On the Density Functional Relationship between Static Dipole Polarizability and Global Softness

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The relationship between global softness and static dipole polarizability is explored from the analogy of the spherical averages defined within density functional theory. A cubic relationship is obtained that is consistent with the experimental observation for atoms. The relationship is found to hold reasonably well for similarly bonded molecules.

Global softness (S) and static electric dipole polarizability (α) are very important properties to characterize the reactive nature of atomic and molecular species. The former, introduced by Pearson,[1] is a measure of the ability of a system to change for any external action; this idea is closely linked with the Huheey's concept[2] of charge capacity, and a reasonable approximation is $(I - A)^{-1}$. The latter describes (to first order) the change of the electron cloud due to the presence of an electric field. The two quantities depend primarily on the valence electrons and play a central role in the establishment of the hard and soft acids and bases (HSAB) principle,[3] which seems to be a universal principle of chemical interactions; hard acids prefer to coordinate to hard bases and soft acids to soft bases. Usually these properties are numerically calculated by means of ab initio procedures. Hence the relations between them, even when formally possible, are difficult to elucidate.

The relationship between global softness and the static electric dipole polarizability was first investigated by Politzer[4] some time ago. Later, it was empirically studied by Fuentealba and Reyes[5] and Ghanty and Ghosh.[6] Both works showed that global softness correlates linearly with $\alpha^{1/3}$. Using empirical arguments Hati and Datta[7] found analytical expressions, including a relationship with the ionization potential, consistent with the above observations. They discussed the application to atoms, ions, and clusters. The paper of Vela and Gázquez[8] represents the first attempt to derive, systematically, from density functional theory the relationship between S and α. This work proposed a linear dependence, which is only approximately consistent with experimental observation. For an empirical study proposing a linear dependence for these quantities, see ref 9.

In this work, we present further evidence for a cubic relationship between the softness and the static dipole polarizability. The starting point is the Berkowitz−Parr equation[10]

$$\chi(\mathbf{r},\mathbf{r}') = -s(\mathbf{r},\mathbf{r}') + \frac{s(\mathbf{r})\, s(\mathbf{r}')}{S} \tag{1}$$

where the linear response function, $\chi(\mathbf{r},\mathbf{r}')$, is related to the softness kernel, $s(\mathbf{r},\mathbf{r}')$, the local softness function, $s(\mathbf{r})$, and the global softness, S.

The static dipole polarizability can be defined in term of the linear response function as

$$\alpha = \frac{1}{2}\int\int \chi(\mathbf{r},\mathbf{r}')\, \delta v(\mathbf{r})\, \delta v(\mathbf{r}')\, d\mathbf{r}\, d\mathbf{r}' \tag{2}$$

where the perturbation $\delta v(\mathbf{r})$ corresponds to an infinitesimal applied static electric field.

For the purposes of this paper, the main observation is that the spherical average global softness is

$$S = 4\pi \int dr\, r^2 s(r) \tag{3}$$

and the spherical average dipole polarizability, in a local approximation of density functional theory, can be written as

$$\alpha = \frac{4\pi}{3} \int dr\, r^4 s(r) \tag{4}$$

Both integrals are in one dimension and over the whole space. Equation 4 was first derived by Vela and Gázquez.[8]

Equations 3 and 4 can be rationalized through an expression of the type

$$\langle n \rangle = c_n \frac{\partial^n}{\partial t^n}\bigg|_{t=0} \int dr\, e^{-tr}\, s(r) \tag{5}$$

where $n = 2$ correspond to the global softness and $n = 4$ to the dipole polarizability. The constant c_n stands for the factor outside the integrals in eqs 3 and 4.

Since an exact expression for the local softness is not known, the evaluation of eq 5 can be done only by resorting to some model for the softness. Hence, in this work the local softness proposed in ref 11 will be used

$$s(r) = \frac{9\rho(r)^{2/3}}{10c_F\rho(r)^{1/3} + 4c} \tag{6}$$

where c is an adjustable parameter and $\rho(r)$ the spherical

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TABLE 1: Parameters and Calculated Atomic Softness and Dipole Polarizabilities for Some p-Atoms[a]

