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Detemination of The Best Method (HF, MP2 and B3LYP) in Calculation of Chemical Hardness

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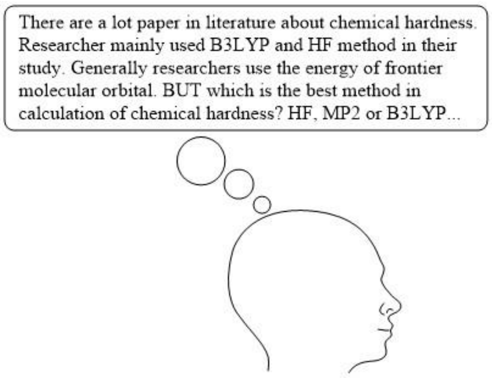
Abstract: Chemical hardness of 62 molecules are calculated at different 18 levels. No imaginargy frequency is observed in optimization results for each level. Correlation between experimental and calculated hardness values are investigated. To analyze this investigation, correlation coefficient and scale factor are calculated for each level. As a results, HF method is better in calculation of chemical hardness and moleculer orbital energy than B3LYP and MP2 methods.

Keywords: *Molecular Orbital Energy, Chemical Hardness, HF, B3LYP, MP2*

Graphical Abstract



- Investigations of the best method in calculation of chemical hardness were performed.
- Some organic and inorganic molecules were optimized at different level.
- Calculated and Experimental chemical hardness values were compared with each other.
- It was found that HF method is the best in calculation of chemical hardness.

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1. Introduction

Chemical hardness is hot topic in chemistry and there are a lot of published papers over it [1-9]. Story of chemical hardness started in the hands of Pearson [10]. Acording to his opinions hard acids have low polarizability due to the stable electron distributions while soft acids have opposite properties [11]. Pearson' s hard acid/base and soft acid/base principle imply that "hard acids or bases prefer to coordinate to hard bases or acids". This principle is very practical in chemistry field. However, definition of hardness or softness is incomplete in hard-soft-acid-base (HSAB) principle. These troubles were solved in 1983 by Pearson and Parr. According to Pearson study, absolute hardness have been introduced as in Eq. (1) [12, 13].

$$\eta = \frac{(I-A)}{2} \qquad (1)$$

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where I and A are ionization potential and electron affinity of any chemical species (atom, ions, molecule or radical). These parameters is useful in determination of behaviors of chemical species. Ionization potential and electron affinity can be calculated by using Eq. (2) and (3).

$$I = E_{N-1} - E_N \tag{2}$$

$$A = E_N - E_{N+1} \tag{3}$$

where E_{N+1}, E_N and E_{N-1} are total energy of system with (N+1), (N) and (N-1) electron, respectively. In addition to these equations, many researchers have being used the Koopmans theorem, recently. According to this theorem, ionization potential and electron affinity can be calculated from frontier molecular orbital , HOMO and LUMO, and their mathematical definations are given in Eq. (4) and (5).

$$I = -E_{HOMO} \tag{4}$$

$$A = -E_{LUMO} \tag{5}$$

One of the other hardness type is optical hardness (η_O) and can be easily calculated by using Eq. (6).

$$\eta_O = E_{LUMO} - E_{HOMO} \tag{6}$$

This hardness is related to polarizabilities of chemical species and can be used in investigation of optical properties of related chemical species. According to hardness equations, energies of frontier molecular orbitals are important to calculation of hardness.

As for the quantum chemical calculations, some quantum chemical descriptors have been calculated by using the energy of frontier molecular orbitals [14-21]. These parameters have been used in determination of reactivity of molecules towards enzyme, protein and metal surface etc. Additionally, some theoretical formulas are derived by using some quantum chemical descriptors in quantitave structure-activity relationship (QSAR) studies. Because of that, calculation of these parameters is important to correct results. Generally, DFT methods have been used in calculation of these parameters.

Recently, computational chemistry has been fashion in academic invstigations. In this study, performance of HF, B3LYP and MP2 methods in calculation of chemical hardness is investigated in detail. Experimental hardness values of 62 molecules are optimized. In calculations, HF, B3LYP and MP2 methods are used. In addition to mentioned methods, 6-31++G(d,p), 6-311G, LANL2DZ, LANL2MB, SDD and SDDALL basis sets are used. Corelations between experimental and calculated results are examined by plotting distribution graphs and correlation coefficient are founds for each graph.

