

# Platinum Difluoride: A Theoretical and Computational Based Study

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**How to cite this paper:** Soni, A.K. and Sahu, V.K. (2023) Platinum Difluoride: A Theoretical and Computational Based Study. *Advances in Biological Chemistry*, 13, 236-246.

<https://doi.org/10.4236/abc.2023.136017>

**Received:** October 13, 2023

**Accepted:** December 3, 2023

**Published:** December 6, 2023

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## Abstract

Platinum on reaction with halogen forms three halides viz., platinum (II) chloride, platinum (II) bromide and platinum (II) iodide, except platinum (II) fluoride. In this research work, the not existence of PtF<sub>2</sub> has been studied theoretically. For this thermodynamic, valence bond theory and molecular orbital theory based study have also been performed on this molecule. In order to obtain minimum energy structure we optimized the geometry of this halide by opting AM1 for thermodynamic work and EHT for population analysis. All the calculations were performed on CAChe software. The thermodynamic study supported the presumption of disproportionation reaction: 2PtF<sub>2</sub> → Pt + PtF<sub>4</sub>. V.B.T showed sd-hybridization rather than sp-hybridization. This was supported by our data as evaluated theoretically by adopting Landis concept, which showed negligible contribution of 5s-orbital of platinum. Mulliken's population analysis based studies have pointed that the overlap is very poor due to the dis-similarity of energy of combining orbitals of Pt and F atom. The Σφ is very small that is 0.2. This also proved that PtF<sub>2</sub> failed to match the criteria of overlapping and thus MOT too. Using eigenvalues and population analysis MO diagram has also been drawn, which clearly supported non-existence of PtF<sub>2</sub> in nature but its existence *in situ* and thus also supported the presumption of disproportionation reaction.

## Keywords

PtF<sub>2</sub>, Molccecular Mechanics, Quantum Mechanism, VBT and MOT

## 1. Introduction

Platinum occurs naturally as the elements, generally with small amounts of the other platinum metals [1]. The ability of platinum to exist in many oxidation

states is an important property of this element (0, +2, +3, +4, +5 and +6), which plays an important role in its applications [2] [3]. A number of complexes are formed by the platinum metal in +2 oxidation state.  $\text{Pt}^{2+}$  is soft acid so stable complexes are formed with S or P as donor atoms but few with O-donors, though there are important amines. +4 oxidation state is more stable for platinum fluoride: “ $2\text{PtF}_2 \rightarrow \text{Pt} + \text{PtF}_4$ ”, that is why  $\text{PtF}_2$  is unknown, presumably unstable with respect to disproportionation: This would occur as a consequence of the stability of low spin  $d^6$  platinum (IV) state and of the oxidizing power of fluorine. The terms “stable” and “unstable” are used to refer to the thermodynamic properties of the complex species considered. Low-spin complexes generally undergo rapid one-electron oxidation or reduction. Due to lower ionization energies (Scheme 1), platinum forms large number of compounds in higher states.

Platinum readily form coordinate complexes and these complexes have their applications in diverse fields: sensors and switches, as catalysts, antimicrobial agents, as biomarkers, as metallopharmaceuticals in treatment of cancer, activate or help to generate redox reactions in photochemistry [4] [5], in biological system [6] [7] [8], materials science [9] [10] [11] and nanoscience [12]. Generally, the compounds formed by platinum are less liable. A survey of literature shows that designing of new ligands that can complexes with platinum in different oxidation states can lead to the develop of new materials [13]. For new materials of diverse applications, there are and will be a continuous step-by-step study to discover new ligands and their new platinum complex.

