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# Study of Molecular Orbitals of Ruthenium (II) Bromide Based on Molecular Mechanics

<sup>1</sup>Gayasuddin Khan\* and <sup>2</sup>Rajendra Prasad Tewari

<sup>1</sup>Department of Physics, K. S. Saket Post Graduate College, Ayodhya, Faizabad, (U.P.) INDIA

<sup>2</sup>Department of Physics, M. L. K. (P. G.) College, Balrampur, (U.P.), INDIA

## ABSTRACT

We have studied the molecular orbitals of ruthenium (II) bromide, in order to study the extent of contribution of 4d, 5s and 5p orbitals in the formation of molecular orbitals. The 3D modeling and geometry optimization of the ruthenium (II) bromide have been done by CAChe software using molecular mechanics with EHT option. Eigenvector analysis shows that  $4dx^2-y^2$  and  $4dxy$  orbitals of ruthenium play a major role in bonding between ruthenium and bromide, 5s orbital is next and 4p orbitals have a negligible role. There is a difference in energy levels of s and p orbitals of bromide are 0.6090 eV. The overlap population analysis shows that the nonbonding orbitals are present in 6<sup>th</sup> and 7<sup>th</sup> molecular orbitals. No molecular orbital is formed by only two atomic orbitals. All molecular orbitals have contribution from many atomic orbitals; the difference is only in extent of involvement.

**Keywords:** Ruthenium (II) bromide, sd hybridization, Population analysis, Overlap population analysis, Eigenvector, Eigenvalues.

## 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 electrons 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. As support for 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

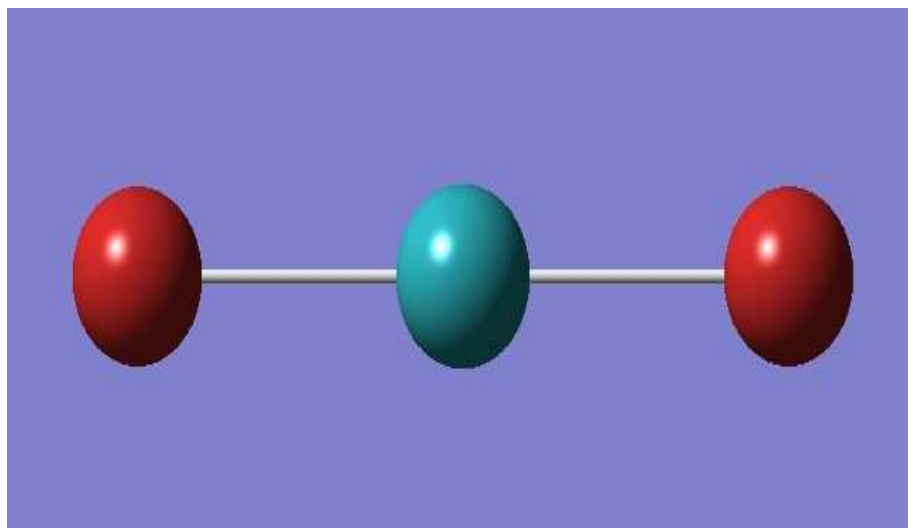
the transition metal-hydrogen bonds, which show dominantly  $sd^n$  hybridized bond orbitals and negligible  $np$  participation [2]. However, there is a serious technical flaw in the analysis. The NBO method requires preselection of those orbitals, which are considered as valence orbitals, and may become occupied in the population analysis. In this paper we present the calculations of eigenvalues, eigenvector, overlap matrix and population analysis of ruthenium (II) bromide, in order to study the extent of contribution of 4d, 5s and 5p orbitals in the formation of molecular orbitals. Such a quantitative study will provide correct information about the involvement of 5p orbital of ruthenium in bonding.

