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Supporting Information

Atomic Partitioning of M-H_2 Bonds in [NiFe] Hydrogenase-

A Test case of Concurrent Binding

Swaminathan Angeline Vedha, Rajadurai Vijay Solomon, &

Ponnambalam Venuvanalingam

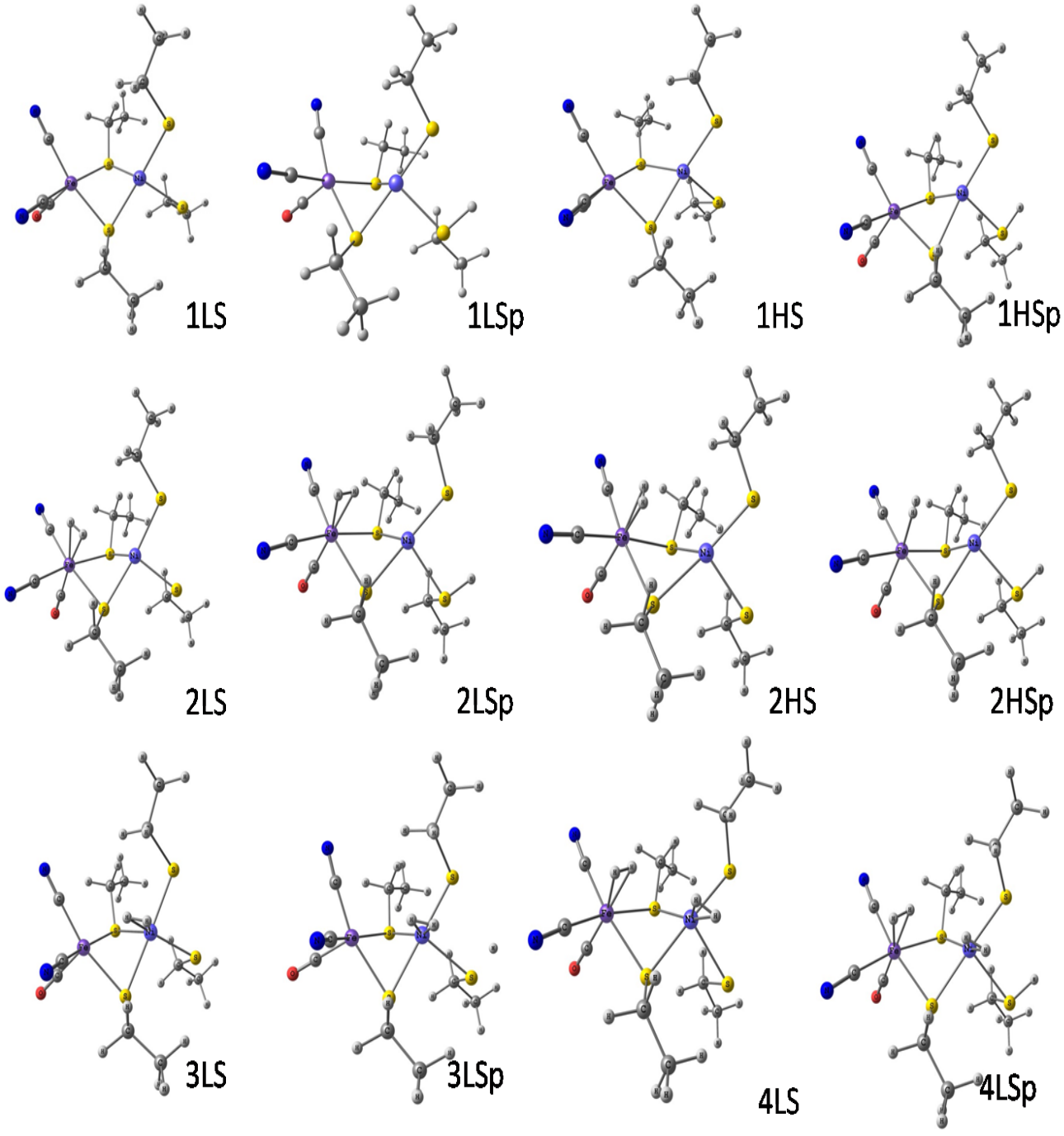
Theoretical and Computational Chemistry Laboratory, School of Chemistry,

Bharathidasan University, Tiruchirappalli – 620024, Tamil Nadu, INDIA

Tel: +91 431 2407053, Fax: +91 431 2407045

E-mail: *venuvanalingam@yahoo.com*

SIF1. Geometries of the twelve cases of the active site of the [NiFe] Hase in the as isolated Ni-SI state.Figure shows Ni in blue, Fe in purple,O in red, S in yellow, Nin deep blue and C & H in ash colors.



Introduction to QTAIM

The Quantum theory of atoms in molecules (QTAIM) is mainly based on electron density $\rho(r)$ and it provides useful insights on the nature of bonding and non-bonding interactions in a chemical system[88, 89]. According to Bader's (QTAIM theory, the presence of (3,-1) bond critical point (*bcp*) between any two atoms is accepted as a criterion for the existence of interactions between them[90, 91]. Further the topological properties at *bcp* namely, electron density $\rho(r)$, its second derivative $\nabla^2\rho(r)$, Kinetic energy density G(r) and the potential energy density V(r) and their signs describes the type and nature of a chemical bond. The molecular graph of the studied systems is given in figure below, where the big spheres correspond to attractors attributed to positions of atoms and critical points such as (3, -1) bond critical point (red) and (3, +1) ring critical point (yellow) & (3,+3) cage critical point (green) indicated by small spheres. The bond ellipticity (ε), which is defined as $(\lambda_1/\lambda_2) - 1$, where λ is the eigen value at the *bcp*, also provides quantitative evidence for the π character of the bond under investigation. When $\varepsilon \rightarrow 0$, the bond belongs to a typical σ bond, and larger is the ε value, stronger will be the π character.

