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Molecular mechanics based study of molecular orbitals of ferrous halides

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ABSTRACT

LCAO approximation studies of iron halides have been made to study the quantitative nature of contribution of 3d, 4s, and 4p atomic orbitals in the formation of molecular orbital. The contribution of electrons in each occupied molecular orbitals have been calculated by adopting population analysis method of Mulliken. The bonding, non-bonding, and anti-bonding nature of molecular orbitals have been identified by the overlap population analysis. The results indicate that in bonding between iron and halogens, $3d_{xz}$ and $3d_{yz}$ orbitals of iron are the main contributors, $3d_{z^2}$ are the next and the 4p orbitals have the negligible role. The non-bonding orbitals in all the four iron halides are 9th and 10th molecular orbitals. The magnitude of splitting of d orbitals as evaluated by eigenvalues and eigenvector values indicates the following order: $FeBr_2 > FeCl_2 > FeI_2 > FeI_2$

KEYWORDS

Iron (II) halides;
Population analysis;
Eigenvalues;
Eigenvector;
Overlap matrix.

INTRODUCTION

In the recent years Landis[1-4] and others[5, 6] have considered only ns and (n-1) d orbitals as valence orbitals of the transition metals. They have ignored the involvement of np orbitals. It has been shown that in hybridization only s and d orbitals are involved. They have also described the hybridization angles and idealized molecular shapes of sd, sd^2, sd^3, sd^4 and sd^5 hybridizations[7-9]. The restriction to valence s and d functions of transition metals suggested by Landis[2-4] means that 12 electron will fill the transition metal valence shell rather than the 18 electrons that can be accommodated if np orbitals were also part of the valence shell. This is astonishing in the light of 18e rule of transition metal compounds. In support of the hypothesis of 12-electron valence space, Landis presented the result of DFT calculation of transition metal hydride[2-4]. He also gave the results of an NBO analysis of the transition metal-hydrogen bonds, which shows dominantly sd^n hybridized bond orbitals and negligible np participation[2]. However, there is a serious technical flaw in the analysis. The NBO method requires preselection of those orbitals, which are considered as valence orbitals, and may become occupied in the population analysis.

In the last decade, there has been a phenomenal advancement in theoretical inorganic chemistry. Commercial programs incorporating the latest methods have become widely available, and are capable of providing more information about molecular orbitals with a simple input of chemical formula. The focus of attention, has been on computational transition-metal chemistry[10,11]. This is largely due to the successful employment of gradient corrected density functional theory in calculating molecule; particularly of the heavier atoms[12-15] and in the use of small-core relativistic effective core potential[16-18] which set the stage for calculation of geometries, bond energies, and chemical reaction and other

important properties of transition metal compounds with impressive accuracy[15,19,20]. Application of molecular mechanics to organometallic and transition metal compounds is growing[21]. Molecular orbital parameters such as eigenvectors, overlap matrix and eigenvalues are well calculated with this method. In this paper we present the calculations of eigenvalues, eigenvector, overlap matrix and population analysis of ferrous halides, in order to study the extent of contribution of 3d, 4s and 4p orbitals in the formation of molecular orbitals. Such a quantitative study will provide correct information about the involvement of 4p orbital of iron in bonding.

EXPERIMENTAL

Techniques described in our earlier paper[22] have been adopted in this paper also.

RESULTS AND DISCUSSION

TABLE 1(a)

Eigen vector values of molecular orbitals of ferrous fluoride

Atom no.	Atom(χ)	Eigen vector values of atomic orbitals																
		AO,s	MO-1	MO-2	MO-3	MO-4	MO-5	MO-6	MO-7	MO-8	MO-9	MO-10	MO-11	MO-12	MO-13	MO-14	MO-15	MO-16	MO-17
1	Fe	4s	0.0260	0.0000	0.0812	0.0002	0.0237	0.0000	0.0000	0.0000	0.0000	0.0473	0.0000	0.2271	-0.0005	-0.7730	0.0000	-0.6999	0.0053
		4px	-0.0017	-0.0021	0.0037	-0.0119	0.0165	0.0000	0.0000	-0.0115	0.0000	0.0203	0.0000	0.0377	-0.1156	0.5023	0.0004	-0.6695	0.6653
		4py	-0.0012	-0.0028	-0.0027	-0.0159	-0.0124	0.0000	0.0000	-0.0155	0.0000	-0.0152	0.0000	-0.0281	-0.1549	-0.3736	-0.0003	0.5080	0.8838
		4pz	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	-0.0209	0.0000	0.0128	0.0000	0.0001	0.0000	0.0000	0.0003	-1.0063	-0.0004	0.0000
		$3dx^2-y^2$	-0.0042	0.0268	-0.0272	-0.1557	0.0239	0.0000	0.0000	0.0134	0.0001	-0.1741	0.0004	0.2222	0.9326	0.0312	0.0000	0.0404	0.2451
		$3dz^2$	-0.0181	0.0000	-0.0907	-0.0002	-0.0250	0.0000	0.0000	0.0000	-0.0008	0.7890	0.0000	0.5832	-0.0008	0.1080	0.0000	0.1818	-0.0015
		3dxy	0.0142	0.0080	0.0928	-0.0462	-0.0801	0.0000	0.0000	0.0040	-0.0004	0.5840	0.0001	-0.7400	0.2793	-0.1047	0.0000	-0.1304	0.0745
		3dxz	0.0000	0.0000	0.0000	0.0000	0.0000	0.0623	-0.0506	0.0000	-0.7994	-0.0007	-0.5975	-0.0001	0.0002	0.0000	-0.0129	-0.0001	0.0001
		3dyz	0.0000	0.0000	0.0000	-0.0001	0.0000	0.0831	0.0381	0.0000	0.5986	0.0005	-0.7980	0.0001	0.0004	0.0000	0.0095	0.0001	0.0001
2	F	2s	0.7009	0.7045	-0.0319	0.0229	-0.0056	0.0000	0.0000	0.0350	0.0000	0.0070	0.0000	0.0308	-0.0579	0.0816	0.0000	0.2907	-0.3091
		2px	0.0034	0.0007	-0.6708	0.5459	0.1079	-0.0002	0.0002	0.4165	0.0000	0.0062	0.0000	-0.1236	0.1107	-0.1217	0.0000	-0.2193	0.2567
		2py	0.0006	0.0011	-0.1044	0.4039	-0.6900	0.0002	0.0002	-0.5679	0.0000	-0.0775	0.0000	0.0554	0.1233	0.0174	0.0000	-0.1499	0.6110
		2pz	0.0000	0.0000	-0.0002	0.0001	0.0002	0.7011	-0.6992	0.0003	0.0718	0.0000	0.1210	-0.0001	0.0000	0.0000	0.0969	0.0000	0.0001
3	F	2s	0.6992	-0.7062	-0.0317	-0.0230	-0.5700	0.0000	0.0000	-0.0035	0.0000	0.0071	0.0000	0.0309	0.0579	0.0817	0.0000	0.0000	0.3043
		2px	0.0004	0.0008	-0.0929	0.2289	0.6905	0.0002	0.0002	-0.6655	0.0000	0.0759	0.0000	-0.0881	0.0863	-0.0515	0.0000	0.0805	-0.1600
		2py	-0.0034	0.0010	0.6685	0.6427	0.0961	-0.0002	-0.0002	0.2367	0.0000	0.0164	0.0000	0.1027	0.1412	0.1117	0.0000	0.2563	0.2596
		2pz	0.0000	0.0000	-0.0002	0.0001	0.0002	-0.6956	-0.7048	-0.0003	0.0722	0.0000	-0.1203	-0.0001	0.0000	0.0000	0.0967	0.0000	-0.0001

TABLE 1(b)

Eigen vector values of molecular orbitals of ferrous chloride

Atom no.	Atom (χ)	AO,s	Eigen vector values or coefficients of atomic orbital																
			MO-1	MO-2	MO-3	MO-4	MO-5	MO-6	MO-7	MO-8	MO-9	MO-10	MO-11	MO-12	MO-13	MO-14	MO-15	MO-16	MO-17
1	Fe	4s	0.0793	-0.0000	-0.2048	0.0157	-0.0000	-0.0000	-0.0000	0.0000	0.1372	-0.0000	-0.0000	-0.2090	-0.0001	0.6092	0.0000	-0.0122	1.0375
		4px	0.0107	0.0169	-0.0003	0.0351	0.0292	-0.0000	0.0000	-0.0389	0.0324	-0.0000	-0.0000	0.2440	0.1349	-0.6295	-0.0004	0.7431	0.6631
		4py	0.0079	0.0227	0.0003	-0.0261	0.0393	0.0000	-0.0000	-0.0523	-0.2420	0.0000	0.0000	-0.0184	0.1810	0.4684	0.0003	1.0147	-0.4744
		4pz	0.0000	-0.0000	-0.0000	0.0000	-0.0000	0.0002	-0.0601	0.0000	0.0000	0.0509	0.0001	0.0000	-0.0000	-0.0004	1.0246	-0.0000	0.0004
		$3dx^2\_y^2$	-0.0089	0.0623	0.3440	0.1056	0.4323	-0.0002	0.0000	0.1450	-0.0644	0.0001	0.0004	-0.2543	-0.8280	-0.0361	-0.0000	0.2781	-0.0368
		$3dz^2$	-0.0395	0.0000	0.1586	-0.0124	0.0000	-0.0000	-0.0002	-0.0000	0.9542	-0.0008	0.0000	-0.2025	-0.0001	-0.0722	0.0000	0.0024	-0.2047
		3dxy	0.0299	0.0187	-0.1149	-0.3516	0.1295	-0.0000	-0.0001	0.0434	0.2155	-0.0004	0.0001	0.8520	-0.2471	0.1206	0.0000	0.0816	0.1358
		3dxz	0.0000	0.0000	-0.0001	0.0001	0.0001	0.2481	-0.2267	0.0000	-0.0007	-0.7695	-0.5481	-0.0002	-0.0002	-0.0000	0.0373	0.0001	0.0001
		3dyz	-0.0000	0.0000	0.0000	-0.0001	0.0002	0.3312	0.1706	0.0001	0.0005	-0.0000	-0.7347	0.0001	-0.0003	-0.0000	-0.0277	0.0001	-0.0001
2	Cl	3s	0.6808	0.6932	0.1020	0.0018	-0.0615	0.0000	0.0000	0.0055	0.0140	-0.0000	-0.0000	-0.0206	0.0517	-0.0395	0.0000	-0.3864	-0.4116
		3px	0.0092	0.0135	0.5452	0.2103	-0.5013	-0.0002	0.0002	0.3881	-0.0331	-0.0001	-0.0001	0.1803	-0.1897	0.2091	0.0001	0.5264	0.5301
		3py	0.0003	0.0089	0.2296	-0.5809	-0.2958	0.0002	-0.0002	-0.5687	-0.0956	0.0001	0.0001	-0.2611	-0.3233	-0.0979	-0.0001	0.1173	0.3052
		3pz	0.0000	0.0000	0.0001	0.0002	-0.0001	0.6180	0.6497	0.0003	0.0000	0.2322	0.3614	0.0001	0.0000	0.0001	-0.2175	0.0002	0.0001
3	Cl	3s	0.6801	-0.6940	0.1019	0.0019	0.0614	-0.0000	0.0000	-0.0055	0.0139	-0.0000	-0.0000	-0.0206	-0.0518	-0.0396	0.0000	0.3957	-0.4015
		3px	0.0025	0.0047	-0.0636	0.6162	-0.1403	0.0002	0.0002	-0.6569	0.0820	-0.0001	0.0001	0.3019	-0.2547	0.1535	0.0001	-0.0350	-0.1411
		3py	-0.0095	0.0155	-0.5879	-0.0352	-0.5652	-0.0002	-0.0002	0.2088	0.0593	0.0001	-0.0001	-0.0974	-0.2748	-0.1723	-0.0001	0.5518	-0.5816
		3pz	0.0000	-0.0000	0.0001	0.0002	0.0001	-0.6130	-0.6546	-0.0003	0.0000	0.2328	-0.3607	0.0001	-0.0000	0.0001	-0.2172	-0.0002	0.0001

