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Molecular Reactivity in the Ground and Excited Electronic States through Density-Dependent Local and Global Reactivity Parameters

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Molecular hardness values have been calculated for a few selected diatomics,viz., H_2, HF, N_2, BF, CO, and F_2 in their ground and first excited electronic configurations using 4-31G double ζ type basis functions. The excited electronic configurations are so chosen that they happen to have the lowest energy for a particular symmetry, keeping in mind the validity of the excited state density functional theory for such systems. It is observed for all the molecules studied that hardness values decrease with electronic excitation. Surface plots of different local quantities like the charge density, the laplacian of the charge density, the quantum potential, the molecular electrostatic potential, and the Fukui function reveal an increase in the molecular reactivity with excitation.

1. Introduction

The concept of chemical hardness (η)[1,2] was first propounded by Pearson through his hard−soft acid−base(HSAB)[3,4] principle. The principle states that "hard acids prefer to coordinate with hard bases, and soft acids with soft bases". The stability of a chemical species was also found to be intimately related to its hardness. Pearson underlined this fact through another principle, viz., the maximum hardness principle (MHP)[1,5] which states that "there seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible". The quantitative definition of hardness is provided within density functional theory(DFT).[6] For a system comprising N electrons in the field of one or more fixed nuclei which generate an external potential $v(\mathbf{r})$, the curvature of the plot representing the change in the electronic energy E with the number of electrons N gives us the hardness, viz.,

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

The operational definition of hardness is obtained by using a finite difference approximation to the second derivative in eq 1 as[7]

$$\eta = (I - A)/2 \tag{2}$$

where I and A are respectively the ionization potential and electron affinity of the system. Equation 2 can be further approximated as follows using the Koopmans' theorem,

$$\eta = (\epsilon_{\mathrm{LUMO}} - \epsilon_{\mathrm{HOMO}})/2 \tag{3}$$

Hard molecules thus have a large HOMO−LUMO gap and soft molecules have a small HOMO−LUMO gap.[7]

It is difficult to calculate η using eq 1 as an analytical form of E as a function of N is not known. Calculation of η from eq 2 has the inherent error introduced by the finite differences. Berkowitz et al.[8] have put forward an alternative definition of η by expressing it as a density functional.

Theoretical calculation of hardness for atoms, ions, radicals, molecules and clusters using ab initio SCF,[9,10] DFT,[11] coupled cluster[12] and other theories have been performed, albeit restricted mostly to the ground state. Very little work[13] has been done to calculate hardness of chemical systems in the excited electronic states. Extension of the ground state DFT formalism for studying hardness to excited states poses a problem. Hohenberg−Kohn theorem is valid strictly for the ground state,[14] and consequently, the energy of an arbitrary excited state cannot be said to be a unique functional of its charge density.[1] This problem disappears, however, if the excited state happens to be the lowest state of a given symmetry.[1,15] Global and local reactivity parameters have been calculated[13] for several excited electronic states of helium isoelectronic systems which satisfy the above criterion as also for different complexions of two-state ensembles[16] of the above systems. For the atomic systems studied, it has been shown[13,16] that "a system is harder in its ground state than in its excited states". The motivation of the present study is to examine the validity of the above statement in the context of molecules. For this purpose we calculate the global hardness for the ground electronic configuration[17] and the first excited electronic configuration[17] of a few diatomics, viz., H_2, HF, N_2, BF, CO, and F_2. We also study several local reactivity descriptors, like the electron density($\rho(\mathbf{r})$), the laplacian of the electron density($\nabla^2\rho(\mathbf{r})$),[18] the quantum potential($V_{\mathrm{qu}}(\mathbf{r})$),[19] the molecular electrostatic potential($V_{\mathrm{es}}(\mathbf{r})$)[20] and the Fukui function($f(\mathbf{r})$)[21,22] for these molecules in both their ground and excited electronic configurations, in terms of their spatial distributions. Theoretical background of the present work is given in section 2 and section 3 provides the computational details. Section 4 contains the results and discussion, while section 5 presents some concluding remarks.

2. Theoretical Background

The global hardness(η) can be expressed in terms of the Fukui function ($f(\mathbf{r})$) and the hardness kernel ($\eta(\boldsymbol{r},\boldsymbol{r}')$) as[8,23]

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$$\eta = \frac{1}{N}\int\int \eta(\mathbf{r},\mathbf{r}')f(\mathbf{r}')\rho(\mathbf{r})\,\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \tag{4}$$

where the hardness kernel is given by[23]

$$\eta(\mathbf{r},\mathbf{r}') = \frac{1}{2}\frac{\delta^2 F[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \tag{5}$$

In eq 5, $F[\rho]$ is the Hohenberg−Kohn−Sham universal functional[14] of DFT and the Fukui function is given as[22]

$$f(\mathbf{r}) = \left(\frac{\partial\rho(\mathbf{r})}{\partial N}\right)_{v(\mathbf{r})} \tag{6}$$

$F[\rho]$ is expressed as the sum of the intrinsic kinetic energy functional, an exchange−correletion energy functional and an electron−electron repulsion term as follows.

$$F[\rho] = T[\rho] + E_{\mathrm{xc}}[\rho] + \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \tag{7}$$

The kinetic energy comprises an atomic part and a molecular part[24−26], viz.,

$$T[\rho] = T_{\mathrm{at}}[\rho] + T_{\mathrm{mol}}[\rho] \tag{8}$$

$T_{\mathrm{at}}[\rho]$ is taken as[26]

$$T_{\mathrm{at}}[\rho] = C_k\int \rho^{5/3}\,\mathrm{d}\mathbf{r} + \frac{1}{8}\int \frac{\nabla\rho.\nabla\rho}{\rho}\,\mathrm{d}\mathbf{r} - a(N)\lambda\int \frac{\rho^{4/3}/r}{1 + r\rho^{1/3}/0.043}\,\mathrm{d}\mathbf{r} \tag{9}$$

$$C_k = \frac{3}{10}(3\pi^2)^{\frac{2}{3}};\quad \lambda = 30\left(\frac{3}{\pi}\right)^{\frac{1}{3}}$$

where $a(N)$ is a constant dependent on the number of electrons N

$$a(N) = a_0 + a_1N^{-1/3} + a_2N^{-2/3}$$

$a_0 = 0.1279$, $a_1 = 0.1811$, and $a_2 = -0.0819$. The first term in eq 9 is the Thomas−Fermi energy functional, and the second term is the Weizsäcker functional.