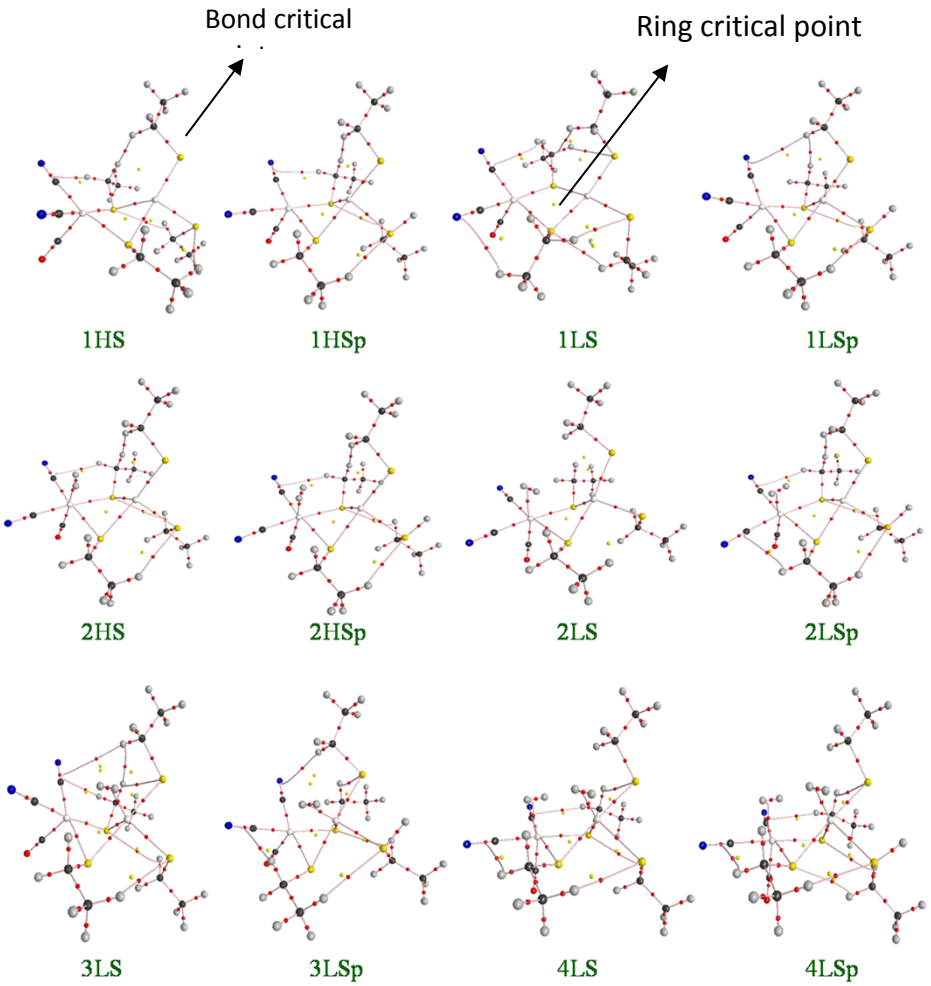


Table 1 Topological properties at the atomic basin of Ni. Computed at the B3LYP/6-311++G with (2d, 2p) polarizations on all atoms.

	Volume @0.01a.u	**Volume @ 0.001a.u**	**ρ(r) (a.u)**	**Energy(a.u)**	**Charge (q in a.u)**
1LS	1.0552e+002	9.4985e+001	2.7392e+001	-1.5090e+003	6.0796e-001
1LSp	1.0778e+002	9.8667e+001	2.7459e+001	-1.5091e+003	5.4026e-001
1HS	1.0596e+002	9.5962e+001	2.7186e+001	-1.5088e+003	8.1340e-001
1HSp	1.1181e+002	1.0136e+002	2.7241e+001	-1.5091e+003	7.5816e-001
2LS	1.0518e+002	9.8198e+001	2.7426e+001	-1.5091e+003	5.7344e-001
2LSp	1.0772e+002	1.0057e+002	2.7263e+001	-1.5091e+003	7.3631e-001
2HS	1.0696e+002	9.9910e+001	2.7229e+001	-1.5091e+003	7.7043e-001
2HSp	1.0531e+002	9.8477e+001	2.7228e+001	-1.5091e+003	7.7115e-001
3LS	8.9656e+001	8.7047e+001	2.7438e+001	-1.5090e+003	5.6176e-001
3LSp	8.5336e+001	8.4547e+001	2.7463e+001	-1.5091e+003	5.3627e-001
4LS	8.6511e+001	8.5533e+001	2.7427e+001	-1.5090e+003	5.7239e-001
4LSp	2.7427e+001	2.7425e+001	2.7427e+001	-1.5090e+003	5.7239e-001

Table 2 Topological properties at the atomic basin of FeComputed at the B3LYP/6-311++G with (2d, 2p) polarizations on all atoms.

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	Volume@0.001 (a.u)	**Volume@0.002 (a.u)**	**Energy(a.u)**	**Charge (q in a.u)**	**ρ(r) (a.u)**
1LS	73.2358	70.21	-1263.96	0.93	25.0658
1LSp	73.2148	71.20	-1264.17	0.90	25.0946
1HS	75.0600	71.75	-1263.95	0.91	25.0908
1HSp	75.2420	72.13	-1264.11	0.92	25.0792
2LS	64.6405	64.1825	-1264.129	0.909	25.0907
2LSp	63.9115	63.52	-1264.09	0.895	25.1044
2HS	64.3881	63.97	-1264.08	0.901	25.0985
2HSp	64.3881	63.97	-1264.08	0.90	25.0985
3LS	70.3595	69.48	-1264.14	0.89	25.1063
3LSp	70.4586	69.32	-1264.16	0.90	25.1040
4LS	64.2546	63.78	-1264.08	0.91	25.0929
4LSp	64.2985	63.83	-1264.16	0.90	25.0970

Table 3. Results of the NBO analysis showing donor and acceptor orbitals with their corresponding interaction energies.In kcal/mol computed at the B3LYP/6-311++G (d, p) level