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TABLE 1(c)

Eigen vector values of molecular orbitals of ferrous bromide

Atom no.	Atom (χ)	AO,s	Eigen vector values or coefficients of atomic orbitals																
			MO-1	MO-2	MO-3	MO-4	MO-5	MO-6	MO-7	MO-8	MO-9	MO-10	MO-11	MO-12	MO-13	MO-14	MO-15	MO-16	MO-17
1	Fe	4s	0.0977	-0.0000	0.2120	0.0000	0.0787	-0.0000	0.0000	0.0000	0.1633	0.0000	0.0000	-0.2151	0.0000	0.6544	-0.0000	0.0437	0.9007
		4px	0.0162	0.0224	0.0032	-0.0189	0.0360	0.0000	0.0000	0.0449	0.0349	0.0000	0.0000	0.0166	0.1268	-0.5900	0.0004	-0.6812	0.6862
		4py	-0.0121	0.0301	-0.0024	-0.0254	-0.0269	-0.0000	-0.0000	0.0604	-0.0260	-0.0000	-0.0000	-0.0125	0.1703	0.4391	-0.0003	-0.9814	-0.4383
		4pz	0.000	-0.0000	0.0000	0.0000	0.0000	-0.0000	-0.0509	-0.0000	0.0000	-0.0512	-0.0000	0.0000	-0.0000	-0.0003	-1.0144	0.0000	0.0004
		$3dx^2\_y^2$	-0.0116	0.0804	-0.0716	-0.5417	0.1362	0.0002	0.0001	-0.0987	-0.0630	-0.0001	-0.0004	-0.2319	-0.7707	-0.0305	0.0000	-0.2414	-0.0245
		$3dz^2$	-0.0517	0.0000	-0.2510	-0.0000	-0.1153	0.0000	-0.0004	0.0000	0.9240	0.0007	-0.0000	-0.2181	-0.0000	-0.0805	-0.0000	-0.0088	-0.1809
		3dxy	0.0390	0.0241	0.2394	-0.1621	-0.4552	0.0001	-0.0002	-0.0296	0.2105	0.0004	-0.0001	0.7747	-0.2307	0.1020	-0.0000	-0.0659	0.1243
		3dxz	0.0000	0.0000	0.0001	-0.0001	0.0002	-0.3401	-0.3851	-0.0000	-0.0006	0.7043	0.4939	-0.0002	-0.0002	0.0000	-0.0240	-0.0001	0.0001
		3dyz	-0.0000	0.0000	-0.0001	-0.0002	-0.0002	-0.4563	0.2870	0.0000	0.0005	-0.5246	0.6630	0.0001	-0.0003	-0.0000	0.0178	-0.0001	-0.0001
2	Br	4s	0.6775	0.6899	-0.1156	0.0826	-0.0142	-0.0000	0.0000	-0.0099	0.0067	0.0000	0.0000	-0.0146	0.0479	-0.0564	-0.0000	0.3116	-0.3567
		4px	0.0072	0.0104	-0.5408	0.4266	0.0879	0.0002	0.0002	-0.4298	-0.0626	0.0001	0.0002	0.2466	-0.2551	0.2210	-0.0001	-0.4641	0.5061
		4py	0.0020	0.0050	-0.1272	0.3049	-0.5672	-0.0002	-0.0002	0.5411	-0.1749	-0.0001	-0.0001	-0.3177	0.3472	-0.0562	0.0001	-0.1032	0.2861
		4pz	0.0000	0.0000	-0.0002	0.0001	0.0002	-0.5494	-0.5943	-0.0003	0.0000	-0.3622	-0.4514	0.0002	0.0000	0.0001	0.1794	-0.0001	0.0001
3	Br	4s	0.6770	-0.6904	-0.1156	-0.0826	-0.0143	0.0000	0.0000	0.0099	0.0067	0.0000	0.0000	-0.0146	-0.0479	-0.0564	-0.0000	-0.3446	-0.3246
		4px	0.0002	0.0018	-0.0333	0.1694	0.5685	-0.0002	0.0002	0.6420	0.1495	0.0001	-0.0002	0.3750	-0.2592	0.1172	-0.0001	0.0217	-0.1315
		4py	-0.0075	0.0114	0.5543	0.4962	0.0790	0.0002	-0.0002	-0.2566	0.1102	-0.0001	0.0001	-0.1449	-0.3441	-0.1956	0.0001	-0.5268	-0.5181
		4pz	0.0000	-0.0000	-0.0002	-0.0001	0.0002	0.5486	-0.5951	0.0003	0.0000	-0.3625	0.4510	0.0002	0.0000	0.0001	0.1793	0.0002	0.0001

TABLE 1(d)

Eigen vectors values of molecular orbitals of ferrous iodide

Atom no.	Atom (χ)	AO,s	Eigen vector values or coefficients of atomic orbital																
			MO-1	MO-2	MO-3	MO-4	MO-5	MO-6	MO-7	MO-8	MO-9	MO-10	MO-11	MO-12	MO-13	MO-14	MO-15	MO-16	MO-17
1	Fe	4s	-0.1390	-0.0000	-0.2089	-0.0000	0.0871	-0.0000	0.0000	0.0000	0.1767	-0.0000	0.0000	0.2041	0.0000	0.6716	-0.0000	-0.8511	-0.0794
		4px	-0.0219	0.0317	-0.0065	0.0191	0.0330	0.0000	0.0000	0.0453	0.0350	-0.0000	0.0000	-0.0135	0.1208	-0.5744	0.0004	-0.5833	-0.7547
		4py	0.0163	0.0425	0.0049	0.0257	-0.0246	-0.0000	-0.0000	0.0608	-0.0260	0.0000	-0.0000	0.0101	0.1623	0.4274	-0.0003	0.5690	-0.8881
		4pz	-0.0000	-0.0000	-0.0000	-0.0000	0.0000	-0.0000	-0.0407	-0.0000	0.0000	0.0513	-0.0000	-0.0000	-0.0000	-0.0003	-1.0103	-0.0004	-0.0000
		$3dx^2\_y^2$	-0.0180	0.1264	0.0808	0.5876	0.1583	0.0003	0.0001	-0.1017	-0.0518	0.0001	-0.0003	0.2172	-0.7327	-0.0261	0.0000	0.0511	-0.2037
		$3dz^2$	0.0801	0.0000	0.2857	0.0001	-0.1751	0.0000	-0.0005	0.0000	0.9055	-0.0006	-0.0000	0.2132	-0.0000	-0.0777	-0.0000	0.1579	0.0147
		3dxy	-0.0602	0.0379	-0.2699	0.1759	-0.5286	0.0001	-0.0003	-0.0305	0.1730	-0.0003	-0.0001	-0.7252	-0.2194	0.0873	-0.0000	-0.1009	-0.0719
		3dxz	-0.0000	0.0000	-0.0001	0.0002	0.0003	-0.3951	-0.5001	-0.0000	-0.0006	-0.6276	0.4501	0.0002	-0.0002	0.0000	-0.0172	-0.0000	-0.0001
		3dyz	0.0000	0.0000	0.0001	0.0002	-0.0002	-0.5302	0.3727	-0.0000	0.0005	0.4675	0.6043	-0.0001	-0.0003	-0.0000	0.0128	0.0001	-0.0001
2	I	5s	-0.6620	0.6810	0.1610	-0.1157	-0.0204	0.0000	-0.0000	-0.0097	0.0030	-0.0000	0.0000	0.0136	0.0574	-0.0726	-0.0000	0.2957	0.3362
		5px	0.0132	0.0041	0.5247	-0.4082	0.0661	0.0002	0.0002	-0.4268	-0.0768	-0.0002	0.0002	-0.2736	-0.2859	0.2240	-0.0001	-0.4242	-0.5085
		5py	0.0057	0.0017	0.1204	-0.2808	-0.5311	-0.0001	-0.0002	0.5442	-0.2198	0.0001	-0.0001	0.3535	-0.3588	-0.0340	0.0000	-0.2542	-0.1415
		5pz	0.0000	0.0000	0.0001	-0.0001	-0.0002	-0.4995	-0.5281	-0.0003	0.0000	0.4565	-0.5045	-0.0002	0.0000	0.0001	0.1567	-0.0001	-0.0001
3	I	5s	-0.6614	-0.6816	0.1609	0.1157	-0.0204	0.0000	-0.0000	0.0097	0.0030	-0.0000	0.0000	0.0136	-0.0574	-0.0726	-0.0000	0.3525	-0.2757
		5px	-0.0016	0.0004	0.0353	-0.1516	0.5276	-0.0002	0.0002	0.6441	0.1884	-0.0002	-0.0002	-0.4171	-0.2614	0.0968	0.0001	0.1177	0.0326
		5py	-0.0143	0.0044	-0.5370	-0.4718	0.0894	0.0001	-0.0002	-0.2527	0.1367	0.0001	0.0001	0.0160	-0.3769	-0.2048	0.0000	0.5683	-0.4300
		5pz	0.0000	-0.0000	0.0002	0.0001	0.0002	0.4988	-0.5288	0.0003	0.0000	0.4570	0.5041	-0.0002	0.0000	0.0001	0.1566	-0.0001	0.0001

Iron (II) halides are triatomic molecules having the following optimized geometry as obtained by DFT method.

