A Relationship between the Static Dipole Polarizability, the Global Softness, and the Fukui Function

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Received June 16, 1989

Abstract: A local approximation to the softness kernel is used to derive an expression for the static–density linear response function in terms of local and nonlocal components that are proportional to the fukui function and the global softness. This relation is applied to the case of a uniform electric field to show that the static dipole polarizability has a linear dependence on the global softness.

The hard and soft acid–base (HSAB) principle has been successfully used to explain some chemical reactions.[1,2] However, the absence of a precise definition to quantify hardness (η), or softness (S), has limited its applications. Parr and Pearson were able to overcome this situation by showing that the HSAB principle may be explained by making use of the definition[3,4]

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_\vartheta = \left(\frac{\partial \mu}{\partial N}\right)_\vartheta \tag{1}$$

where E is the electronic binding energy, N is the total number of electrons, μ is the chemical potential, and ϑ is the external potential. This definition allows one to quantify the hardness of different species, and the values obtained show the same tendencies of qualitative scales formulated in the past.[3]

In terms of the definition given by eq 1, the global softness is given by[5]

$$S = \frac{1}{\eta} = \left(\frac{\partial N}{\partial \mu}\right)_\vartheta \tag{2}$$

which leads to the finite differences formula

$$S \simeq \frac{1}{I - A} \tag{3}$$

where I is the first ionization potential, and A is the electron affinity. The right-hand side of eq 3 corresponds to Huheey's definition of charge capacity,[6] a quantity closely related to the static dipole polarizability (α) as shown by Politzer,[7] who found through a least-squares fit an approximate linear relationship between $(I - A)^{-1}$ and α.

The purpose of the present work is to make use of the thermodynamic like structure of density functional theory[8-13] to prove the relation between α and $(I - A)^{-1}$ or S. The relation between global softness and the static dipole polarizability had been inferred long ago;[2] however, it has never been proven.

In order to prove the relationship between S and α, we will develop first an approximate expression for the static density linear response function in terms of the global softness and the fukui function. Later on, we will use this expression to determine the static dipole polarizability in terms of S.

The linear response of a many-electron system to some small static perturbation $\delta\vartheta(\mathbf{r}')$ can be conveniently expressed in terms of the induced electronic density $\delta\rho(\mathbf{r})$ in the form

$$\delta\rho(\mathbf{r}) = \int \left(\frac{\delta\rho(\mathbf{r})}{\delta\vartheta(\mathbf{r}')}\right)_N \delta\vartheta(\mathbf{r}')\, d\mathbf{r}' \tag{4}$$

where the functional derivative $(\delta\rho(\mathbf{r})/\delta\vartheta(\mathbf{r}'))_N$ is known as the static–density response function. The calculation of the induced density through eq 4 has been successfully applied in several contexts within the framework of the Kohn–Sham approach to density functional theory, because the response of the Kohn–Sham system to a change in the one-body effective potential $\delta\vartheta_{\text{eff}}(\mathbf{r})$ corresponds to that of a system of non-interacting electrons. Thus, one can write the induced density as

$$\delta\rho(\mathbf{r}) = \int \chi^0(\mathbf{r},\mathbf{r}')\, \delta\vartheta_{\text{eff}}(\mathbf{r}')\, d\mathbf{r}' \tag{5}$$

where $\chi^0(\mathbf{r},\mathbf{r}')$, the non-interacting static–density response function, can be expressed in terms of the retarded single-particle Green's functions which can be obtained directly as solutions of relatively simple differential equations.[14,15] Thus, this approach provides a great simplification and it leads to good predictions of several properties. For example, the atomic static dipole polarizabilities of closed shell atoms agree with the experimental values within a few percent.

