J. Braz. Chem. Soc., Vol. 00, No. 00, 1-xx, 2006.
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0103 - 5053 $6.00+0.00

Concerning the FERMO Concept and Pearson's Hard and Soft Acid-Base Principle

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We decide to calculate the FERMO-LUMO gaps using the 6-31G** basis set for all compounds, since we have to used it for the enolate ion for solve MO composition problem (see Table S3). It was observed a shift when the diffuse function is added, but a important feature is that the difference between the hard and soft FERMO-LUMO gaps are constant, independently of the basis set used to calculate the MO energy. The only exception was the enolate ion – as should be expected, since the enolate ion presents an anomalous result with the basis set 6-31+G**. Nevertheless, the variation along the basis set is really small (0.2 eV in the HF method).

As one can notice, the values between HF and DFT methods are quite different. However, this effect is expected due to MO energy differences.

Table S1. ½ FERMO-LUMO gaps for different methods and basis set

	½ FERMO-LUMO gap (eV)			
Molecules	DFT/6-31+G**	DFT/6-31G**	HF/6-31+G**	HF/6-31G**
SCN^-				
S	2.6	3.9	4.7	7.5
N	4.3	5.6	7.4	10.2
NO_2^-				
N	2.5	2.5	6.3	7.3
O	3.1	3.1	7.1	8.1
$CH_3COCH_2^-$				
C (enolic)	1.8	3.2	3.9	6.6
O	2.2	3.6	5.2	7.7
DMSO				
S	3.2	3.6	5.9	7.5
O	3.7	4.1	6.5	8.1

Table S2. MO numeration

Molecules	DFT/6-31+G**	DFT/6-31G**	HF/6-31+G**	HF/6-31G**
SCN^-				
HOMO	15	15	15	15
S–FERMO	15	15	15	15
N-FERMO	11	13	11	11
NO_2^-				
HOMO	12	12	12	12
N-FERMO	12	12	12	12
O-FERMO	11	11	10	10
$CH_3COCH_2^-$				
HOMO	16	16	16	16
C-FERMO	16	16	16	16
O-FERMO	15	15	15	15
DMSO				
HOMO	21	21	21	21
S-FERMO	21	21	21	21
O-FERMO	20	20	20	20

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Table S3. MO compositions. We are displaying the MO compositions for the five last occupied MOs. MO compositions for DFT/6-31+G** and HF/6-31+G** methodologies. For the enolate ion the MO compositions for the DFT/6-31G** and HF/6-31G** methodologies are also displayed. All MO compositions are in percentage. Atoms in blue are the soft sites and in red the harder ones

SCN^-

DFT/6-31+G**
Five last occupied MOs

	11	12	13	14[a]	15[a]
C1	20.61	44.08	44.08	1.38	1.38
N2	63.07	36.61	36.61	20.76	20.76
S3	16.32	19.31	19.31	77.87	77.87

HF/6-31+G**
Five last occupied MOs

	11	12	13	14[a]	15[a]
C1	22.27	39.24	39.24	1.71	1.71
N2	45.51	41.82	41.82	17.55	17.55
S3	32.22	18.94	18.94	80.75	80.75

[a] Degenerated MOs.

NO_2^-

DFT/6-31+G**
Five last occupied MOs

	8	9	10	11	12
N1	47.89	48.44	0.28	1.41	52.35
O2	26.13	25.84	49.80	49.26	23.82
O3	25.98	25.72	49.93	49.34	23.84

HF/6-31+G**
Five last occupied MOs

	8	9	10	11	12
N1	25.38	36.54	1.49	0.38	46.93
O2	37.27	31.81	49.20	49.73	26.52
O3	37.34	31.65	49.30	49.89	26.55

$CH_3COCH_2^-$

DFT/6-31+G**
Five last occupied MOs

	12	13	14	15	16
C1	20.56	15.31	28.23	17.88	5.84
O2	35.78	27.41	49.40	14.77	33.06
C3	14.17	15.09	6.62	46.91[a]	57.39
H4	5.46	12.67	0.00	0.06	0.02
H5	0.00	11.51	0.00	0.24	0.03
C6	10.86	15.70	6.34	19.71	0.62
H7	2.77	1.14	4.72	0.00	1.52
H8	7.60	0.01	0.00	0.43	0.00
H9	2.80	1.17	4.68	0.00	1.52