## 2. Materials and Methods

In this study platinum (II) fluoride is the study material, which does not exist. That is why it is selected for study rather than other platinum dihalides. The adopted methods for various calculations of platinum difluoride are based on Mulliken’s population analysis [14]. Mulliken defined  $\phi_i$  (molecular orbital),  $n_{r,i}$  (the contributions of electrons in each occupied MO) and  $n_{r-s,i}$  (overlap population that explain bonding, antibonding and nonbonding nature of bond), as below:

$$\phi_i = \sum_{rk} c_{irk} \chi_{rk} \quad (1)$$

$$n_{r,i} = n_i c_{ri}^2 \quad (2)$$

$$n_{r-s,i} = n_i (2c_{ri} c_{si} S_{rs}) \quad (3)$$

here  $n_i$  is the number of electron in  $\phi$ ,  $i = 1 - 17$ ,  $c_{ri}$  is the coefficient of atomic orbitals for Pt-atom,  $c_{si}$  is the coefficient of AOs for other (X-2 or X-3) and  $S_{rs}$  is the overlap integral between the two AOs (one of an atom Pt-1

Pt	IE <sub>1</sub>	IE <sub>2</sub>	IE <sub>3</sub>	IE <sub>4</sub>
KJmol <sup>-1</sup>	870	1791	(2800)	(3900)

Values in parentheses are estimated

**Scheme 1.** Ionization energy/enthalpy of platinum.

or X-2 and one of another atom X-2 or X-3). In order to obtain minimum energy structure we optimized the geometry of each halide by opting Extended Hückel Theory (EHT). All the calculations were performed on CAChe software as described in our recent work [14]. From minimum energy structure, we have extracted values of eigenvectors, overlap matrix and eigenvalues. By submitting the values of eigenvector (Table 1) and overlap matrix (Table 2) in Equation (3), we have derived the values of overlap population and tabulated in Table 3. And the summation of values of overlap population was obtained to describe bonding, nonbonding and antibonding molecular orbitals have also been incorporated in this Table. After that using all above along with eigenvalues molecular orbital diagram has been drawn. Before this, we have also examined the nature and contribution of atomic orbitals and then their mixing (valence bond theory) or overlapping (molecular orbital theory). V.B. Theory and M.O. theory on their refinements gave same wave function for the molecule but they differ in their approximations only. Mulliken (1955) [15] [16] [17] [18] also correlated the bonded interaction of V.B.T. with positive overlap population and non-bonded repulsion of V.B.T. with negative population analysis.

### 3. Results and Discussion

To check the validity of the disproportionation concept that is “ $2\text{PtF}_2 \rightarrow \text{Pt} + \text{PtF}_4$ ” [1], thermodynamics works have also been performed. The enthalpy ( $H^\circ$ ), entropy (S) and free energy (G) of platinum metal are zero, zero and 1.3432 (kcal/mol), respectively. And that of  $\text{PtF}_2$  are 30.176 (kcal/mol), 62.008 (cal/mol) and 11.692 (kcal/mol), respectively. And of  $\text{PtF}_4$  are 4140.219 (kcal/mol), 4139.767 (cal/mol) and +57.193 (kcal/mol), respectively. The change in enthalpy ( $\Delta H$ ), entropy ( $\Delta S$ ) and free energy ( $\Delta G$ ) are (kcal/mol) for the reaction is 4089.867, 4015.751 and  $-1,192,603$ , respectively. And after that of bonding nature in platinum difluoride has been studied. The optimized geometry as obtained from molecular mechanics method of platinum (II) fluoride is shown in Figure 1.

The MOs of this molecule as formed by linear combination of nine orbitals (five 4d-orbitals, one 5s orbital and three 5p orbitals) from ruthenium and four orbitals (three 2p orbitals and one 2s orbital) from each bromine are shown below

$$\text{Pt-1} = 5dx^2-y^2, 5dz^2, 5dxy, 5dxz, 5dyz, 6s, 6px, 6py, 6pz = 9$$

$$\text{F-2} = 2s, 2px, 2py, 2pz = 4$$

$$\text{F-3} = 2s, 2px, 2py, 2pz = 4$$

$$\text{Total} = 17$$

In order to examine the contribution of various atomic orbitals in the formation of molecular orbitals the LCAO has been studied. The 17 AOs on LCAO approximations give 17 MOs. Thus,  $\chi_1 - \chi_9$  are AOs of platinum ( $\chi_1 = 6s, \chi_2 = 6px, \chi_3 = 6py, \chi_4 = 6pz, \chi_5 = 5dx^2 - y^2, \chi_6 = 5dz^2, \chi_7 = 5dxy, \chi_8 = 5dxz, \chi_9 = 5dyz$ )

