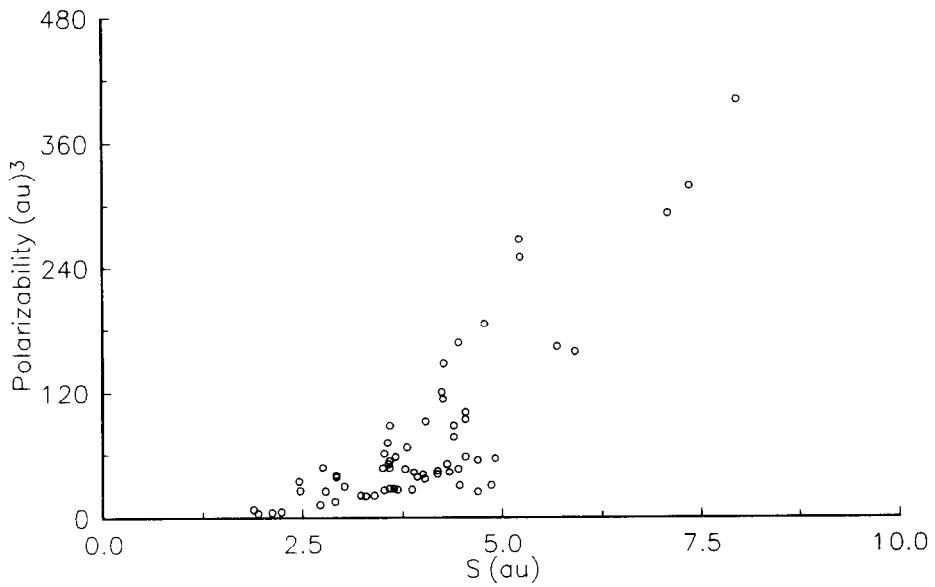

Fig. 1. Electric dipole polarizability vs. softness for all elements.

(Numerical results) we discuss some empirical correlations.

Theory

The energy of an atomic or molecular system in the presence of a static electric field ϵ can be expanded in a Taylor series as

$$E = E_0 - \mu_\alpha \epsilon_\alpha - \tfrac{1}{2}\alpha_{\alpha\beta}\epsilon_\alpha\epsilon_\beta + \dots \quad (1)$$

where E_0 is the energy of the free system, ϵ_α is the α-component of the electric field, μ_α given by

$$\mu_\alpha = -\left(\frac{\partial E}{\partial \epsilon_\alpha}\right)_{\epsilon_\alpha=0} \quad (2)$$

is the α-component of the permanent electric dipole moment, and

$$\alpha_{\alpha\beta} = -\left(\frac{\partial^2 E}{\partial\epsilon_\alpha \partial\epsilon_\beta}\right)_{\epsilon_\alpha\epsilon_\beta=0} \quad (3)$$

is the α,β-component of the dipole polarizability tensor. The greek subscript denotes cartesian coordinates x, y, z. A repeated subscript in Eq. (1) denotes a summation over the three cartesian coordinates. For a spherical atom the dipole moment vanishes and the electric field can be assumed in the z-direction, $\epsilon = \epsilon r\cos\theta\hat{z}$, where ϵ is the field strength. Hence, Eq. (1) reads

$$E - E_0 = \frac{1}{2}\left(\frac{\partial^2 E}{\partial\epsilon^2}\right)_{\epsilon=0}\epsilon^2 + \dots \quad (4)$$

and the mean value of the polarizability is

$$\alpha = -\left(\frac{\partial^2 E}{\partial\epsilon^2}\right)_{\epsilon=0} \quad (5)$$

Equations (4) and (5) are the working equations of all the finite field methods for calculating polarizabilities.