[a] The MO composition from C3 (the enolic carbon atom) is large because the diffuse function creates an anomalous carbon 4s contribution. This became clearer when the total contribution from the C3 atom is splited in terms of its atomic orbitals (AOs). As it can be seem, the 4s AO is responsible for more than 85% of the MO contribution for the C3 AOs. Since the 4s AO is included only when diffuse functions are added into the basis set, this large 4s contribution was a basis set effect caused by the diffuse function. To avoid this effect, we were forced to remove the diffuse function, and the FERMOs from C and O were better characterized. The effect is present in both HF and DFT calculations.

C3 Atomic Orbitals	DFT/6-31+G** Five last occupied MOs				
	12	13	14	15	16
1S	0.32	0.00	0.00	0.08	0.00
2S	1.43	0.01	0.00	0.37	0.00
2PX	74.49	44.88	0.00	0.63	0.00
2PY	3.22	42.45	0.00	0.81	0.00
2PZ	0.00	0.00	77.53	0.00	47.16
3S	2.90	0.06	0.00	2.88	0.00
3PX	9.48	3.82	0.00	0.30	0.00
3PY	1.29	2.33	0.00	0.30	0.00
3PZ	0.00	0.00	21.35	0.00	28.97
4S	4.97	0.42	0.00	88.04	0.00
4PX	1.73	2.75	0.00	3.04	0.00
4PY	0.03	2.51	0.00	3.54	0.00
4PZ	0.00	0.00	0.77	0.00	23.85
5XX	0.03	0.37	0.00	0.00	0.00
5YY	0.00	0.37	0.00	0.00	0.00
5ZZ	0.00	0.00	0.00	0.00	0.00
5XY	0.09	0.03	0.00	0.00	0.00
5XZ	0.00	0.00	0.18	0.00	0.01
5YZ	0.00	0.00	0.17	0.00	0.00

DFT/6-31G**
Five last occupied MOs

	12	13	14	15	16
C1	16.38	14.70	31.69	2.74	2.73
O2	25.83	40.13	47.59	57.62	36.29
C3	20.39	7.68	8.29	11.79	54.30
H4	12.25	10.16	0.00	0.95	0.02
H5	0.72	12.19	0.00	1.53	0.02
C6	10.62	13.63	4.11	21.36	1.71
H7	3.87	0.37	4.17	0.32	2.47
H8	6.03	0.77	0.00	3.36	0.00
H9	3.92	0.37	4.14	0.32	2.47

HF/6-31+G**
Five last occupied MOs

	12	13	14	15	16
C1	19.84	13.23	19.78	16.17	6.42
O2	37.77	17.75	60.39	27.50	29.36
C3	9.34	25.12	5.03	38.11[a]	61.00
H4	2.20	14.27	0.00	0.17	0.02
H5	0.70	12.23	0.00	0.37	0.03
C6	13.86	13.63	6.51	17.00	0.32
H7	2.65	1.70	4.16	0.02	1.43
H8	10.96	0.34	0.00	0.64	0.00
H9	2.68	1.74	4.13	0.02	1.43

[a] Same basis set effect observed for DFT calculations.

Table S3. Cont.