The molecular contribution to the intrinsic kinetic energy is given as[24−26]

$$T_{\mathrm{mol}}[\rho] = \int\int \frac{1}{N^2}\left[\frac{1}{R^{12}} - \left(\frac{N}{10}\right)^{14} R^2\exp(-0.8R)\right]\rho(\mathbf{r})\rho(\mathbf{r}')\,\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \tag{10}$$

where R is taken as the equilibrium internuclear separation of the diatomic. This functional properly explains the following facts:[24] (a) It goes to zero as R goes to infinity, (b) it reproduces the kinetic energies of diatomics for the equilibrium internuclear distances, and (c) it shows the proper behavior of $\Delta T(R) = T(R) - T(\infty)$ versus R curve during molecule formation. For given N and R values $T_{\mathrm{mol}}[\rho]$ is a constant and being a part of the interacting kinetic energy[6,27] may not scale homogeneously.

The exchange−correlation energy functional $E_{\mathrm{xc}}[\rho]$ is written as the sum of the exchange and correlation energy functionals

$$E_{\mathrm{xc}}[\rho] = E_{\mathrm{x}}[\rho] + E_{\mathrm{c}}[\rho] \tag{11}$$

In eq 11 $E_{\mathrm{x}}[\rho]$ is taken as[28] the Dirac exchange functional modified as follows in the spirit of Becke's functional[29]

$$E_{\mathrm{x}}[\rho] = -C_x\left[\int \rho^{4/3}\,\mathrm{d}\mathbf{r} + \int \frac{\rho^{4/3}}{1 + r^2\rho^{2/3}/0.0244}\,\mathrm{d}\mathbf{r}\right];\quad C_x = \left(\frac{3}{4\pi}\right)(3\pi^2)^{1/3} \tag{12}$$

and $E_{\mathrm{c}}[\rho]$ is a Wigner-type parametrized correlation energy functional given by[30]

$$E_{\mathrm{c}}[\rho] = -\int \frac{\rho}{9.81 + 21.437\rho^{-1/3}}\,\mathrm{d}\mathbf{r} \tag{13}$$

Considering the difficulty in evaluating $f(\mathbf{r})$ from eq 6 one would prefer to express $f(\mathbf{r})$ as a density functional. A completely satisfactory and straightforward Fukui density functional for practical atomic and molecular calculations is still not available. Attempts have been made[31,32] in writing $f(\mathbf{r})$ with $\rho(\mathbf{r})$ as the only input. We model $f(\mathbf{r})$ in the lines of Fuentealba[32] by considering the following local form of $F[\rho]$.

$$F^{\mathrm{loc}}[\rho] = T^{\mathrm{loc}}[\rho] + V_{\mathrm{ee}}^{\mathrm{loc}}[\rho] \tag{14}$$

The local kinetic energy is taken as[28]

$$T^{\mathrm{loc}}[\rho] = C_k\int \rho^{5/3}\,\mathrm{d}\mathbf{r} + C_x\int \frac{\rho^{4/3}/r}{1 + r\rho^{1/3}/0.043}\,\mathrm{d}\mathbf{r} \tag{15}$$

The form of the electron-electron repulsion energy $V_{\mathrm{ee}}^{\mathrm{loc}}$ is taken as a modified Parr functional[33]

$$V_{\mathrm{ee}}^{\mathrm{loc}}[\rho] = \alpha(N-1)^{2/3}\int \rho^{4/3}\mathrm{d}\mathbf{r} \tag{16}$$

where α is a parameter. Such a model for $f(\mathbf{r})$ has been successfully utilized to study the dynamics of various chemical reactivity parameters.[26,34] Substitution of the above value of $F^{\mathrm{loc}}[\rho]$ in eq 5 enables us to obtain $\eta(\mathbf{r},\mathbf{r}')$, which, in this local model becomes diagonal as follows[32]

$$\eta(\mathbf{r},\mathbf{r}') = \frac{1}{2}g(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}') \tag{17a}$$

and hence the softness kernel becomes[32]

$$s(\mathbf{r},\mathbf{r}') = \frac{\delta(\mathbf{r}-\mathbf{r}')}{g(\mathbf{r})} \tag{17b}$$

which leads to the simple expression for the local softness as[32]

$$s(\mathbf{r}) = \int s(\mathbf{r},\mathbf{r}')\mathrm{d}\mathbf{r}' = \frac{1}{g(\mathbf{r})} \tag{17c}$$

where $g(\mathbf{r})$ is the second derivative of the integrand[32] of the local $F[\rho]$ given in eq 14, with respect to $\rho(\mathbf{r})$.

The Fukui function $f(\mathbf{r})$ is expressed as the normalized $s(\mathbf{r})$

$$f(\mathbf{r}) = \frac{s(\mathbf{r})}{\int s(\mathbf{r})\mathrm{d}\mathbf{r}} \tag{18}$$

Substitution of $f(\mathbf{r})$ in eq 4 helps us evaluate the global hardness η.