### MATERIALS AND METHODS

The study materials of this paper are ruthenium (II) bromide. The 3D modeling and geometry optimization of the ruthenium (II) bromide have been done by CAChe software using molecular mechanics with EHT option. Eigenvalues, eigenvectors and overlap matrix values have been obtained with the same software, using the same option. With the help of these values, eigenvector analysis, magnitude of contribution of atomic orbital in MO formation, population analysis and overlap population analysis have been made and discussed. The theory on which various calculations are made is defined elsewhere [10].

### RESULTS AND DISCUSSION

Ruthenium (II) bromide is triatomic molecule, having the following optimized geometry [11-12] as obtained from molecular mechanics [13–16] method.



**Figure.1 Optimized geometry of ruthenium (II) bromide.**

The MOs of ruthenium (II) bromide are formed by linear combination of 9 ruthenium orbitals and 4 orbitals from bromide as detailed below-

$$\begin{array}{rcl}
 \text{Ru-1} = 5s, 5p_x, 5p_y, 5p_z, 4d_{x^2-y^2}, 4d_z^2, 4d_{xy}, 4d_{xz}, 4d_{yz} & = & 9 \\
 \text{Br-2} = 4s, 4p_x, 4p_y, 4p_z & = & 4 \\
 \text{Br-3} = 4s, 4p_x, 4p_y, 4p_z & = & 4 \\
 \text{Total} & = & 17
 \end{array}$$

**Table 1. Eigenvector values of molecular orbitals of Ruthenium (II) bromide.**

Atom	AOs ( $\chi$ )	Eigenvector 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
Ru-1	5s	-0.1235	0.0000	0.0412	0.0000	0.0000	-0.0000	-0.0000	-0.0000	0.0000	-0.0000	-0.4988	0.0000	-0.0000	0.0000	-0.0000	1.0382	0.0000
	5px	-0.0000	-0.0872	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	-0.1950	0.0014	-0.0000	0.0000	0.0000	-0.0000	-0.0110	0.0000	0.0000	1.3478
	5py	0.0000	-0.0009	0.0000	-0.0000	-0.0000	0.0000	0.0000	-0.0021	-0.1254	0.0000	-0.0000	-0.0000	0.0000	1.0113	-0.0010	0.0000	0.0146
	5pz	-0.0000	-0.0000	-0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.1254	0.0000	0.0000	0.0000	-0.0010	-1.0113	0.0000	0.0000
	4dx <sup>2</sup> -y <sup>2</sup>	-0.1425	-0.0000	0.5982	0.0008	0.0192	0.0000	0.4999	0.0000	-0.0000	0.0000	0.5494	-0.0000	0.0103	0.0000	-0.0000	0.3682	0.0000
	4dz <sup>2</sup>	0.0823	-0.0000	-0.3455	-0.0000	-0.0000	0.0000	0.8660	-0.0000	0.0000	-0.0000	-0.3173	0.0000	-0.0000	-0.0000	0.0000	-0.2127	-0.0000
	4dxy	-0.0031	0.0000	0.0130	-0.0355	-0.8852	0.0000	0.0108	-0.0000	-0.0000	0.0000	0.0119	0.0019	-0.4749	0.0000	-0.0000	0.0080	-0.0000
	4dxz	-0.0000	-0.0000	0.0000	-0.8853	0.0355	0.0108	-0.0000	-0.0000	-0.0000	-0.0000	0.0000	-0.4750	-0.0019	-0.0000	-0.0000	0.0000	0.0000
	4dyz	-0.0000	0.0000	-0.0000	-0.0096	0.0004	-0.9999	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0051	-0.0000	0.0000	0.0000	-0.0000	0.0000
Br-2	4s	-0.6531	-0.6794	-0.1904	-0.0000	-0.0000	0.0000	0.0000	0.0796	-0.0000	0.0000	0.0328	-0.0000	0.0000	-0.0000	0.0000	-0.3224	-0.4462
	4px	-0.0020	-0.0175	-0.4025	0.0001	0.0029	0.0000	0.0000	0.6271	0.0074	-0.0000	0.3706	0.0000	-0.0071	0.0024	-0.0000	0.5882	0.6113
	4py	-0.0000	-0.0002	-0.0044	-0.0108	-0.2691	0.0000	0.0000	0.0068	-0.6854	0.0002	0.0040	-0.0026	0.6580	-0.2246	0.0002	0.0064	0.0066
	4pz	0.0000	-0.0000	-0.0000	-0.2691	0.0108	0.0000	0.0000	0.0000	0.0002	0.6846	0.0000	0.6580	0.0026	0.0002	0.2246	-0.0000	0.0000
Br-3	4s	-0.6531	0.6794	-0.1904	0.0000	0.0000	0.0000	0.0000	-0.0796	-0.0000	0.0000	0.0328	0.0000	-0.0000	-0.0000	0.0000	0.3224	0.4462
	4px	0.0020	-0.0175	0.4025	-0.0001	-0.0029	-0.0000	-0.0000	0.6271	0.0074	-0.0000	-0.3706	-0.0000	0.0071	0.0024	-0.0000	-0.5882	0.6113
	4py	0.0000	-0.0002	0.0044	0.0108	0.2691	0.0000	0.0000	0.0068	-0.6845	0.0002	-0.0040	0.0026	-0.6580	-0.2246	0.0002	-0.0064	0.0066
	4pz	0.0000	-0.0000	-0.0000	0.2691	-0.0108	0.0000	0.0000	0.0000	0.0002	0.6846	0.0000	-0.6580	-0.0026	0.0002	0.2246	-0.0000	0.0000