	Donor NBO(i)	**Acceptor NBO(j)**	$\Delta E_{i\rightarrow j}$
1LS	σ S_3 -Ni_{20}	σ*S_{12} -Ni_{20}	6.41
	σ C_4-H_{27}	σ*C_5 - S_6	4.79
	σ C7-H_{23}	σ*C_8 - S_9	4.69
	σ S_9 -Ni_{20}	σ*S_6-Ni_{20}	5.35
	σ C_{10} -H_{30}	σ*C_{11} - S_{12}	4.94
	σ S_{12} -Ni_{20}	n*Fe_{13}	17.58
	σ S_{12} -Ni_{20}	σ*S_3 -Ni_{20}	5.75
	σ Fe_{13} - C_{14}	σ*Fe_{13} -C_{14}	10.05
	σ Fe_{13} - C_{14}	σ*Fe_{13}-C_{18}	10.48
	σ Fe_{13} - C_{16}	σ*S_{12}-Fe_{13}	7.31
	σ Fe_{13} - C_{18}	σ*Fe_{13}-C_{18}	6.77
	n S_3	σ*S_3-Ni_{20}	4.7
	n Fe_{13}	σ*C_{18} -O_{19}	21.63
	n Fe_{13}	π*C_{18} -O_{19}	24.38
	n Ni_{20}	n*Fe_{13}	5.10
	σ S_{12}-Ni_{20}	n*Fe_{13}	17.58
	σ Fe_{13}-C_{16}	σ*Fe_{13}-C_{16}	10.37
	σ Fe_{13}-C_{16}	σ*Fe_{13}-C_{18}	11.18
	σ Fe_{13}-C_{18}	σ*Fe_{13}-C_{14}	10.21
	σ Fe_{13}-C_{18}	σ*Fe_{13}-C_{16}	10.68
2LS	σ S_6-Ni_{20}	σ*S_9-Ni_{20}	6.88
	σ S_{12}-Fe_{13}	n*Ni_{20}	21.07
	σ Fe_{13}- C_{14}	σ*Fe_{13}-C_{14}	11.68
	σ Fe_{13}- C_{14}	σ*Fe_{13}-C_{18}	10.59
	σ Fe_{13}- C_{18}	σ*Fe_{13} -C_{14}	10.71
	σ Fe_{13}- C_{18}	σ*Fe_{13}-C_{16}	10.28
	n Fe_{13}	σ*C_{18}-O_{19}	19.20
	n Fe_{13}	σ*C_{18}-O_{19}	16.61
	σ Fe_{13}- C_{14}	σ*H_{41}-H_{42}	4.88
	n S_{12}	n*Ni $_{20}$	78.60
	σ S_{12}-Fe_{13}	n*Ni_{20}	21.07
	n Fe_{13}	σ*C_{18}-O_{19}	19.20
	n Fe_{13}	π*C_{18}-O_{19}	16.61
	σ Fe-C_{14}	σ*Fe_{13}-C_{14}	11.68
	n Fe	σ* H_{41}-H_{42}	2.39
3LS	σ S_3-Ni_{20}	σ*S_{12} -Ni_{20}	5.20
	σ S_6-Ni_{20}	n*Fe_{13}	9.35
	σ S_{12} -Ni_{20}	n*Fe_{13}	20.93
	σ Fe_{13}-C_{14}	σ*Fe_{13}-C_{14}	10.00
	σ Fe_{13}-C_{14}	σ*Fe_{13} -C_{16}	5.15
	σ Fe_{13}-C_{14}	σ*Fe_{13}-C_{18}	9.91
	σ Fe_{13}-C_{16}	σ*Fe_{13} -C_{16}	10.46
	σ Fe_{13}-C_{18}	σ*Fe_{13} -C_{16}	9.94
	σ Fe_{13}-C_{18}	σ*Fe_{13} -C_{14}	9.64
	σ Fe_{13}-C_{18}	σ*Fe_{13} -C_{18}	6.24
	n Fe_{13}	σ*C_{18} -O_{19}	22.26
	n Fe_{13}	π*C_{18} -O_{19}	24.83
	n Ni_{20}	n*Fe_{13}	7.17
	n Ni_{20}	σ*S_{12}-Ni_{20}	9.64

	n Ni_{20}	σ*H_{41}-H_{42}	10.46
	σ H_{41}-H_{42}	n*Ni_{20}	93.90
	n Ni_{20}	σ*H_{41}-H_{42}	0.06
	n Ni_{20}	σ*H_{41}-H_{42}	10.46
	n Ni_{20}	σ*H_{41}-H_{42}	0.14
4LS	σ Fe_{13}-C_{14}	σ*Fe_{13}-C_{18}	10.30
	σ Fe_{13}-C_{16}	σ*Fe13-C_{16}	11.89
	σ Fe_{13}-C_{16}	σ*Fe13-C_{18}	10.26
	σ Fe_{13}-C_{16}	π*C_{18}-O_{19}	5.11
	σ Fe_{13}-C_{18}	σ*Fe_{13}-C_{14}	10.67
	σ Fe_{13}-C_{18}	σ*Fe_{13}-C_{16}	10.67
	n Fe_{13}	π*C_{14}-N_{15}	5.46
	n Fe_{13}	σ*C_{18}-O_{19}	15.27
	n Fe_{13}	π*C_{18}-O_{19}	13.66
	σ Fe_{13}-C_{16}	σ*H_{43}-H_{44}	5.41
	σ H_{41}-H_{42}	n*Ni_{20}	73.51
	σ H_{41}-H_{42}	σ*S_3-Ni_{20}	5.15
	σ H_{43}-H_{44}	n*Fe_{13}	132.19
	n Ni_{20}	σ*H_{43}-H_{44}	0.68
	n Ni_{20}	σ*H_{41}-H_{42}	10.12
	n Fe_{13}	σ*H_{43}-H_{44}	1.69
	n Fe_{13}	σ*H_{43}-H_{44}	0.83
	n Fe_{13}	σ*H_{43}-H_{44}	0.08
	σ C_{16}-N_{17}	σ*H_{43}-H_{44}	0.20
	π C_{16}-N_{17}	σ* H_{43}-H_{44}	0.29
	π C_{16} -N_{17}	σ* H_{43}-H_{44}	0.12
	n Ni_{20}	σ*H_{43}-H_{44}	0.19

Table.4. Results of the atomic integrations carried out on all the atoms of 1LS state (a.u) at B3LYP/6-311++G with (2d, 2p) polarizations on all atoms.