**Table 1.** Eigenvector values of atomic orbitals ( $\chi$ ) in molecular orbitals ( $\phi$ ) of PtF<sub>2</sub>.

Atom	$\phi_1$	$\phi_2$	$\phi_3$	$\phi_4$	$\phi_5$	$\phi_6$	$\phi_7$	$\phi_8$	$\phi_9$	$\phi_{10}$	$\phi_{11}$	$\phi_{12}$	$\phi_{13}$	$\phi_{14}$	$\phi_{15}$	$\phi_{16}$	$\phi_{17}$
Pt-1	$\chi_1$	-0.0229	-0.0000	0.0751	0.0000	0.0000	-0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.3609	-0.0005	0.0000	0.9884	0.0000
	$\chi_2$	0.0000	-0.0024	0.0000	0.0000	0.0470	0.0032	-0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.1013	-0.0020	0.0000	1.1344
	$\chi_3$	0.0000	-0.0000	0.0000	-0.0000	-0.0004	-0.0012	0.0188	0.0000	0.0000	-0.0000	-0.0000	-0.0000	0.0631	-1.0023	-0.0000	-0.0095
	$\chi_4$	0.0000	0.0002	0.0000	0.0000	-0.0048	-0.0188	-0.0012	-0.0000	0.0000	-0.0000	-0.0000	0.0000	0.9972	0.0636	0.0005	-0.1146
	$\chi_5$	-0.0270	-0.0000	0.1456	-0.0098	-0.0010	-0.0000	0.0000	-0.0017	-0.5050	0.0103	-0.1006	-0.7948	-0.0002	0.0000	0.3438	0.0000
	$\chi_6$	0.0153	-0.0000	-0.0824	0.0168	-0.0011	0.0000	-0.0000	0.0000	-0.8573	0.0108	0.1724	0.4496	0.0001	-0.0000	-0.1945	-0.0000
	$\chi_7$	0.0005	0.0000	-0.0024	-0.0060	-0.0965	0.0000	0.0000	-0.1005	0.0085	0.9902	-0.0604	0.0133	-0.0000	0.0000	-0.0058	0.0000
	$\chi_8$	0.0055	0.0000	-0.0294	-0.0950	0.0061	0.0000	-0.0000	-0.0083	-0.1000	-0.0620	-0.9751	0.1606	-0.0000	-0.0000	-0.0695	-0.0000
	$\chi_9$	0.0000	0.0000	0.0002	0.0014	0.0097	-0.0000	-0.0000	-0.9949	0.0008	-0.0996	0.0144	-0.0013	0.0000	0.0000	0.0006	0.0000
F-2	$\chi_{10}$	-0.6995	0.7077	-0.0367	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0471	0.0001	-0.0000	-0.2300	-0.3013
	$\chi_{11}$	-0.0044	-0.0044	-0.6640	-0.0701	-0.0014	-0.6929	-0.0711	0.0014	-0.0000	-0.0002	0.0114	-0.1374	-0.0082	0.0002	0.2663	0.2713
	$\chi_{12}$	0.0000	-0.0004	0.0056	-0.0440	-0.6981	0.0058	-0.0443	0.7043	0.0000	-0.1126	0.0070	0.0011	-0.0051	0.0804	-0.0022	-0.0023
	$\chi_{13}$	0.0004	0.0000	0.0670	-0.6946	0.0443	0.0695	-0.7007	-0.0447	0.0000	0.0070	0.1121	0.0139	-0.0800	-0.0051	-0.0269	-0.0274
F-3	$\chi_{14}$	-0.6995	0.0000	-0.0367	-0.0000	-0.0000	0.0124	0.0000	-0.0000	0.0000	0.0000	-0.0000	0.0471	0.0001	0.0000	-0.2300	0.3013
	$\chi_{15}$	0.0044	-0.7078	0.6640	0.0711	0.0014	-0.6928	-0.0713	0.0014	0.0000	0.0002	-0.0114	0.1374	-0.0080	0.0002	-0.2663	0.2713
	$\chi_{16}$	-0.0000	0.0000	-0.0056	0.0440	0.6980	0.0058	-0.0443	0.7043	0.0000	0.1126	-0.0070	-0.0012	-0.0051	0.0804	0.0022	-0.0023
	$\chi_{17}$	-0.0004	0.0000	-0.0672	0.6944	-0.0443	0.0705	-0.7007	-0.0447	0.0000	-0.0070	-0.1121	-0.0139	-0.0800	-0.0051	0.0269	-0.0274

**Table 2.** Overlap matrix or overlap integrals values ( $S_{rs}$ ) of various overlaps of atomic orbitals of constituent atoms in PtF<sub>2</sub>.