**Table 2. Overlap matrix (Overlap integrals values) of Ruthenium (II) bromide.**

AOs	5s (Ru-1)	5px (Ru-1)	5py (Ru-1)	5pz (Ru-1)	4dx <sup>2</sup> -y <sup>2</sup> (Ru-1)	4dz <sup>2</sup> (Ru-1)	4dxy (Ru-1)	4dxz (Ru-1)	4dyz (Ru-1)	4s (Br-2)	4px (Br-2)	4py (Br-2)	4pz (Br-2)	4s (Br-3)	4px (Br-3)	4py (Br-3)	4pz (Br-3)	
5s (Ru-1)	1.0000																	
5px (Ru -1)	-0.0000	1.0000																
5py (Ru -1)	-0.0000	-0.0000	1.0000															
5pz (Ru -1)	0.0000	0.0000	0.0000	1.0000														
4dx <sup>2</sup> -y <sup>2</sup> (Ru -1)	0.0000	0.0000	-0.0000	0.0000	1.0000													
4dz <sup>2</sup> (Ru -1)	-0.0000	-0.0000	-0.0000	0.0000	0.0000	1.0000												
4dxy (Ru -1)	-0.0000	0.0000	0.0000	0.0000	-0.0000	0.0000	1.0000											
4dxz (Ru 1)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000										
4dyz (Ru -1)	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0000	0.0000	-0.0000	1.0000									
4s (Br-2)	0.1947	0.2991	0.0032	0.0000	0.0849	-0.0490	0.0018	0.0000	0.0000	1.0000								
4px (Br-2)	-0.2872	-0.3759	-0.0056	0.0000	-0.1261	0.0728	-0.0035	0.0000	0.0000	-0.0000	1.0000							
4py (Br-2)	-0.0031	-0.0056	0.1361	0.0000	-0.0030	0.0008	0.0731	0.0000	0.0000	-0.0000	0.0000	1.0000						
4pz (Br-2)	0.0000	0.0000	0.0000	0.1361	0.0000	0.0000	0.0000	0.0731	0.0008	0.0000	0.0000	0.0000	1.0000					
4s (Br-3)	0.1947	-0.2991	-0.0032	0.0000	0.0849	-0.0490	0.0018	0.0000	0.0000	0.0001	-0.0008	-0.0000	0.0000	1.0000				
4px (Br-3)	0.2872	-0.3759	-0.0056	0.0000	0.1261	-0.0728	0.0035	0.0000	0.0000	0.0008	-0.0036	-0.0000	0.0000	0.0000	1.0000			
4py (Br-3)	0.0031	-0.0056	0.1361	0.0000	0.0030	-0.0008	-0.0731	0.0000	0.0000	0.0000	-0.0000	0.0003	0.0000	0.0000	0.0000	1.0000		
4pz (Br-3)	0.0000	0.0000	0.0000	0.1361	0.0000	0.0000	0.0000	-0.0731	-0.0008	0.0000	0.0000	0.0000	0.0003	0.0000	0.0000	0.0000	1.0000	

