A Density Functional Treatment of Chemical Reactivity and the Associated Electronic Structure Principles in the Excited Electronic States

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Global reactivity parameters like the softness and the polarizability and local reactivity parameters like the Fukui function and the local hardness have been calculated for the ground (^{1}S) and several excited electronic states (^{1}P, ^{1}D, ^{1}F) of various helium isoelectronic systems (He, Li^+, Be^{2+}, B^{3+}, C^{4+}). Only the lowest energy state of a given symmetry is chosen because of the validity of the excited state density functional theory exclusively for this type of states. The softness varies linearly with the cube root of the polarizability for both the ground and the excited states. It has been demonstrated for the first time for the systems studied that *a system is harder and less polarizable in its ground state than in any of its excited states*. Radial distributions of the charge density, the Fukui function, and the local hardness exhibit characteristic shell structures in both the ground and the excited states.

Density functional theory[1] (DFT) has been quite successful in rationalizing popular qualitative chemical concepts. Electronegativity[2] (χ) and hardness[3,4] (η) are two such cardinal indices of chemical reactivity. Pauling[5] introduced the concept of electronegativity as the power of an atom in a molecule to attract electrons to itself while the idea of hardness was given by Pearson[6] in the context of the hard−soft acid−base (HSAB) principle which states that "hard likes hard and soft likes soft". For an N-electron system with external potential $v(\mathbf{r})$ and total energy E, electronegativity[7] (χ) and hardness[8] (η) are respectively defined as follows:

$$\chi = -\mu = -(\partial E/\partial N)_{v(\mathbf{r})} \tag{1}$$

and

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

In eqs 1 and 2, μ is the chemical potential, the Lagrange multiplier associated with the normalization constraint in Euler−Lagrange equation of DFT.[1] The hardness can equivalently be expressed as[9]

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

where $f(\mathbf{r})$ is the Fukui function[10,11] and the hardness kernel is given by[9]

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

where $F[\rho]$ is the Hohenberg−Kohn−Sham[12] universal functional of DFT. It may be noted that while χ and η are global reactivity parameters defined for the system as a whole, the Fukui function is a local index of the reactivity having different values at different sites of the system and hence is a better descriptor of the site selectivity in a molecule.

There are some widely used electronic structure principles based on these chemical concepts. According to Sanderson's electronegativity equalization principle,[13] all the constituent atoms in a molecule have the same electronegativity value given by the geometric mean of the electronegativity values of the pertinent isolated atoms. An important principle based on the hardness concept is the maximum hardness principle[14] which states that "there seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible". Formal proofs for the electronegativity equalization,[15] HSAB,[3,8,16] and maximum hardness[3,17] principles have been provided within DFT.

For complete characterization of the many-particle wave function one needs only N and $v(\mathbf{r})$. The response of the system when N is varied at fixed $v(\mathbf{r})$ is described by χ and η. On the other hand, polarizability (α) measures the response of the system when $v(\mathbf{r})$ changes at constant N. A minimum polarizability principle[18,19] can be stated as "the natural direction of evolution of any system is toward a state of minimum polarizability". This principle can be thought of as a consequence[18] of the inverse relationship[20] between α and η and the validity of the maximum hardness principle.[14] Pearson[21] has pointed out that "Actually this can be proved by the Parr-Chattaraj method.[17a] The polarizability of a system is proportional to fluctuations of the local polarization from the average value. The variance is minimum for the equilibrium system". In order to know the actual relationship between α and η, several studies[20] have been carried out and it has been finally observed [20c−f] for various atoms, molecules, and clusters that the softness ($S = 1/(2\eta)$) correlates linearly with the cube root of the polarizability ($\alpha^{1/3}$).

All the studies described above have been restricted to ground states. To our knowledge, hardly any attempt has been made so far in extending these studies to excited states. In the present paper, we investigate the validity of the linear relationship between S and $\alpha^{1/3}$ for various excited states of different helium isoelectronic systems. Since excited states are generally more

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reactive than the ground state, it is expected that the ground state would be harder[22] and hence less polarizable than any excited state. This fact may as well be considered to be a natural consequence of the maximum hardness and minimum polarizability principles. In the present study, we verify this prognosis through actual numerical calculation of these reactivity parameters.