AOs	6s (Pt-1)	6px (Pt-1)	6py (Pt-1)	6pz (Pt-1)	5dx <sup>2</sup> -y <sup>2</sup> (Pt-1)	5dz <sup>2</sup> (Pt-1)	5dxy (Pt-1)	5dxz (Pt-1)	5dyz (Pt-1)	2s (F-2)	2px (F-2)	2py (F-2)	2pz (F-2)	3s (F-3)	2px (F-3)	2py (F-3)	2pz (F-3)
6s (Pt-1)	1.0000																
6px (Pt-1)	0.0000	1.0000															
6py (Pt-1)	0.0000	0.0000	1.0000														
6pz (Pt-1)	0.0000	0.0000	0.0000	1.0000													
5dx <sup>2</sup> -y <sup>2</sup> (Pt-1)	0.0000	0.0000	0.0000	0.0000	1.0000												
5dz <sup>2</sup> (Pt-1)	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000											
5dxy (Pt-1)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000										
5dxz (Pt-1)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000									
5dyz (Pt-1)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000								
2s (F-2)	0.1701	0.2642	-0.0022	-0.0267	0.0876	-0.0495	-0.0015	-0.0177	0.0001	1.0000							
2px (F-2)	-0.1400	-0.2106	0.0023	0.0280	-0.0901	0.0505	0.0019	0.0227	-0.0002	0.0000	1.0000						
2py (F-2)	0.0012	0.0023	0.0669	-0.0002	0.0015	-0.0004	0.0442	-0.0002	-0.0045	0.0000	0.0000	1.0000					
2pz (F-2)	0.0141	0.0280	-0.0002	0.0641	0.0136	-0.0128	-0.0002	0.0414	-0.0003	0.0000	0.0000	0.0000	1.0000				
2s (F-3)	0.1701	-0.2641	0.0022	0.0267	0.0876	-0.0495	-0.0015	-0.0177	0.0001	0.0000	0.0000	0.0000	0.0000	1.0000			
2px (F-3)	0.1400	-0.2106	0.0023	0.0281	0.0901	-0.0505	-0.0019	-0.0227	0.0002	0.0000	-0.0001	0.0000	0.0000	0.0000	1.0000		
2py (F-3)	-0.0012	0.0023	0.0669	-0.0002	-0.0015	0.0004	-0.0442	0.0002	0.0045	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	
2pz (F-3)	-0.0142	0.0281	-0.0002	0.0641	-0.0136	0.0128	0.0002	-0.0414	0.0003	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000

**Table 3.** Coefficient values of 4dxy, 4dxz, 4dx<sup>2</sup> - y<sup>2</sup>, 5s, 5px, 5py, 5pz AOs of PtF<sub>2</sub>.