Even though this method is based on density functional theory (because it makes use of the Kohn–Sham formalism), the basic relations are formulated in terms of the non-interacting static–density response function which does not have as origin density functional theory. However, the thermodynamic-like structure of density functional theory[8-13] allows one to express the static–density response function in terms of other derivatives without having to invoke $\chi^0(\mathbf{r},\mathbf{r}')$. In particular, Berkowitz and Parr[16] have shown that

$$\left(\frac{\delta\rho(\mathbf{r})}{\delta\vartheta(\mathbf{r}')}\right)_N = -s(\mathbf{r},\mathbf{r}') + S f(\mathbf{r}) f(\mathbf{r}') \tag{6}$$

where $s(\mathbf{r},\mathbf{r}')$ is the softness kernel, and $f(\mathbf{r})$ is the fukui function.[10] These quantities are defined by the formulas[16]

$$s(\mathbf{r},\mathbf{r}') = -\frac{\delta\rho(\mathbf{r})}{\delta u(\mathbf{r}')} \tag{7}$$

$$s(\mathbf{r}) = \int s(\mathbf{r},\mathbf{r}')\, d\mathbf{r}' \tag{8}$$

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and

$$f(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)_{\vartheta} = \left(\frac{\delta \mu}{\delta \vartheta(\mathbf{r})}\right)_{N} \tag{9}$$

The relations given above lead to

$$S = \int s(\mathbf{r})\ \mathrm{d}\mathbf{r} = \left(\frac{\partial N}{\partial \mu}\right)_{\vartheta} \tag{10}$$

The function $s(\mathbf{r})$ is the local softness, and

$$u(\mathbf{r}) = \vartheta(\mathbf{r}) - \mu = \frac{\delta F[\rho]}{\delta \rho(\mathbf{r})} \tag{11}$$

where $F[\rho]$ is a universal functional that contains the electronic kinetic energy and the electron–electron interaction energy contributions.[17]

Since eq 6 provides an exact relation, Berkowitz and Parr have suggested that it can be used to calculate the softness kernel because $f(\mathbf{r})$ and S may be determined from an orbital theory, and $(\delta\rho(\mathbf{r})/\delta\vartheta(\mathbf{r}'))_N$ may be determined from perturbation theory. In this work we adopt a different point of view: we will consider a simple approximation to $s(\mathbf{r},\mathbf{r}')$ to derive an approximate relation between the static–density response function, the fukui function, and the global softness. That is, let us consider a local approximation to describe the relation between the electronic density and the modified potential $u(\mathbf{r})$. In this case, $\rho(\mathbf{r})$ is a function of $u(\mathbf{r})$ (instead of a functional), and according to eq 7 and 8 one obtains

$$s(\mathbf{r},\mathbf{r}') \simeq S f(\mathbf{r})\ \delta(\mathbf{r} - \mathbf{r}') \tag{12}$$

Substituting eq 12 in eq 6 one finds that within the local approximation for the softness kernel, the static–density response function is given by

$$\left(\frac{\delta \rho(\mathbf{r})}{\delta \vartheta(\mathbf{r}')}\right)_{N} = S f(\mathbf{r})[f(\mathbf{r}') - \delta(\mathbf{r} - \mathbf{r}')] \tag{13}$$

the induced density is given by

$$\delta\rho(\mathbf{r}) = S f(\mathbf{r})\left[\int f(\mathbf{r}')\ \delta\vartheta(\mathbf{r}')\ \mathrm{d}\mathbf{r}' - \delta\vartheta(\mathbf{r})\right] \tag{14}$$

and the energy change, up to second order in $\delta\vartheta(\mathbf{r})$, is given by

$$\mathrm{d}E = \int \rho(\mathbf{r})\ \delta\vartheta(\mathbf{r})\ \mathrm{d}\mathbf{r} + \frac{1}{2}S\left[\left(\int f(\mathbf{r})\ \delta\vartheta(\mathbf{r})\ \mathrm{d}\mathbf{r}\right)^2 - \int f(\mathbf{r})\ (\delta\vartheta(\mathbf{r}))^2\ \mathrm{d}\mathbf{r}\right] \tag{15}$$

One may note that eq 13 satisfies the Maxwell relation[8] $(\delta\rho(\mathbf{r})/\delta\vartheta(\mathbf{r}'))_N = (\delta\rho(\mathbf{r}')/\delta\vartheta(\mathbf{r}))_N$, and eq 14 satisfies the condition $\int\delta\rho(\mathbf{r})\ \mathrm{d}\mathbf{r} = 0$ because $\int f(\mathbf{r})\ \mathrm{d}\mathbf{r} = 1$.

The first term of eq 14 is the nonlocal component, which determines the change in the electronic density at point **r** due to the change in the external potential at every point in space, while the second term is the local component which determines the change in the electronic density at point **r** due to the change in the external potential at this point.