2. Computational Details

Computational processes of were performed by using GaussView 5.0.8 [22], Gaussian 09 AML64-G09 Revision-D01 programs [23], Gaussian 09 IA32W-G09 Revision-A02 programs [24]. Firstly, geometries of investigated compounds were optimized by using universal force field (UFF) method which is one of the molecular mechanics methods. After that, the geometries of mentioned complexes reoptimized at HF, B3LYP and MP2 methods with 6-31++G(d,p), 6-311G, LANL2DZ, LANL2MB, SDD and SDDALL basis sets. The vibrational frequency analyses indicate that optimized structures of relevant molecules are at stationary points corresponding to local minima without imaginary frequencies. Chemical hardness of these molecules are calculated by using Eq. (1).

3. Results and discussion

3.1. Chemical Hardness in HF Method

The fully optimizations of related molecules are done at each basis set in vacuum. Experimental hardness values (η) of investigated molecules are given in Table 1 [25]. Chemical hardness value of mentioned molecules are calculated at 6-31++G(d,p), 6-311G and LANL2DZ basis sets and given in Table 2 – 4, respectively. As for the other basis sets, Calculated results in LANL2MB, SDD and SDDALL basis sets are given in Supp. Table S1 – S3, respectively.

Table 1. Studied molecules and their experimental hardness values

Molecule	η [a]	Molecule	η [a]	Molecule	η [a]	Molecule	η [a]
SF_6	7.40	BBr_3	4.85	C_5H_5N	5.00	cyclohexene	5.50
BF_3	9.70	PBr_3	4.20	butadiene	4.90	DMF	5.80
SO_3	5.50	S_2	3.85	H_2S	6.20	$C_6H_5NH_2$	4.40
Cl_2	4.60	$C_6H_5NO_2$	4.40	C_2H_2	7.00	$CH_3CH{=}C(CH_3)_2$	5.50
H_2	8.70	PCl_3	4.70	$HCONH_2$	6.20	CH_3F	9.40
SO_2	5.60	N_2O	7.60	styrene	4.36	H_2O	9.50
N_2	8.90	acrylonitrile	5.56	CH_3COCH_3	5.60	$(CH_3)_3As$	5.70
Br_2	4.00	CS_2	5.56	PH_3	6.00	$(CH_3)_3P$	5.90
O_2	5.90	CO_2	8.80	C_6H_6	5.30	$(CH_3)_2S$	6.00
CO	7.90	HF	11.00	toluene	5.00	NH_3	8.20
BCl_3	5.64	HCl	8.00	propylene	5.90	CH_4	10.3
CS	5.23	CH_3CN	7.50	C_6H_5OH	4.80	$C(CH_3)_4$	8.30
HNO_3	5.23	CH_2O	6.20	C_6H_5SH	4.60	$(CH_3)_2O$	8.00
CH_3NO_2	5.34	HCO_2CH_3	6.40	CH_3Cl	7.50	$(CH_3)_3N$	6.30
PF_3	6.70	CH_3CHO	5.70	p-xylene	4.80	-	-
HCN	8.00	C_2H_4	6.20	1,2,5-trimethylbenzene	4.72	-	-

[a] Experimental values are taken from *Ref. 25*.

Table 2. Calculated chemical hardness values of mentioned molecules at HF/6-31++G(d,p) level in vacuum

Molecule	η	Molecule	η	Molecule	η	Molecule	η
SF_6	10.251	BBr_3	6.275	C_5H_5N	5.294	cyclohexene	6.174
BF_3	9.742	PBr_3	5.705	butadiene	5.047	DMF	5.592
SO_3	7.669	S_2	3.769	H_2S	5.782	$C_6H_5NH_2$	4.558
Cl_2	6.380	$C_6H_5NO_2$	5.485	C_2H_2	6.222	$CH_3CH{=}C(CH_3)_2$	5.110
H_2	9.156	PCl_3	6.359	$HCONH_2$	6.242	CH_3F	7.792
SO_2	6.864	N_2O	7.945	styrene	4.771	H_2O	7.515
N_2	10.341	acrylonitrile	5.938	CH_3COCH_3	6.124	$(CH_3)_3As$	4.987
Br_2	5.444	CS_2	5.639	PH_3	5.770	$(CH_3)_3P$	5.002
O_2	6.651	CO_2	8.223	C_6H_6	5.169	$(CH_3)_2S$	5.151
CO	8.695	HF	9.457	toluene	4.982	NH_3	6.330
BCl_3	6.927	HCl	7.032	propylene	5.503	CH_4	8.028
CS	7.065	CH_3CN	6.834	C_6H_5OH	4.839	$C(CH_3)_4$	6.721
HNO_3	7.304	CH_2O	6.575	C_6H_5SH	5.228	$(CH_3)_2O$	6.310
CH_3NO_2	6.736	HCO_2CH_3	6.911	CH_3Cl	6.471	$(CH_3)_3N$	5.319
PF_3	7.327	CH_3CHO	6.327	p-xylene	4.838	-	-
HCN	7.341	C_2H_4	5.824	1,2,5-trimethylbenzene	4.773	-	-