MOs	5d <sub>z<sup>2</sup></sub> (Pt-1)	5d <sub>xy</sub> (Pt-1)	5d <sub>xz</sub> (Pt-1)	6s (Pt-1)	6p <sub>x</sub> (Pt-1)	6p <sub>y</sub> (Pt-1)	6p <sub>z</sub> (Pt-1)
$\phi_1$	0.0153	0.0005	0.0055	0.0229	0.0000	0.0000	0.0000
$\phi_2$	0.0000	0.0000	0.0000	0.0000	0.0024	0.0000	0.0002
$\phi_3$	0.0824	0.0024	0.0294	0.0751	0.0000	0.0000	0.0000
$\phi_4$	0.0168	0.0060	0.0950	0.0000	0.0000	0.0000	0.0000
$\phi_5$	0.0011	0.0965	0.0061	0.0000	0.0000	0.0000	0.0000
$\phi_6$	0.0000	0.0000	0.0000	0.0000	0.0470	0.0004	0.0048
$\phi_7$	0.0000	0.0000	0.0000	0.0000	0.0032	0.0012	0.0188
$\phi_8$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0188	0.0012
$\phi_9$	0.0000	0.1005	0.0083	0.0000	0.0000	0.0000	0.0000
$\phi_{10}$	0.8573	0.0085	0.1000	0.0000	0.0000	0.0000	0.0000
$\phi_{11}$	0.0108	0.9902	0.0620	0.0000	0.0000	0.0000	0.0000
$\phi_{12}$	0.1724	0.0604	0.9751	0.0000	0.0000	0.0000	0.0000
$\Sigma =$	<b>1.1561</b>	<b>1.2650</b>	<b>1.2814</b>	<b>0.0980</b>	<b>0.0526</b>	<b>0.0204</b>	<b>0.0250</b>



Bond Length=2.019Å

Bond Angle=179.99°

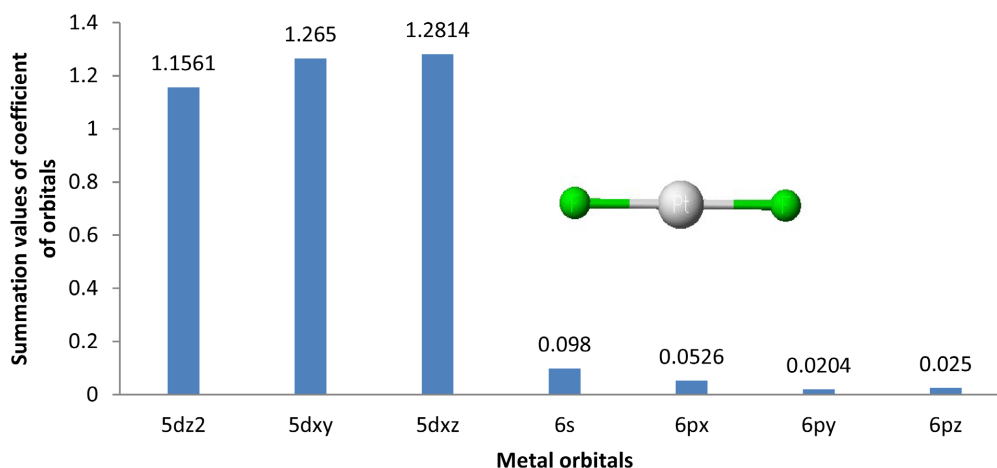
**Figure 1.** Structure of PtF<sub>2</sub>.**Table 4.** Quantitative and qualitative nature of occupied molecular orbitals of platinum difluoride.

MO No.	$\Sigma n_{r-s,l}$	sign	MOs	MO No.	$\Sigma n_{r-s,l}$	sign	MOs
$\phi_1$	0.0198	+	BMO	$\phi_7$	0.0035	+	BMO
$\phi_2$	-0.0016	+	ABMO	$\phi_8$	0.0036	+	BMO
$\phi_3$	0.0720	+	BMO	$\phi_9$	0.0000	0	NBO
$\phi_4$	0.0121	+	BMO	$\phi_{10}$	0.0000	0	NBO
$\phi_5$	0.0121	+	BMO	$\phi_{11}$	-0.0200	-	ABMO
$\phi_6$	0.0275	+	BMO	$\phi_{12}$	-0.0200	-	ABMO