For calculating the hardness from eq 3 one needs to know $f(\mathbf{r})$ and $\eta(\mathbf{r},\mathbf{r}')$. We propose a local model[19,23] for the Fukui function which was successfully made use of[19] in monitoring a time-dependent process in terms of the dynamics of various reactivity indices. For this purpose, we write the Hohenberg–Kohn–Sham[12] universal functional as follows:

$$F[\rho] = T[\rho] + V_{ee}[\rho] \tag{5}$$

In eq 5 the kinetic energy functional is taken as given by Ghosh and Deb,[24] viz.,

$$T[\rho] = T_0[\rho] + C_x \int \frac{\rho^{4/3}/r}{1 + (r\rho^{1/3}/0.043)}\,\mathrm{d}\mathbf{r}; \quad C_x = \left(\frac{3}{4\pi}\right)(3\pi^2)^{1/3} \tag{6}$$

where $T_0[\rho]$ is the Thomas–Fermi functional given as

$$T_0[\rho] = C_k \int \rho(r)^{5/3}\,\mathrm{d}\mathbf{r}; \quad C_k = \frac{3}{10}(3\pi^2)^{2/3} \tag{7}$$

and the total electron–electron repulsion energy $V_{ee}[\rho]$ is written as follows in the spirit of the corresponding local formula suggested by Parr[25]

$$V_{ee}[\rho] = \lambda \int \rho(r)^{4/3}\,\mathrm{d}\mathbf{r} \tag{8}$$

where λ is a parameter.

Substitution of this $F[\rho]$ (eq 5) in eq 4 gives the hardness kernel $\eta(\mathbf{r},\mathbf{r}')$ which in this local model[19,23] is related to the local softness $s(\mathbf{r})$ as follows:

$$s(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}')/2\eta(\mathbf{r}, \mathbf{r}') \tag{9}$$

The Fukui function can now be expressed as the normalized $s(\mathbf{r})$, i.e.

$$f(\mathbf{r}) = s(\mathbf{r})/S \tag{10}$$

where S is the global softness given by

$$S = 1/2\eta = \int s(\mathbf{r})\,\mathrm{d}\mathbf{r} \tag{11}$$

It may be noted that the calculation of S here does not require the ionization potential and the electron affinity or the orbital energy values as is the case with any standard approach[3] of calculating it.

A local hardness can also be obtained by averaging over $\eta(\mathbf{r},\mathbf{r}')$ as[9,19,23]

$$\eta(\mathbf{r}) = \frac{1}{N}\int \eta(\mathbf{r}, \mathbf{r}')\,\rho(\mathbf{r}')\,\mathrm{d}\mathbf{r}' = \frac{1}{2N}\frac{\rho(\mathbf{r})}{s(\mathbf{r})} \tag{12}$$

We make use of the local softness to calculate the static electric dipole polarizability[23,26] for spherically averaged densities as

$$\alpha = (4\pi/3)\int_0^\infty s(\mathbf{r})r^4\,\mathrm{d}r \tag{13}$$

after carrying out the integrations over the angular variables.

TABLE 1: Calculated Softness (au) and Polarizability Values (au) for the Ground States of the Atoms

atom	S	α[a]
H	1.76	4.50 (4.50)
He	1.51	1.86 (1.38)
Li	5.20	48.37 (163.98)
Be	5.02	25.73 (37.79)
B	4.78	17.78 (20.45)
C	4.34	11.51 (11.88)
N	3.82	7.42 (7.42)
O	3.70	6.34 (5.41)
F	3.45	4.99 (3.76)
Ne	3.20	3.91 (2.67)
Na	6.98	59.82 (159.26)
Mg	7.22	43.14 (71.53)
Al	7.65	44.71 (45.89)
Si	7.44	33.15 (36.31)
P	7.01	24.25 (24.50)
S(^{1}D)	6.84	20.86 (19.57)
Cl	6.43	16.17 (14.71)
Ar	6.08	13.11 (11.07)

[a] The α values in parentheses are from ref 34.

TABLE 2: Calculated Softness (au) and Polarizability Values (au) for the Ground and the Different Excited States of the Helium Isoelectronic Systems

atom/ion	electronic configuration	state	S	α
He	1s^2	^{1}S	1.51	1.86
He	1s2p	^{1}P	6.89	117.92
He	1s3d	^{1}D	13.09	728.71
He	1s4f	^{1}F	21.95	3536.36
Li$^+$	1s^2	^{1}S	0.78	0.40
Li$^+$	1s2p	^{1}P	3.20	14.11
Li$^+$	1s3d	^{1}D	6.48	100.29
Li$^+$	1s4f	^{1}F	10.76	441.43
Be^{2+}	1s^2	^{1}S	0.49	0.16
Be^{2+}	1s2p	^{1}P	1.97	3.97
Be^{2+}	1s3d	^{1}D	4.15	28.90
Be^{2+}	1s4f	^{1}F	6.99	128.28
B^{3+}	1s^2	^{1}S	0.34	0.09
B^{3+}	1s2p	^{1}P	1.38	1.59
B^{3+}	1s3d	^{1}D	2.98	11.87
B^{3+}	1s4f	^{1}F	5.10	53.11
C^{4+}	1s^2	^{1}S	0.25	0.06
C^{4+}	1s2p	^{1}P	1.03	0.78

We choose the parameter λ in eq 8 to have a value 5 so that the exact value of the dipole polarizability of the hydrogen atom is reproduced by eq 13 in case its exact density is made use of.