Table 3. Calculated chemical hardness values of mentioned molecules at HF/6-311G level in vacuum

Molecule	η	Molecule	η	Molecule	η	Molecule	η
SF_6	7.864	BBr_3	6.248	C_5H_5N	6.398	cyclohexene	7.459
BF_3	11.193	PBr_3	5.229	butadiene	6.016	DMF	6.945
SO_3	6.374	S_2	3.774	H_2S	6.947	$C_6H_5NH_2$	5.806
Cl_2	5.954	$C_6H_5NO_2$	5.548	C_2H_2	7.943	$CH_3CH{=}C(CH_3)_2$	6.591
H_2	10.458	PCl_3	5.968	$HCONH_2$	7.602	CH_3F	9.399
SO_2	5.769	N_2O	8.424	styrene	5.568	H_2O	8.796
N_2	10.647	acrylonitrile	6.648	CH_3COCH_3	7.550	$(CH_3)_3As$	6.405
Br_2	5.193	CS_2	5.680	PH_3	6.979	$(CH_3)_3P$	6.449
O_2	6.783	CO_2	9.769	C_6H_6	6.467	$(CH_3)_2S$	6.648
CO	9.383	HF	10.628	toluene	6.292	NH_3	7.591
BCl_3	7.139	HCl	8.017	propylene	7.121	CH_4	9.646
CS	7.083	CH_3CN	8.243	C_6H_5OH	6.134	$C(CH_3)_4$	8.117
HNO_3	7.441	CH_2O	7.660	C_6H_5SH	6.298	$(CH_3)_2O$	7.802
CH_3NO_2	7.033	HCO_2CH_3	8.462	CH_3Cl	7.771	$(CH_3)_3N$	6.646
PF_3	8.028	CH_3CHO	7.719	p-xylene	6.140	-	-
HCN	8.967	C_2H_4	7.359	1,2,5-trimethylbenzene	6.143	-	-

Table 4. Calculated chemical hardness values of mentioned molecules at HF/LANL2DZ level in vacuum

Molecule	η	Molecule	η	Molecule	η	Molecule	η
SF_6	7.980	BBr_3	6.242	C_5H_5N	6.288	cyclohexene	7.459
BF_3	10.906	PBr_3	4.986	butadiene	5.869	DMF	7.381
SO_3	6.150	S_2	3.765	H_2S	7.766	$C_6H_5NH_2$	5.691
Cl_2	5.892	$C_6H_5NO_2$	5.460	C_2H_2	8.036	$CH_3CH{=}C(CH_3)_2$	7.023
H_2	11.680	PCl_3	6.070	$HCONH_2$	7.951	CH_3F	10.320
SO_2	5.568	N_2O	8.279	styrene	5.422	H_2O	9.869
N_2	10.425	acrylonitrile	6.508	CH_3COCH_3	7.672	$(CH_3)_3As$	6.738
Br_2	5.008	CS_2	5.727	PH_3	7.578	$(CH_3)_3P$	7.134
O_2	6.735	CO_2	9.644	C_6H_6	6.338	$(CH_3)_2S$	7.147
CO	9.164	HF	11.635	toluene	6.166	NH_3	8.748
BCl_3	7.265	HCl	8.784	propylene	7.121	CH_4	11.504
CS	6.997	CH_3CN	9.051	C_6H_5OH	6.022	$C(CH_3)_4$	9.389
HNO_3	7.268	CH_2O	7.523	C_6H_5SH	6.237	$(CH_3)_2O$	8.851
CH_3NO_2	6.942	HCO_2CH_3	8.314	CH_3Cl	8.143	$(CH_3)_3N$	7.876
PF_3	8.140	CH_3CHO	7.626	p-xylene	6.029	-	-
HCN	9.082	C_2H_4	7.117	1,2,5-trimethylbenzene	6.054	-	-