	HF/6-31+G**				
C3 Atomic Orbitals	Five last occupied MOs				
	12	13	14	15	16
1S	0.29	0.00	0.00	0.15	0.00
2S	1.42	0.01	0.00	0.62	0.00
2PX	66.39	37.81	0.00	2.05	0.00
2PY	18.70	30.93	0.00	1.96	0.00
2PZ	0.00	0.00	72.44	0.00	45.28
3S	0.07	0.04	0.00	3.76	0.00
3PX	9.65	9.90	0.00	0.91	0.00
3PY	2.14	7.16	0.00	0.55	0.00
3PZ	0.00	0.00	26.78	0.00	37.72
4S	0.09	11.35	0.00	84.24	0.00
4PX	0.87	0.28	0.00	2.54	0.00
4PY	0.08	1.82	0.00	3.20	0.00
4PZ	0.00	0.00	0.29	0.00	16.95
5XX	0.00	0.32	0.00	0.00	0.00
5YY	0.03	0.33	0.00	0.00	0.00
5ZZ	0.00	0.00	0.00	0.00	0.00
5XY	0.26	0.03	0.00	0.01	0.00
5XZ	0.00	0.00	0.27	0.00	0.04
5YZ	0.00	0.00	0.22	0.00	0.01

	HF/6-31G**				
	Five last occupied MOs				
	12	13	14	15	16
C1	18.30	10.70	21.78	3.15	4.30
O2	39.20	23.08	59.55	64.49	31.29
C3	12.48	17.58	6.28	9.48	59.67
H4	3.98	16.79	0.00	0.92	0.02
H5	0.38	15.68	0.00	1.19	0.02
C6	10.08	13.42	5.28	17.79	0.85
H7	2.88	1.34	3.56	0.29	1.93
H8	9.78	0.03	0.00	2.40	0.00
H9	2.92	1.37	3.53	0.29	1.93

DMSO

	DFT/6-31+G**				
	Five last occupied MOs				
	17	18	19	20	21
S1	38.00	21.52	48.79	3.40	40.61
O2	38.18	4.53	34.24	63.43	36.61
C3	8.37	22.92	3.78	14.57	10.21
H4	1.03	0.46	3.16	0.03	0.75
H5	0.81	12.62	0.13	0.21	0.19
H6	1.72	0.96	1.42	1.77	0.24
C7	8.36	22.92	3.79	14.57	10.21
H8	0.79	12.64	0.13	0.21	0.19
H9	1.03	0.46	3.16	0.03	0.75
H10	1.71	0.98	1.41	1.77	0.24

	HF/6-31+G**				
	Five last occupied MOs				
	17	18	19	20	21
S1	38.42	22.03	39.09	6.13	44.29
O2	37.05	10.84	44.34	61.79	36.73
C3	8.59	21.59	3.89	13.98	8.12
H4	1.45	0.13	2.39	0.01	1.03
H5	0.76	10.89	0.07	0.45	0.16
H6	1.47	0.93	1.93	1.60	0.18
C7	8.59	21.61	3.90	13.99	8.11
H8	0.74	10.90	0.07	0.45	0.17
H9	1.46	0.13	2.39	0.01	1.03
H10	1.46	0.95	1.93	1.60	0.18

Table S4. Cartesian Coordinates for stationary points

SCN^-

C1	0.000000	0.000000	0.637074
N2	0.000000	0.000000	1.819856
S3	0.000000	0.000000	-1.035090

NO_2^-

N1	0.013083	0.000000	-0.056588
O2	0.026637	0.000000	1.207123
O3	1.138074	0.000000	-0.633735

$CH_3COCH_2^-$

C1	0.015835	0.311493	-0.116499
O2	-0.102313	0.762312	1.073236
C3	1.189027	0.083529	-0.826497
H4	2.155147	0.293538	-0.371974
H5	1.174033	-0.303325	-1.842826
C6	-1.315617	-0.013412	-0.835469
H7	-1.934731	0.893181	-0.879033
H8	-1.180424	-0.400820	-1.854380
H9	-1.874434	-0.752590	-0.245272

DMSO

S1	0.084657	0.081765	0.222669
O2	0.193386	0.305735	1.721467
C3	1.799515	-0.044133	-0.422620
H4	2.378825	0.814872	-0.073438
H5	2.222046	-0.964763	-0.015578
H6	1.781616	-0.092847	-1.515221
C7	-0.301962	1.710572	-0.531473
H8	-1.306232	1.980598	-0.199384
H9	0.417976	2.451125	-0.172970
H10	-0.278632	1.629359	-1.621957