

# Calculation of Ionization energies , electron affinities , hardnesses and electro negativites , using many bases set of many methods

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**Abstract-** Representative atomic and molecular systems, including various inorganic and organic molecules with covalent and ionic bonds, have been studied by using density functional theory. The calculations were done with the commonly used exchange-correlation functional B3LYP followed by a comprehensive analysis of the calculated highest-occupied and lowest-unoccupied Kohn-Sham orbital (HOMO and LUMO) energies. DFT calculations of vibration spectra of many organic systems [1, 2], Density Functional Theory (DFT) calculations have been performed to support our wave number assignments. The theoretically predicted IR is well in agreement with that of experimental spectral data.

## 1. Introduction

The global properties may explain the reactivity and selectivity. One of these global quantities is hardness  $\eta$ . The relation of the hardness with the HOMO-LUMO gap is physically clear. It is obvious that the more stable structure has the largest HOMO-LUMO energy gap. Therefore, an electronic system with a larger HOMO-LUMO gap should be less reactive than one having a smaller gap. It is the base of the maximum hardness principle. Another global property is the electric dipole polarizability.

Hardness measures the stability and polarizability measures the reactivity [8-9]. The minimum polarizability principle (MPP) [15] has been postulated which expected that 'the natural direction of evolution of any system is towards a state of minimum polarizability'. Molecular properties such as dipole polarizabilities have been studied in thiophene monomers and polythiophenes by many methods.

## 2. Methods

**2.1 Computational method** The ionization potential is calculated in present work as the energy difference between the energy of the molecule derived from electron-transfer (radical cation) and the respective neutral molecule [2, 3, 4, 5, and 6]:

$$IP = E_{cation} - E_n \dots (2.1)$$

The EA was computed as the energy difference between the neutral molecule and the anion molecule:

$$EA = E_n - E_{anion} \dots (2.2)$$

The HOMO and LUMO energy was also used to estimate the IP and EA in the framework of Koopmans' theorem [6, 7, 8, 9, and 10]:

$$IP = -\epsilon_{HOMO} \dots (2.3)$$

$$EA = -\epsilon_{LUMO} \dots (2.4)$$

## 2.2 Chemical potential , chemical hardness and softness

Within the framework of the density functional theory (DFT), one of the global quantities is chemical potential ( $\kappa$ ), which measures the escaping tendency of an electronic cloud. It is a constant, through all space, for the ground state of an atom, molecule or solid, and equals the slope of the energy versus  $N$  (number of electrons) curve at external potential  $v(r)$  [9,10,11]:

$$\kappa = [\partial E / \partial N]_{v(r)} \dots (2.5)$$

Finite difference approximation to Chemical Potential gives,

$$\kappa \approx -\chi = -((IP + EA))/2 \dots (2.6)$$

Where  $\chi$  is electro negativity, the electro negativity is a measure of the tendency to attract electrons by an atom in a chemical bond and defined as the negative of the chemical potential in DFT [7,18]

The chemical hardness is a measure of the resistance to charge transfer. The theoretical definition of chemical hardness has been provided by the density functional theory as the second derivative of electronic energy with respect to the number of electrons  $N$ , for a constant external potential  $v(r)$  [9, 10,11,12]:

$$\eta = 1/2 [( \partial^2 E / \partial N^2 )_{v(r)}] = 1/2 [ \partial \kappa / \partial N ]_{v(r)} \dots (2.7)$$

Finite difference approximation to Chemical hardness gives,

$$\eta = (IP - EA)/2 \dots (2.8)$$

The chemical hardness of a given system is, as can be seen by equation (3.13), a resistance of the chemical potential to change in its number of electrons. For insulator and semiconductor, hardness is half of the energy gap.

The global chemical softness,  $S$ , is a property of molecules that measures the extent of chemical reactivity. It is the inverse of the chemical hardness  $\eta$  [12,13,14]:

$$S = 1/2\eta = ((\partial^2 N) / (\partial E)^2)_{v(r)} = (\partial N / \partial \kappa)_{v(r)} \dots (2.9)$$

## 2.3 Electrophilic Index

Electrophilicity is a measure of energy lowering due to maximal electron flow between donor and acceptor. Electrophilicity ( $\omega$ ) is defined as [13,15,16, 17]:

$$\omega = \kappa^2 / (2\eta) \dots (2.10)$$

## 3. Calculation Method

Geometries of all of the molecules considered in this study were fully optimized by using gradient corrected DFT with Becke's three-parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP)[19] we also performed single point energy calculations on the neutral systems using basis sets, Semi empirical methods Pm6, Hartree Fock with basis set 6-311G\*, and density functional theory the B3LYP with a larger basis set, 6-311G\*, 6-311G\*\*, aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ, SDD

## 4. Results and Discussion

Basis Set Dependence of the DFT Results. Before exploring any correlation of the DFT HOMO /LUMO energies with molecular properties, we need to understand the basis set dependence of the HOMO/LUMO energies. Previous DFT calculations[15] tested a series of correlation-consistent basis sets, starting from the 6-311G\*, 6-311G\*\*, aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ, SDD to obtain HOMO and LUMO energies for developing correlations with molecular properties.

We note that in the previous study, quite small molecules were used and there was no issue in terms of the computational resources needed, whereas we are interested in developing correlations for much larger molecular systems where a smaller basis set is needed in order to perform efficient computations.

The calculated results are collected in Tables together with available experimental data. Note that the calculated vertical IP and EA values listed in the tables 1 and 2 were determined from the total energy calculations on the neutral systems.