In order to examine the contribution of various atomic orbitals in the formation of molecular orbitals the LCAO has been studied. The 17 AOs give LCAO approximations to the 17 MOs of ruthenium (II) bromide. The various AOs are represented by  $\chi$  and MOs by  $\phi$ .  $\chi_1$  to  $\chi_9$  are 5s, 5px, 5py, 5pz,  $4dx^2-y^2$ ,  $4dz^2$ , 4dxy, 4dxz, 4dyz, respectively are atomic orbitals of ruthenium and  $\chi_{10}$  to  $\chi_{13}$  and  $\chi_{14}$  to  $\chi_{17}$  are 4s, 4px, 4py, 4pz for Br-2 and Br-3, respectively are atomic orbitals of bromide.

The eigenvalues of 17 MOs ( $\phi_1$  to  $\phi_{17}$ ) of ruthenium (II) bromide are -0.8280, -0.8154, -0.5702, -0.5626, -0.5626, -0.5476, -0.5476, -0.4972, -0.4854, -0.4854, -0.4838, -0.4579, -0.4579, -0.2274, -0.2274, -0.0181 and 0.3273, respectively. The coefficients of  $\chi$  are the eigenvector and overlap matrix which has been taken from Table-1 and Table- 2.

In order to examine the extent of involvement of 4d, 5s and 5p orbitals in the formation of molecular orbitals the values of coefficient of these orbitals have been added to see the total involvement in all the eleven MOs. The summation values of 4dxy, 4dxz,  $4dx^2-y^2$ , 5s, 5px, 5py, and 5pz are 0.9595, 0.9316, 1.8100, 0.6635, 0.2836, 0.1284 and 0.1254, respectively. The nonbonding orbitals  $4dz^2$  and 4dyz are excluded. It is clearly indicated that the maximum involvement is of  $4dx^2-y^2$  orbital and the minimum of 5pz orbital. The involvement of p orbital is negligible. The value of coefficient is between 0.2836 to 0.1254 which is very low in comparison to d orbitals (dxy, dxz,  $dx^2-y^2$ ) which is in the range 1.8100 to 0.9316. The value for 5s is 0.6635. The extent of involvement of 4d, 5s and 5p orbitals of ruthenium in the formation of MOs in the bromide is well demonstrated by the graph (Fig-2) drawn between the orbitals and the summation values of their coefficients. The graph showing below clearly shows that the involvement of p orbitals is negligible.