It is important to mention that the above functionals were originally proposed for the ground state. In this work, it is tacitly assumed that they are valid for the excited states as well, since, to our knowledge, no functional is known till date which is explicitly derived for the excited states.[27] Hohenberg–Kohn theorems have only been proved for the ground state,[12] the lowest excited state of a given symmetry,[28] and the ensemble of states.[29] Excited state calculations within the ensemble formalism[29,30] and time-dependent density functional theory[19,31] have been reported in recent years. Change in reactivity for different complexions of an ensemble is currently being studied in our laboratory.

In order to test the efficacy of the present scheme we first calculate the softness and the polarizability values for the ground states of the atoms H through Ar using near-Hartree–Fock densities (except S, for which ^1D density is used due to the nonavailability of the ground state density of the same quality) of Clementi and Roetti.[32] Table 1 reports the softness and the polarizability values for the ground states of these atoms. Miller and Bederson[33] have shown that the best recommended polar-

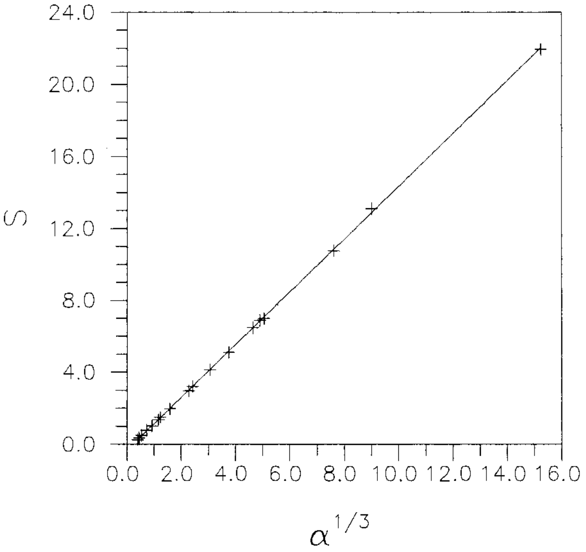

Figure 1. Plot of the softness (au) vs the cube root of the polarizability (au) for the different electronic states of various He isoelectronic systems.

izability values (both experimental and theoretical) for many atoms are within an error of ±50%. Considering the problems associated with the accurate theoretical or experimental determination of the polarizabilities and the simplicity of the scheme adopted here, it is quite gratifying to note that the calculated polarizability values in the present work compare so well with the corresponding literature values.[34] The calculated softness values also mimic the expected chemical trends in most cases.[35,36] On the average both α and S decrease along a period and increase along a group. Therefore, for a given period the corresponding noble gas atom is the hardest and the least polarizable. This fact is expected because of the exceptional stability of any noble gas atom vis-á-vis the maximum hardness and the minimum polarizability principles. Very good S vs $\alpha^{1/3}$ plots have been observed[37] for these systems with an average correlation coefficient greater than 0.9 for any period. We calculate S and α values for different helium isoelectronic systems in ^1S, ^1P, ^1D, and ^1F electronic states. While the ground state densities (^1S) are taken from Clementi and Roetti,[32] the corresponding excited state densities of the near-Hartree–Fock quality are taken from Mukherjee et al.[38] It must be pointed out that the excited state densities are not widely available. We have chosen only those excited states which are of lowest energy for a given symmetry. The excited state DFT is valid only for this type of excited states.[28] The softness and the polarizability values of He, Li^+, Be^{2+}, B^{3+}, and C^{4+} in various electronic states (^1S, ^1P, ^1D, and ^1F) are reported in Table 2. ^1D and ^1F densities for C^{4+} are not available in ref 38. Very large polarizability values for the excited states are already known.[39,40] As expected, in a given electronic state both S and α decrease as the nuclear charge increases for the systems with same number of electrons, studied in the present work. For all the systems studied, the ground state is the hardest and the least polarizable. This may be treated as a new electronic structure principle if not a consequence of the maximum hardness and the minimum polarizability principles. It is quite unlikely that this inference would change in case different functionals and/or better quality densities, if available, are used. Figure 1 depicts the plot of S vs $\alpha^{1/3}$ for all the systems in all the electronic states. A beautiful linear correlation with a correlation coefficient of 1.00 is easily discernible.

