J. Phys. Chem. A **1999,** *103,* 1274−1275

Chemical Reactivity and Excited-State Density Functional Theory

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Received: September 22, 1998; In Final Form: November 18, 1998

Softness and polarizability are calculated for different complexions of two-state ensembles of various helium isoelectronic systems (He, Li^+, Be^{2+}, B^{3+}, C^{4+}). It is shown for the first time for the systems studied that an increase in the excited-state contribution in a two-state ensemble makes the system softer and more polarizable, as expected from the principles of maximum hardness and minimum polarizability.

Chemical reactivity parameters such as electronegativity[1] (χ) and hardness[2,3] (η) have been defined within density functional theory (dft)[4] as follows:

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(r)} \tag{1}$$

and

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

where μ is the chemical potential of an N-electron system with external potential $v(r)$ and total energy E. An equivalent expression for hardness[5] is

$$\eta = \frac{1}{N}\int\int \eta(r, r')f(r')\rho(r)\,\mathrm{d}r\,\mathrm{d}r' \tag{3}$$

where $f(r)$ is the Fukui function[6,7] and the hardness kernel is given by[5]

$$\eta(r, r') = \frac{1}{2}\,\frac{\delta^2 F[\rho]}{\delta\rho(r)\delta\rho(r')} \tag{4}$$

where $F[\rho]$ is the Hohenberg−Kohn−Sham[8] universal functional of dft.

These reactivity parameters are better appreciated through the associated electronic structure principles. The electronegativity equalization principle[9] states that “all the constituent atoms in a molecule have the same electronegativity value”. Two important hardness related principles are the HSAB[2,10] and maximum hardness[2,11] principles. According to the former,[2,10] “hard likes hard and soft likes soft”, and the latter states that[2,11] “there seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible”.

A many-particle system is completely characterized by N and $v(r)$. While χ and η describe the response of the system when N changes at fixed $v(r)$; the linear density response function,[4] $R(r,r')$ depicts the same for the variation of $v(r)$ for constant N; that is,

$$R(r,r') = \left[\frac{\delta\rho(r)}{\delta v(r')}\right]_N \tag{5}$$

This response function can be expressed within dft as follows:[4,5]

$$R(r,r') = \frac{s(r)s(r')}{S} - s(r,r') \tag{6}$$

where $s(r,r')$, $s(r)$, and S are the softness kernel, local softness, and global softness, respectively. The linear response of the electronic cloud of a chemical species to a weak external electric field is measured in terms of the static electric dipole polarizability (α). A simple perturbation calculation shows[4,12−14] that the first-order perturbation correction vanishes and the second-order correction is related to α as follows:

$$\alpha = -\int\int R(r,r')v(r)v(r')\,\mathrm{d}r\,\mathrm{d}r' \tag{7}$$

where $v(r)$ is the external electric potential. A minimum polarizability principle may be stated as[15,16] “the natural direction of evolution of any system is towards a state of minimum polarizability”.

To the best of our knowledge, the calculations of all the reactivity parameters and verification of the associated structure principles have been restricted to ground states and hardly any progress has been made in extending these studies to excited states. Here, we report the study of chemical reactivity involving excited states. For this purpose, the excited-state dft is made use of. The ground-state formulation of dft has been extended to the lowest state of a given symmetry[17] and the ensemble of states.[18] Time-dependent dft[16,19] and the ensemble formalism[18,20] have been used for the excited-state calculations. Time evolution of various reactivity parameters such as χ, η, α, and entropy associated with an ion−atom collision process and an atom-field interaction process have been studied[16] for both the ground and the excited electronic states, within a quantum fluid density functional framework. Dynamic variants of the related structure principles have been found to be operative for both the electronic states.