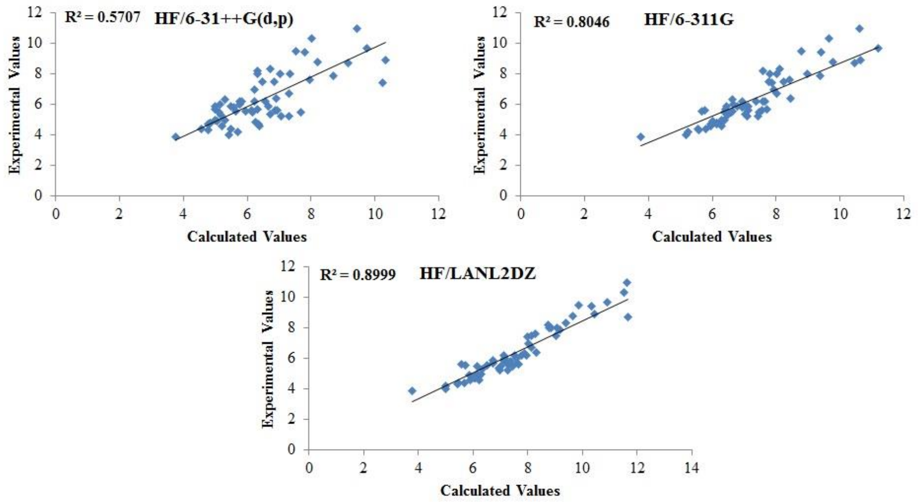

Fig. 1. Distribution graphs between experimental and calculated values at HF/6-31++G(d,p), HF/6-311G and HF/LANL2DZ levels in vacuum.

Table 5. Calculated chemical hardness values of mentioned molecules at B3LYP/6-31++G(d,p) level in vacuum

Molecule	η	Molecule	η	Molecule	η	Molecule	η
SF_6	2.190	BBr_3	2.973	C_5H_5N	3.186	cyclohexene	1.192
BF_3	5.337	PBr_3	1.856	butadiene	3.239	DMF	3.520
SO_3	1.618	S_2	0.435	H_2S	4.940	$C_6H_5NH_2$	3.131
Cl_2	1.711	$C_6H_5NO_2$	2.180	C_2H_2	5.532	$CH_3CH=C(CH_3)_2$	4.130
H_2	11.664	PCl_3	2.232	$HCONH_2$	3.409	CH_3F	6.671
SO_2	1.405	N_2O	3.502	styrene	3.006	H_2O	6.127
N_2	4.913	acrylonitrile	3.562	CH_3COCH_3	3.041	$(CH_3)_3As$	4.309
Br_2	1.446	CS_2	2.726	PH_3	5.412	$(CH_3)_3P$	4.566
O_2	0.894	CO_2	4.591	C_6H_6	3.828	$(CH_3)_2S$	4.076
CO	4.606	HF	6.500	toluene	3.719	NH_3	6.996
BCl_3	3.369	HCl	5.486	propylene	4.529	CH_4	11.090
CS	2.981	CH_3CN	5.405	C_6H_5OH	3.179	$C(CH_3)_4$	8.519
HNO_3	3.255	CH_2O	3.008	C_6H_5SH	3.690	$(CH_3)_2O$	5.701
CH_3NO_2	2.441	HCO_2CH_3	3.510	CH_3Cl	4.431	$(CH_3)_3N$	5.931
PF_3	3.388	CH_3CHO	3.042	p-xylene	3.620	-	-
HCN	5.581	C_2H_4	4.529	1,2,5-trimethylbenzene	3.593	-	-

According to HF results, calculated chemical hardness values are mainly in agreement with experimental results except results in HF/6-31++G(d,p) and HF/LANL2MB levels. In these levels, there are big deviations in results.

3.2. Chemical Hardness in B3LYP Method

The fully optimizations of related molecules are performed in each basis set. In this method, the best results are calculated by using B3LYP/6-31++G(d,p) level in vacuum. Calculated hardness values of related molecules are given in Table 5 at B3LYP/6-31++G(d,p) level.