In density functional theory [5] the energy of a system of N electrons can be expressed as a functional of the density $\rho(\boldsymbol{r})$ and the external potential $v(\boldsymbol{r})$

$$E[\rho, v] = F[\rho] + \int \rho(\boldsymbol{r})v(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} \quad (6)$$

where $F[\rho]$ is a universal functional consisting of kinetic, classical electrostatic and exchange correlation contributions. The energy functional obeys a variational principle, so one has the Euler equation

$$\mu = \frac{\delta E}{\delta \rho} = v(\boldsymbol{r}) + \frac{\delta F}{\delta \rho} \tag{7}$$

where the Lagrange multiplier μ represents the chemical potential of the electron cloud. Note that the same symbol μ was used above for the dipole moment. In all subsequent equations μ means the chemical potential.

Consider now the change in the energy density functional of Eq. (6) due to a change in the external potential (i.e. an infinitesimal electric field) at number of electrons N constant. One can perform a Taylor series functional expansion around the reference electron density $\rho_0(r)$ and external potential $v_0(r)$ corresponding to the free system (i.e. no electric field). Following the work of Gazquez and Vela [8]

$$E[\rho, v] = E[\rho_0, v_0] + \int \rho_0(\boldsymbol{r}) \delta v(\boldsymbol{r})\, \mathrm{d}\boldsymbol{r} + \frac{1}{2} \int\int \left(\frac{\delta^2 E}{\delta \rho(\boldsymbol{r}) \delta \rho(\boldsymbol{r}')} \right) \Bigg|_{\rho_0, v_0} \times \delta \rho(\boldsymbol{r}) \delta \rho(\boldsymbol{r}')\, \mathrm{d}\boldsymbol{r}\, \mathrm{d}\boldsymbol{r}' + \ldots \tag{8}$$

where the relation

$$\rho_0(\boldsymbol{r}) = \left[\frac{\delta E}{\delta v(\boldsymbol{r})} \right]_{\rho} \Bigg|_{\rho_0, v_0} \tag{9}$$

was used. The change in the density due to a modification of the external potential can be written as

$$\delta \rho(\boldsymbol{r}) = \int \left[\frac{\delta \rho(\boldsymbol{r})}{\delta v(\boldsymbol{r}')} \right]_N \delta v(\boldsymbol{r}')\, \mathrm{d}\boldsymbol{r}' \tag{10}$$

Suppose now that the variation of the external potential corresponds to an infinitesimal electric field $\delta v(\boldsymbol{r}) = \delta \epsilon r \cos\theta$. Using ϵ as an infinitesimal parameter which defines the variation, Eq. (8) becomes

$$E[\rho, v] = E[\rho_0, v_0] + \tfrac{1}{2} \epsilon^2 \int\int \left[\frac{\delta \mu}{\delta \rho(\boldsymbol{r})} \right]_v \times \frac{\delta \rho(\boldsymbol{r})}{\delta \epsilon} \frac{\delta \rho(\boldsymbol{r}')}{\delta \epsilon} \mathrm{d}\boldsymbol{r}\, \mathrm{d}\boldsymbol{r}' + \ldots \tag{11}$$

Equations (7), (10) and the spherical symmetry of the atomic density were used. Equation (11) is equivalent to those derived by Gasquez and Vela [8] and Ghosh [9]. Comparison of Eqs. (4) and (11) yields

$$\alpha = \int\int \left[\frac{\delta \mu}{\delta \rho(\boldsymbol{r}')} \right]_v \frac{\delta \rho(\boldsymbol{r})}{\delta \epsilon} \frac{\delta \rho(\boldsymbol{r}')}{\delta \epsilon} \mathrm{d}\boldsymbol{r}\, \mathrm{d}\boldsymbol{r}' \tag{12}$$

which is an exact expression for the electric dipole polarizability in terms of the variation of the density and the chemical potential. The terms under the integral sign can be related to the hardness and softness kernels. The first term is merely the definition of the hardness kernel

$$\eta(\boldsymbol{r}, \boldsymbol{r}') = \frac{1}{2} \frac{\delta^2 F}{\delta \rho(\boldsymbol{r}) \delta \rho(\boldsymbol{r}')} = \frac{1}{2} \left[\frac{\delta \mu}{\delta \rho(\boldsymbol{r}')} \right]_v \tag{13}$$

and the second term is the derivative of the density with respect to the electric field, which is directly related to the linear response function.