and  $\chi_{10}$  -  $\chi_{17}$  are AOs of chlorine ( $\chi_{10} = 3s$ ,  $\chi_{11} = 3px$ ,  $\chi_{12} = 3py$ ,  $\chi_{13} = 3pz$  for F-2 and  $\chi_{14} = 3s$ ,  $\chi_{15} = 3px$ ,  $\chi_{16} = 3py$ ,  $\chi_{17} = 3pz$  for F-3). The magnitude of contribution of various AOs ( $\chi$ ) in the formation of 17 MOs ( $\phi_1$  to  $\phi_{17}$ ) is demonstrated in **Table 4** reflected that nine AOs ( $\chi_2$ ,  $\chi_3$ ,  $\chi_4$ ,  $\chi_7$ ,  $\chi_9$ ,  $\chi_{12}$ ,  $\chi_{13}$ ,  $\chi_{16}$ ,  $\chi_{17}$ ) have no contribution in the formation of 1<sup>st</sup> MO ( $\phi_1$ ) as these have zero or near zero coefficient values. And the rest eight AOs ( $\chi_1$ ,  $\chi_5$ ,  $\chi_6$ ,  $\chi_8$ ,  $\chi_{10}$ ,  $\chi_{11}$ ,  $\chi_{14}$ ,  $\chi_{15}$ ) have their contribution in  $\phi_1$ . By adopting same view the contributions AOs in  $\phi_2$  to  $\phi_{17}$  MOs can also be described. The characteristics of transition metal (TM) elements are due to their d orbitals of (n - 1) shell and s and p

orbitals of  $n$  shell. As the atom of TM elements form compound they adopt either concept of bonded attraction and non-bonded repulsion of VB (Valence Bond) theory and or positive and negative overlap populations of MO (Molecular Orbital) theory [17] [18] [19] [20]. In the first case, they may undergo various type of hybridization that depends upon the oxidation state of TM and number and nature of combining atoms or ions, and in the second case formation of molecular orbital by LCAO approximation [19]. At first we have to examine the extent of involvement of 4d, 5s and 5p AOs of Pt-1 in the formation of MOs in platinum dihalides. For this, values of coefficient " $\chi$ " of  $5d_z^2$ ,  $5d_{xy}$ ,  $5d_{xz}$ , 6s,  $6p_x$ ,  $6p_y$  and  $6p_z$  have presented in **Table 3**. The " $\chi$ " of non-bonding orbitals  $5d_{x^2-y^2}(\chi_5)$  and  $5d_{yz}(\chi_9)$  are excluded. It was Landis, who discovered  $sd^n$ -hybridization ( $n = 1$  to 5) along with molecular shape and bond angles in his seminal publications [20] [21] [22]. Further, he also explained co-relationship between  $sd^n$ -hybridization and its bond angle by plotting a graph between energy and bond angle. In order to explore atomic orbitals detail with respect to hybridization, we have examined the contribution of 5d, 6s and 6p AOs of Pt-1 in  $PtF_2$ . For this only occupied MO ( $\phi_1 - \phi_{12}$ ) were considered. And values of  $c_i$  of each  $\chi$  of  $5d_z^2$ ,  $5d_{xy}$ ,  $5d_{xz}$ , 6s,  $6p_x$ ,  $6p_y$  and  $6p_z$  of above twelve molecular orbitals were added and the results were tabulated in **Table 3**. Analysis of this table reflected that major contributions are from orbitals of 5d and 6s. The negligible contribution of 5s-orbital has disclosed  $sd$ -hybridization. The involvement of three p-orbitals is negligible as their summation values are very low in comparison to d-orbital and considerably also low with respect to s-orbital. The graphical point of view of the same is reflected from **Figure 2**.

The shape of each MO ( $\phi_1 - \phi_{17}$ ) has been determined by the relative magnitudes and signs of the different coefficients. For this the  $Pt(II)X_2$  has been decomposed into three parts: Pt-1, F-1 and F-2, and the MO of the complete system has been obtained by allowing the orbitals of Pt-1 (5d, 6s, 6p), F-1 (ns and np) and F-2 (ns and np) to overlap. The combining atomic orbital must have 1)



**Figure 2.** Extent of involvement of metal orbital in the formation of MOs of  $PtF_2$ .

same or nearly same energy *i.e.*, comparable energy, 2) proper orientation *i.e.*, same symmetry about the molecular axis and 3) extent of overlapping of orbitals should be maximum *i.e.*, not less than 40%.