ILS	ENERGY	CHARGE	$\rho(r)$	$-\nabla 2\rho(r)$	VOLUME @0.01	VOLUME @0.001
C16	-3.7536e+001	6.1800e-001	5.3819e+0	-9.1037e-003	8.8245e+001	7.7508e+001
N17	-5.5181e+001	-1.2651e+000	8.2651e+0	-1.0024e-003	1.7902e+002	1.3901e+002
	-92.7187	-0.6471			267.2662	
C14	-3.7536e+001	6.1265e-001	5.3873e+0	-9.7590e-003	9.0247e+001	7.8414e+001
N15	-5.5181e+001	-1.2679e+0	8.2679e+0	-1.1514e-003	1.8024e+002	1.3898e+002
	-92.7178	-0.6552			270.50	
C18	-3.7380e+001	9.6097e-001	5.0390e+0	-9.9651e-003	7.1879e+001	6.3968e+001
O19	-7.5933e+001	-1.1647e+00	9.1647e+0	-3.2310e-003	1.3376e+002	1.0804e+002
	-113.3143	-0.2037			205.64	
S12	-3.9839e+002	-3.4582e-001	1.6345e+1	7.3714e-003	1.7613e+002	1.5817e+002
C11	-3.7894e+001	-4.2542e-003	6.0042e+00	-8.3156e-003	6.1173e+001	5.8117e+001
C10	-3.7845e+001	1.2319e-001	5.8768e+00	-8.3350e-003	6.7683e+001	6.0736e+001
H30	-6.3810e-001	-4.8792e-002	1.0487e+00	5.8045e-004	5.3902e+001	4.0679e+001
H31	-6.3569e-001	-4.4866e-002	1.0448e+00	2.8503e-004	5.4154e+001	4.0340e+001
H32	-6.2821e-001	-1.8834e-002	1.0188e+00	4.4902e-004	5.4592e+001	4.0488e+001
H39	-6.2336e-001	1.4327e-002	9.8567e-001	5.1011e-004	4.7686e+001	3.7786e+001
H40	-6.2781e-001	1.5361e-002	9.8463e-001	-1.4061e-004	4.5825e+001	3.8222e+001
	-477.2901	-0.3096			561.15	
S6	-3.9837e+002	-3.6754e-001	1.6367e+01	8.4470e-003	1.7981e+002	1.5968e+002
C5	-3.7899e+001	-2.1994e-002	6.0219e+00	1.1678e-003	6.1290e+001	5.8165e+001
C4	-3.7898e+001	5.5278e-002	5.9447e+00	1.7917e-003	6.8576e+001	6.1560e+001
H27	-6.4134e-001	-6.0088e-002	1.0600e+00	8.8778e-004	5.4542e+001	4.0733e+001
H28	-6.1920e-001	3.8665e-003	9.9613e-001	-5.8473e-005	5.1640e+001	4.0353e+001
H29	-6.3784e-001	-4.6601e-002	1.0466e+00	4.7762e-004	5.4258e+001	4.0438e+001
H37	-6.2898e-001	2.4515e-003	9.9754e-001	7.7038e-004	4.9179e+001	3.8240e+001
H38	-6.2462e-001	1.3678e-002	9.8632e-001	2.0959e-004	4.8945e+001	3.7912e+001
	-477.3253	-0.4209			568.25	
S9	-3.9830e+002	-4.4728e-001	1.6447e+01	7.7608e-003	2.3846e+002	1.9414e+002
C7	-3.7872e+001	1.0153e-001	5.8984e+00	-8.0623e-003	6.7076e+001	6.0334e+001
C8	-3.7853e+001	3.1195e-002	5.9688e+00	-6.5341e-003	6.1897e+001	5.8025e+001
H21	-6.3550e-001	-4.2655e-002	1.0426e+00	5.3394e-004	5.4689e+001	4.0378e+001
H22	-6.3736e-001	-4.7279e-002	1.0472e+00	5.0596e-004	5.4913e+001	4.0617e+001
H23	-6.3811e-001	-5.3547e-002	1.0535e+00	3.3103e-004	5.4417e+001	4.0366e+001
H35	-6.4157e-001	-2.8814e-002	1.0288e+00	8.0251e-004	5.1434e+001	3.8974e+001
H36	-6.3553e-001	-1.5332e-002	1.0153e+00	-2.5600e-004	5.0335e+001	3.9415e+001
	-477.2186	-0.5021			633.22	
S3	-3.9832e+002	-4.4518e-001	1.6445e+01	-3.1898e-003	2.3285e+002	1.9121e+002
C2	-3.7839e+001	3.6651e-002	5.9633e+00	-3.1537e-003	5.9268e+001	5.6314e+001
C1	-3.7870e+001	6.2530e-002	5.9374e+00	-9.1454e-003	6.8288e+001	6.1396e+001
H24	-6.2944e-001	-3.1592e-002	1.0315e+00	-5.2412e-004	5.3885e+001	4.0148e+001
H25	-6.3498e-001	-3.9422e-002	1.0394e+00	7.4187e-004	5.3876e+001	4.0589e+001
H26	-6.4348e-001	-7.1825e-002	1.0718e+00	6.3313e-004	5.5710e+001	4.1790e+001
H34	-6.3190e-001	-2.1667e-003	1.0021e+00	6.9590e-004	4.7155e+001	3.8033e+001
H33	-6.3555e-001	-9.8434e-003	1.0098e+00	5.9303e-004	4.9852e+001	3.9578e+001
	-477.2130	-0.5008			620.90	
Fe	-1.2641e+003	9.0725e-001	2.5092e+01	-4.0083e-004	7.5513e+001	7.2631e+001
Ni	-1.5091e+003	5.5632e-001	2.7443e+01	-8.5709e-003	1.1095e+002	1.0071e+002

Table5. Results of the atomic integrations carried out on all the atoms of 3LS state B3LYP/6-311++G with (2d, 2p) polarizations on all atoms.

	ENERGY (a.u)	CHARGE(q)(in a.u)	ρ(r) in (a.u)	$-\nabla 2\rho(r)$
C16	-3.7539e+1	6.1656e-001	5.3834e+000	-9.0908e-005
N17	-5.5235e+1	-1.3277e+000	8.3277e+000	-7.9045e-005
C14	-3.7539e+001	6.2213e-001	5.3778e+000	1.6244e-004
N15	-5.5234e+001	-1.3227e+000	8.3227e+000	-2.8524e-004
C18	-3.7389e+001	9.5552e-001	5.0444e+000	-1.4572e-004
O19	-7.5882e+001	-1.1786e+000	9.1786e+000	1.0077e-003
S12	-3.9839e+002	-3.6083e-001	1.6360e+001	2.4316e-003
C11	-3.7919e+001	-3.84885e-002	6.0384e+000	6.7247e-004
C10	-3.7889e+001	6.1922e-002	5.9380e+000	7.8677e-004
H30	-6.3821e-001	-5.2921e-002	1.0529e+000	2.7411e-004
H31	-6.3556e-001	-4.6274e-002	1.0462e+000	1.7442e-005
H32	-6.2723e-001	-1.7674e-002	1.0176e+000	2.6465e-004
H39	-6.2301e-001	1.5441e-002	9.8455e-001	1.3763e-004
H40	-6.2579e-001	1.7384e-002	9.8261e-001	1.2409e-004
S6	-3.9838e+002	-3.4468e-001	1.6344e+001	2.5413e-003
C5	-3.7906e+001	-2.6682e-002	6.0266e+000	1.7169e-004
C4	-3.7896e+001	5.8883e-002	5.9411e+000	5.5970e-004
H27	-6.3939e-001	-5.7688e-002	1.0576e+000	2.1420e-004
H28	-6.1900e-001	2.7920e-003	9.9720e-001	1.8562e-004
H29	-6.3505e-001	-4.0863e-002	1.0408e+000	2.5947e-004
H37	-6.2857e-001	5.1172e-004	9.9948e-001	3.0610e-004
H38	-6.2346e-001	1.7181e-002	9.8281e-001	1.7851e-004
S9	-3.9832e+002	1.5441e-002	9.8455e-001	1.3763e-004
C7	-3.7901e+001	6.5881e-002	5.9341e+000	1.9558e-004
C8	-3.7903e+001	-2.9288e-002	6.0292e+000	4.3756e-004
H21	-6.3358e-001	-3.7388e-002	1.0373e+000	2.6959e-004
H22	-6.3552e-001	-4.3670e-002	1.0436e+000	2.7737e-004
H23	-6.3816e-001	-5.2812e-002	1.0528e+00	2.3600e-004
H35	-6.4032e-001	-3.0791e-002	1.0307e+000	1.7770e-004
H36	-6.2946e-001	4.0570e-004	9.9959e-001	2.0074e-004
S3	-3.9833e+002	-4.2442e-001	1.6424e+001	2.9099e-003
C2	-3.7886e+001	-2.1367e-002	6.0213e+000	8.0529e-004
C1	-3.7879e+001	5.5072e-002	5.9449e+000	1.4485e-004
H24	-6.3478e-001	-4.2594e-002	1.0425e+000	3.2959e-004
H25	-6.3422e-001	-4.0809e-002	1.0408e+000	3.0639e-004
H26	-6.4086e-001	-6.5252e-002	1.0652e+000	3.4688e-004
H34	-6.3009e-001	1.3577e-004	9.9986e-001	2.0186e-004
H33	-6.3302e-001	-3.8334e-003	1.0038e+000	2.0727e-004
Fe	-1.2641e+003	8.9313e-001	2.5106e+001	-2.9376e-003
Ni	-1.5090e+003	5.6176e-001	2.7438e+001	-1.2633e-003
H41	-5.7905e-001	-1.3858e-002	1.0138e+000	1.5455e-004
H42	-5.9019e-001	-1.8419e-002	1.0184e+000	1.9501e-004

Table.6 Results of the atomic integrations carried out on all the atoms of 2LS state B3LYP/6-311++G with (2d, 2p) polarizations on all atoms.