Experimental and calculated results are used to plot the distribution graph. It is represented in Fig. 2 and it is seen that correlation coefficient (R^2) values is 0.5907. As for the other results in B3LYP method, correlation coefficient is calculated as lower than 0.5907. Therefore, performance of B3LYP in calculations of chemical hardness is under the expectations. Calculated results in 6-311G, LANL2DZ, LANL2MB SDD and SDDALL basis sets are given in Supp. Table S4 – S8, respectively.

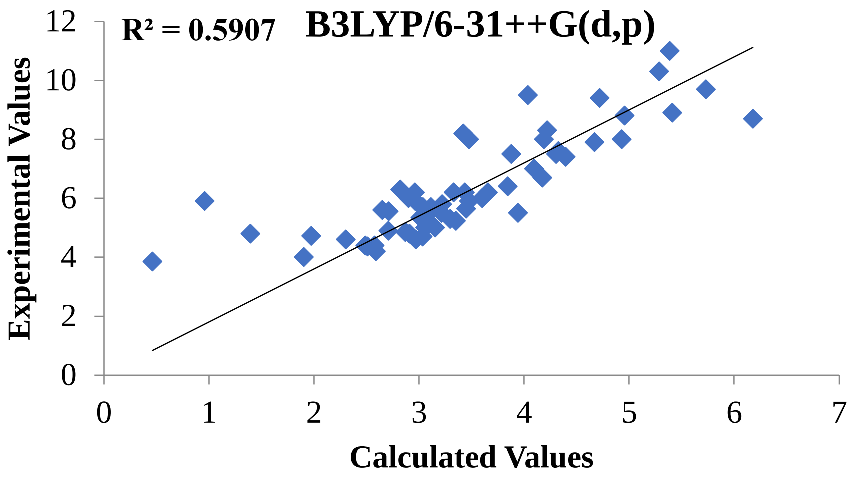

Fig. 2. Distribution graphs between experimental and calculated values at B3LYP/6-31++G(d,p) levels in vacuum.

Table 6. Calculated chemical hardness values of mentioned molecules at MP2/LANL2DZ level in gas phase

Molecule	η	Molecule	η	Molecule	η	Molecule	η
SF_6	6.792	BBr_3	6.219	C_5H_5N	6.072	cyclohexene	9.281
BF_3	10.725	PBr_3	4.832	butadiene	5.664	DMF	7.173
SO_3	5.900	S_2	3.719	H_2S	7.678	$C_6H_5NH_2$	5.602
Cl_2	5.721	$C_6H_5NO_2$	5.174	C_2H_2	7.743	$CH_3CH{=}C(CH_3)_2$	6.817
H_2	11.620	PCl_3	2.956	$HCONH_2$	7.689	CH_3F	10.183
SO_2	5.136	N_2O	7.433	styrene	5.360	H_2O	9.738
N_2	9.510	acrylonitrile	6.210	CH_3COCH_3	7.493	$(CH_3)_3As$	6.695
Br_2	4.893	CS_2	5.610	PH_3	7.561	$(CH_3)_3P$	7.098
O_2	6.526	CO_2	9.162	C_6H_6	6.168	$(CH_3)_2S$	7.030
CO	8.965	HF	11.461	toluene	6.013	NH_3	8.678
BCl_3	7.216	HCl	8.692	propylene	6.880	CH_4	11.363
CS	6.727	CH_3CN	8.535	C_6H_5OH	5.895	$C(CH_3)_4$	9.256
HNO_3	6.862	CH_2O	7.397	C_6H_5SH	6.071	$(CH_3)_2O$	8.774
CH_3NO_2	6.480	HCO_2CH_3	8.042	CH_3Cl	8.039	$(CH_3)_3N$	7.887
PF_3	7.982	CH_3CHO	7.468	p-xylene	4.302	-	-
HCN	8.557	C_2H_4	6.922	1,2,5-trimethylbenzene	5.901	-	-

3.3. Chemical Hardness in MP2 Method

The optimizations of related molecules are done in each basis set. In this method, the best results are calculated by using MP2/LANL2DZ level in gas phase. Calculated hardness values of related molecules are given in Table 6 for MP2/LANL2DZ level.