Radial distributions of the charge density, the Fukui function, and the local hardness for He in four different electronic states as representative cases are presented respectively in Figures 2–4. The atomic shell structure in all these plots are very conspicuous. Other systems in different electronic states also exhibit shell structures (not shown here). It may be noted that the Fukui function is positive everywhere. Although the radial distributions of $\rho(\mathbf{r})$, $f(\mathbf{r})$, and $\eta(\mathbf{r})$ all exhibit shell structures, they are of different nature. It is worth mentioning that the

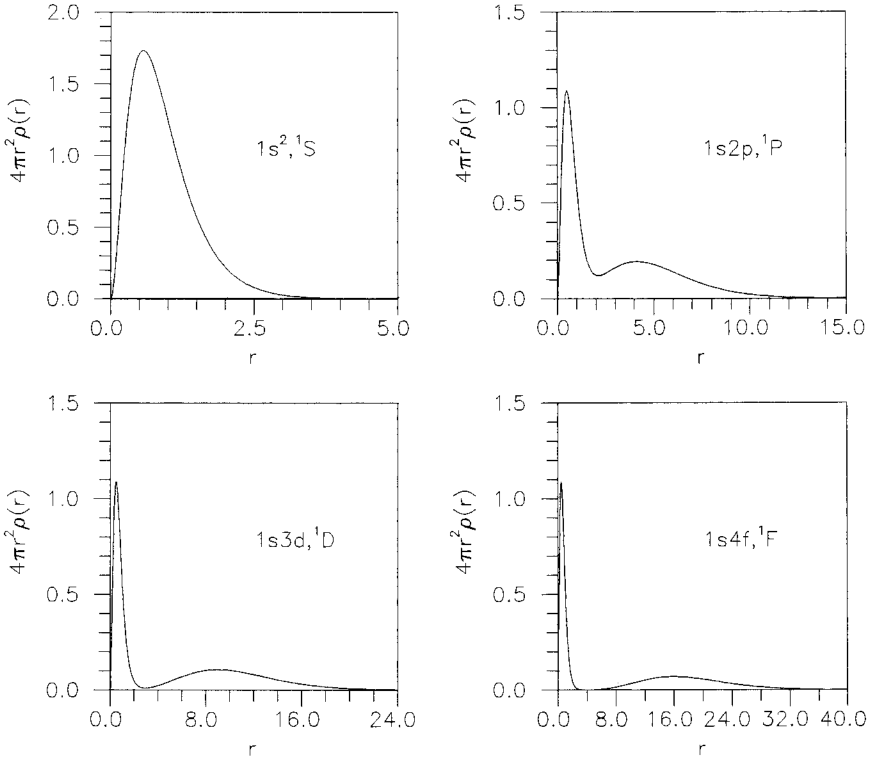

Figure 2. Radial distribution of the electron density (au) of the He atom in four different electronic states.