The molecular orbitals of FeX_2 (X= F, Cl, Br, I) are formed by linear combination of 9 iron orbitals and 4 orbitals from each halogen. The details of the valence orbitals involved in the formation of MOs are as detailed below:

Fe-1 = 4s, $4p_x$, $4p_y$, $4p_z$, $3d_{x^2-y^2}$, $3d_{z^2}$, $3d_{xy}$, $3d_{xz}$, $3d_{yz}$ = 9

X-2 = ns, np_x, np_y, np_z = 4

X-3 = ns, np_x, np_y, np_z = 4

Total =17

Where, n =2 for F, 3 for Cl, 4 for Br, and 5 for I.

In order to examine the contribution of various AOs in the formation of MOs, the LCAO has been studied. The 17 AOs give the LCAO approximation to the 17 MOs of iron halides. The various AOs orbitals are represented by χ and MOs by ϕ. 1-9 χ are atomic orbitals of iron and 10-17 χ are atomic orbitals of halogens (χ_1=4s, χ_2=$4p_x$, χ_3=$4p_y$, χ_4= $4p_z$, χ_5 = $3d_{x^2-y^2}$, χ_6 =$3d_{z^2}$, χ_7=$3d_{xy}$, χ_8=$3d_{xz}$, χ_9 = $3d_{yz,}$ χ_{10}= ns, χ_{11} =np_x, χ_{12} = np_y, χ_{13} = np_z for X-2 and χ_{14} = ns, χ_{15} = np_x, χ_{16} = np_y, χ_{17} = np_z for X-3.

The forms of the 17 MOs that is the magnitude of contribution of various AOs in the formation of MOs of the halides are demonstrated in the TABLE 1a-d. In this TABLE, the coefficient of χ is the eigenvector value.

In order to examine the extent of involvement of 3d, 4s, and 4p orbitals in the formation of molecular orbitals, the value of coefficient of these orbitals have been separately tabulated for each molecular orbital and are given in TABLE 2. To see the total involvement in the molecular orbital ($\phi_1\phi_{11}$) the coefficient values of each orbital have been added. The summation values

TABLE 2

Coefficient values of 3dxy, 3dyz, 3dxz, $3d^2$-y^2, $3dz^2$, 4s, 4px, 4py, 4pz orbitals

MO,s	Ferrous Halides	3dxy	3dxz	3dyz	$3dx^2$-y^2	$3dz^2$	4s	4px	4py	4pz
$\phi_?$	Ferrous fluoride	0.0142	0.0000	0.0000	0.0042	0.0181	0.0260	0.0017	0.0012	0.0000
	Ferrous chloride	0.0299	0.0000	0.0000	0.0089	0.0395	0.0793	0.0107	0.0079	0.0000
	Ferrous bromide	0.0390	0.0000	0.0000	0.1160	0.0517	0.0977	0.0162	0.0121	0.0000
	Ferrous iodide	0.0602	0.0000	0.0000	0.0180	0.0801	0.1390	0.0219	0.0163	0.0000
ϕ_2	Ferrous fluoride	0.0080	0.0000	0.0000	0.0268	0.0000	0.0000	0.0021	0.0028	0.0000
	Ferrous chloride	0.0187	0.0000	0.0000	0.0623	0.0000	0.0000	0.0169	0.0227	0.0000
	Ferrous bromide	0.0241	0.0000	0.0000	0.0804	0.0000	0.0000	0.0224	0.0301	0.0000
	Ferrous iodide	0.0379	0.0000	0.0000	0.1264	0.0000	0.0000	0.0317	0.0425	0.0000
ϕ_3	Ferrous fluoride	0.0928	0.0000	0.0000	0.0272	0.0907	0.0812	0.0037	0.0027	0.0000
	Ferrous chloride	0.1149	0.0001	0.0000	0.0344	0.1586	0.2048	0.0003	0.0003	0.0000
	Ferrous bromide	0.2394	0.0001	0.0001	0.0716	0.2510	0.2120	0.0032	0.0024	0.0000
	Ferrous iodide	0.2699	0.0001	0.0001	0.0808	0.2857	0.2089	0.0065	0.0049	0.0000
ϕ_4	Ferrous fluoride	0.0462	0.0000	0.0001	0.1557	0.0002	0.0002	0.0119	0.0159	0.0000
	Ferrous chloride	0.3516	0.0001	0.0001	0.1056	0.0124	0.0157	0.0351	0.0261	0.0000
	Ferrous bromide	0.1621	0.0001	0.0002	0.5417	0.0000	0.0000	0.0189	0.0254	0.0000
	Ferrous iodide	0.1759	0.0002	0.0002	0.5876	0.0001	0.0000	0.0191	0.0257	0.0000
ϕ_5	Ferrous fluoride	0.0801	0.0000	0.0000	0.0239	0.0250	0.0237	0.0165	0.0124	0.0000
	Ferrous chloride	0.1295	0.0001	0.0002	0.4323	0.0000	0.0000	0.0292	0.0393	0.0000
	Ferrous bromide	0.4552	0.0002	0.0002	0.1362	0.1153	0.0787	0.0360	0.0269	0.0000
	Ferrous iodide	0.5286	0.0030	0.0002	0.1583	0.1751	0.0871	0.0330	0.0246	0.0000
ϕ_6	Ferrous fluoride	0.0000	0.0623	0.0831	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001
	Ferrous chloride	0.0000	0.2481	0.3312	0.0002	0.0000	0.0000	0.0000	0.0000	0.0002
	Ferrous bromide	0.0001	0.3401	0.4563	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000
	Ferrous iodide	0.0001	0.3951	0.5302	0.0003	0.0000	0.0000	0.0000	0.0000	0.0000
ϕ_7	Ferrous fluoride	0.0000	0.0506	0.0381	0.0000	0.0000	0.0000	0.0000	0.0000	0.0209
	Ferrous chloride	0.0001	0.2267	0.1706	0.0000	0.0002	0.0000	0.0000	0.0000	0.0601
	Ferrous bromide	0.0002	0.3851	0.2870	0.0001	0.0004	0.0000	0.0000	0.0000	0.0509
	Ferrous iodide	0.0003	0.5000	0.3727	0.0001	0.0005	0.0000	0.0000	0.0000	0.0407
ϕ_8	Ferrous fluoride	0.0040	0.0000	0.0000	0.0134	0.0000	0.0000	0.0115	0.0155	0.0000
	Ferrous chloride	0.0434	0.0000	0.0055	0.1450	0.0000	0.0000	0.0389	0.0523	0.0000
	Ferrous bromide	0.0296	0.0000	0.0000	0.0987	0.0000	0.0000	0.0449	0.0604	0.0000
	Ferrous iodide	0.0305	0.0000	0.0000	0.1017	0.0000	0.0000	0.0453	0.0608	0.0000
ϕ_9	Ferrous fluoride	0.0004	0.7994	0.5986	0.0001	0.0008	0.0000	0.0000	0.0000	0.0128
	Ferrous chloride	0.2155	0.0007	0.0005	0.0644	0.9542	0.1372	0.0324	0.0242	0.0000
	Ferrous bromide	0.2105	0.0006	0.0005	0.0630	0.9240	0.1633	0.0349	0.0260	0.0000
	Ferrous iodide	0.1730	0.0006	0.0005	0.0518	0.9055	0.0177	0.0350	0.0260	0.0000
$\phi_{??}$	Ferrous fluoride	0.5840	0.0007	0.0005	0.1741	0.7890	0.0473	0.0203	0.0152	0.0000
	Ferrous chloride	0.0004	0.7695	0.5741	0.0001	0.0008	0.0000	0.0000	0.0000	0.0509
	Ferrous bromide	0.0004	0.7043	0.5246	0.0001	0.0007	0.0000	0.0000	0.0000	0.0512
	Ferrous iodide	0.0003	0.6276	0.4675	0.0001	0.0006	0.0000	0.0000	0.0000	0.0513
$\phi_{??}$	Ferrous fluoride	0.0001	0.5975	0.7980	0.0004	0.0000	0.0000	0.0000	0.0000	0.0001
	Ferrous chloride	0.0001	0.5481	0.7347	0.0004	0.0000	0.0000	0.0000	0.0000	0.0001
	Ferrous bromide	0.0001	0.4939	0.6630	0.0004	0.0000	0.0000	0.0000	0.0000	0.0000
	Ferrous iodide	0.0001	0.4501	0.6043	0.0003	0.0000	0.0000	0.0000	0.0000	0.0000
	Summation									
	Ferrous fluoride	0.8296	1.5105	1.5184	0.4258	0.9238	0.1784	0.0677	0.0657	0.0339
	Ferrous chloride	0.9041	1.8294	1.8110	0.8536	1.1657	0.4370	0.1635	0.1728	0.1113
	Ferrous bromide	1.1607	1.9244	1.9319	1.0040	1.3431	0.5517	0.1785	0.1833	0.1021
	Ferrous iodide	1.2804	1.9741	1.9757	1.1254	1.4476	0.6117	0.1925	0.2008	0.0920

of $(\phi_1\phi_{11})$ have been placed at the bottom of the TABLE and it clearly indicates that maximum involvement is of $3d_{yz}$ and the minimum is of 4pz orbital. The involvement of p orbital is negligible. It has the value of coefficient in between 0.2008 to 0.0339. It is very low in comparison to all the five d-orbitals, which is in the range of

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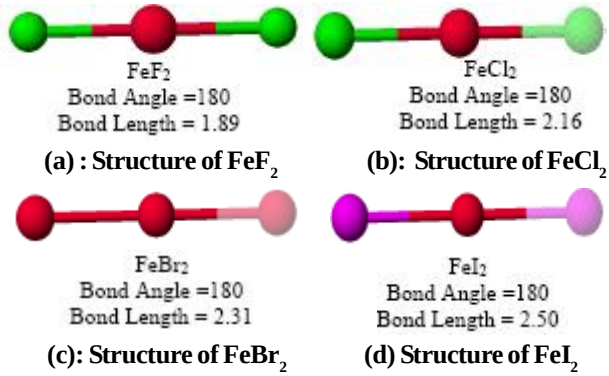