Now

$$\mathrm{d}\rho(\boldsymbol{r}) = \frac{\delta \rho(\boldsymbol{r})}{\delta \epsilon} \epsilon \tag{14}$$

or, in terms of $\delta v(\boldsymbol{r})$

$$\mathrm{d}\rho(\boldsymbol{r}) = \int \left[\frac{\delta \rho(\boldsymbol{r})}{\delta v(\boldsymbol{r}')} \right]_N \delta v(\boldsymbol{r}')\, \mathrm{d}\boldsymbol{r}' \tag{15}$$

and (after Berkowitz and Parr [10])

$$\left[\frac{\delta \rho(\boldsymbol{r})}{\delta v(\boldsymbol{r}')} \right]_N = -s(\boldsymbol{r}, \boldsymbol{r}') + Sf(\boldsymbol{r}) f(\boldsymbol{r}') \tag{16}$$

All the displayed quantities are very well related between themselves [5]. The softness kernel $s(\boldsymbol{r}, \boldsymbol{r}')$ obeys the equations

$$2 \int s(\boldsymbol{r}, \boldsymbol{r}') \eta(\boldsymbol{r}', \boldsymbol{r}'')\, \mathrm{d}\boldsymbol{r}' = \delta(\boldsymbol{r} - \boldsymbol{r}'') \tag{17}$$

and

$$S = \int\int s(\boldsymbol{r}, \boldsymbol{r}')\, \mathrm{d}\boldsymbol{r}\, \mathrm{d}\boldsymbol{r}' \tag{18}$$

where S is the global softness. The Fukui function $f(\boldsymbol{r})$ is related to them through the equation

$$Sf(\boldsymbol{r}) = \int s(\boldsymbol{r}, \boldsymbol{r}')\, \mathrm{d}\boldsymbol{r}' \tag{19}$$

Hardness and softness kernels are necessary in order to evaluate the dipole polarizability using Eq.

Table 1
Softness S and electric dipole polarizabilities μ

	α (a.u.)	S (a.u.)		α (a.u.)	S^a (a.u.)
Li	165.0	5.69	Be	36.28	2.92
Na	164.0	5.92	Mg	70.70	3.56
K	293.0	7.09	Cs	157.0	4.45
Rb	321.0	7.36	Sr	200.0	4.78
Cs	402.0	7.96	Ba	280.0	5.22
Be^+	24.70	3.07	Mg^+	35.10	3.68
B^{2+}	7.92	2.13	Al^{2+}	14.40	2.83
C^{3+}	3.50	1.64	Si^{3+}	9.03	2.33
N^{4+}	1.81	1.33	P^{4+}	4.50	1.99
O^{5+}	1.05	1.12	S^{5+}	2.95	1.75
F^{6+}	0.65	0.97	Cl^{6+}	2.00	1.55
			Ar^{7+}	1.50	1.40

[a] For the alkaline earth metal atoms the softness values tabulated by Parr and Yang [5] are wrong. We recalculate them using the ionization potentials given by Moore [11].

(12). Unfortunately, they are not known. In practice, they are much more difficult to obtain than the polarizability itself. Hence, Eq. (12) has its value as a way of understanding the kind of relation between softness and polarizability more than as an equation for evaluating the polarizability.

In the next section (Numerical results) we present some empirical correlations between electric dipole polarizabilities and softness.

Numerical results

In the finite difference approximation the atomic softness is simple to calculate. It is the reciprocal of the difference between the ionization potential and the electroaffinity. Numerical values are compiled in the book of Parr and Yang [5]. For some ions, we calculate the softness using as input the data given by Moore [11]. All the numerical values used in this paper are listed in Table 1.