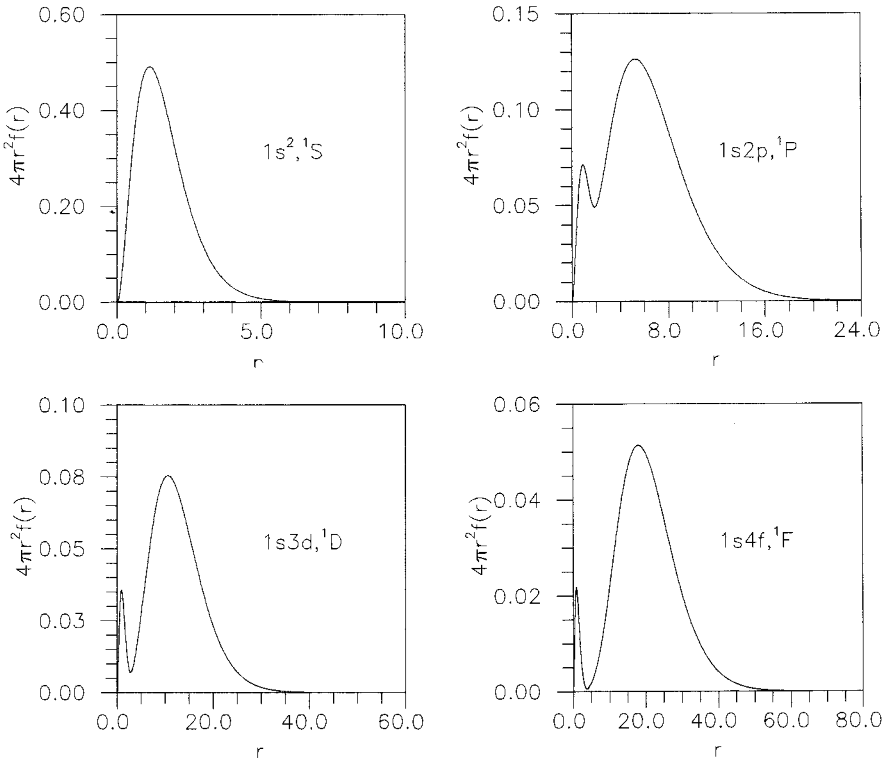

Figure 3. Radial distribution of the Fukui function (au) of the He atom in four different electronic states.

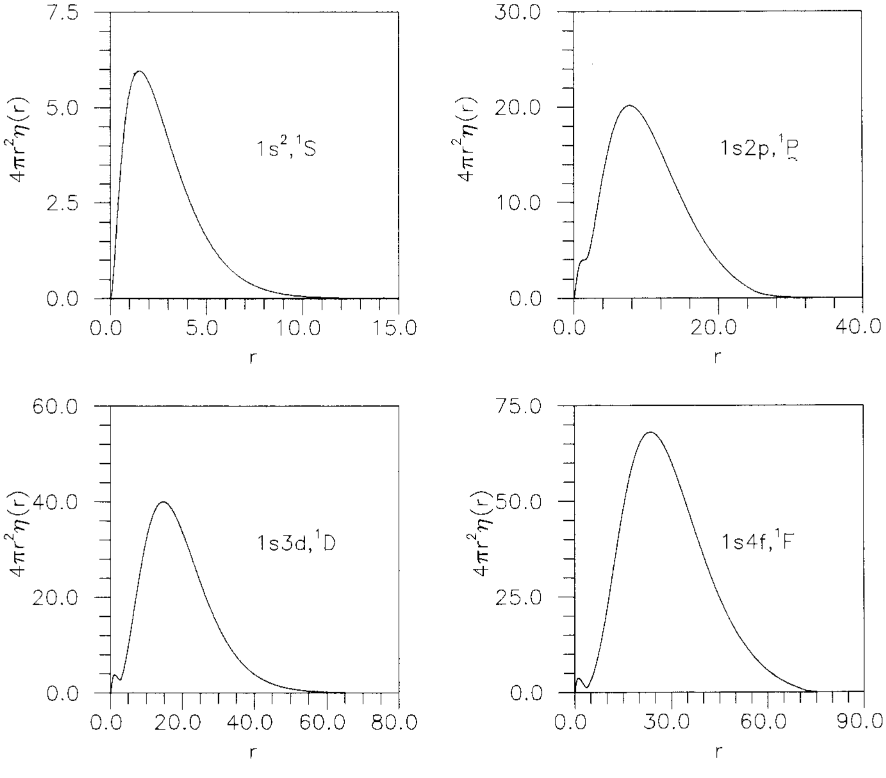

Figure 4. Radial distribution of the local hardness (au) of the He atom in four different electronic states.

shell structure in radial density does not necessarily imply the same for the radial distributions of all density-dependent quantities. It is known[41] that the hard−hard interactions are ionic in character and hence charge-controlled whereas the soft−soft interactions are covalent in nature and hence frontier-controlled. It may be expected that for a hard species the radial distribution of $\eta(\mathbf{r})$ will resemble that of $\rho(\mathbf{r})$ while for a soft species it will resemble that of $f(\mathbf{r})$. It is quite heartening to note that *He* being a very hard species at the ground state its $4\pi r^2\eta(\mathbf{r})$ plot looks more like $4\pi r^2\rho(\mathbf{r})$. However, as it becomes softer with excitation the $4\pi r^2\eta(\mathbf{r})$ behavior gradually changes toward that of $4\pi r^2 f(\mathbf{r})$.

In the present work we have calculated the Fukui function, the local hardness, the softness, and the polarizability values for the ground and the excited states of various helium isoelectronic systems and have demonstrated for the first time the following: (a) The softness varies linearly with the cube root of the polarizability also for the excited states, (b) for the systems studied in the present work the ground state of a system is harder and less polarizable than any of its excited states considered here, and (c) prominent atomic shell structures are exhibited by the radial distributions of the charge density, the Fukui function, and the local hardness in both the ground and the excited states.

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