(a) : Structure of FeF_2 (b): Structure of $FeCl_2$

(c): Structure of $FeBr_2$ (d) Structure of FeI_2

Figure 1

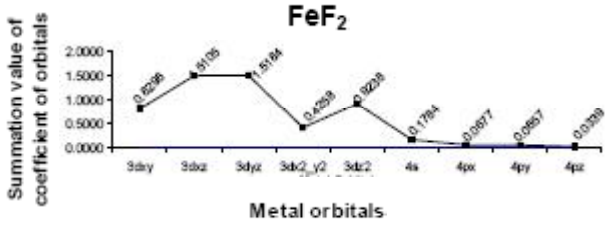

Figure 2 : Extent of involvement of molecular orbital in the formation of MOs of FeF_2

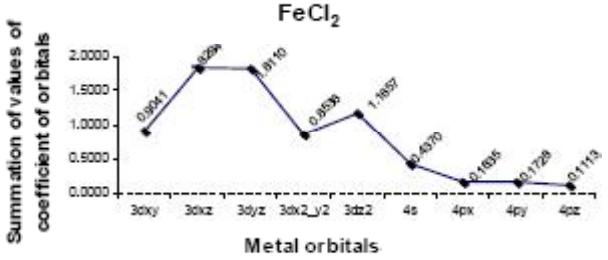

Figure 3: Extent of involvement of molecular orbital in the formation of MOs of $FeCl_2$

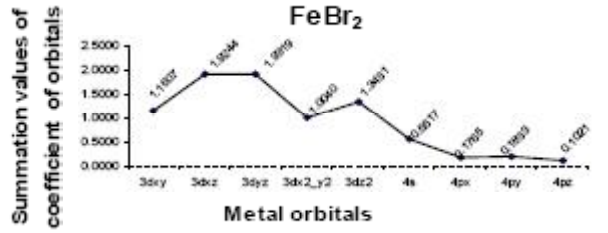

Figure 4 : Extent of involvement of molecular orbital in the formation of MOs of $FeBr_2$

1.9757 to 0.4258. The value of s orbital is in between 0.6117 to 0.1784. The extent of involvement of various iron orbitals in the formation of MO in FeF_2, $FeCl_2$, $FeBr_2$ and FeI_2 are very well demonstrated by the TABLE 2 and also by graphs (figures 2, 3, 4, and 5) drawn between the metal orbitals and the summation value of their coefficient or eigenvector. The graph again

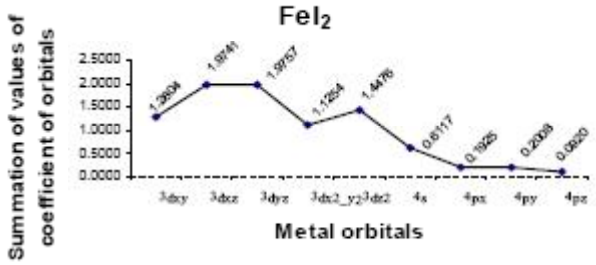

Figure 5 : Extent of involvement of molecular orbital in the formation of MOs of FeI_2

TABLE (S-1)

Summation of coefficient values of orbitals

Orbitals	FeF_2	$FeCl_2$	$FeBr_2$	FeI_2
3dxy	0.8296	0.9041	1.1607	1.2804
3dxz	1.5105	1.8294	1.9244	1.9741
3dyz	1.5184	1.8110	1.9319	1.9757
$3dx^2\_y^2$	0.4258	0.8536	1.0040	1.1254
$3dz^2$	0.9238	1.1657	1.3431	1.4476
4s	0.1784	0.4370	0.5517	0.6117
4px	0.0677	0.1635	0.1765	0.1925
4py	0.0657	0.1728	0.1833	0.2008
4pz	0.0339	0.1113	0.1021	0.0920

indicates that involvement of p orbital is negligible. The summations of coefficient values of various orbitals are highest in case of iodide and lowest in fluoride. It is perhaps on this account the splitting of d orbitals as discussed later is maximum in iodide and minimum in fluoride.

Population analysis

The population analysis method, introduced by Mulliken is applied to calculate the contribution of electrons in each occupied MO. This method apportions the electron of n- electron molecule into net population, n_r in the basic function χ_r.

Suppose, n_i represent the number of electron in MO ϕ_i (where n_i =0,1,2) and $n_{r,i}$ represent the contribution of electron in the MO ϕ_i to the net population χ_r, then-

$$\mathbf{n_{ri} = n_i c_{ri}^2} \quad \textbf{(1)}$$

where c_{ri} is the coefficient of atomic orbitals for the ith MO (r =1-17).

Equation (1) has been solved for 22 electrons of 11 molecular orbitals, each having 2 electrons. The six molecular orbitals having no electrons are left out. The data relating to c_{ri} have been taken from TABLE 1a-d. The results of solution of equation (1) are included in TABLE 3a-d, which enlist the contribution of electrons in molecular orbitals under two heads: major and mi-

TABLE 3(a)

Contribution of electrons in MO of FeF_2

MO no.(i)	n_i	Major contribution		Minor contribution	
		Basic functions(c_r)	$n_{r,i}=n_i c^2_{ri}$	Basic functions(c_r)	$n_{r,i}=n_i c^2_{ri}$
1	2	4s(Fe 1)	0.0014	$3dz^2$(Fe-1)	0.0006
	2	2s(F 2)	0.9825	-	-
	2	2s(F 3)	0.9778	-	-
2	2	$3dx^2\_y^2$(Fe 1)	0.0014	-	-
	2	2s(F-2)	0.9926	-	-
	2	2s(F 3)	0.9974	-	-
3	2	3dxy(Fe 1)	0.0172	$3dz^2$(Fe-1)	0.0165
	2	-	-	4s(Fe 1)	0.0132
	2	-	-	4py(Fe-1)	0.0015
	2	2px(F-2)	0.8999	2py(F-2)	0.0218
	2	-	-	2s(F-2)	0.002
	2	2py(F-3)	0.8938	2px(F-3)	0.0173
	2	-	-	2s(F 3)	0.002
4	2	$3dx^2\_y^2$(Fe 1)	0.0485	3dxy(Fe 1)	0.0043
	2	2px(F-2)	0.596	2py(F-2)	0.3263
	2	2py(F-3)	0.8938	2px(F-3)	0.0173
5	2	3dxy(Fe-1)	0.0128	-	-
	2	2py(F-2)	0.9522	2px(F-2)	0.0233
	2	2px(F-3)	0.9536	2py(F-3)	0.0185
6	2	3dyz(Fe-1)	0.0138	3dxz(Fe-1)	0.0078
	2	2pz(Fe-2)	0.9831	-	-
	2	2pz(Fe-3)	0.9677	-	-
7	2	3dxz(Fe-1)	0.0051	3dyz(Fe-1)	0.0029
	2	2pz(Fe-2)	0.9778	-	-
	2	2pz(Fe-3)	0.9935	-	-
8	2	4py(Fe-1)	0.0005	$3dx^2\_y^2$(Fe 1)	0.0004
	2	2py(F-2)	0.645	2px(F-2)	0.3469
	2	2px(F-3)	0.8858	2py(F-3)	0.1121
9	2	3dxz(Fe-1)	-	3dyz(Fe-1)	0.7166
	2	-	-	4pz(Fe-1)	0.0003
	2	2pz(F-2)	0.0103	-	-
	2	2pz(F-3)	0.0104	-	-
10	2	$3dz^2$(Fe-1)	0.0125	3dxz(Fe-1)	0.6821
	2	-	-	$3dx^2\_y^2$(Fe 1)	0.0606
	2	-	-	4s(Fe 1)	0.0045
	2	2py(F-2)	0.012	-	-
	2	2px(F-3)	0.0115	2py(F-3)	0.0005
11	2	3dyz(Fe-1)	1.2736	3dxz(Fe-1)	0.0005
	2	2pz(F-2)	0.0293	-	-
	2	2pz(F-3)	0.0289	-	-

nor. It is evident that major contribution is from 3d and 4s orbitals. The p orbitals have negligible contribution.

Besides contribution of electrons, the Mullikens method is also used for evaluating overlap population in order to distinguish bonding, non-bonding and anti-bonding molecular orbitals. This method allocates proportionally the overlap population $n_{r\text{-}s}$ for all possible pairs of basic function, which is shown by equation (2).

$$\mathbf{n_{r\text{-}s\text{-}i} = n_i\,(2.c_{ri}.c_{si}\,S_{rs})} \qquad \mathbf{(2)}$$

where c_{ri} = the coefficient of atomic orbitals for one atom; c_{si} = the coefficient of atomic orbitals for other atom; S_{rs} = the overlap integral between the two atomic orbitals (one from an atom and one from other atom).

TABLE 3(b)