An accurate evaluation of the atomic electric dipole polarizability remains a great challenge to theoreticians and experimentalists. The point is well exemplified in the review of Miller and Bederson [12] in which for many atoms the best quoted value of the electric dipole polarizability is given with an estimated accuracy of only 50%. Hence, in order to use a set of values of comparable quality we calculate the electric dipole polarizability using a finite field method and a pseudopotential model as previously described [13]. In fact, the only

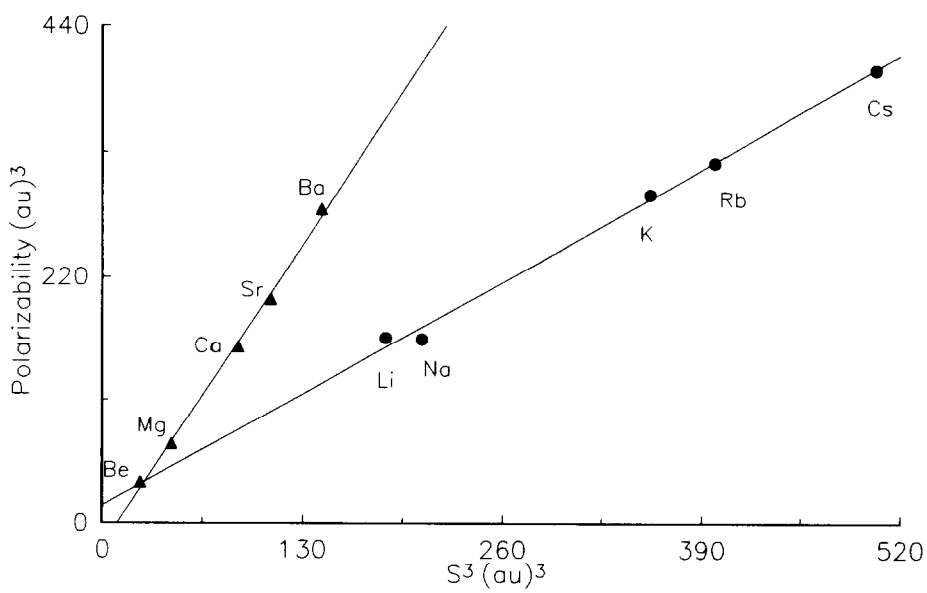

Fig. 2. Electric dipole polarizability vs. the third power of the softness for the alkali metal atoms (●) and the alkaline earth metal atoms (▲).

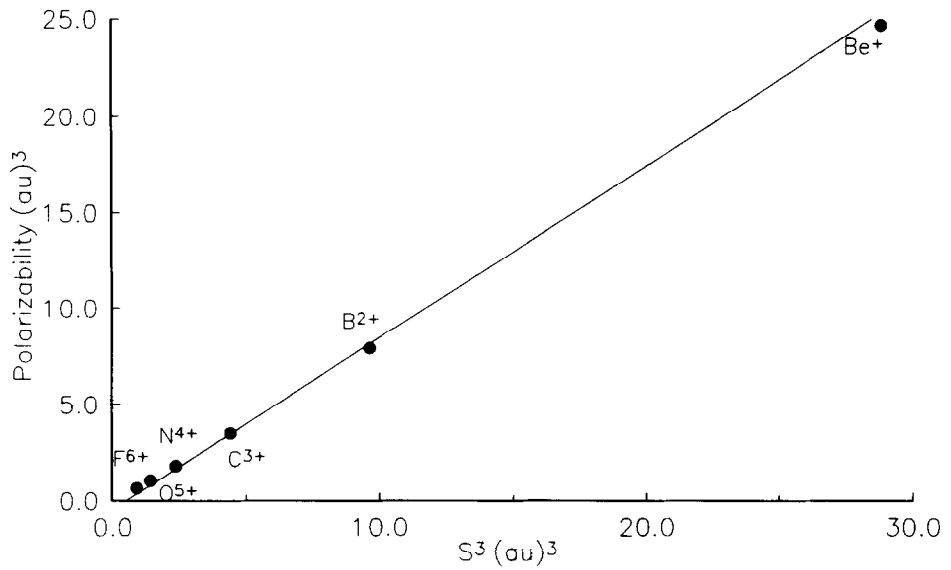

Fig. 3. Electric dipole polarizability vs. the third power of the softness for some ions of the Li isoelectronic sequence.

new values are those for the Na sequence of ions, the others being already published [13–15]. All the systems studied in this work (with the exception of the alkaline earth metal atoms) have only a single valence electron so we do not need to consider the valence correlation contribution to the electric dipole polarizability. Hence, the calculated values of the electric dipole polarizability are very reliable. All the numerical values used in this work are listed in Table 1.