atoms	λ	S_{cal} (au)	S_{exp} (au)	α_{cal} (au)	α_{exp} (au)
B	1.634	7.062	7.070	23.770	20.447
Al	1.250	9.232	9.823	53.094	56.279
Ga	1.288	8.960	9.383	48.532	54.795
In	1.230	9.382	9.717	55.727	55.824
C	1.939	5.951	5.442	14.224	11.877
Si	1.454	7.940	8.050	33.735	36.305
Ge	1.460	7.904	8.002	33.321	40.962
Sn	1.367	8.442	8.921	40.595	51.960
N	2.248	5.133	3.763	9.128	7.423
P	1.660	6.952	5.576	22.670	24.496
As	1.626	7.097	6.047	24.122	29.084
Sb	1.509	7.647	7.160	30.179	44.537
O	2.542	4.540	4.475	6.313	5.412
S	1.866	6.184	6.572	15.960	19.570
Se	1.788	6.454	7.031	18.141	25.441
Te	1.644	7.019	7.730	23.338	37.115
F	2.843	4.059	3.881	4.513	3.779
Cl	2.065	5.588	5.814	11.776	14.711
Br	1.947	5.927	6.447	14.050	20.582
I	1.774	6.505	7.373	18.574	33.133

[a] Experimental values from refs 15 and 16.

averaged electron density. For atoms, the electron density in the valence region can be approximated by

$$\rho(r) = A\, e^{-\lambda r} \tag{7}$$

For one-electron atoms, this is the exact expression with $A = Z^3/\pi$ and $\lambda = 2Z$. For the rest of the atoms, Sen et al.[12] have found the best A, λ values to fit the electronic densities in the valence region. Guided by the expression for the hydrogen atom a relation of the type $A = k\lambda^3$ has been postulated, where k is a different constant for elements having different valence structures.

Inserting eqs 6 and 7 into eq 5, we obtain (see Appendix)

$$S = \frac{191 k^{2/3}}{c}\frac{1}{\lambda} \tag{8}$$

and

$$\alpha = \frac{1717.5 k^{2/3}}{c}\frac{1}{\lambda^3} \tag{9}$$

Table 1 shows a comparison of the experimental values of global softness and dipole polarizability with the calculated values by eqs 8 and 9 for p-elements. We take the values $c = 4.96$, ref 12, and $k = 0.164$. Given its simple derivation, eqs 8 and 9 are reasonably accurate. The softnesses are calculated within 10% of the experimental values with the only exception of nitrogen atom. The dipole polarizabilities are in reasonably good agreement with the experimental values considering that α is a very sensitive quantity and experimental measurements sometimes have a large uncertainty. The main point in this work is the relation of α and S. Combining eqs 8 and 9, the following relationship between α and S is obtained:

$$\alpha = \frac{0.000\,25 c^2}{k^{4/3}} S^3 \tag{10}$$

The present DFT approach vindicates the cubic relationship proposed earlier[5,6] on empirical grounds. For molecules, using the arithmetic average principle[13] for the global softness, one can write

$$S = \frac{1}{J}\sum_j S_j = \frac{K'}{J}\sum_j (\alpha_j)^{1/3} \tag{11}$$

and according to classical arguments and the jellium model, $\alpha \sim r_a^3$, with r_a the atomic radius. Taking the atomic radius as the r value corresponding to the Hartree–Fock density of 10^{-3} au, one obtains a reasonable result for the dipole polarizability.[14] Substituting in eq 11, one obtains,

$$S = K\sum_j r_{a_j} \tag{12}$$

which is an acceptable approximation for the global softness of the molecule or cluster.

In the following we try to give additional proofs for the validity of this relation. Figures 1, 2, and 3 show the plotted α against S^3 for s, p, and d-elements (data from refs 16 and 17). For p-elements the slope of the plot is 0.063, very close to the value 0.068 suggested by the relation in eq 10. For s and d-elements it is necessary to take groups of elements with similar behavior. For the alkali and alkaline earth metal atoms, there is clear the break in the slope going from Li to Na and Mg to Ca. This is clearly an effect of the $n = 3$ shell where the excitations to the 3d-states play an important role. For d-elements the analysis is more difficult owing to the major complexity of these atoms and the lack of reliable experimental values. Nevertheless the 3d-elements, except V and Cr, and the platinum metals seems to obey the cubic relation.
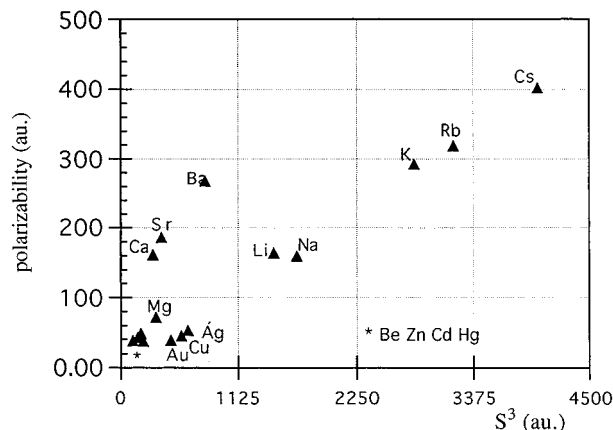