Contribution of electrons in MO of $FeCl_2$

MO no.(i)	n_i	Major contribution		Minor contribution	
		Basic functions(c_r)	$n_{r,i}=n_i c^2_{ri}$	Basic functions(χ_r)	$n_{r,i}=n_i c^2_{ri}$
1	2	4s(Fe-1)	0.0126	$3dz^2$(Fe-1)	0.0031
	2	-	-	3dxy(Fe-1)	0.0018
	2	3s(Cl-2)	0.9270	-	-
	2	3s(Cl-3)	0.9251	-	-
2	2	$3dx^2\_y^2$(Fe 1)	0.0078	4py(Fe-1)	0.0010
	2	-	-	3dxy(Fe-1)	0.0007
	2	3px(Cl-2)	0.9611	3px(Cl-2)	0.0004
	2	3s(Cl-3)	0.9633	3px(Cl-3)	0.0005
3	2	4s(Fe-1)	0.0839	$3dz^2$(Fe-1)	0.0503
	2	-	-	3dxy(Fe-1)	0.0264
	2	3px(Cl-2)	0.5945	3py(Cl-2)	0.1054
	2	-	-	3s(Cl-2)	0.0208
	2	3py(Cl-3)	0.6913	3s(Cl-3)	0.0208
	2	-	-	3px(Cl-3)	0.0081
4	2	3dxy(Fe-1)	0.2472	$3dx^2\_y^2$(Fe 1)	0.0223
	2	-	-	4px(Fe-1)	0.0025
	2	3py(Cl-2)	0.6749	3px(Cl-2)	0.0885
	2	3px(Cl-3)	0.7594	3py(Cl-3)	0.0025
5	2	$3dx^2\_y^2$(Fe 1)	0.3738	3dxy(Fe-1)	0.0335
	2	-	-	4py(Fe-1)	0.0031
	2	3px(Cl-2)	0.5945	3py(Cl-2)	0.1054
	2	-	-	3s(Cl-2)	
	2	3py(Cl-3)	0.6913	3px(Cl-3)	0.0208
6	2	3dyz(Fe-1)	0.2194	3dxz(Fe-1)	0.1231
	2	3pz(Cl-2)	0.7638	-	-
	2	3pz(Cl-3)	0.7515	-	-
7	2	3dyz(Fe-1)	0.1028	3dxz(Fe-1)	0.0582
	2	-	-	-	0.0072
	2	3pz(Cl-2)	0.8442	-	-
	2	3pz(Cl-3)	0.8570	-	-
8	2	$3dx^2\_y^2$(Fe 1)	0.0421	4py(Fe-1)	0.0055
	2	-	-	3dxy(Fe-1)	0.0038
	2	-	-	3dxy(Fe-1)	0.0030
	2	3py(Cl-2)	0.6468	3px(Cl-2)	0.3012
	2	3px(Cl-3)	0.8630	3py(Cl-3)	0.0872
9	2	$3dz^2$(Fe-1)	1.8210	3dxy(Fe-1)	0.0929
	2	-	-	4s(Fe-1)	0.0376
	2	-	-	$3dx^2\_y^2$(Fe 1)	0.0083
	2	3py(Cl-2)	0.0183	3px(Cl-2)	0.0022
	2	3px(Cl-3)	0.0134	3py(Cl-3)	0.0070
10	2	3dxz(Fe-1)	-	3dyz(Fe-1)	0.6592
	2	-	-	4px(Fe-1)	0.0052
	2	3pz(Cl-2)	0.1078	-	-
	2	3pz(Cl-3)	0.1084	-	-
11	2	3dyz(Fe-1)	1.0796	3dxz(Fe-1)	0.6008
	2	3pz(Cl-2)	0.2612	-	-
	2	3pz(Cl-3)	0.2602	-	-

From equation (2) it is evident that for overlap population analysis of MOs of molecule, eigenvector value (coefficient), value of overlap matrix (overlap integrals), and number of electrons in each MO are needed. The

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TABLE 3(c)

Contribution of electrons in MO of $FeBr_2$

MO no.(i)	n_i	Major contribution		Minor contribution	
		Basic functions(χ_r)	$n_{r,i}=n_ic^2_{ri}$	Basic functions(χ_r)	$n_{r,i}=n_ic^2_{ri}$
1	2	4s(Fe-1)	0.0191	$3dz^2$(Fe-1)	0.0053
	2	-	-	3dxy(Fe-1)	0.0030
	2	4s(Br-2)	0.9180	-	-
	2	4s(Br-3)	0.0092	-	-
2	2	$3dx^2\_y^2$(Fe 1)	0.0129	3dxy(Fe-1)	0.0012
	2	-	-	4px(Fe-1)	0.0010
	2	4s(Br-2)	0.9519	4px(Br-2)	0.0002
	2	4s(Br-3)	0.9533	4py(Br-3)	0.0003
3	2	$3dz^2$(Fe-1)	0.1260	3dxy(Fe-1)	0.1146
	2	-	-	4s(Fe-1)	0.0899
	2	4px(Br-2)	0.5849	4py(Br-2)	0.0324
	2	-	-	4s(Br-2))	0.0267
	2	4py(Br-3)	0.6145	4s(Br-3))	0.0267
	2	-	-	4px(Br-3)	0.2218
4	2	$3dx^2\_y^2$(Fe 1)	0.5869	3dxy(Fe-1)	0.0526
	2	4px(Br-2)	0.3640	4py(Br-2)	0.1859
	2	-	-	4s(Br-2))	0.0136
	2	4py(Br-3)	0.4924	4px(Br-3)	0.0574
	2	-	-	4s(Br-3))	0.0136
5	2	3dxy(Fe-1)	0.4144	$3dx^2\_y^2$(Fe 1)	0.0371
	2	-	-	$3dz^2$(Fe-1)	0.0266
	2	-	-	4s(Fe-1)	0.0124
	2	4py(Br-2)	0.6434	4px(Br-2)	0.0155
	2	4px(Br-3)	0.6464	4py(Br-3)	0.0125
6	2	3dyz(Fe-1)	0.4164	3dxz(Fe-1)	0.2313
	2	4pz(Br-2)	0.6037	-	-
	2	4pz(Br-3)	0.6019	-	-
7	2	3dxz(Fe-1)	0.2966	3dyz(Fe-1)	0.1647
	2	-	-	4pz(Fe-1)	0.0052
	2	4pz(Br-2)	0.7064	-	-
	2	4pz(Br-3)	0.7083	-	-
8	2	$3dx^2\_y^2$(Fe 1)	0.0195	4py(Fe-1)	0.0073
	2	-	-	4px(Fe-1)	0.0040
	2	4py(Br-2)	0.5856	4px(Br-2)	0.3695
	2	4px(Br-3)	0.8243	4py(Br-3)	0.1317
9	2	$3dz^2$(Fe-1)	1.7076	3dxy(Fe-1)	0.0886
	2	-	-	4s(Fe-1)	0.0005
	2	-	-	$3dx^2\_y^2$(Fe 1)	0.0079
	2	4py(Br-2)	0.0612	-	0.0447
	2	4px(Br-3)	0.0078	-	0.0243
10	2	3dxz(Fe-1)	0.9921	3dyz(Fe-1)	0.5504
	2	-	-	4pz(Fe-1)	0.0052
	2	4pz(Br-2)	0.2624	-	-
	2	4pz(Br-3)	0.2628	-	-
11	2	3dyz(Fe-1)	0.8791	3dxz(Fe-1)	0.4879
	2	4pz(Br-2)	0.4075	----	----
	2	4pz(Br-3)	0.4068	----	----

TABLE 3(d)

Contribution of electrons in MO of FeI_2

MO no.(i)	n_i	Major contribution		Minor contribution	
		Basic functions(χ_r)	$n_{r,i}=n_ic^2_{ri}$	Basic functions(χ_r)	$n_{r,i}=n_ic^2_{ri}$
1	2	4s(Fe-1)	0.0387	$3dz^2$(Fe-1)	0.0128
	2	-	-	3dxy(Fe-1)	0.0072
	2	5s(I-2)	0.8765	5px(I-2)	0.0003
	2	5s(I-3)	0.8749	5py(I-3)	0.0004
2	2	$3dx^2\_y^2$(Fe 1)	0.0320	4py(Fe-1)	0.0360
	2	5s(I-2)	0.9275	-	-
	2	5s(I-3)	0.9292	-	-
3	2	$3dz^2$(Fe-1)	0.1632	3dxz(Fe-1)	0.1457
	2	-	-	4s(Fe-1)	0.0873
	2	-	-	$3dx^2\_y^2$(Fe 1)	0.0130
	2	5px(I-2)	0.5506	5s(I-2)	0.0518
	2	-	-	5py(I-2)	0.0290
	2	5py(I-3)	0.5767	5s(I-3)	0.0518
4	2	$3dx^2\_y^2$(Fe 1)	0.6905	3dxy(Fe-1)	0.0620
	2	5px(I-2)	0.3332	5py(I-2)	0.1577
	2	-	-	5s(I-2)	0.0268
	2	5py(I-3)	0.4452	5px(I-3)	0.0460
	2	-	-	5s(I-3)	0.0268
5	2	3dxy(Fe-1)	0.5882	$3dz^2$(Fe-1)	0.0613
	2	-	-	$3dx^2\_y^2$(Fe 1)	0.0501
	2	-	-	4s(Fe-1)	0.0158
	2	5py(I-2)	0.5641	5px(I-2)	0.0087
	2	5px(I-3)	0.5567	5py(I-3)	0.0160
6	2	3dyz(Fe-1)	0.5622	3dxz(Fe-1)	0.3122
	2	5pz(I-2)	0.4990	-	-
	2	5pz(I-2)	0.4976	-	-
7	2	3dxz(Fe-1)	0.5002	-	-
	2	-	-	4pz(Fe-1)	0.0033
	2	5pz(I-2)	0.5578	-	-
	2	5pz(I-3)	0.5593	-	-
8	2	$3dx^2\_y^2$(Fe 1)	0.0207	4s(Fe-1)	0.0074
	2	-	-	4px(Fe-1)	0.0041
	2	5py(I-2)	0.5923	5px(I-2)	0.3643
	2	5px(I-3)	0.8297	5py(I-3)	0.1277
9	2	$3dz^2$(Fe-1)	1.6399	4s(Fe-1)	0.0624
	2	-	-	3dxy(Fe-1)	0.0599
	2	-	-	$3dx^2\_y^2$(Fe 1)	0.0054
	2	5py(I-2)	0.0966	5px(I-2)	0.0118
	2	5px(I-3)	0.0710	5py(I-3)	0.0374
10		3dxz(Fe-1)	0.7878	3dyz(Fe-1)	0.4371
	2	-	-	4pz(Fe-1)	0.0052
	2	5pz(I-2)	0.4168	-	-
	2	5pz(I-3)	0.4177	-	-
11	2	3dxy(Fe-1)	0.7303	3dxz(Fe-1)	0.4052
	2	5pz(I-2)	0.5090	-	-
	2	5pz(I-3)	0.5082	-	-

eigenvector and overlap integral value for halides of iron have been taken from TABLE 1a-d and TABLE 4a-d respectively and the number of electron is taken as two for all 11 MOs. With the help of these, TABLE 5 is constructed for overlap population contribution $n_{r\text{-}s\text{-}i}$ of one molecular orbital of FeF_2. 17 such TABLES are constructed for 17 molecular orbitals of each halide, but only 11 TABLES are considered and remaining 6 having no electrons are left out. In this way, there will

TABLE 4(a)