In Figs. 2–4 we present the atomic electric dipole polarizability vs. the third power of the softness.

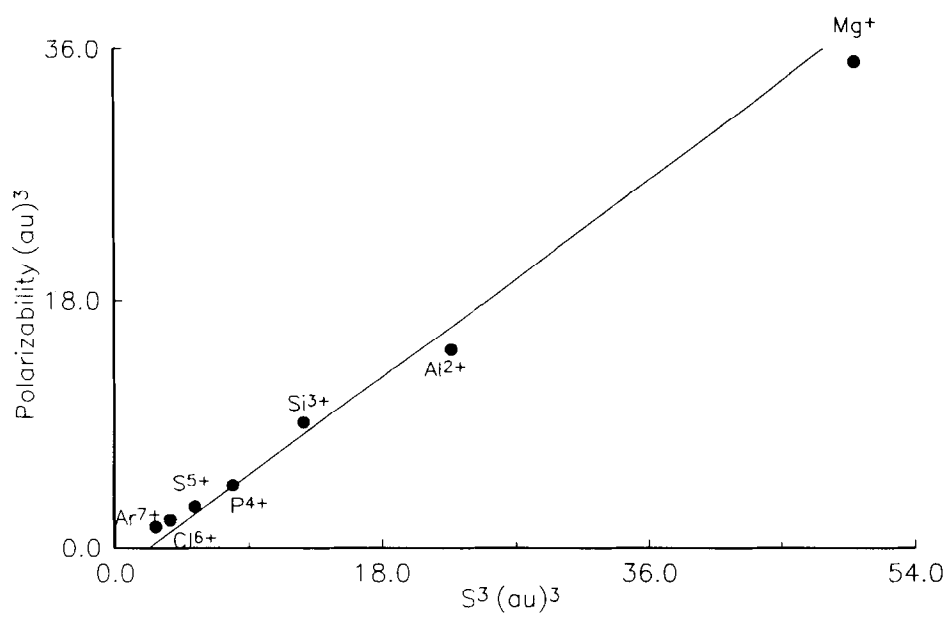

Fig. 4. Electric dipole polarizability vs. the third power of the softness for some ions of the Na isoelectronic sequence.

Using the specific characteristics given by the periodic table of the elements, an interesting correlation is found. All curves are near perfect straight lines with a correlation factor of near 1.0. In Fig. 2 the atoms are ordered according to the columns of the periodic table of the elements. Hence, in each curve the number of valence electrons is constant. The best fitted curve is $\alpha = 0.77S^3 + 15.09$ for the alkaline metal atoms and $\alpha = 2.07S^3 - 20.46$ for the alkaline earth metal atoms. In Figs. 3 and 4 the results for the Li and Na isoelectronic sequences are shown. Here, the total number of electrons is constant. For Fig. 3 the best fitted curve is $\alpha = 0.89S^3 - 0.47$. For Fig. 4 the best fitted curve is $\alpha = 0.79S^3 - 1.82$. All the curves have different slopes, showing the dependence on the number of electrons. Note that for the one valence electron series the slopes are very similar and near to unity, whereas for the two electron series the slope is near to two.

It is remarkable that in all the curves the electric dipole polarizability depends on the third power of the softness. Of course, this is nothing else but an empirical fact. It is an open question whether a theoretical explanation exists.

The analysis is very sensitive to the numerical values. An error of one tenth in the polarizability can change a cubic equation into a quadratic one. Thus, very accurate values of the electric dipole polarizability and softness are necessary. For many atoms these quantities are not well known so it is difficult to check the observed relation in other atomic series. Furthermore, other important effects should be considered, namely the electronic correlation and the relativistic contributions.

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