	Energy (a.u)	Charge(q in a.u)	ρ(r) in a.u	$-\nabla 2\rho(r)$
C16	-3.7536e+001	6.2835e-001	5.3716e+000	-1.9221e-004
N17	-5.5238e+001	-.3284e+000	8.3284e+000	-2.0154e-004
	-92.7753			
C14	-3.7536e+001	6.2044e-001	5.3795e+000	-1.1654e-004
N15	-5.5232e+001	-1.3192e+00	8.3192e+000	-6.3873e-005
	-92.7686			
C18	-3.7364e+001	1.0069e+000	4.9930e+000	-1.9567e-004
O19	-7.5905e+001	-1.1683e+00	9.1683e+000	9.5673e-004
	-113.2708			
S12_brdg	-3.9840e+002	-3.8426e-001	1.6384e+001	2.2916e-003
C11	-3.7915e+001	-3.8062e-002	6.0380e+000	5.9230e-004
C10	-3.7888e+001	6.5252e-002	5.9347e+000	1.3195e-003
H30	-6.3810e-001	-5.1472e-002	1.0514e+000	3.1064e-004
H31	-6.3447e-001	-4.1704e-002	1.0417e+000	2.1869e-004
H32	-6.2712e-001	-1.7415e-002	1.0174e+000	2.1593e-004
H39	-6.2480e-001	7.0523e-003	9.9294e-001	1.7348e-004
H40	-6.3107e-001	5.7833e-003	9.9421e-001	2.6930e-004
	-477.3688			
S6_brdg	-3.9836e+002	-3.6345e-001	1.6363e+001	2.9615e-003
C5	-3.7857e+001	3.2970e-002	5.9670e+000	-6.1376e-003
C4	-3.7897e+001	5.7140e-002	5.9428e+000	7.1261e-004
H27	-6.3920e-001	-5.7212e-002	1.0572e+000	2.2841e-004
H28	-6.1688e-001	8.3496e-003	9.9165e-001	2.7286e-004
H29	-6.3357e-001	-3.7505e-002	1.0375e+000	2.4001e-004
H37	-6.2046e-001	2.2070e-002	9.7792e-001	2.7156e-004
H38	-6.3110e-001	-8.0772e-003	1.0080e+000	2.0820e-004
	-477.2653			
S9	-3.9830e+002	-4.6874e-001	1.6468e+001	1.7997e-003
C7	-3.7902e+001	6.6807e-002	5.9331e+000	-8.7084e-004
C8	-3.7887e+001	-2.1007e-002	6.0210e+000	1.0727e-003
H21	-6.32783e-001	-3.7072e-002	1.0370e+000	2.7689e-004
H22	-6.3486e-001	-4.2753e-002	1.0427e+000	2.9411e-004
H23	-6.3952e-001	-5.8348e-002	1.0583e+000	2.9494e-005
H35	-6.4286e-001	-3.7186e-002	1.0371e+000	1.7094e-004
H36	-6.3851e-001	-2.3578e-002	1.0235e+000	2.1779e-004
	-477.2864			
S3	-3.9834e+002	-4.4165e-001	1.6441e+001	2.1221e-003
C2	-3.7881e+001	-2.2395e-002	6.0223e+000	-3.0771e-005
C1	-3.7879e+001	5.6383e-002	5.9436e+000	-1.4627e-004
H24	-6.3390e-001	-3.8648e-002	1.0386e+000	2.9839e-004
H25	-6.3370e-001	-3.7838e-002	1.0378e+000	2.3634e-004
H26	-6.4067e-001	-6.5309e-002	1.0653e+000	3.4697e-004
H34	-6.2859e-001	5.3181e-003	9.9468e-001	2.0631e-004
H33	-6.3268e-001	-3.6944e-003	1.0036e+000	1.8816e-004
	-477.2784			
Fe	-1.2641e+003	9.0899e-001	2.5091e+001	-5.6179e-005
Ni20	-1.5091e+003	5.7344e-001	2.7426e+001	-1.3468e-003
H41	-5.8461e-001	2.6558e-002	9.7344e-001	2.2065e-004
H42	-5.9630e-001	-1.5313e-002	1.0153e+000	1.6993e-004
	-1.1809			

Table.7 Results of the atomic integrations carried out over all the atoms of 4LS state B3LYP/6-311++G with (2d, 2p) polarizations on all atoms.