The energy gap between overlapping orbitals of Pt and halogen (F, Cl, Br, I) atoms in platinum halides as demonstrated in **Scheme 2** also proved the not existence of PtF<sub>2</sub> molecule. As orbital of the metal, Pt and halogen, F of this molecule has maximum instability *i.e.*, having different energy. The possible overlaps between the various AOs of ruthenium (Pt-1) and halogens (F-2 and F-2) in each MO will be 88. To solve Equation (3) for these 88 overlaps in MOs of platinum difluoride, we need eigenvector values ( $C_{ri}$  and  $C_{si}$ ), values of overlap matrix ( $S_{rs}$ ) and number of electrons ( $n_i$ ) in each MO. The eigenvector and overlap integral values for platinum difluoride have been taken from **Table 1** and **Table 2**, respectively. The number of electrons is taken as two for  $\phi_1$  to  $\phi_{12}$  and zero for  $\phi_{13}$  to  $\phi_{17}$ . Finally, Equation (3) has been solved for twelve MOs. The summation values of overlap population of these twelve MOs have been presented in **Table 4**.

In order to get a precise description, the sum of overlap population for the twelve MOs of PtF<sub>2</sub> has also been worked out and results are presented in **Table 4**. As can be seen from the table among the twelve molecular orbitals, seven are bonding, two are nonbonding and three are antibonding. The bonding molecular orbitals are  $\phi_1$  and  $\phi_3 - \phi_8$ . The nonbonding molecular orbitals are  $\phi_9$  and  $\phi_{10}$ , which are purely two d atomic orbitals of platinum namely  $dx^2-y^2$  and  $dyz$ . The three antibonding molecular orbitals are  $\phi_2$  and  $\phi_{11} - \phi_{12}$ . All these have also been clearly shown by **Figure 3**.

## 4. Conclusions

1) The thermodynamic study supported the presumption of disproportionation reaction:  $2PtF_2 \rightarrow Pt + PtF_4$ .

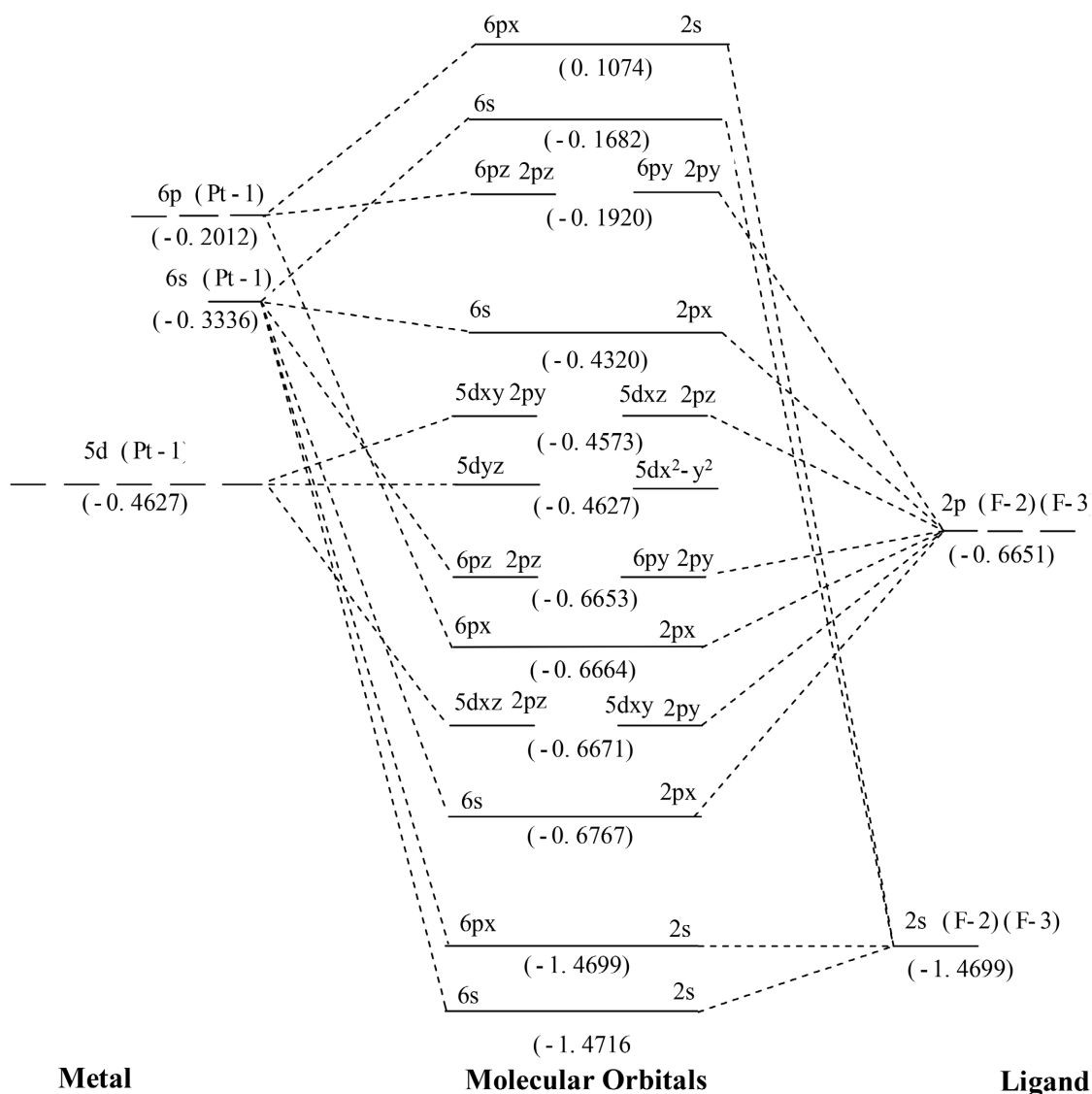
2) V.B.T showed sd-hybridization rather than sp-hybridization. This was supported by our data as evaluated theoretically by adopting Landis concept, which showed negligible contribution of 5s-orbital of platinum.