Overlap matrix (overlap integrals) of FeF_2

AO,S		4s	$4p_x$	$4p_y$	$4p_z$	$3dx^2\_y^2$	$3dz^2$	3dxy	3dxz	3dyz	2s	$2p_x$	$2p_y$	$2p_z$	2s	$2p_x$	$2p_y$	$2p_z$
		Fe-1	Fe-1	Fe-1	Fe-1	Fe-1	Fe-1	Fe-1	Fe-1	Fe-1	F-2	F-2	F-2	F-2	F-3	F-3	F-3	F-3
4s	Fe-1	1.0000																
4px	Fe-1	-0.0000	1.0000															
4py	Fe-1	-0.0000	0.0000	1.0000														
4pz	Fe-1	0.0000	0.0000	0.0000	1.0000													
$3dx^2\_y^2$	Fe-1	-0.0000	0.0000	-0.0000	0.0000	1.0000												
$3dz^2$	Fe-1	-0.0000	-0.0000	-0.0000	0.0000	0.0000	1.0000											
3dxy	Fe-1	-0.0000	-0.0000	-0.0000	0.0000	-0.0000	-0.0000	1.0000										
3dxz	Fe-1	0.0000	0.0000	0.0000	-0.0000	0.0000	0.0000	0.0000	1.0000									
3dyz	Fe-1	0.0000	0.0000	0.0000	-0.0000	0.0000	-0.0000	0.0000	-0.0000	1.0000								
2s	F-2	0.1938	0.2756	0.1131	0.0001	0.0726	-0.0589	0.0717	0.0000	0.0000	1.0000							
2px	F-2	-0.1355	-0.1722	-0.1038	-0.0001	-0.0486	0.0514	-0.0775	-0.0000	-0.0000	0.0000	1.0000						
2py	F-2	-0.0556	-0.1038	0.0381	-0.0000	-0.0621	0.0211	0.0109	-0.0000	0.0000	-0.0000	-0.0000	1.0000					
2pz	F-2	-0.0000	-0.0001	-0.0000	0.0807	-0.0000	0.0000	-0.0000	0.0514	0.0211	0.0000	0.0000	0.0000	1.0000				
2s	F-3	0.1935	-0.0294	-0.2960	0.0001	-0.0999	-0.0588	0.0200	-0.0000	-0.0001	0.0005	-0.0005	-0.0006	0.0000	1.0000			
2px	F-3	0.0144	0.0777	-0.0290	0.0000	-0.0201	-0.0055	-0.0522	0.0000	-0.0000	0.0005	-0.0004	-0.0006	0.0000	-0.0000	1.0000		
2py	F-3	0.1456	-0.0290	-0.2118	0.0001	-0.0927	-0.0552	0.0242	0.0000	-0.0001	0.0006	-0.0006	-0.0007	0.0000	0.0000	0.0000	1.0000	
2pz	F-3	-0.0000	0.0000	0.0001	0.0806	0.0000	0.0000	-0.0000	-0.0055	-0.0551	-0.0000	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000	1.0000

TABLE 4(b)

Overlap matrix (overlap integrals) of $FeCl_2$

AO,s		4s	$4p_x$	$4p_y$	$4p_z$	$3dx^2\_y^2$	$3dz^2$	3dxy	3dxz	3dyz	3s	$3p_x$	$3p_y$	$3p_z$	3s	$3p_x$	$3p_y$	$3p_z$
		Fe-1	Fe-1	Fe-1	Fe-1	Fe-1	Fe-1	Fe-1	Fe-1	Fe-1	Cl-2	Cl-2	Cl-2	Cl-2	Cl-3	Cl-3	Cl-3	Cl-3
4s	Fe-1	1.0000																
4px	Fe-1	0.0000	1.0000															
4py	Fe-1	0.0000	-0.0000	1.0000														
4pz	Fe-1	0.0000	0.0000	0.0000	1.0000													
$3dx^2\_y^2$	Fe-1	-0.0000	0.0000	-0.0000	0.0000	1.0000												
$3dz^2$	Fe-1	-0.0000	-0.0000	-0.0000	0.0000	0.0000	1.0000											
3dxy	Fe-1	-0.0000	-0.0000	0.0000	0.0000	0.0000	-0.0000	1.0000										
3dxz	Fe-1	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0000	0.0000	1.0000									
3dyz	Fe-1	0.0000	0.0000	0.0000	-0.0000	0.0000	0.0000	0.0000	-0.0000	1.0000								
3s	Cl-2	0.2217	0.2923	0.1172	0.0001	0.0669	-0.0534	0.0638	0.0000	0.0000	1.0000							
3px	Cl-2	-0.3066	-0.3040	-0.1872	-0.0001	-0.0541	0.0612	-0.0969	-0.0001	-0.0000	0.0000	1.0000						
3py	Cl-2	-0.1229	-0.1872	0.0881	-0.0000	-0.0870	0.0245	0.0296	-0.0000	0.0000	-0.0000	-0.0000	1.0000					
3pz	Cl-2	-0.0001	-0.0001	-0.0000	0.1631	-0.0000	0.0000	-0.0000	0.0815	0.0327	0.0000	0.0000	0.0000	1.0000				
3s	Cl-3	0.2215	-0.0284	-0.3134	0.0001	-0.0908	-0.0533	0.0166	-0.0000	-0.0000	0.0034	-0.0097	-0.0130	0.0000	1.0000			
3px	Cl-3	0.0298	0.1585	-0.0487	0.0000	-0.0258	-0.0059	-0.0841	0.0000	-0.0000	0.0097	-0.0127	-0.0263	0.0000	0.0000	1.0000		
3py	Cl-3	0.3288	-0.0487	-0.3745	0.0001	-0.1105	-0.0657	0.0282	-0.0000	-0.0001	0.0130	-0.0263	-0.0284	0.0000	0.0000	0.0000	1.0000	
3pz	Cl-3	-0.0001	0.0000	0.0001	0.1629	0.0001	0.0001	-0.0000	-0.0079	-0.0874	-0.0000	0.0000	0.0000	0.0069	0.0000	0.0000	0.0000	1.0000

TABLE 4(c)

Overlap matrix (overlap integrals) of $FeBr_2$

AO,s		4s	$4p_x$	$4p_y$	$4p_z$	$3dx^2\_y^2$	$3dz^2$	3dxy	3dxz	3dyz	4s	4px	4py	4pz	4s	4px	4py	4pz
		Fe-1	Fe-1	Fe-1	Fe-1	Fe-1	Fe-1	Fe-1	Fe-1	Fe-1	Br-2	Br-2	Br-2	Br-2	Br-3	Br-3	Br-3	Br-3
4s	Fe-1	1.0000																
4px	Fe-1	0.0000	1.0000															
4py	Fe-1	-0.0000	-0.0000	1.0000														
4pz	Fe-1	0.0000	0.0000	0.0000	1.0000													
$3dx^2\_y^2$	Fe-1	0.0000	0.0000	-0.0000	0.0000	1.0000												
$3dz^2$	Fe-1	-0.0000	-0.0000	-0.0000	0.0000	0.0000	1.0000											
3dxy	Fe-1	-0.0000	0.0000	-0.0000	0.0000	0.0000	0.0000	1.0000										
3dxz	Fe-1	0.0000	0.0000	0.0000	-0.0000	0.0000	-0.0000	0.0000	1.0000									
3dyz	Fe-1	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0000	0.0000	-0.0000	1.0000								
4s	Br-2	0.1886	0.2546	0.1021	0.0001	0.0575	-0.0459	0.0550	0.0000	0.0000	1.0000							
4px	Br-2	-0.2707	-0.2962	-0.1705	-0.0001	-0.0568	0.0599	-0.0906	-0.0001	-0.0000	-0.0000	1.0000						
4 py	Br-2	-0.1086	-0.1705	0.0604	-0.0000	-0.0752	0.0240	0.0184	-0.0000	0.0000	-0.0000	0.0000	1.0000					
4pz	Br-2	-0.0001	-0.0001	-0.0000	0.1287	-0.0000	0.0000	-0.0000	0.0653	0.0262	0.0000	0.0000	0.0000	1.0000				
4s	Br-3	0.1886	-0.0248	-0.2731	0.0001	-0.0782	-0.0459	0.0143	-0.0000	-0.0000	0.0014	-0.0044	-0.0058	0.0000	1.0000			
4px	Br-3	0.0263	0.1247	-0.0444	0.0000	-0.0225	-0.0058	-0.0671	0.0000	-0.0000	0.0044	-0.0070	-0.0131	0.0000	0.0000	1.0000		
4py	Br-3	0.2904	-0.0444	-0.3605	0.0001	-0.1083	-0.0642	0.0263	-0.0000	-0.0001	0.0058	-0.0131	-0.0148	0.0000	-0.0000	-0.0000	1.0000	
4pz	Br-3	-0.0001	0.0000	0.0001	0.1287	0.0000	0.0000	-0.0000	-0.0064	-0.0700	-0.0000	0.0000	0.0000	0.0027	0.0000	0.0000	0.0000	1.0000

be 44 TABLES for all the four halides. This TABLE constitutes 7 columns as-

Column 1- number of electron (n_i); Column 2,4- atomic orbitals of iron and halogens; Column 3- coefficient of AOs of one atom (c_{ri}); Column 5-coefficient of AOs of other atom (c_{si}) ; Column 6- overlap integrals between two AOs for different atoms (S_{rs}); Column 7-overlap population contribution (n_{r-s-i}).

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TABLE 4(d)

Overlap matrix (overlap integrals) of FeI_2

AO,s		4s	$4p_x$	$4p_y$	$4p_z$	$3dx^2\_y^2$	$3dz^2$	3dxy	3dxz	3dyz	5s	$5p_x$	$5p_y$	$5p_z$	5s	$5p_x$	$5p_y$	$5p_z$
		Fe-1	Fe-1	Fe-1	Fe-1	Fe-1	Fe-1	Fe-1	Fe-1	Fe-1	I-2	I-2	I-2	I-2	I-3	I-3	I-3	I-3
4s	Fe-1	1.0000																
4px	Fe-1	0.0000	1.0000															
4py	Fe-1	-0.0000	0.0000	1.0000														
4pz	Fe-1	0.0000	0.0000	0.0000	1.0000													
$3dx^2\_y^2$	Fe-1	0.0000	-0.0000	-0.0000	0.0000	1.0000												
$3dz^2$	Fe-1	-0.0000	-0.0000	-0.0000	0.0000	-0.0000	1.0000											
3dxy	Fe-1	-0.0000	0.0000	-0.0000	0.0000	0.0000	0.0000	1.0000										
3dxz	Fe-1	0.0000	0.0000	0.0000	-0.0000	-0.0000	-0.0000	0.0000	1.0000									
3dyz	Fe-1	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0000	-0.0000	-0.0000	1.0000								
5s	I-2	0.1779	0.2351	0.0941	0.0001	0.0504	-0.0402	0.0480	0.0000	0.0000	1.0000							
5px	I-2	-0.2598	-0.2904	-0.1605	-0.0001	-0.0541	0.0551	-0.0814	-0.0000	-0.0000	-0.0000	1.0000						
5py	I-2	-0.1040	-0.1605	0.0464	-0.0000	-0.0649	0.0220	0.0128	-0.0000	0.0000	0.0000	0.0000	1.0000					
5pz	I-2	-0.0001	-0.0001	-0.0000	0.1106	-0.0000	0.0000	-0.0000	0.0504	0.0216	0.0000	0.0000	0.0000	1.0000				
5s	I-3	0.1778	-0.0226	-0.2522	0.0001	-0.0684	-0.0402	0.0124	-0.0000	-0.0000	0.0018	-0.0041	-0.0055	0.0000	1.0000			
5px	I-3	0.0250	0.1068	-0.0414	0.0000	-0.0194	0.0053	-0.0554	0.0000	-0.0000	0.0041	-0.0060	-0.0109	0.0000	0.0000	1.0000		
5py	I-3	0.2786	-0.0414	-0.3509	0.0001	-0.0997	-0.0590	0.0233	-0.0000	-0.0001	0.0055	-0.0109	-0.0126	0.0000	0.0000	0.0000	1.0000	
5pz	I-3	-0.0001	0.0000	0.0001	0.1106	0.0000	0.0000	-0.0000	-0.0052	-0.0579	-0.0000	0.0000	0.0000	0.0021	0.0000	0.0000	0.0000	1.0000

