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Molecular Electronic Excitations and the Minimum Polarizability Principle

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The validity of the minimum polarizability principle upon electronic excitation is studied as a companion principle of that obtained by Chattaraj and Poddar in the case of the maximum hardness principle. Twelve diatomic molecules have been selected and, both the hardness and the dipole polarizability for the ground and excited states have been calculated by means of ab initio density functional calculations using Sadlej's basis set. It has been found that a molecule is less polarizable in its ground state than in an electronically excited state of the same spin multiplicity.

1. Introduction

The chemical hardness (η) has been shown to be a useful index of reactivity in atoms, molecules, clusters, and solids.[1−4] The success is in part due to the maximum hardness principle (MHP)[6] which states that "there seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible". A theoretical definition of hardness has been provided in the context of density functional theory,[4] where hardness has been defined[5] as the second derivative of the electronic energy, E, with respect to the number of electrons, N, for a constant external potential, $\upsilon(\vec{r})$.

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{\upsilon(\vec{r})} \qquad (1)$$

Further, in a finite difference approximation and using Koopmans' theorem, a practical equation for the calculation of hardness has been given[1]

$$\eta = (\epsilon_L - \epsilon_H)/2 \qquad (2)$$

where ϵ_L and ϵ_H are the lowest unoccupied and highest occupied molecular orbital (LUMO and HOMO) energies, respectively. The relation of the hardness with the HOMO−LUMO gap is physically clear. An electronic system with a larger HOMO−LUMO gap should be less reactive than one having a smaller gap.

A very recent study of the MHP has shown its validity upon electronic excitation in atoms[7] and molecules.[8] In the later work the molecular hardness has been calculated for some diatomic molecules in their ground and first excited electronic states, and it has been observed that for all the molecules studied the hardness values decrease with electronic excitation revealing an increase in the molecular reactivity.

It has been for some years suggested that the hardness is inversely proportional to the electric dipole polarizability (α). Politzer[9] showed numerically that atomic hardness is inversely proportional to approximated Hartree−Fock atomic polarizabilities. Later on, Fuentealba and Reyes[10] and Ghanty and Ghosh[11] using more elaborated calculations of the polarizabilities found that polarizabilities are inversely proportional to the third power of the hardness. This was more recently analytically demostrated by Simón−Manso and Fuentealba[12] using a local functional model for the hardness kernel. The relationship between the hardness and the dipole polarizability is important because the dipole polarizability is a well-defined observable which can be measured whereas the hardness is not. On the basis of this inverse relationship, a minimum polarizability principle (MPP)[13] has been postulated as a complement to the MHP. Hence, it is expected that "the natural direction of evolution of any system is towards a state of minimum polarizability". Since a theoretical proof of such a principle does not exist, the numerical testing of it in different chemical systems and situations is important.

The electric dipole polarizability is a measure of the linear response of the electron density in the presence of an infinitesimal electric field, F, and represents a second-order variation in the energy, viz.,

$$\alpha_{a,b} = -\left(\frac{\partial^2 E}{\partial F_a \partial F_b}\right) \quad a, b = x, y, z \qquad (3)$$

The observable quantity is its mean value

$$\langle\alpha\rangle = {}^1/_3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \qquad (4)$$

In this paper the validity of the MPP upon electronic excitation will be studied as a companion principle of that obtained by Chattaraj and Poddar[8] in the case of the MHP. Twelve diatomic molecules have been selected, and both the hardness and the dipole polarizability for the ground and excited states have been calculated. The computational details are presented in section 2. The results are presented and discussed in section 3. In section 4 the final remarks are presented.

2. Computational Details

The calculation of the dipole polarizability is very sensitive to the quality of the basis set. To allow for the distortion of the

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TABLE 1: Bond Lengths, Energies, Polarizabilities (in au), and Hardness Values (eV) of Diatomic Molecules