The Hohenberg−Kohn universal functional $F[\rho]$ (eq 4) used in this work is as follows:

$$F[\rho] = T[\rho] + V_{ee}[\rho], \tag{8}$$

where the kinetic energy functional is[21]

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10.1021/jp983821n CCC: \$18.00

TABLE 1: Calculated Softness (au) and Polarizability (au) Values for Two-State Ensembles of the Helium Isoelectronic Systems

atom/ ion	S				α			
	$\omega = 0$	$\omega = 0.25$	$\omega = 0.5$	$\omega = 1$	$\omega = 0$	$\omega = 0.25$	$\omega = 0.5$	$\omega = 1$
He	1.507	3.715	4.979	6.888	1.856	48.461	75.490	117.824
Li^+	0.778	1.774	2.345	3.205	0.398	5.970	9.169	14.133
Be^{2+}	0.490	1.104	1.453	1.975	0.160	1.734	2.629	4.005
B^{3+}	0.342	0.774	1.018	1.379	0.091	0.727	1.084	1.630
C^{4+}	0.254	0.582	0.764	1.033	0.064	0.378	0.553	0.817

$$T[\rho] = \frac{3}{10}(3\pi^2)^{2/3}\int \rho(r)^{5/3}\,\mathrm{d}r + \left(\frac{3}{4\pi}\right)(3\pi^2)^{1/3}\int \frac{\rho^{4/3}/r}{1 + ((r\rho^{1/3})/0.043)}\,\mathrm{d}r \quad (9)$$

and the total electron−electron repulsion energy is a modified Parr functional[22] as given below.

$$V_{\mathrm{ee}}[\rho] = \lambda \int \rho(r)^{4/3}\,\mathrm{d}r \quad (10)$$

with λ being a parameter.

We can write the global softness (S) and the polarizability (α) as follows:[13,14]

$$S = \int s(r)\,\mathrm{d}r; \quad \mathrm{s}(r) = \frac{\delta(r - r')}{2\eta(r,r')} \quad (11a)$$

$$\alpha = \frac{4\pi}{3}\int_0^\infty s(r) r^4\,\mathrm{d}r \quad (11b)$$

Equation 11b is valid for spherically averaged densities.The value of the parameter λ (eq 10) is taken as 5, which reproduces the exact dipole polarizability (eq 11b) of the hydrogen atom using its exact density.

We have calculated the S and α values of a two-state ensemble for the He isoelectronic series comprising He, Li^+, Be^{2+}, B^{3+}, and C^{4+}. The ensemble density is chosen as

$$\rho_{\mathrm{ensemble}} = (1 - \omega)\rho_{\mathrm{gs}} + \omega\rho_{\mathrm{es}} \quad (12)$$

where ρ_{gs} and ρ_{es} are ground-state[23] and excited-state[24] (1^1P, 1s2p configuration) densities, respectively. In eq 12, ω is a real number[18,20] that measures the relative weights of various electronic states present in the ensemble.

Table 1 presents the S and α values for the He isoelectronic systems with $\omega = 0$, 0.25, and 0.5. For comparison we have also included the corresponding values for $\omega = 1$. It may be noted that $\omega = 1$ corresponds to the pure excited states[17,25] and the excited states chosen here are the lowest energy states of the ^{1}P-type. For a given ω value, as the nuclear charge increases, for the same number of electrons (2 here), systems become harder and less polarizable, as expected. For a given system, as ω increases, both S and α increase, which implies that with an increase in the excited-state contribution in an ensemble the system becomes softer and more polarizable.

Local reactivity parameters such as radial distributions of ρ, $\nabla\rho$, $-\nabla^2\rho$, and $f(r)$, local hardness, electrostatic potential, and quantum potential exhibit(not shown here) characterestic shell structures and signatures of increasing softness and polarizability with an increase in the excited-state contribution.

In conclusion, a system is the hardest and the least polarizable in its ground state and becomes gradually softer and more polarizable as the excited-state contribution in a two-state ensemble increases, a fact in conformity with the principles of maximum hardness and minimum polarizability.

Acknowledgment. Dedicated to Professor Ralph G. Pearson, the father of the hardness concept. We thank the referee for constructive criticism and CSIR, New Delhi for financial assistance.

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