	Energy(a.u)	Charge(q in a.u)	ρ(r) in a.u	$-\nabla 2\rho(r)$
C16	-3.7536e+001	6.1674e-001	5.3832e+000	-7.6890e-003
N17	-5.5221e+001	-1.3165e+0	8.3165e+0	-1.4037e-003
C14	-3.7530e+001	6.3707e-001	5.3629e+000	-7.7785e-003
N15	-5.5206e+001	-1.2883e+000	8.2883e+000	-3.5253e-005
C18	-3.7351e+001	1.0130e+000	4.9869e+000	-8.9518e-003
O19	-7.5888e+001	-1.1465e+000	9.1465e+000	-2.2240e-003
S12_brdg	-3.9840e+002	-3.3530e-001	1.6335e+001	4.1121e-003
C11	-3.7889e+001	-3.0361e-004	6.0003e+000	-4.9672e-003
C10	-3.7844e+001	1.3223e-001	5.8677e+000	-6.1391e-003
H30	-6.4221e-001	-5.8754e-002	1.0587e+000	7.3912e-004
H31	-6.3360e-001	-3.6759e-002	1.0367e+000	2.1105e-004
H32	-6.2674e-001	-1.6737e-002	1.0167e+000	3.9122e-004
H39	-6.1829e-001	2.1798e-002	9.7820e-001	-1.3147e-003
H40	-6.2479e-001	1.33915e-002	9.8660e-001	-1.3461e-003
S6_brdg	-3.9837e+002	-3.3754e-001	1.6337e+001	4.0039e-003
C5	-3.7864e+001	2.7071e-002	5.9729e+000	-5.2519e-003
C4	-3.7894e+001	6.1983e-002	5.9380e+000	-1.1791e-003
H27	-6.4549e-001	-6.7415e-002	1.0674e+000	8.1565e-004
H28	-6.1977e-001	1.0950e-003	9.9890-001	-6.3854e-005
H29	-6.3427e-001	-3.4076e-002	1.0340e+000	6.0816e-004
H37	-6.1881e-001	2.4588e-002	9.7541e-001	-1.6763e-004
H38	-6.3309e-001	-1.6215e-002	1.0162e+000	-3.6465e-004
S9	-3.9833e+002	-3.9921e-001	1.6399e+001	3.7372e-003
C7	-3.7854e+001	1.4262e-001	5.8573e+000	-2.3069e-003
C8	-3.7863e+001	3.6656e-002	5.9633e+000	-6.7299e-003
H21	-6.3342e-001	-3.4397e-002	1.0343e+000	6.2475e-004
H22	-6.3671e-001	-4.2979e-002	1.0429e+000	9.7836e-004
H23	-6.4317e-001	-6.2975e-002	1.0629e+000	3.7863e-004
H35	-6.4614e-001	-4.5279e-002	1.0452e+000	7.3319e-004
H36	-6.3902e-001	-2.7305e-002	1.0273e+000	2.1068e-004
S3	-3.9831e+002	-5.3192e-001	1.6531e+001	-1.6467e-003
C2	-3.7852e+001	2.8199e-002	5.9718e+000	-4.9907e-003
C1	-3.7830e+001	1.3774e-001	5.8622e+000	-3.2860e-003
H24	-6.3703e-001	-4.3202e-002	1.0432e+000	8.4822e-004
H25	-6.3573e-001	-4.3293e-002	1.0432e+000	7.3804e-004
H26	-6.4930e-001	-8.2177e-002	1.0821e+000	6.2367e-004
H34	-6.3546e-001	-5.3485e-003	1.0053e+000	2.5154e-004
H33	-6.36800e-001	-8.5319e-003	1.0085e+000	1.5030e-005
Fe	-1.2640e+003	9.0675e-001	2.5093e+001	-3.6933e-003
Ni	-1.5090e+003	5.7239e-001	2.7427e+001	-2.1234e-003
H41	-6.0071e-001	-4.4204e-002	1.0442e+000	-2.2405e-005
H42	-5.7409e-001	1.5119e-002	9.8488e-001	1.8152e-004
H43(Fe)	-5.9607e-001	-1.0975e-002	1.0109e+000	1.7408e-004
H44(Fe)	-5.8848e-001	2.1251e-002	9.7874e-001	2.1160e-004

Table.8 H-H *bcp* properties computed at B3LYP/6-31g(f) for Fe,6-311g++(2d,2p) for Ni and 6-31g(d) on all other atoms

System	**Ellipticity**	**ρ(r) in a.u**	**G(r)**	$-\nabla 2\rho(r)$	**V(r)**
2HS	3.0984e-002	2.2566e-001	1.0555e-002	1.9773e-001	2.1884e-001
2HSp	5.8201e-002	5.9924e-002	4.7541e-002	-3.2206e-002	6.2876e-002
2LS	2.8263e-002	2.2650e-001	9.9426e-003	2.0130e-001	2.2118e-001
2LSp	3.1664e-002	2.2557e-001	1.0237e-002	1.9799e-001	2.1846e-001
3LS	3.0226e-002	2.1055e-001	1.5097e-002	1.6410e-001	1.9429e-001
3LSp	2.5754e-002	2.2153e-001	9.2918e-003	1.9394e-001	2.1252e-001
4LS(Ni)	1.9344e-002	2.2358e-001	1.1267e-002	1.9716e-001	2.1970e-001
4LS(Fe)	2.8469e-002	2.2740e-001	9.9225e-003	2.0273e-001	2.2257e-001
4LSp(Fe)	2.8867e-002	2.2731e-001	9.6609e-003	2.0296e-001	2.2228e-001
4LSp(Ni)	2.3267e-00	2.2412e-001	9.5373e-003	1.9933e-001	2.1841e-001

Table.9 Topological properties at the *bcps* between Fe & CN

Fe-C	Ellipticity	ρ(r) (a.u)	G(r)	K(r)	$-\nabla 2\rho(r)$	V(r)
2HS	1.1235e-001	1.1776e-001	1.2498e-001	4.0002e-002	-8.4980e-002	1.6498e-001
2HSp	8.2613e-002	1.2261e-001	1.2669e-001	4.4643e-002	-8.2050e-002	1.7133e-001
2LS	1.4221e-001	1.1744e-001	1.2354e-001	3.9769e-002	-8.3771e-002	1.6331e-001
2LSp	8.4798e-002	1.2218e-001	1.2645e-001	4.4234e-002	-8.2222e-002	1.7069e-001
3LS	4.3700e-002	1.1276e-001	1.2244e-001	3.7411e-002	-8.5029e-002	1.5985e-001
3LSp	4.3700e-002	1.1276e-001	1.2244e-001	3.7411e-002	-8.5029e-002	1.5985e-001
4LS(Ni)	5.7303e-002	1.1364e-001	1.2289e-001	3.8071e-002	-8.4820e-002	1.6096e-001
4LS(Fe)	5.5810e-002	1.1516e-001	1.1948e-001	3.9506e-002	-7.9979e-002	1.5899e-001
4LSp(Fe)	8.0862e-002	1.1487e-001	1.2285e-001	3.8779e-002	-8.4072e-002	1.6163e-001
4LSp(Ni)	1.0061e-001	1.2103e-001	1.2533e-001	4.3354e-002	-8.1978e-002	1.6868e-001
2HS	3.3739e-002	1.1497e-001	1.2543e-001	3.8884e-002	-8.6545e-002	1.6431e-001
2HSp	3.6236e-002	1.1602e-001	1.2280e-001	3.9907e-002	-8.2893e-002	1.6270e-001

Table.10 Topological properties at the *bcps* between C & N in proximal CN group

C-N	Ellipticity	Rho(r) (a.u)	G(r) (a.u)	K(r) (a.u)	$-\nabla 2\rho(r)$ (a.u)	V(r) (a.u)
1hs	2.6605e-003	4.6170e-001	7.0857e-001	8.1346e-001	1.0489e-001	1.5220e
1hsp	5.9265e-003	4.7556e-001	7.1331e-001	8.8273e-001	1.6942e-001	1.5960
1ls	1.9167e-003	4.6870e-001	7.3648e-001	8.3223e-001	9.5752e-002	1.5687
1lsp	6.3157e-003	4.7525e-001	7.1170e-001	8.8185e-001	1.7014e-001	1.5935
2hs	8.5102e-004	4.7544e-001	7.0774e-001	8.8280e-001	1.7506e-001	1.5905
2hsp	8.5102e-004	4.7544e-001	7.0774e-001	8.8280e-001	1.7506e-001	1.5905
2ls	1.2077e-003	4.7543e-001	7.0690e-001	8.8265e-001	1.7574e-001	1.5895
2lsp	2.5593e-004	4.7455e-001	7.1495e-001	8.8044e-001	1.6548e-001	1.5954
3ls	5.5695e-003	4.7446e-001	7.0038e-001	8.7963e-001	1.7924e-001	1.5800
3lsp	7.5575e-003	4.7512e-001	7.0924e-001	8.8135e-001	1.7211e-001	1.5905
4ls	1.4147e-003	4.7719e-001	7.1305e-001	8.8773e-001	1.7468e-001	1.6007
4lsp	9.2965e-004	4.7640e-001	7.1833e-001	8.8556e-001	1.6723e-001	1.6039

Table.11 Natural spin densities at the triplet cases computed at B3LYP/6-311++G (d, p) level.