Among the other local quantities, the quantum potential($V_{\mathrm{qu}}(\mathbf{r})$) is given by[19]

$$V_{\mathrm{qu}}(\mathbf{r}) = -\frac{\nabla^2\rho^{1/2}(\mathbf{r})}{2\rho^{1/2}(\mathbf{r})} \tag{19}$$

TABLE 1: Calculated Hardness Values (au) for the Ground and the First Excited Electronic Configurations[38] of Different Diatomics

molecule	electronic configuration	η^a
H_2	$(\sigma_g 1s)^2$	0.319 (0.319)
	$(\sigma_g 1s)(\sigma_u 1s)$	0.197
HF	$(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^4$	0.501 (0.404)
	$(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^3(4\sigma)$	0.397
N_2	$(\sigma_g 1s)^2(\sigma_u 1s)^2(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^4(\sigma_g 2p)^2$	0.292 (0.327)
	$(\sigma_g 1s)^2(\sigma_u 1s)^2(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^4(\sigma_g 2p)(\pi_g 2p)$	0.279
CO	$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2$	0.291 (0.290)
	$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)(2\pi)$	0.278
BF	$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2$	0.286
	$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)(2\pi)$	0.275
F_2	$(\sigma_g 1s)^2(\sigma_u 1s)^2(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^4$	0.335 (0.231)
	$(\sigma_g 1s)^2(\sigma_u 1s)^2(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^3(\sigma_u 2p)$	0.291

[a] The η values in parantheses are from refs 1 and 7.

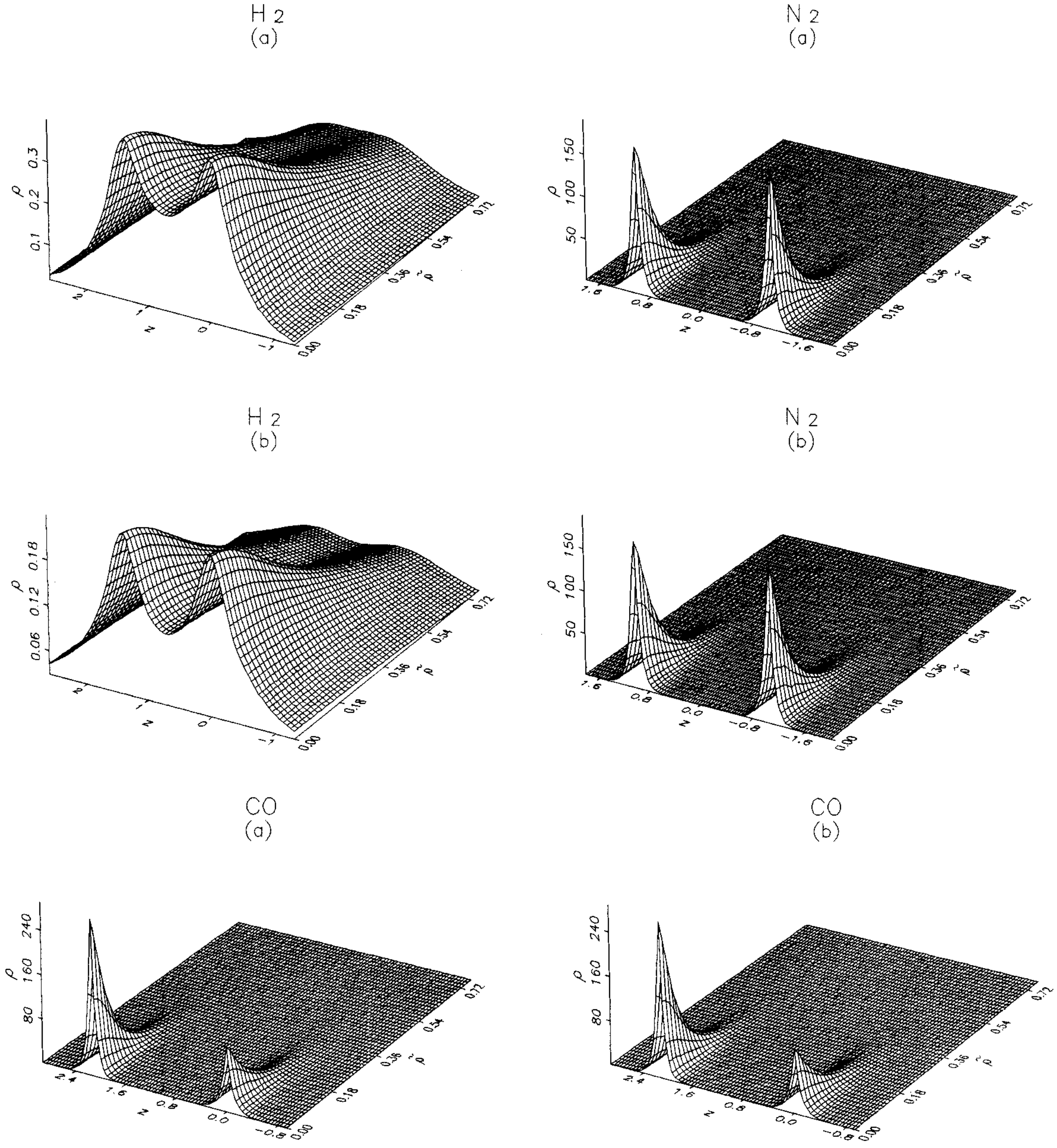


Figure 1. Surface plots of the charge density (ρ) of the diatomics in their (a) ground electronic configuration and (b) first excited electronic configuration. The basal rectangular mesh is the molecular plane. For H_2, $0.0 \leq \tilde{\rho} \leq 0.77$ and $-1.3 \leq z \leq 2.61$; for N_2, $0.0 \leq \tilde{\rho} \leq 0.77$ and $-2.0 \leq z \leq 1.83$; for CO, $0.0 \leq \tilde{\rho} \leq 0.77$ and $-0.93 \leq z \leq 2.92$. The z-coordinates of the nuclei are[38] H_2 (H, 0.0, H, 1.40165); N_2 (N, −1.03704999, N, 1.03704999) and CO (C, 0.0, O.2.132).

Quantum potential based theories, viz., quantum fluid dynamics[35] and quantum theory of motion,[36] have been successfully used[37] in understanding the quantum domain behavior of classically chaotic systems.