Thus, even though we have made use of a local approximation for $s(\mathbf{r},\mathbf{r}')$, we have found an expression for the static density response function that takes into account nonlocal effects and satisfies some basic properties. For atoms and molecules the relation between the static density response function, the fukui function, and the global softness may be very useful because $f(\mathbf{r})$ and S can be determined by calculating the charge density and the energy for several values of N and performing a numerical differentiation of these data. This procedure implies that even though the derivation of eq 13 is based on the formal theoretical framework provided by density functional theory, one can avoid the problem of the unknown functional by making use of conventional wave function theory to determine the energy and the electronic density.

It is also worth noting that eq 15 provides a very interesting interpretation of the second-order correction to the energy. $E^{(2)}$ provides a measure of the fluctuations of the expectation value of the change in the external potential with respect to the fukui function.

Now consider the static dipole polarizabilities. In this case the change in the external potential is given by

$$\delta\vartheta(\mathbf{r}) = \mathbf{r}\cdot\hat{\xi} \tag{16}$$

where $\hat{\xi}$ represents a uniform electric field of unit amplitude. By noting that

$$E^{(2)} = -\tfrac{1}{2}\hat{\xi}\cdot\alpha\cdot\hat{\xi} \tag{17}$$

one finds, using eqs 15 and 16, that

$$\alpha = -S\left[\left(\int \mathbf{r}\ f(\mathbf{r})\ \mathrm{d}\mathbf{r}\right)^2 - \int \mathbf{r}\mathbf{r}\ f(\mathbf{r})\ \mathrm{d}\mathbf{r}\right] \tag{18}$$

which shows that the polarizability tensor can be interpreted as a measure of the fluctuations of the expectation value of the dyadic **rr** of the fukui function. At the same time, it allows one to see that the main contribution to the polarizability of an atom or a molecule comes from the valence electrons, since the larger values of $f(\mathbf{r})$ are located in the valence region. In fact, $f(\mathbf{r}) \simeq \phi^*_{\mathrm{H}}(\mathbf{r})\phi_{\mathrm{H}}(\mathbf{r})$ (where ϕ_{H} is the highest occupied atomic or molecular orbital) when relaxation effects are neglected. On the other hand, one can see that eq 18 predicts a linear relationship between the static dipole polarizability and the global softness.

For the specific case of an atomic system one can show (using the fact that the angular dependence of the fukui function is equal to the angular dependence of the electronic density) that the first term in the right-hand side of eq 18 is equal to zero, while for the second term one just has to consider the diagonal elements of the polarizability tensor. Thus

$$\alpha = S\int r^2 \cos^2\theta\ f(\mathbf{r})\ \mathrm{d}\mathbf{r} \tag{19}$$

From eq 14 one has that the induced dipole moment density is directly proportional to $Sf(\mathbf{r})$, since the first term in the right-hand side vanishes for the atomic case. The comparison of the plots of $\alpha(r)$ given by Stott and Zaremba[14] with the plots of the fukui function[18] provides evidence that supports this result.

In order to test the relationship between α and S, one needs to calculate the fukui function and the global softness. By noting that

$$\int r^2 \cos^2\theta\ f(\mathbf{r})\ \mathrm{d}\mathbf{r} = \left(\frac{\partial}{\partial N}\int r^2 \cos^2\theta\ \rho(\mathbf{r})\ \mathrm{d}\mathbf{r}\right) \tag{20}$$

and using a finite difference scheme, one can approximate the polarizability as

$$\alpha = \frac{1}{2}\frac{1}{I - A}\left[\int r^2 \cos^2\theta\rho^-(\mathbf{r})\ \mathrm{d}\mathbf{r} - \int r^2 \cos^2\theta\ \rho^+(\mathbf{r})\ \mathrm{d}\mathbf{r}\right] \tag{21}$$

where ρ^- and ρ^+ are the electronic densities for the anion and cation of the corresponding atom. Thus, all quantities can be obtained from any self-consistent-field calculation. For a Hartree–Fock electron density the integrals in eq 21 can be written just in terms of the expectation value r^2. In Figure 1 we present the plot of the experimental values of the polarizability versus the quantity $(I - A)^{-1} \simeq S$, while in Figure 2 one can see the plot of the experimental values of α versus the values calculated from eq 21. It is clear from these plots that the factor in square brackets improves substantially the linear relationship between α and S. In fact, by multiplying the values of α obtained through eq 21