The possible overlap between the various AOs of metal and halogens in each molecular orbital will be 88, as described below-

8 overlap- 4s AO of iron with ns, np_x, np_y, np_z AOs of both halogens; 8 overlap- 4px AO of iron with ns, np_x, np_y, np_z AOs of both halogens; 8 overlap- 4py AO of iron with ns, np_x, np_y, np_z AOs of both halogens; 8 overlap- 4pz AO of iron with ns, np_x, np_y, np_z AOs of both halogens; 8 overlap- $3d_{x^2-y^2}$ AO of iron with ns, np_x, np_y, np_z AOs of both halogens; 8 overlap- $3d_{z^2}$ AO of iron with ns, np_x, np_y, np_z AOs of both halogens; 8 overlap- $3d_{xy}$ AO of iron with ns, np_x, np_y, np_z AOs of both halogens; 8 overlap- $3d_{xz}$ AO of iron with ns, np_x, np_y, np_z AOs of both halogens; 8 overlap- $3d_{yz}$ AO of iron with ns, np_x, np_y, np_z AOs of both halogens; 4 overlap- ns AO of X-2 with ns, np_x, np_y, np_z AOs of X-3; overlap- np_x AO of X-2 with ns, np_x, np_y, np_z AOs of X-3; overlap- np_y AO of X-2 with ns, np_x, np_y, np_z AOs of X-3;overlap- np_z AO of X-2 with ns, np_x, np_y, np_z AOs of X-3;

Total - 88 overlaps.

For the study of overlap population we have to construct 11 TABLES for each halide, each having 88 possible overlaps, but while building up TABLE we have dropped the values of zero eigenvector values (TABLE 1a-d), hence each TABLE of overlap population contribution differ in its number of orbitals. For obtaining the values of overlap population contribution ($n_{r\text{-}s\text{-}i}$), we have to discuss each TABLE separarately, but for brevity we here discuss TABLE 5 for molecular orbital number 1 of iron fluoride only.

This TABLE has 45 possible overlaps, out of which 36 provide coefficient values of ferrous orbitals and 9 for F-2 in column 3,i.e. c_{ri}. Column 5 is the coefficient value c_{si} for both the fluorine. Up to 36, both the fluorine are involved and for the remaining nine only F-3.Column 6 is overlap integral S_{rs} and exhibits the magnitude of overlap between the AOs represented in column 2 and 4.Column 7 of TABLE 5 enlists the values of overlap population, derived from eqn.(2). The values are self-explanatory for indicating the magnitude.

The overlap population analysis also shows negligible involvement of 4p orbital of iron. It has earlier been suggested that much smaller radius of the 3d orbital than the 4s orbital makes the involvement of 4s orbital dominant contribution in the bonding. This hypothesis is the central theme of a recent textbook of transition metal chemistry by Gerloch and Constable[23]. While the importance of the valence ns and (n-1)d functions for the description for transition metal bond is undisputed, the status of the empty np orbital is controversially discussed.

Our result indicates that the involvement of np orbital in transition metal bond is negligible and the main role is played by ns and by (n-1) d orbital. Landis[1-4] has also empathetically denied the involvement of np orbital in hybridization. He has supported the sd hybridization and has based his observation on the bond angles. The idealized sd hybridization has been shown to have angles of 90°C. This is because the energy curve are a function of the bond angles and have two minima, one below 90°C and one above 90°C. The bond angles as presented in figure 1 also supports the Landis concept.

The sum of the values of overlap populations, decides the nature of MO in a covalent molecule. If the sum of this interatomic overlap population contribution

TABLE 5

Overlap population contributions of 1st molecular orbital of FeF_2

n_i	Aos	C_{ri}	Aos	C_{si}	S_{rs}	$n_{r-s,i}=n_i(2C_{ri}.C_{si}.S_{rs})$
2	4s(Fe-1)	0.0260	2s(F-2)	0.7009	0.1938	0.0141
2	4s(Fe-1)	0.0260	$2p_x$(F-2)	0.0034	-0.1355	0.0000
2	4s(Fe-1)	0.0260	$2p_y$(F-2)	0.0006	-0.0556	0.0000
2	4s(Fe-1)	0.0260	2s(F-3)	0.6992	0.1935	0.0141
2	4s(Fe-1)	0.0260	$2p_x$(F-3.)	0.0004	0.0144	0.0000
2	4s(Fe-1)	0.0260	$2p_y$(F-3)	-0.0034	0.1456	-0.0001
2	$4p_x$(Fe-1)	-0.0017	2s(F-2)	0.7009	0.2756	-0.0013
2	$4p_x$(Fe-1)	-0.0017	$2p_x$(F-2)	0.0034	-0.1722	0.0000
2	$4p_x$(Fe-1)	-0.0017	$2p_y$(F-2)	0.0006	-0.1038	0.0000
2	$4p_x$(Fe-1)	-0.0017	2s(F-3)	0.6992	-0.0294	0.0001
2	$4p_x$(Fe-1)	-0.0017	$2p_x$(F-3.)	0.0004	0.0777	0.0000
2	$4p_x$(Fe-1)	-0.0017	$2p_y$(F-3)	-0.0034	-0.0290	0.0000
2	$4p_y$(Fe-1)	-0.0012	2s(F-2)	0.7009	0.1131	-0.0004
2	$4p_y$(Fe-1)	-0.0012	$2p_x$(F-2)	0.0034	-0.1038	0.0000
2	$4p_y$(Fe-1)	-0.0012	$2p_y$(F-2)	0.0006	0.0381	0.0000
2	$4p_y$(Fe-1)	-0.0012	2s(F-3)	0.6992	-0.2960	0.0010
2	$4p_y$(Fe-1)	-0.0012	$2p_x$(F-3.)	0.0004	-0.0290	0.0000
2	$4p_y$(Fe-1)	-0.0012	$2p_y$(F-3)	-0.0034	-0.2118	0.0000
2	$3dx^2$-y^2(Fe-1)	-0.0042	2s(F-2)	0.7009	0.0726	-0.0009
2	$3dx^2$-y^2(Fe-1)	-0.0042	$2p_x$(F-2)	0.0034	-0.0486	0.0000
2	$3dx^2$-y^2(Fe-1)	-0.0042	$2p_y$(F-2)	0.0006	-0.0621	0.0000
2	$3dx^2$-y^2(Fe-1)	-0.0042	2s(F-3)	0.6992	-0.0999	0.0012
2	$3dx^2$-y^2(Fe-1)	-0.0042	$2p_x$(F-3.)	0.0004	-0.0201	0.0000
2	$3dx^2$-y^2(Fe-1)	-0.0042	$2p_y$(F-3)	-0.0034	-0.0927	0.0000
2	$3dz^2$(Fe-1)	-0.0181	2s(F-2)	0.7009	-0.0589	0.0030
2	$3dz^2$(Fe-1)	-0.0181	$2p_x$(F-2)	0.0034	0.0514	0.0000
2	$3dz^2$(Fe-1)	-0.0181	$2p_y$(F-2)	0.0006	0.0211	0.0000
2	$3dz^2$(Fe-1)	-0.0181	2s(F-3)	0.6992	-0.0588	0.0030
2	$3dz^2$(Fe-1)	-0.0181	$2p_x$(F-3.)	0.0004	-0.0055	0.0000
2	$3dz^2$(Fe-1)	-0.0181	$2p_y$(F-3)	-0.0034	-0.0552	0.0000
2	3dxy(Fe-1)	0.0142	2s(F-2)	0.7009	0.0717	0.0029
2	3dxy(Fe-1)	0.0142	$2p_x$(F-2)	0.0034	-0.0775	0.0000
2	3dxy(Fe-1)	0.0142	$2p_y$(F-2)	0.0006	0.0109	0.0000
2	3dxy(Fe-1)	0.0142	2s(F-3)	0.6992	0.0200	0.0008
2	3dxy(Fe-1)	0.0142	$2p_x$(F-3.)	0.0004	-0.0522	0.0000
2	3dxy(Fe-1)	0.0142	$2p_y$(F-3)	-0.0034	0.0242	0.0000
2	2s(F-2)	0.7009	2s(F-3)	0.6992	0.0005	0.0010
2	2s(F-2)	0.7009	$2p_x$(F-3.)	0.0004	0.0005	0.0000
2	2s(F-2)	0.7009	$2p_y$(F-3)	0.0034	0.0006	0.0000
2	$2p_x$(F-2)	0.0034	2s(F-3)	0.6992	-0.0005	0.0000
2	$2p_x$(F-2)	0.0034	$2p_x$(F-3.)	0.0004	-0.0004	0.0000
2	$2p_x$(F-2)	0.0034	$2p_y$(F-3)	-0.0034	-0.0006	0.0000
2	$2p_y$(F-2)	0.0006	2s(F-3)	0.6992	-0.0006	0.0000
2	$2p_y$(F-2)	0.0006	$2p_x$(F-3.)	0.0004	-0.0006	0.0000
2	$2p_y$(F-2)	0.0006	$2p_y$(F-3)	-0.0034	-0.0007	0.0000
					$\Sigma n_{r-s,i}$ =	0.0384

is substantially positive, the MO is bonding; if substantially negative, the MO is antibonding and if zero or near zero, the MO is non-bonding. TABLE 5 indicates that the sum of overlap population contribution in first MO of FeF_2 is 0.0384. Similarly, the sum of overlap population contribution has been worked out for $FeCl_2$, $FeBr_2$ and FeI_2 and the values are found to be 0.1295, 0.1364, and 0.1853 respectively, which are positive indicating or supporting the bonding nature of MO.