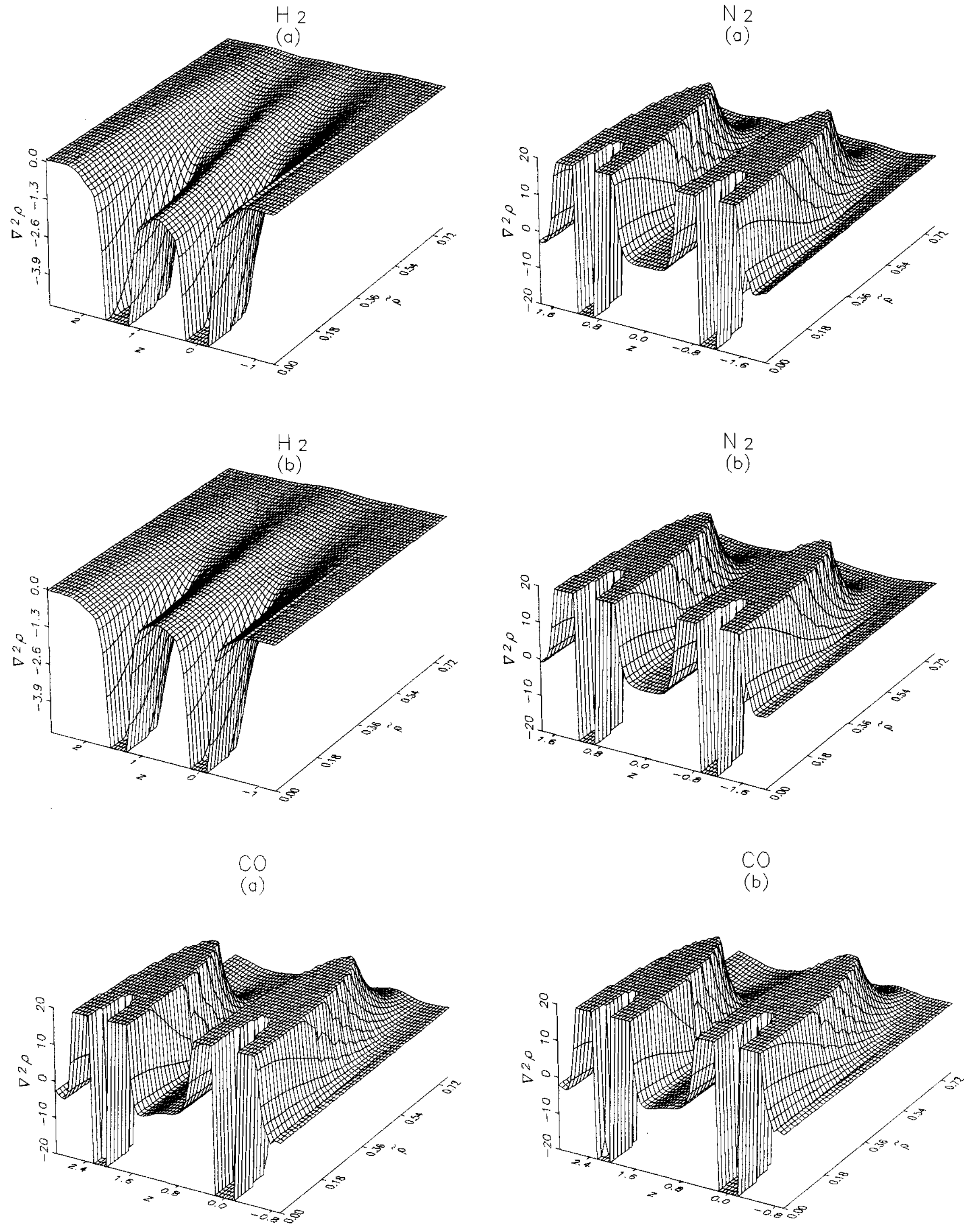


Figure 2. Surface plots of the laplacian of the charge density ($\nabla^2\rho$) of the diatomics in their (a) ground electronic configuration and (b) first excited electronic configuration. Mesh sizes are same as those in Figure 1. For H_2, plots have been truncated at −5.0 au, while for N_2 and CO, plots have been truncated at ±20 au.

The molecular electrostatic potential ($V_{es}(\mathbf{r})$) is expressed as[20]

$$V_{es}(\mathbf{r}) = \sum_{A=1}^{\text{no.of nuclei}} \frac{Z_A}{|\mathbf{r}-\mathbf{R}_A|} - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}' \qquad (20)$$

where Z_A is the charge of the Ath nucleus located at $\mathbf{R}_A$.

3. Computational Details

Electron density distributions have been computed at the equilibrium geometries for H_2, HF, N_2, BF, CO, and F_2. The basis sets used are the 4-31G double-ζ basis sets of Snyder and Basch.[38] Owing to the cylindrical symmetry of the diatomics, we have used cylindrical polar coordinates ($\tilde{\rho}$, ϕ, z) in our calculations. The internuclear axis is taken along the z direction and the $\tilde{\rho}-z$ plane as the molecular plane. Because of the cylindrical symmetry all local quantities are evaluated at the ($\tilde{\rho}-z$) points. It may be noted that the last term in eq 9 is origin dependent. The origin of the coordinate system is taken from Snyder and Basch.[38] Global quantities are calculated by carrying out an analytical integration over the azimuthal angle $0 \le \phi \le 2\pi$. We also make use of a transformation $\tilde{\rho} = \tilde{x}^2$ and use a