A graph is plotted by using experimental and calculated chemical hardness values and it is represented in Fig. 3. It is seen that correlation coefficient (R^2) values is 0.8147. Calculated chemi,cal hardness values in 6-31++G(d,p), 6-311G, LANL2MB, SDD and SDDALL basis sets are given in Supp. Table S9 – S13, respectively.

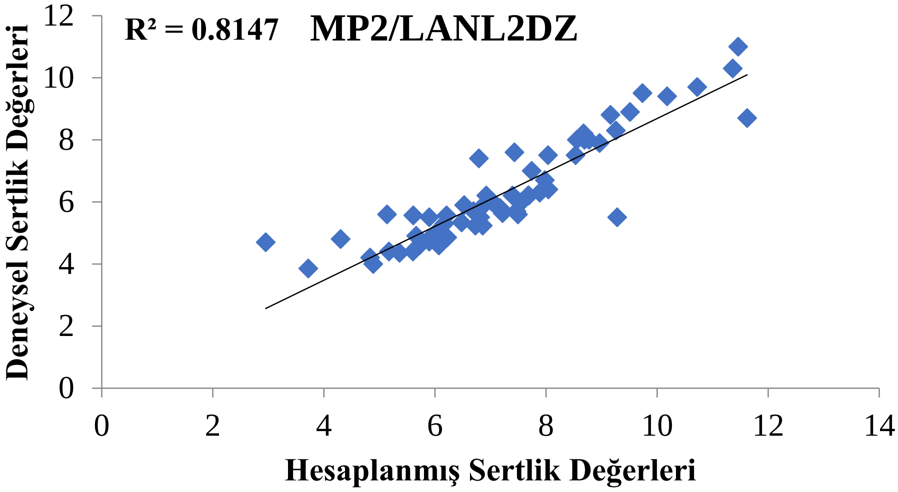

Fig. 3. Distribution graphs between experimental and calculated values at MP2/LANL2DZ levels in gas phase.

Table 7. Calculated scale factor ($\lambda_{Average}$) and correlation coefficient (R^2) values for each level

Basis Set	HF		B3LYP		MP2	
	$\lambda_{Average}$	R^2	$\lambda_{Average}$	R^2	$\lambda_{Average}$	R^2
6-31++G(d,p)	0.9825	0.5707	2.0241	0.5907	0.9916	0.5863
6-311G	0.8598	0.8046	1.9667	0.4986	0.9459	0.7200
LANL2DZ	0.8375	0.8999	1.9526	0.3803	0.8754	0.8147
LANL2MB	0.7404	0.5388	1.8528	0.5630	0.7606	0.5630
SDD	0.8313	0.8970	1.9923	0.2719	0.8646	0.6057
SDDALL	0.8426	0.8178	1.9534	0.3611	0.8764	0.7708

3.4. Scale Factor for Chemical Hardness

Scale factors are mainly used in vibrational spectroscopy to determination of anharmonic frequencies. In this study, scale factor is calculated for determination of accuracy and harmony. Scale factor ($\lambda_{Hardness}$) is calculated for each level by using Eq. (7) and (8).

$$\lambda_{Hardness} = \frac{\eta_{experimental}}{\eta_{calculated}} \quad (7)$$

$$\lambda_{Average} = \frac{\sum_0^N \lambda_{Hardness}}{N} \quad (8)$$

It is expected that scale factor is equal to one. If scale factor is equal to one, it is expected that accuracy and harmony is high. Calculated scale factor and R^2 values are given in Table 7.

To determine the best method n calculation of chemical hardness, both scale factor and correlation coefficient must be taken into consideration. Scale factor and correlation coefficient must be equal or close to “1”. Therefore, results in HF method are better than those of B3LYP and MP2. Additionally, HF method is better in calculation of molecular orbital energies than those of B3LYP and MP2, since chemical hardness is calculated by using HOMO and LUMO energies.

4. Conclusion

62 molecules are optimized at three different methods and six different basis set in gas phase. Chemical hardnesses are calculated in each level by taking into considerations Koopmans theorem. Distribution graphs are plotted in each level and correlation coefficient are calculated for each graph. In addition to these results, average scale factor for chemical hardness are calculated by using experimental and calculated hardness values. As a results, HF method is better in calculation of chemical hardness and moleculer orbital energy than B3LYP and MP2 methods.

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