3) Mulliken's population-based studies have pointed that the overlap is very poor due to dissimilarity of energy of combining orbitals of Pt and F atom. The  $\Sigma\phi$  is very much low that is 0.2. This also proved that PtF<sub>2</sub> failed to match the criteria of overlapping and thus MOT, too.

PtF <sub>2</sub>	$\Delta_{5d-2s} = 1.007$	$\Delta_{5d-2p} = 0.202$	$\Delta_{6s-2s} = 1.136$	$\Delta_{6s-2p} = 0.332$	$\Delta_{6p-2s} = 1.269$	$\Delta_{6p-2p} = 0.464$
PtCl <sub>2</sub>	$\Delta_{5d-3s} = 0.504$	$\Delta_{5d-3p} = 0.059$	$\Delta_{6s-3s} = 0.633$	$\Delta_{6s-3p} = 0.188$	$\Delta_{6p-3s} = 0.765$	$\Delta_{6p-3p} = 0.321$
PtBr <sub>2</sub>	$\Delta_{5d-4s} = 0.348$	$\Delta_{5d-4p} = 0.019$	$\Delta_{6s-4s} = 0.477$	$\Delta_{6s-4p} = 0.148$	$\Delta_{6p-4s} = 0.610$	$\Delta_{6p-4p} = 0.280$
PtI <sub>2</sub>	$\Delta_{5d-5s} = 0.199$	$\Delta_{5d-5p} = 0.016$	$\Delta_{6s-5s} = 0.328$	$\Delta_{6s-5p} = 0.113$	$\Delta_{6p-5s} = 0.460$	$\Delta_{6p-5p} = 0.246$

**Scheme 2.** Energy gap between overlapping orbitals of Pt and halogen (F, Cl, Br, I) in platinum halides.





**Figure 3.** MO diagram of PtF<sub>2</sub> along with the energy of AOs and MOs in eV as shown in parenthesis.

4) Using eigenvalues and population analysis MO diagram has also been drawn, which clearly supported non-existence of PtF<sub>2</sub> in nature but its existence *in situ* and thus also supported presumption of the disproportionation reaction.

### Acknowledgements

Authors are thankful to the Principal, Shia P.G. College, Sitapur Road, Lucknow for laboratory facilities and support. Anil Kumar Soni also gratefully acknowledges the financial support (Letter No./Reginal office Lucknow/5496-99/2021-22, Dated; 15-03-2022) given by Research & Development, Lucknow (U.P.).

### Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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