Figure 1. Dipole polarizability vs cubic global softness for atoms with a valence s-shell.
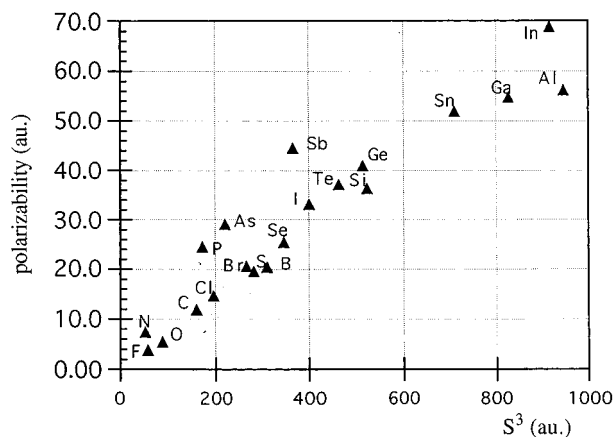

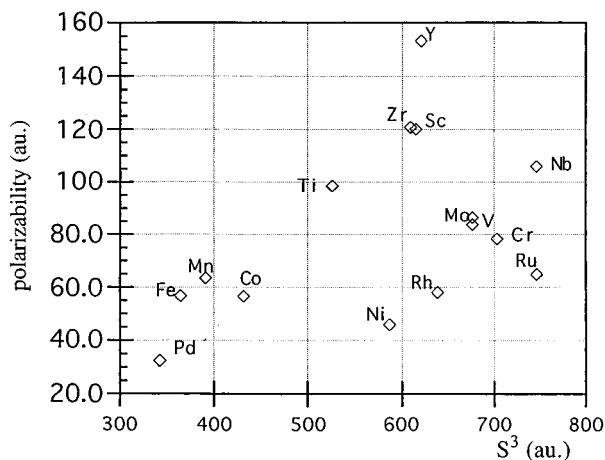**Figure 2.** Dipole polarizability vs cubic global softness for atoms with a valence p-shell.

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Figure 3. Dipole polarizability vs cubic global softness for atoms with a valence d-shell.
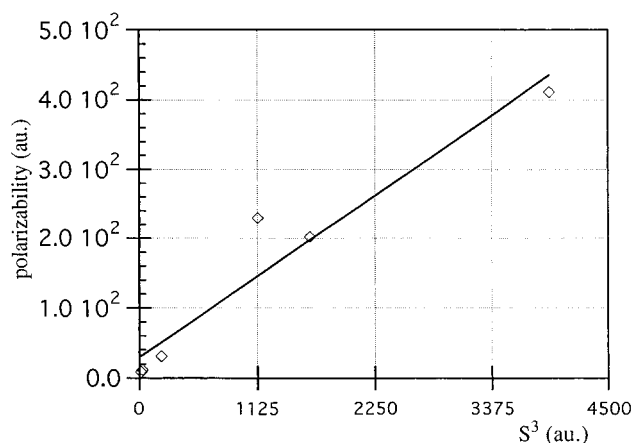

Figure 4. Dipole polarizability vs cubic global softness for diatomic molecules of Table 2.
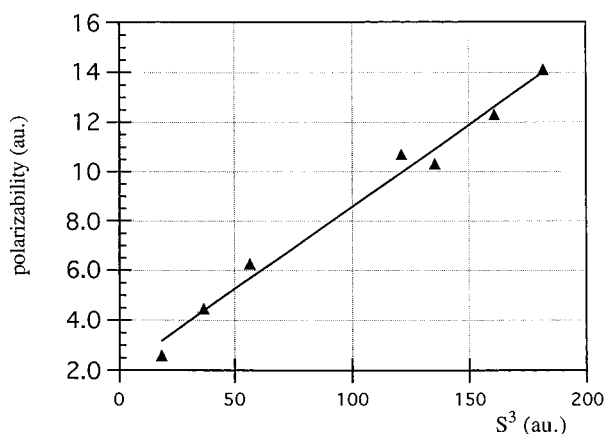

Figure 5. Dipole polarizability vs cubic global softness for hydrocarbon molecules of Table 2.