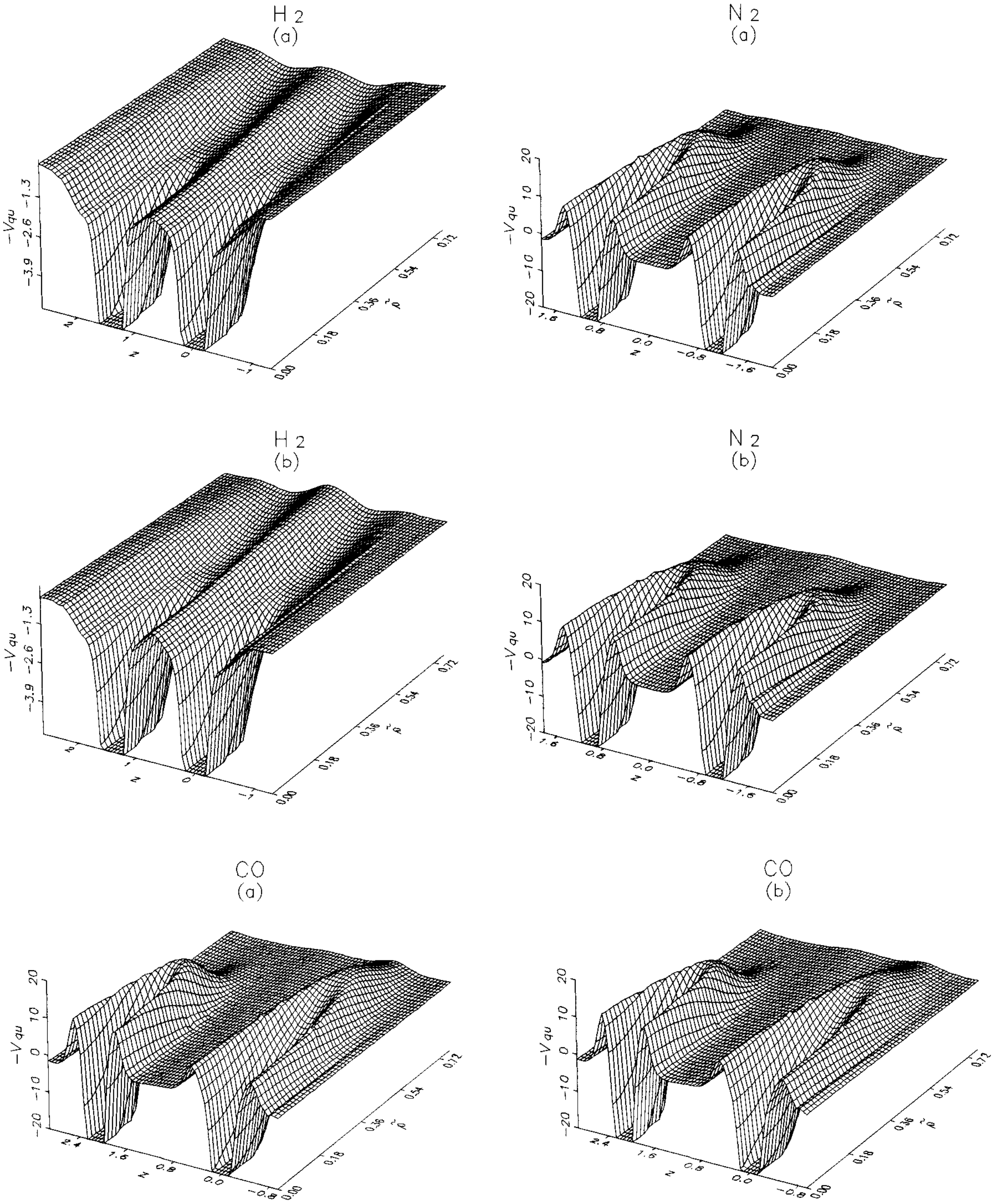


Figure 3. Surface plots of the negative of the quantum potential ($-V_{qu}$) of the diatomics in their (a) ground electronic configuration and (b) first excited electronic configuration. Mesh sizes are same as those in Figure 1. For H_2, plots have been truncated at -5.0 au while for N_2 and CO, plots have been truncated at -20 au.

very dense mesh along the z direction to have more points near the nuclei both along the $\tilde{\rho}$ and z directions. This is required as the electron density shoots up as one approaches the nuclear sites. The spatial grid sizes along the $\tilde{\rho}$ or $\tilde{x}$ and z directions are taken as $\Delta\tilde{x} = 0.01$ and $\Delta z = 0.001$, respectively. The density at any ($\tilde{\rho}-z$) point has been generated by transforming the cartesian coordinates x_A, y_A, and z_A, appearing in the expansion of the primitive Gaussians[38] in the 4-31G basis set, into the corresponding cylindrical coordinates. The calculations, being relatively simple, do not require any software package. Analytical codes have also been written for the evaluation of the laplacian of the charge density and the quantum potential. The electrostatic potential, the Fukui function, and the hardness have been evaluated numerically.

4. Results and Discussion

The hardness (η) values for the molecules in their ground and first excited electronic configurations have been presented in Table 1. The value of the parameter α in eq 16 is chosen as 50.0 so that the ground state hardness value of H_2 as reported by Pearson[7] is reproduced. Pearson utilized eq 2 to determine η from experimentally or theoretically obtained I and A values. The value of η for CO as obtained by us tallies with that obtained by Pearson, and the value of N_2 turns out to be little