TABLE 6

MO	**Nature of occupied** Mos: Sum of overlap-population contribution(Σn_{r-s-i})		Nature of Mos
	Ferrous fluoride		
1	0.0384	(Positive)	Bonding
2	0.0082	(Positive)	Bonding
3	0.1074	(Positive)	Bonding
4	0.0911	(Positive)	Bonding
5	-0.0075	(Negative)	Anti-bonding
6	0.0274	(Positive)	Bonding
7	0.0196	(Positive)	Bonding
8	0.0087	≈zero	Nonbonding
9	-0.0158	≈zero	Nonbonding
10	-0.0181	(Negative)	Anti-bonding
11	-0.0458	(Negative)	Anti-bonding
	Ferrous chloride		
1	0.1295	(Positive)	Bonding
2	0.0402	(Positive)	Bonding
3	0.4144	(Positive)	Bonding
4	0.2006	(Positive)	Bonding
5	0.2168	(Positive)	Bonding
6	0.1421	(Positive)	Bonding
7	0.1315	(Positive)	Bonding
8	0.0474	(Positive)	Bonding
9	0.0225	≈zero	Nonbonding
10	-0.0357	≈zero	Nonbonding
11	-0.2018	(Negative)	Anti-bonding
	Ferrous bromide		
1	0.1364	(Positive)	Bonding
2	0.0772	(Positive)	Bonding
3	0.3719	(Positive)	Bonding
4	0.2314	(Positive)	Bonding
5	1.7599	(Positive)	Bonding
6	0.1467	(Positive)	Bonding
7	0.1188	(Positive)	Bonding
8	0.0561	(Positive)	Bonding
9	0.0007	≈zero	nonbonding
10	-0.0729	≈zero	nonbonding
11	-0.1812	(Negative)	Anti-bonding
	Ferrous iodide		Bonding
1	0.1853	(Positive)	Bonding
2	0.1029	(Positive)	Bonding
3	0.3285	(Positive)	Bonding
4	0.2256	(Positive)	Bonding
5	0.0056	(Positive)	Bonding
6	0.0630	(Positive)	Bonding
7	0.0749	(Positive)	Bonding
8	0.0513	(Positive)	Bonding
9	0.0192	≈zero	Nonbonding
10	0.0150	≈zero	Nonbonding
11	-0.1495	(Negative)	Anti-bonding

Similarly, the sum of overlap population for the 11 MOs in all the halides has been worked out, and the results are tabulated in TABLE 6 that gives information

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TABLE 7

Splittig of d orbitals in iron(II) halides

Energy	Fe^{++}	FeF_2	$FeCl_2$	$FeBr_2$	FeI_2
-0.4630	$3d_{x^2-y^2}$, $3d_{z^2}$, $3d_{z^2}$, $3d_{xy}$, $3d_{xz}$, $3d_{yz}$	$3d_{z^2}$, $3d_{xy}$	$3d_{z^2}$, $3d_{xy}$	$3d_{z^2}$, $3d_{xy}$	$3d_{z^2}$, $3d_{xy}$
-0.4569	-	$3d_{x^2-y^2}$	-	-	-
-0.4381	-	-	-	-	$3d_{x^2-y^2}$
-0.4380	-	-	$3d_{x^2-y^2}$	-	-
-0.4376	-	-	-	$3d_{x^2-y^2}$	-

TABLE 8: Eigen value of molecular orbitals of ferrous halides

M.O.	FeF_2	$FeCl_2$	$FeBr_2$	FeI_2
1	-1.4718	-0.9746	-0.8188	-0.6727
2	-1.4702	-0.9669	-0.8136	-0.6658
3	-0.6737	-0.5628	-0.5235	-0.5088
4	-0.6717	-0.5443	-0.5114	-0.4999
5	-0.6675	-0.5363	-0.5031	-0.4884
6	-0.6674	-0.5356	-0.5007	-0.4875
7	-0.6662	-0.5324	-0.4933	-0.4802
8	-0.6653	-0.5202	-0.4818	-0.4672
9	-0.4609	-0.4581	-0.4562	-0.4557
10	-0.4600	-0.4540	-0.4517	-0.4501
11	-0.4569	-0.4380	-0.4376	-0.4381
12	-0.4456	-0.4347	-0.4331	-0.4344
13	-0.4330	-0.4140	-0.4121	-0.4132
14	-0.2554	-0.2169	-0.2298	-0.2339
15	-0.1867	-0.1634	-0.1766	-0.1819
16	-0.0223	0.2855	0.1248	0.0563
17	-0.1012	0.3344	0.1276	0.0576

about the nature of occupied MO of all halides. The TABLE clearly indicates that the non-bonding electrons are present in 9th and 10th molecular orbitals of all the four halides of iron.

The eigenvector analysis as presented in TABLE 1a- 1d indicates that these orbitals are $3d_{z^2}$ and $3d_{xy}$. The energies of these orbitals in iron ions and in the halides are demonstrated in TABLE 7.

From the TABLE 7 it is clear that all the d orbitals in iron ion are degenerate and their energy is –0.4630 eV. The energy of $3d_{z^2}$ and $3d_{xy}$ in all the halides is also the same. The energy of 11th orbital in the case of FeF_2 is -0.4569eV, in case of $FeCl_2$ is -0.4380 eV, in $FeBr_2$ is -0.4376eV, and in case of FeI_2 is -0.4381eV. The energy difference between non-bonding orbitals and the next higher orbitals that is 11th orbital is as below:

FeF_2 = 0.0061eV, $FeCl_2$ = 0.0259eV, $FeBr_2$ = 0.0263eV, FeI_2 = 0.0258eV

The order of d orbital splitting in various halides is: $FeBr_2 > FeCl_2 > FeI_2 > FeF_2$. The eigenvalues of the molecular orbitals of the halides are included in TABLE 8.

The position of non-bonding molecular orbitals, which are not exactly but approximately degenerate for all the four halides.

From the above discussion it is clear that no molecular orbital is formed by only two atomic orbitals. All MOs have contribution of many basic functions or atomic orbitals; as a result, every MO has a definite shape having contributions from many basic functions.

CONCLUSIONS

1. Eigenvector analysis shows that $3d_{xz}$ and 3dyz orbitals of iron play a major role in bonding between iron and halogen, $3d_{z^2}$ orbital is next and 4p orbitals have a negligible role. This supports the Landis observation and concept of sd hybridization. The bond angles are also in the range prescribed for sd hybridization.
2. The overlap population analysis shows that non-bonding orbitals are 9th and 10th in all the four halides. The eigen values of these orbitals and that of free ions are approximately the same and are in the close range of 0.4360eV.
3. No molecular orbital is formed by two atomic orbitals only. All MOs have contribution from many atomic orbitals; the difference is only in extent of involvement.
4. The splitting of d orbitals as evaluated by the difference in energy of the non-bonding orbitals and the orbitals next higher to them indicates the following order:

$FeBr_2$ > $FeCl_2$ > FeI_2 > FeF_2

REFERENCES

[1] C.R.Landis, T.Cleveland, T.K.Firman; J.Am.Chem. Soc., **117**, 1859 **(1995)**.

[2] C.R.Landis, T.K.Firman, D.M.Root, T.Cleveland; J. Am.Chem.Soc., **120**, 1842 **(1998)**.

[3] C.R.Landis, T.Cleveland, T.K.Firman; J.Am. Chem.Soc., **120**, 2641 **(1998)**.

[4] T.K.Firman,, C.R.Landis; J.Am.Chem.Soc., **120**, 12650 **(1998)**.

[5] L.G.Vanquickenborne, K.Pierloot, D.Devoghel; J.Chem.Educ., **71**, 469 **(1994)**.

[6] M.P.Melrose, E.R.Sceri; J.Chem.Educ., **73**, 498

(1996).

[7] A.J.Shortland, G.Wilkinson; Soc., J.Chem.Soc., Dalton Trans., 872 **(1973)**.

[8] V.Pfenning, K.Seppelt; Science, **271**, 626 **(1996)**.

[9] M.Kaupp; J.Am.Chem.Soc., **118**, 3018 **(1996)**.

[10] E.R.Davidson; Chem.Rev.,**100**, 351 **(2000)**.

[11] E.R.Davidson; Chem.Rev., **91**, 649 **(1991)**.

[12] 'Topics in Current Chemistry', R.F.Nalewajski (Ed.); Springer, Verlag, Berlin, 180-183 **(1996)**.

[13] 'Density Functional Theory of Atoms and Molecules', R.G.Parr, W.Yang (Eds.); Oxford University Press, New York, **(1988)**.

[14] 'Density Functional Methods in Chemistry', J. Labanowski, J.Andzelm (Eds.); Springer, Verlag Heidelberg, **(1991)**.

[15] T.Ziegler; Chem.Rev., **91**, 651, **(1991)**.

[16] L.Szasz; 'Pseudopotential Theory of Atoms and Molecules', J.Wiley and Sons; New York **(1986)**.

[17] M.Krauss, W.Stevens; J.Ann.Rev.Phys.Chem., **35**, 357 **(1984)**.

[18] P.Durand, J.P.Malrieu; Adv.Chem.Phys., **67**, 321 **(1987)**.

[19] G.Freking, I.Antes, M.Bochme, S.Dapprich, A.W. Ehlers, V.Jenas, A.Neuhans, M.Otto, R.Stegmann, A.Veldkamp, S.F.Vyboishchikow; in: K.B.Lipkoeitz, D.B.Boyd (Eds.); 'Reviev in Computational Chemistry', VCH, New York, **8**, 63-144 **(1996)**.

[20] T.R.Cundari, M.T.Benson, M.L.Lutj, S.O. Sommerer; 'Reviews in Computational Chemistry', K.B.Lipkowitz, D.B.Boyd (Eds.); VCH: New York, **8**, 145-202, **(1996)**.

[21] I.N.Levine; 'Quantum Chemistry', 5th ed. Prentice Hall, New Jersey, 664-667, **(2000)**.

[22] R.K.Singh, P.D.Sharma,P.P.Singh; As.J.Chem., **19**, 121 **(2007)**.

[23] M.Gerloch, E.C.Constable; Transition Metal Chemistry, VCH Weinheim, **(1994)**.