	R_e (Å)	config[a]	E (au)	α_{xx}	α_{yy}	α_{zz}	$\langle\alpha\rangle$	η (eV)
H_2	0.769	$\sigma_g^2\ {}^1\Sigma_g^+$	−1.172	4.76	4.76	7.38	5.60	12.0
	0.769	$\sigma_g\sigma_u\ {}^1\Sigma_u^+$	−0.764	19.2	19.2	154.4	64.1	7.45
	0.769	$\sigma_g\sigma_u\ {}^3\Sigma_u^+$	−0.799	14.3	14.3	92.5	40.4	3.10[b]
Li_2	2.665	$\sigma_g^2\ {}^1\Sigma_g^+$	−14.983	162.0	162.0	252.01	92.0	2.23
	2.665	$\sigma_g\sigma_u\ {}^1\Sigma_u^+$	−14.938	178.6	178.6	379.9	246.0	1.65
N_2	1.108	$\sigma_g^2\ {}^1\Sigma_g^+$	−109.547	10.24	10.24	15.501	1.99	10.8
	1.108	$\sigma_g\pi_g\ {}^1\Pi_g$	−109.250	15.57	17.41	26.57	19.85	2.57
F_2	1.398	$\pi_u^4\,\pi_g^4\ {}^1\Sigma_g^+$	−199.577	6.53	6.53	12.65	8.57	7.09
	1.398	$\pi_u^4\,\pi_g^3\,\sigma_u^1\ {}^1\Pi_u$	−199.443	6.95	6.84	18.71	10.8	4.13
	1.398	$\pi_u^4\,\pi_g^3\,\sigma_u^1\ {}^3\Pi_u$	−199.464	6.94	6.85	18.74	10.8	6.88
HF	0.928	$\sigma^2\pi^4\ {}^1\Sigma^+$	−100.481	5.43	5.43	6.72	5.86	10.8
	0.928	$\sigma^2\pi^3\sigma^1\ {}^1\Pi$	−100.113	34.8	34.8	49.1	39.5	3.91
	0.928	$\sigma^2\pi^3\sigma^1\ {}^3\Pi$	−100.118	33.0	35.6	46.7	38.4	4.97
BF	1.274	$\pi^4\sigma^2\ {}^1\Sigma^+$	−124.703	18.96	18.96	21.13	20.4	6.44
	1.274	$\pi^4\sigma\pi\ {}^1\Pi$	−124.542	22.03	20.73	45.65	29.5	5.18
	1.274	$\pi^4\sigma\pi\ {}^3\Pi$	−124.577	18.55	18.25	26.73	21.2	5.60
LiH	1.593	$\sigma^2\ {}^1\Sigma$	−8.069	30.35	30.35	29.18	30.0	3.92
	1.593	$\sigma\sigma\ {}^3\Sigma$	−7.947	227.0	227.0	80.8	178.0	1.90[b]

[a] Only the configuration of the highest orbitals has been shown. [b] Energy gap for the majority spin.

TABLE 2: Bond Lengths, Energies, Polarizabilities (in au), and Hardness Values (eV) of Diatomic Molecules Having Triplet Ground States

	R_e (Å)	config[a]	E (au)	α_{xx}	α_{yy}	α_{zz}	$\langle\alpha\rangle$	η
O_2	1.21	$\pi_g\pi_g\ {}^3\Sigma_g^-$	−150.372	8.29	8.29	15.62	10.74	4.84
	1.21	$\pi_g^2\ {}^1\Sigma_g^+$	−150.311	8.87	7.99	14.85	10.57	0.95
OS	1.48	$\pi\pi\ {}^3\Sigma^-$	−473.404	20.31	20.31	29.94	23.52	3.54
	1.48	$\pi^2\ {}^1\Sigma$	−473.359	18.76	24.30	29.60	24.22	0.60
S_2	1.89	$\pi_g\pi_g\ {}^3\Sigma_g^-$	−796.416	31.88	31.88	59.37	41.05	2.86
	1.89	$\pi_g^2\ {}^1\Sigma_g^+$	−796.380	35.61	29.92	57.90	41.14	0.46
NH	1.05	$\sigma^2\pi\pi\ {}^3\Sigma^-$	−55.237	9.34	9.34	12.47	10.38	4.08
	1.05	$\sigma\pi^2\pi\ {}^1\Sigma^+$	−55.156	12.51	8.41	12.82	11.25	0.93
LiN	1.71	$\pi\pi\ {}^3\Sigma^-$	−62.131	31.19	20.30	29.62	27.04	1.61
	1.71	$\pi^2\ {}^1\Sigma^+$	−62.038	31.40	31.40	26.31	29.70	0.60

TABLE 3: Bond Lengths, Energies, Polarizabilities (in au), and Hardness Values (eV) of Diatomic Molecules for Adiabatic Excitations