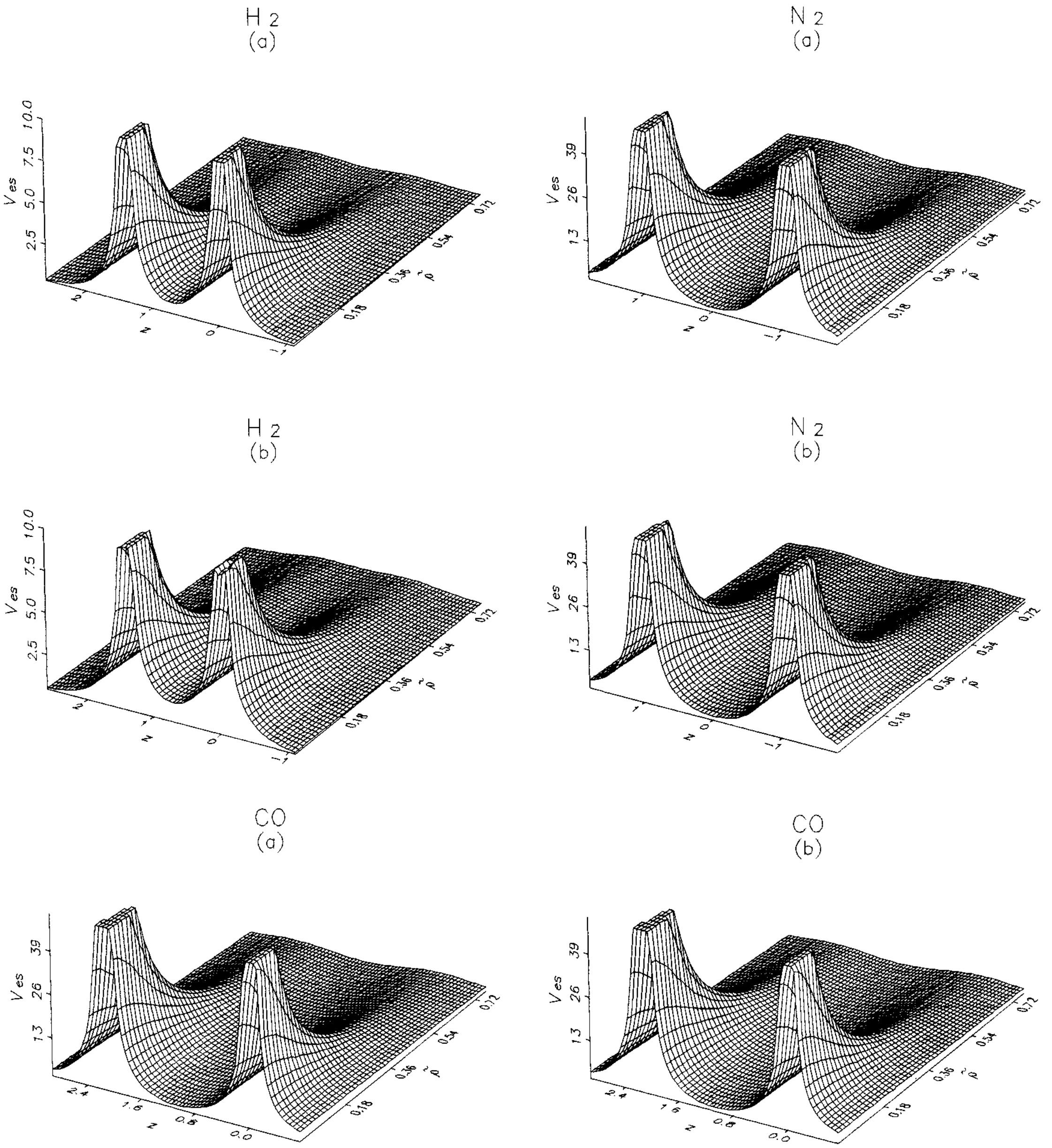
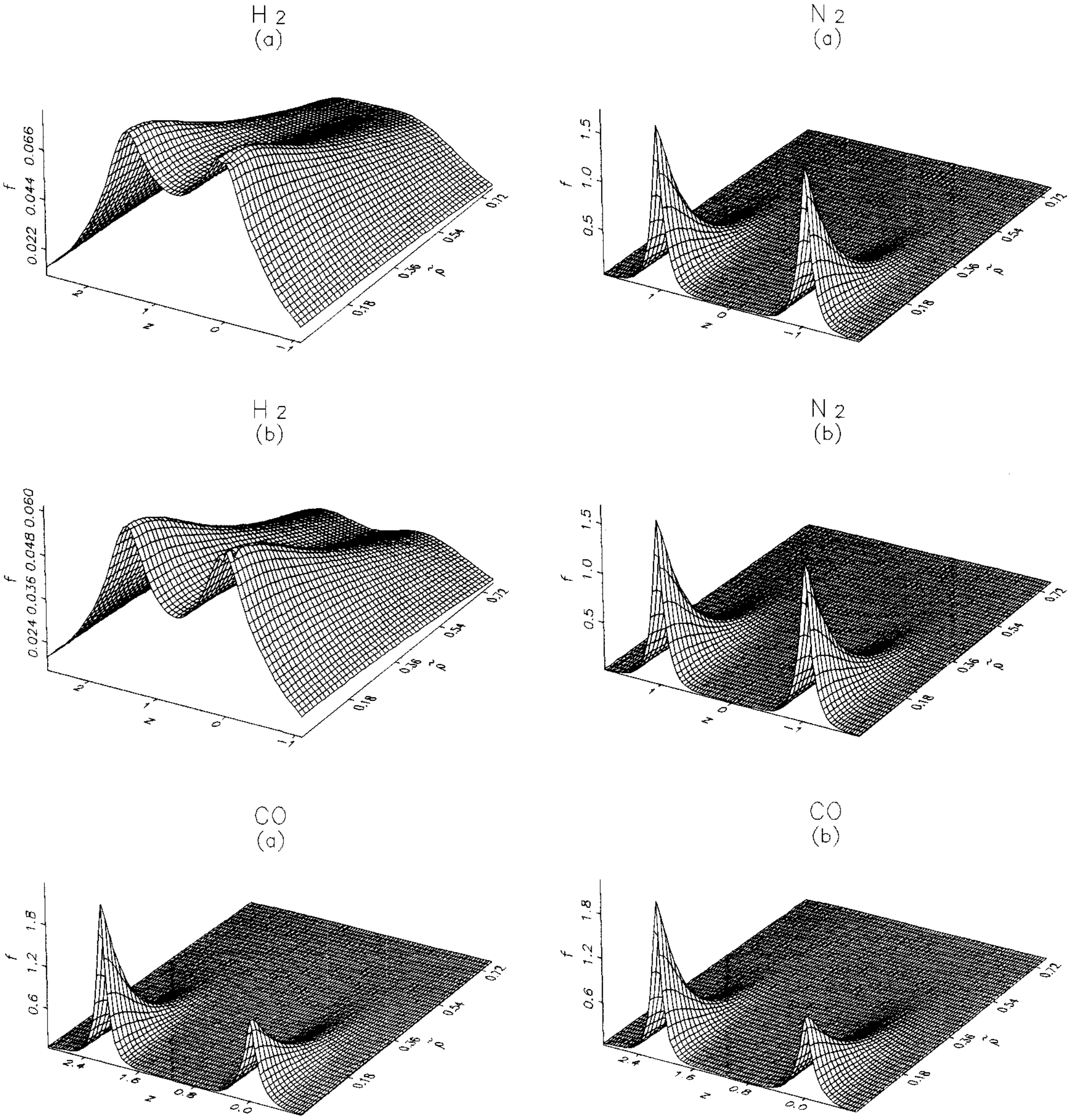