	1HS	1HSp	2HS	2HSp
Fe	0.005	0.181	0.111	-0.009
Ni	1.399	-0.003	-0.001	1.416
S	0.103	-0.005	0.249	0.097
S	0.144	-0.007	0.097	0.249
S	0.079	0.000	0.121	0.121
S	0.245	-0.009	0.111	0.111
Total Spin density	2.000	2.000	2.00	2.000
Spin contamination <s2> value	2.0083	2.0114	2.0094	2.0097
Spin assigned to Fe	αß	αß	αß	αß
Spin assigned to Ni	αßαα	αßαα	αßαα	αßαα
Net Charge of the complex	-2	-1	-2	-1

Table.12 Relative energies of the 12 states and their total charges computed at the B3LYP/6-311++G with (2d, 2p) polarizations on all atoms.

	1HS	1HSp	1LS	1LSp	2HS	2HSp	2LS	2LSp	3LS	3LSp	4LS	4LSp
CHARGE	**-2**	**-1**	**-2**	**-1**	**-2**	**-1**	**-2**	**-1**	**-2**	**-1**	**-2**	**-1**
MULTIPLICIY	**3**	**3**	**1**	**1**	**3**	**3**	**1**	**1**	**1**	**1**	**1**	**1**
RELATIVE ENERGY (IN Hatree)	**-0.73024**	**0**	-0.7489	**-0.0105**	**0.5772**	**1.1835**	**0.5605**	**0.5541**	**0.5595**	**1.1715**	**1.7235**	**2.3474**

Results of the computations carried out at B3LYP/LANL2DZ.

Figure.1 Plot of ρ(r) at the M-H_2*bcp* (represented in black) and at the H-H *bcp* (represented in red).where ρ(r) values are in a.u

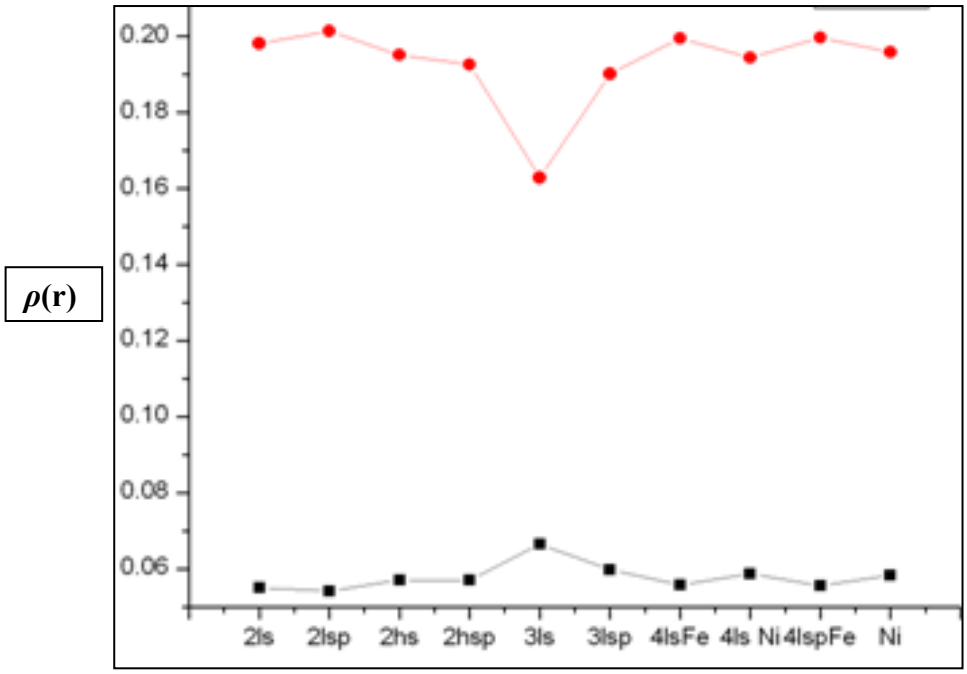


Figure.2 Volume of Ni atom at an isodensity surface of 0.001 a.u ,X-axis is volume of the Ni atom in au^3

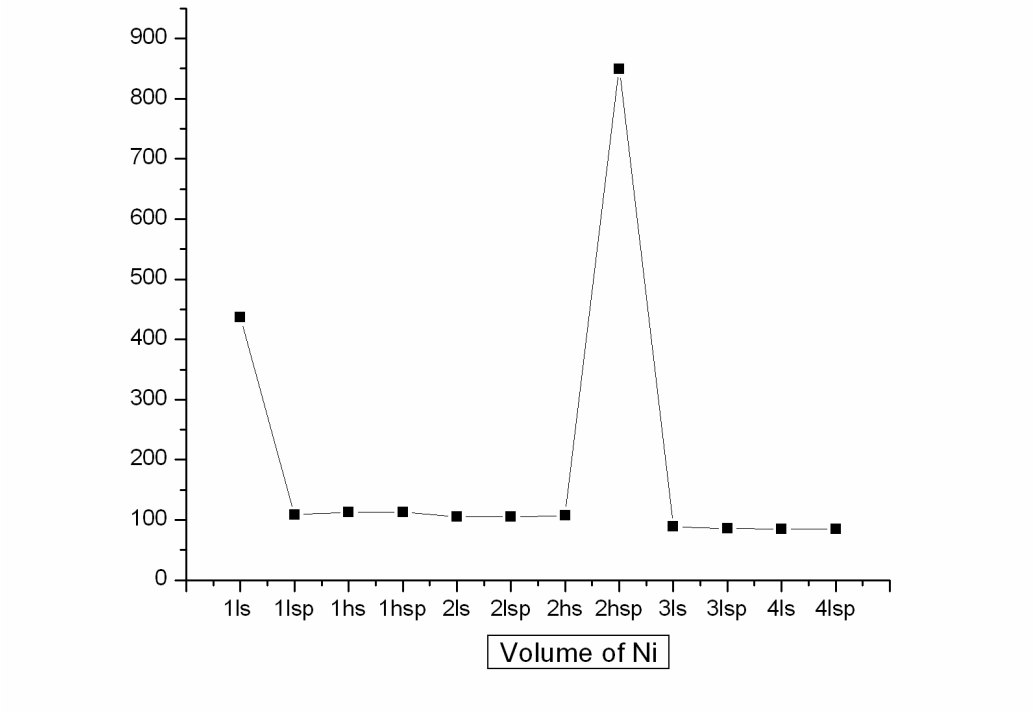


Figure.3 Electron density ρ(r) at the Fe atom at the various states. X-axis represents ρ(r)values in eÅ^{-3}