Figures 4 and 5 and Table 2 show the dependence of dipole polarizability on the global softness for diatomic and hydrocarbon molecules, respectively. The dipole polarizabilities of hydrocarbon molecules follow very nicely the cubic relation. For the diatomic molecules the results are not as good presumably due to the lack of spherical symmetry. For molecules, other effects such as temperature and vibrational contributions are surely important.

Finally, it could be interesting to look at the two quantities, softness and dipole polarizabilities, as two moments of the

TABLE 2: Polarizabilities and Global Softness of Molecules

molecules	α (au)[a]	S (au)[b]
Diatomic Molecules		
F_2	8.380	2.634
Cl_2	31.112	5.915
N_2	11.740	3.057
Na_2	202.462	11.779
Li_2	229.457	10.417
K_2	411.673	15.798
Hydrocarbon Molecules		
methane	17.499	2.642
ethane	30.167	3.328
propene	42.247	3.838
benzene	69.647	5.134
toluene	83.009	5.442
cyclohexene	72.211	4.947
p-xylene	95.157	5.669

[a] From ref 15. [b] Calculated with the approximation $2/(\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}})$ from MP2 results using the basis set 6-31G**. For organic molecules after semiempirical full optimization with PM3 Hamiltonian. The program SPARTAN[18] was used.

moment expression of the local softness. Define

$$S_n = \int r^n s(r) \, dr \qquad (13)$$

so that the global softness (S), corresponds to S_0 and the dipole polarizability is one-third of S_2. In general, it is easy to show that

$$S_n = S \frac{\partial \langle r^n \rangle}{\partial N} \qquad (14)$$

with N the number of electrons and $\langle r^n \rangle$ the expectation value of r^n. If one thinks of S_n as the moments of r over the distribution function $s(\mathbf{r})$, one finds that the mean-square deviation ($S_2 - S_1^2$) is given by

$$\sigma_s = 3\alpha - \left(S \frac{\partial \langle r \rangle}{\partial N} \right)^2 \qquad (15)$$

In conclusion, we have shown that the empirically proposed cubic relationship between the dipole polarizability and the global softness here has been theoretically justified within the local density model. Extensive further numerical tests in support of this relationship have been presented. Finally, the dipole polarizability and the global softness have been connected as two moments of r over the distribution function $s(\mathbf{r})$.

Appendix

Substituting eq 7 into eq 6, we have

$$s(r) = \frac{27 k^{1/3} \beta}{10 c_F} \frac{e^{-2\beta r}}{3^{-\beta r} + \gamma}$$

with $\beta = (^1/_3)\lambda$ and $\gamma = 4c/10 c_F k^{1/3}\lambda$.

After substitution in eq 5 it is necessary to solve the integral

$$\int \frac{dr\, e^{-\alpha r}}{e^{-\beta r} + \gamma}$$

with $\alpha = t + 2\beta$.

Despite its easy appearance, it does not appear tabulated in the commonly used Mathematical Tables. Therefore we explain the procedure used by us.

Transforming

$$\frac{1}{e^{-\beta r} + \gamma} = \frac{1}{\gamma} \frac{1}{1 + \dfrac{e^{-\beta r}}{\gamma}}$$

we expand like $(1 + x)^{-1}$

$$\frac{1}{e^{-\beta r} + \gamma} = \frac{1}{\gamma}\left(1 - \frac{e^{-\beta r}}{\gamma} + \frac{e^{-2\beta r}}{\gamma^2} + ...\right) = \frac{1}{\gamma}\sum_{k=0}^{\infty}(-1/\gamma)^k\, e^{-k\beta r}$$

Then, exchanging the sum and the integral we obtain

$$\int \frac{dr\, e^{-\alpha r}}{e^{-\beta r} + \gamma} = \frac{1}{\gamma}\sum_{k=0}^{\infty}(-1/\gamma)^k \frac{1}{\alpha + k\beta}$$

which is a hypergeometric series[17] that converges very rapidly. In fact, the dipole polarizability of the hydrogen atom does not change in an appreciable way when the series is truncated at the first term. After the truncation one takes the second and fourth derivates with respect to t and evaluates it for $t = 0$. In this way, one obtains eqs 8 and 9 of the text.

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