Figure 4. Surface plots of the molecular electrostatic potential (V_{es}) of the diatomics in their (a) ground electronic configuration and (b) first excited electronic configuration. Mesh sizes adopted are for H_2, $0.0 \leq \tilde{\rho} \leq 0.77$ and $-1.09 \leq z \leq 2.61$; for N_2, $0.0 \leq \tilde{\rho} \leq 0.77$ and $-1.79 \leq z \leq 1.83$; for CO, $0.0 \leq \tilde{\rho} \leq 0.77$ and $-0.73 \leq z \leq 2.92$. For H_2, plots have been truncated at +10.0 au while for N_2 and CO, plots have been truncated at +50 au.

lower, whereas the values for HF and F_2 turn out to be greater. Balawender et al.[39] have also calculated η for some of the above-mentioned diatomics by the ab initio Hartree−Fock self-consistent field method, as an average of a set of terms representing various types of reactivity. Considering the simplicity of the calculation of hardness in the present work it is heartening to note that our η values compare well with the other reported η values.[1,7] Our results corroborate with Pearson's observation that harder molecules possess larger HOMO−LUMO gaps.[7] It is very important to note that our calculation of η does not require any a priori knowledge of the total or orbital energy values of the system as is the case with the most present day prescriptions for the calculation of η. Furthermore, we may completely bypass the solution of the Schrödinger equation in case it is possible to obtain the required electron density from any source, say, from an experiment or as the solution of a single-density equation.[40,41] For all the systems studied here, the molecule with the excited electronic configuration turns out to be less hard than with the ground electronic configuration. The decrease in hardness is, however, not uniform in all the cases. While the decrease is small for CO, N_2 and BF, it is quite appreciable in H_2, HF and F_2 in which the HOMO in the first excited electronic configuration is of σ type. The decrease in hardness of the systems studied with excitation can be thought of as a validation of the maximum hardness principle. It is important to mention that for all the systems studied we have used the same basis set. Consequently the quality[38] of the calculated electron densities remains same for all the molecules studied. We may legitimately assume that the molecule will still turn out to be harder in its ground electronic configuration than in its excited electronic configuration in case a better quality density is made use of. The absolute values of hardness would, however, differ.

We have also presented the topographical plots of $\rho(\mathbf{r})$, $\nabla^2\rho(\mathbf{r})$, $-V_{qu}(\mathbf{r})$, $V_{es}(\mathbf{r})$, and $f(\mathbf{r})$ for the H_2, N_2, and CO molecules both in their ground and excited electronic configurations. The



H 2 (a)

N 2 (a)

H 2 (b)

N 2 (b)

CO (a)

CO (b)

Figure 5. Surface plots of the Fukui function (*f*) of the diatomics in their (a) ground electronic configuration and (*b*) first excited electronic configuration. Mesh sizes are same as those in Figure 4.