	R_e (Å)	config	E (au)	α_{xx}	α_{yy}	α_{zz}	$\langle\alpha\rangle$	η
O_2	1.21	$\pi_g\pi_g\ {}^3\Sigma_g^-$	−150.372	8.29	8.29	15.62	10.74	4.84
	1.23	$\pi_g^2\ {}^1\Sigma_g^+$	−150.310	8.89	8.08	15.14	10.70	0.96
N_2	1.09	$\sigma_g^2\ {}^1\Sigma_g^+$	109.546	10.09	10.09	15.07	11.75	10.9
	1.21	$\sigma_g\pi_g\ {}^1\Pi_g$	−109.240	15.80	16.09	27.23	19.74	1.22
NH	1.05	$\sigma^2\pi\pi\ {}^3\Sigma^-$	−55.237	9.34	9.34	12.47	10.38	4.08
	1.13	$\sigma\pi^2\pi\ {}^1\Sigma^+$	−55.152	12.73	8.56	14.27	11.85	0.94

electron density, it is necessary to have very diffuse basis functions. Hence, in general, the most standard basis sets are not well suited for the calculation of the dipole polarizability. Therefore, the Sadlej basis sets[14] which are specially constructed for the calculation of the dipole polarizability have been used. The density functional methods have already shown to yield reasonable values of the static dipole polarizability of atoms,[15] molecules[15] and clusters.[16] The analytical second derivative method to calculate the dipole polarizability as it is implemented in the GAUSSIAN 98 program[17] has been used.

The hardness values have been calculated using eq 2. For the open shell systems an average between the gaps for different spins has been taken. This procedure has been proposed and used by many workers.[18] However, there are problems in its implementation which will be discussed later in this paper.

The excited electronic states have been chosen to be the lowest state for the particular symmetry. Hence, the validity of the fundamental theorems of density functional theory is assured. All the calculations have been done by solving the Kohn−Sham equations with the B3LYP[19] exchange-correlation functional, which is a hybrid functional including part of the Hartree−Fock exchange calculated with the Kohn−Sham orbitals. The B3LYP density functional method has already demostrated to be a reliable method for the calculation of energies and polarizabilities in this type of molecules.[15] The excited configurations have been generated by orbital substitution in the Slater determinant followed by the Kohn−Sham minimization.

3. Results and Discussion

In Table 1 the bond lengths, energies, dipole polarizabilities, and hardness values for some diatomic molecules are shown. They are all chosen to have a ${}^1\Sigma$ ground state. The bond lengths have been optimized for ground states, and no relaxation has been permitted after excitation. Hence, the calculations are for a vertical excitation. For the ground state of some molecules there are experimental values of the dipole polarizability to compare with. For O_2, F_2, and HF molecules the experimental values after correction for vibrational contributions[15] are 10.66, 8.36, and 5.60 au, respectively. They compare very well with the calculated values of 10.74, 8.57, and 5.86 au, respectively. Hence, the comparison yields some confidence in the results reported in this paper.

For all the molecules, the MPP is obeyed for the excitation to a singlet state. However, the situation is more complicated in the comparison between the singlet ground state and the triplet excited state. In some cases, especially for the F_2 molecule, comparing the singlet and triplet Π states, the difference in polarizability values is negligible so that within the accuracy of our calculations no conclusive prediction can be made. It is also worth mentioning that all molecules obey the MHP. However, the finite difference approximation for the calculation of hardness seems to be inadequate in calculating the hardness of the excited states. For excited open shell states the LUMO is not well defined and, in some cases, for one spin component, lies below the HOMO giving a negative contribution to the hardness. For systems with a high spin polarization, like the triplet states of H_2 and LiH, the energy gap has only sense for the majority spin.

In light of the different behavior encountered for the triplet states, another set of five diatomic molecules having triplet ground states has been studied. The results are presented in Table 2. In almost all the studied molecules the dipole polarizability of the excited singlet state is very close to and slightly bigger than the dipole polarizability of the triplet ground state. This is a clear indication that the MPP is not applicable in comparing states of different multiplicities. It seems that the dipole polarizability is not very sensitive to a change of just the spin polarization without a change in the orbital occupation (in the case of O_2 and others the change is just between the degenerate π orbitals). On the other hand, the MHP is followed in case of all the molecules.

Since all the discussed calculations have been done for vertical excitations, the study of the effect of geometry relaxation is in order. For the molecules of O_2, N_2 and NH the calculations have been repeated using the experimental bond lengths[20] for ground and excited states. The results are presented in Table 3. It is clear that the values do not change in any significant amount mainly because the change in bond length upon excitation is small.

4. Final Remarks

The validity of the minimum polarizability principle upon electronic excitation has been studied. It has been found that for singlet−singlet excitations the excited-state polarizability is always greater than the ground-state polarizability in accord with the minimum polarizability principle. However, for transitions involving a change in the spin multiplicity the minimum polarizability principle is not always obeyed. The polarizability is not sensitive to a change in spin polarization without a change in the orbital occupation.

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