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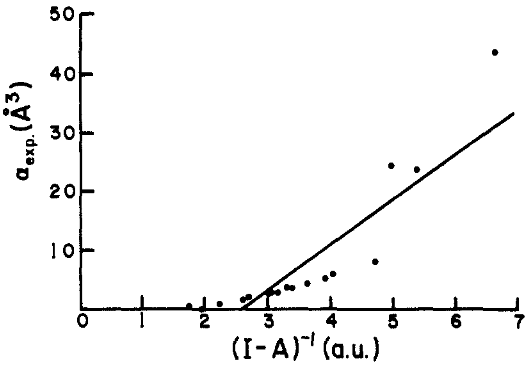

Figure 1. Plot of the experimental polarizability of some neutral atoms versus the quantity $(I - A)^{-1}$. The values of α_{exp} were taken from ref 19, and the only cases considered are those in which the estimated accuracy is less or equal to 2%. The values of I and A were obtained from the total energies reported in ref 20. The correlation factor of the linear least-squares fit is 0.76895.

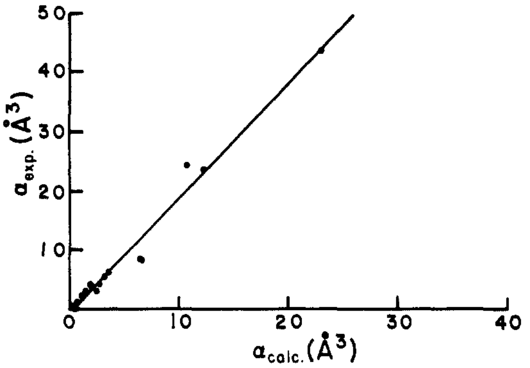

Figure 2. Plot of the experimental polarizability of some neutral atoms versus the values calculated from eq 21. The expectation values of r^2 were taken from ref 21 (see Figure 1 for the other quantities). The correlation factor of the linear least-squares fit is 0.97557, and the slope is 1.94.

by a factor of 2, one obtains rather accurate estimates of the atomic static dipole polarizabilities.

It is worth analyzing the case when the static perturbation corresponds to a point charge Q located at the position $\mathbf{R}$ far away from the unperturbed system

$$\delta\vartheta(\mathbf{r}) = -\frac{Q}{|\mathbf{R} - \mathbf{r}|} \tag{22}$$

Substituting eq 22 in eq 15 one finds that

$$dE = \frac{ZQ}{R} - Q\int \frac{\rho(\mathbf{r})}{|\mathbf{R} - \mathbf{r}|}\,d\mathbf{r} + \frac{1}{2}S\left[\left(Q\int \frac{f(\mathbf{r})}{|\mathbf{R} - \mathbf{r}|}\,d\mathbf{r}\right)^2 - \int f(\mathbf{r})\left(\frac{Q}{|\mathbf{R} - \mathbf{r}|}\right)^2 d\mathbf{r}\right] \tag{23}$$

where we have included the interaction with the atomic nucleus.

For simplicity let us consider that the unperturbed system is a spherically symmetric neutral atom. In this case the leading term when $R \gg r$ can be obtained by using the appropriate binomial expansions in eq 23. After some algebraic manipulations one obtains

$$dE = -\frac{1}{2}\frac{\alpha Q^2}{R^4} \tag{24}$$

where we have used eq 19. This expression is equal to the exact asymptotic expression for the induction energy or charge induced–dipole interaction energy. In this case the approximations associated with eq 13 are absorbed in the definition of polarizability given by eq 19 and one recovers the exact result.

The relationship between α and S developed here strengthens the definitions of hardness and softness, eqs 1 and 2, and the results presented here seem to indicate that eq 13 provides a reasonable approximation to the static–density response function, and it may be useful to study a wide variety of problems in the linear response regime.

Acknowledgment. The valuable comments of Prof. R. G. Parr are gratefully acknowledged. We also thank J. Robles, M. Galvân, and A. Garritz for many encouraging discussions. This work was supported in part by the Secretaria de Educaciôn Pûblica (PRONAES) and by CONACYT through the Programa de Fortalecimiento del Posgrado Nacional.