surface plot in each case is on the molecular plane specified by the $\tilde{\rho}-z$ coordinates. Only one half of the surface distributions have been shown. The other half is symmetrical about the molecular axis. Figure 1 shows the surface plots of $\rho(\mathbf{r})$ for the molecules in their ground and first excited electronic configurations. The charge density is evenly distributed about the nuclear centers for the homonuclear diatomics. The peaks in $\rho(\mathbf{r})$ occur at the nuclear sites. For the excited electronic configuration of H_2, $\rho(\mathbf{r})$ decreases at the nuclear sites but spreads out more as one goes radially away from the nuclei. The same is true for N_2 and CO though in a less conspicuous manner. For the molecules the average position of the overall electron cloud is near the midpoint between the nuclei. The excited CO electronic configuration is formed by the transfer of an electron from the 5σ orbital centered around the C atom to a 2π orbital centered mainly around the O atom. The resulting electronic distribution has its center displaced a little toward the O atom resulting in an increase in the dipole moment on electronic excitation.[17b] Figure 2 shows the surface plots of $\nabla^2\rho(\mathbf{r})$ for the same systems. The shell strucure[18] is clearly revealed in all these plots. All the three molecules, H_2, N_2, and CO, illustrate shared interactions[23] wherein the laplacian assumes negative values over the binding region of each interacting pair of nuclei as a result of the fusion of valence shell charge concentration (VSCC) of the two interacting atoms. In N_2 the radius(r_0) of the VSCC about each N_2 atom is found to be 0.720 au and the corresponding magnitude of $\nabla^2\rho(\mathbf{r})$ to be 2.89 au. The values are close to those of Chan and Hamilton,[19] viz., $r_0 = 0.737$ au and corresponding $|\nabla^2\rho(\mathbf{r})| = 2.61$ au. In CO the values of the nonbonded minima from O and C atoms are found to be 0.636 au and 0.844 au respectively. The values of the laplacian at these positions are found to be -4.46 au and -1.45 au, respectively. All these values are close to those reported by Bader et al.[18] The regions of nonbonded charge concentrations and charge depletions so obtained given by the minima and maxima in $\nabla^2\rho(\mathbf{r})$ respectively identify the sites of electrophilic and nucleophilic attack in CO.[18,42] Moreover, the values of r_0 and corresponding $|\nabla^2\rho(\mathbf{r})|$ suggest[18] that O is a hard site and C is a soft site in the CO molecule. It is interesting to observe that in the first excited electronic state of CO the values of r_0 and the corresponding $|\nabla^2\rho(\mathbf{r})|$ for O are 0.654 au and 3.26 au and for C are 1.006 au and 0.24 au, respectively. The softness of the site corresponding to C in CO increases further compared to that of O. Figure 3 shows the surface distributions of $-V_{qu}(\mathbf{r})$ and Figure 4 shows those of $V_{es}(\mathbf{r})$. The topography of $-V_{qu}(\mathbf{r})$ shows shell strucures in the same way as $\nabla^2\rho(\mathbf{r})$. However, its magnitude at a given point is much less than that of $\nabla^2\rho(\mathbf{r})$ at the same point. $V_{es}(\mathbf{r})$ shows positive values in and around nuclear sites signifying an affinity for nucleophiles.[43] It may be noted that this inference is based on an approximation that "the areas in a molecule where an electrophilic attack is less likely to happen can be considered as suited for a nucleophilic attack".[43] One should be cautious in making use of this approximation[43] as it has already been pointed out[18] that "the positive potentials exhibited by such maps, are not necessarily indicative of a corresponding affinity for nucleophiles". Politzer and co-workers[44] have explicitly demonstrated the situations when a positive channel refers to an electrophilic center. It is also important to note that $V_{es}(\mathbf{r})$ cannot have any local maximum except at the nuclear sites.[20] This is one of the reasons for the difference in the topographies of $V_{es}(\mathbf{r})$ and $\nabla^2\rho(\mathbf{r})$ apart from the fact that, unlike $\nabla^2\rho(\mathbf{r})$, $V_{es}(\mathbf{r})$ does not take care of the exchange−correlation effects.[20] With excitation $V_{es}(\mathbf{r})$ diffuses radially outwards from the nuclear sites as does the charge density, hinting thereby at the possibility that the affinity for a nucleophilic attack is no longer restricted to the nuclear sites but pervades the whole molecule as such. The local behavior of $f(\mathbf{r})$ is presented in the form of its surface plots in Figure 5. The Fukui function is also known to be a measure of intramolecular reactivity. It has been used[45] before to predict the type of attack (electrophilic, nucleophilic, or radical), the site of attack and the orientation of the attacking molecule. A high value of $f(\mathbf{r})$ at a particular site implies a high reactivity of that site[45] but for the hard−hard interactions where a site with minimum $f(\mathbf{r})$ value has been argued[46] to be the most reactive, for example, in protonation reactions, as a consequence of the local HSAB principle.[46,47] However, we feel that Fukui's frontier molecular orbital theory[21] properly augmented by Klopman's ideas,[48] viz., hard−hard interactions are mainly ionic in nature and hence charge-controlled and soft−soft interactions are mainly of covalent character and thus frontier controlled, is adequate in explaining both reactivity and selectivity of a molecule. While the site with the maximum value of the Fukui function is best suited for a soft−soft interaction, the site having the largest value of the gross charge, obtainable from a reliable population analysis scheme, is most favorable toward a hard−hard interaction. It is evident from our surface plots that $f(\mathbf{r})$ attains the highest values close to the nuclear sites and shows a trough in the internuclear bonding region. The plots resemble those of the charge density implying an approximate homogeneous electron gas behavior.[31] It also reveals that[32] local hardness varies relatively slowly in comparison to $\rho(\mathbf{r})$. In fact $f(\mathbf{r})$ can be approximated as $\rho(\mathbf{r})/n(\mathbf{r})$ where $n(\mathbf{r})$ is a slowly varying function of $\mathbf{r}$. As we go radially outward, $n(\mathbf{r})$ is greater than N near the nucleus and is less than N away from it. Departure from the homogeneous electron gas behavior is more pronounced for larger N. In CO, for example, the high values of $f(\mathbf{r})$ near the sites of the carbon and oxygen nuclei suggest that these regions are more prone to attack from outside. For the excited electronic configuration of the molecules, $f(\mathbf{r})$ decreases near the nuclear sites and increases radially outwards from them. This feature is easily discernible in the plot for H_2. However, one needs to carefully examine the profiles of $f(\mathbf{r})$ (not presented here) on or parallel to the internuclear axis for both the electronic configurations of N_2 and CO to be certain that the same holds true for these molecules as well. Since local softness $s(\mathbf{r})$ is nothing but scaled $f(\mathbf{r})$, increase/decrease in $f(\mathbf{r})$ implies a proportional increase/decrease in $s(\mathbf{r})$. We may thus infer that with excitation the Fukui function as well as the local softness increase, albeit a little, over most parts of the molecule away from the nuclei, leading to greater reactivity and a decrease in the global hardness of the molecule as a whole. In general the molecules are more reactive in their excited states than in their ground states.[1] It is expected from the maximum hardness principle[1,5] that the hardness values would decrease with excitation[13,16] and the related local quantities would also exhibit changes reflecting greater reactivity. The densities associated with the excited electronic states considered here do not differ conspicuously in comparison to the corresponding ground state densities and accordingly the other density-dependent local reactivity parameters also do not exhibit markedly different behavior in the two electronic states.

5. Concluding Remarks

The global hardness values for the diatomics H_2, HF, N_2, BF, CO, and F_2 have been calculated as density functionals using double-ζ type 4-31G basis functions for their ground and the first excited electronic configurations. These values compare favorably with other existing values. For all the systems studied the hardness is larger in the ground electronic state than in the excited electronic one, a case in conformity with the maximum hardness principle. The decrease in η with excitation is pronounced in the cases of H_2 and HF. This decrease is manifested in the increase in the radii of the valence shell charge concentrations of the constituent atoms of the diatomics in the excited electronic configurations as also in the decrease in the magnitudes of $\nabla^2\rho(\mathbf{r})$ and $-V_{qu}(\mathbf{r})$ at the VSCCs. The diffusivity of the Fukui function radially outwards from the nuclear sites throughout a molecule implies an increase in reactivity and decrease in global hardness of the molecule with excitation.

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