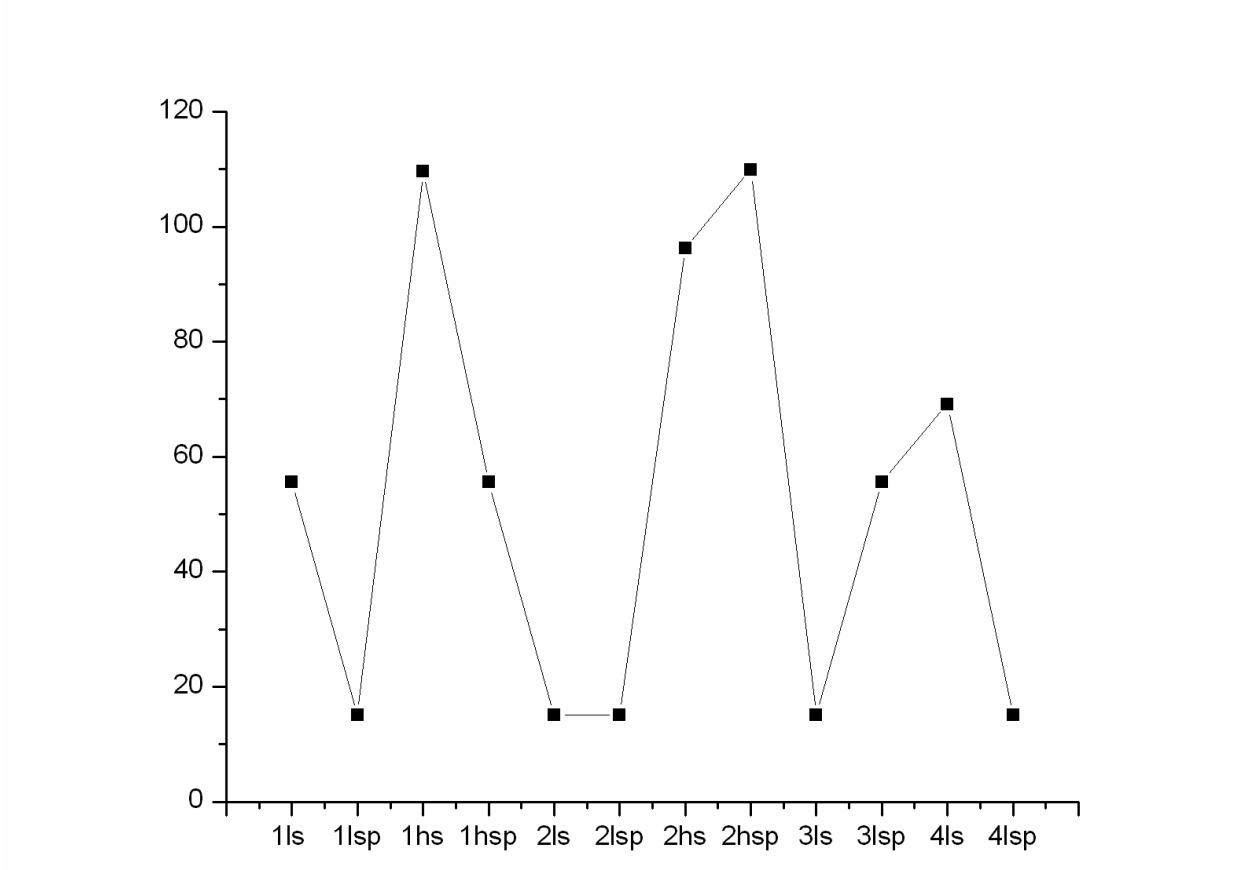
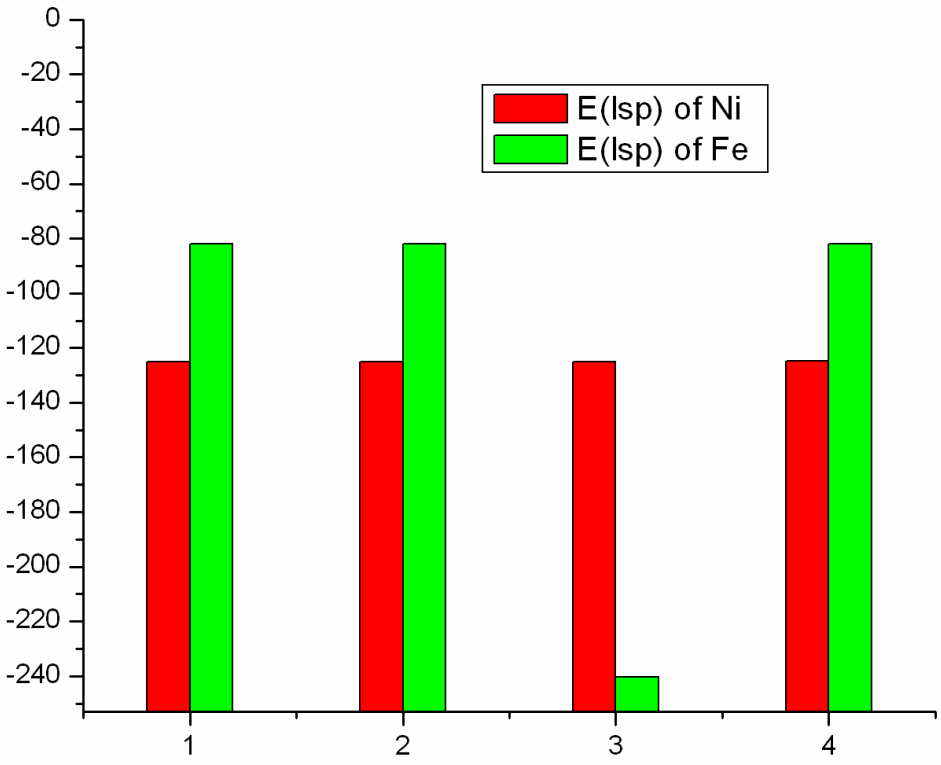


Figure.4 Energy of the atomic basins of Fe in green and Ni in red in the lowspin protonated cases. x-axis represents the energy at the atomic basins ΔE(Ω) in a.u



References:

[88] R. F. W. Bader, *Acc. Chem. Res.* **1985**, *18*, 9-15.

[89] R. F. W. Bader, *Atoms in Molecules – A Quantum Theory*, Oxford University Press, New York, **1990**.

[90] R. Bader, *J. Phys. Chem. A* **1998**, *102*, 7314-7323.

[91] R. F. W. Bader, *Chem. Rev.* **1991**, *91*, 893-928.