**Table (1): Experimental and Calculated Ionization Potential (IP) for molecules**

molecules	Ionization Potential(IP)								
	semi	HF	Density functional theory / B3LYP						
	pm6	6-311G*	6-311G**	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	SDD	reference	
CO <sub>2</sub>	12.9222	14.7535	9.2213	10.0018	10.1447	10.4666	10.3313	13.7731 <sup>[10]</sup>	11.796 <sup>[20,21]</sup>
H <sub>2</sub> O	12.3168	13.6107	8.1476	7.9301	8.332	8.6316	8.484	12.621 <sup>[10]</sup>	12.77 <sup>[1]</sup>
O <sub>3</sub>	11.3537	13.3804	9.0162	9.5831	9.5602		9.3964		11.77 <sup>[10]</sup>
H <sub>2</sub> S	9.4415	12.473	7.3182	7.2859	7.3248	7.3216	7.1174		10.47 <sup>[20]</sup>

**Table (2): Calculated energy luma inversion for molecules**

molecules	Electron affinities (EA)						
	semi	HF	Density functional theory / B3LYP				
	pm6	6-311G*	6-311G**	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	SDD
CO <sub>2</sub>	-0.2506	-6.2754	-0.7788	-0.8988	-0.7377	0.5894	0.4103
H <sub>2</sub> O	-4.062	-4.0844	1.8697	-1.3396	-0.6814	-0.2754	-1.6564
O <sub>3</sub>	1.7603	0.1456	5.1976	5.4303	5.3949		6.0989
H <sub>2</sub> S	-0.4558	-3.5443	-0.2544	0.621	0.6063	0.6104	-0.8139

**Table (3): Calculated energy gap for molecules**

molecules	energy gap						
	semi	HF	Density functional theory / B3LYP				
	pm6	6-311G*	6-311G**	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	SDD
CO <sub>2</sub>	13.2428	21.8912	11.0573	10.9006	11.0824	9.8772	9.9209
H <sub>2</sub> O	16.3789	17.6953	8.9264	9.1697	8.1387	8.909	9.8048
O <sub>3</sub>	9.7663	13.2348	4.0937	4.153	4.1712		3.4975
H <sub>2</sub> S	9.8974	14.0198	7.5626	6.6749	6.7185	6.7122	7.9313

**Table (4): Calculated chemical potential for molecules**

molecules	chemical potential ( $\mu$ )						
	semi	HF	Density functional theory / B3LYP				
	pm6	6-311G*	6-311G**	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	SDD
CO <sub>2</sub>	6.3708	4.2402	4.5009	4.5515	-4.8035	-5.528	5.3708
H <sub>2</sub> O	-4.1274	-4.0844	-3.6844	-3.24525	-4.0693	-4.1791	-3.246
O <sub>3</sub>	-6.643	-6.763	-7.24445	-7.5068	-7.48055		7.84765
H <sub>2</sub> S	4.49285	3.46535	3.5269	3.95845	3.96555	3.9665	3.15175

**Table (5): Calculated Chemical hardness for molecules**

molecules	Chemical hardness ( $\eta$ )						
	semi	HF	Density functional theory / B3LYP				
	pm6	6-311G*	6-311G**	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	SDD
CO <sub>2</sub>	6.6214	10.5156	5.5287	5.4503	5.412	4.9386	4.9605
H <sub>2</sub> O	8.1894	8.84765	4.4632	4.58485	4.7507	4.4545	4.9024
O <sub>3</sub>	4.8827	6.6174	2.04685	2.0765	2.08565		1.74875
H <sub>2</sub> S	4.94865	7.07133	3.7813	3.33745	3.35925	3.3561	3.96565

**Table (6): Calculated softness for molecules**

molecules	softness (S)						
	semi	HF	Density functional theory / B3LYP				
	pm6	6-311G*	6-311G**	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	SDD
CO <sub>2</sub>	0.075513	0.047548	0.090437	0.091738	0.090233	0.101243	0.100796
H <sub>2</sub> O	0.061055	0.056512	0.112027	0.109055	0.105248	0.112246	0.101991
O <sub>3</sub>	0.102402	0.075558	0.244278	0.24079	0.239733		0.285919
H <sub>2</sub> S	0.101038	0.07133	0.13223	0.149815	0.148843	0.148982	0.1252446

**Table (7): Electrophilicity Calculated for molecules**

molecules	Electrophilicity ( $\omega$ )						
	semi	HF	Density functional theory / B3LYP				
	pm6	6-311G*	6-311G**	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	SDD
CO <sub>2</sub>	3.064842	0.854887	2.019921	1.90046	2.082005	3.093871	2.907519
H <sub>2</sub> O	1.04009	1.282179	1.520748	1.148527	1.742817	1.960363	1.074628
O <sub>3</sub>	4.51896	3.455902	12.8202	13.569	13.41515		17.60847
H <sub>2</sub> S	2.039516	0.85658	1.644808	2.3475	2.34064	2.343959	1.252446

## Conclusions

1. Energy gap and hardness presented an assistance to predict reactive molecules.
2. The Semi empirical methods Pm6, HartreeFock presented good results in calculation of total energy
- 3.

he ionization potential and electron affinity of a molecules calculated by using energy-vertical method were found in a good agreement with experimental results and better than those calculated by using KT/DFT and KT/AM1, thus Koopman's theorem was not satisfied accurately.

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