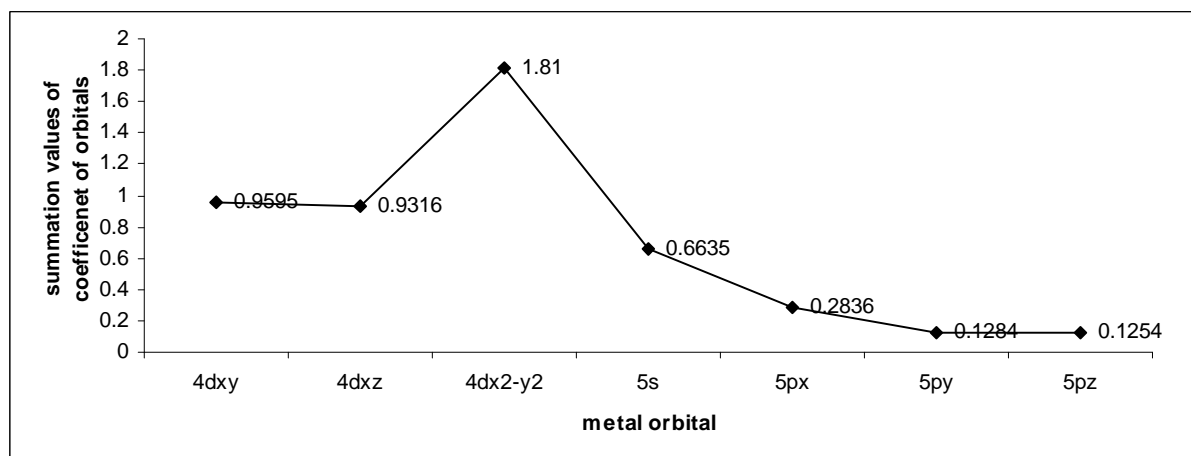


Figure.2 Trend of extent of involvement of metal orbital in the formation of MOs of RuBr<sub>2</sub>.

### Population Analysis:

The contribution of electrons in each occupied MO is calculated by using the population analysis method, introduced by Mulliken. This method apportions the electrons of n-electron molecule into net population  $n_r$  in the basis function  $\chi_r$ .

**Table 3: Contribution of electrons in MO of Ruthenium (II) bromide.**

MO. No	$n_i$	Major contribution		Minor contribution	
		Basis function ( $\chi_r$ )	$n_{r,i} = n_i c_{ri}^2$	Basis function ( $\chi_r$ )	$n_{r,i} = n_i c_{ri}^2$
1	2	5s (Ru 1)	0.0305		
		$4dx^2-y^2$ (Ru 1)	0.0406		
		$4dz^2$ (Ru 1)	0.0135		
		3s (Br 2)	0.8530		
		3s (Br 3)	0.8530		
2	2	5px (Ru 1)	0.0152	4px (Br 2)	0.0006
		4s (Br 2)	0.9231	4px (Br 3)	0.0006
		4s (Br 3)	0.9231		
3	2	$4dx^2-y^2$ (Ru 1)	0.7156	5s (Ru 1)	0.0033
		$4dz^2$ (Ru 1)	0.2387	4dxy (Ru 1)	0.0003
		4s (Br 2)	0.0725		
		4px (Br 2)	0.3240		
		4s (Br 3)	0.0725		
		4px (Br 3)	0.3240		
4	2	4dxz (Ru 1)	1.5675	4dxy (Ru 1)	0.0025
		4pz (Br 2)	0.1448		
		4pz (Br 3)	0.1448		
5	2	4dxy (Ru 1)	1.5671	$4dx^2-y^2$ (Ru 1)	0.0007
		4py (Br 2)	0.1448	4dxz (Ru 1)	0.0025
		4py (Br 3)	0.1448		
6	2	4dyz (Ru 1)	1.9996	4dxz (Ru 1)	0.0002
		$4dx^2-y^2$ (Ru 1)	0.4998	4dxy (Ru 1)	0.0002
7	2	$4dz^2$ (Ru 1)	1.4999		
		5px (Ru 1)	0.0760		
		4s (Br 2)	0.0126		
		4px (Br 2)	0.7865		
		4s (Br 3)	0.0126		
8	2	4px (Br 3)	0.7865		
		5py (Ru 1)	0.0314		
		4py (Br 2)	0.9370		
9	2	4py (Br 3)	0.9370		
		5pz (Ru 1)	0.0314		
		4pz (Br 2)	0.9373		
10	2	4pz (Br 3)	0.9373		
		5s (Ru 1)	0.4976	4dxy (Ru 1)	0.0002
		$4dx^2-y^2$ (Ru 1)	0.6036	4s (Br 2)	0.0021
11	2	$4dz^2$ (Ru 1)	0.2013		
		4px (Br 2)	0.2746		
		4px (Br 3)	0.2746		

Let there be  $n_i$  electrons in the MO  $\phi_i$  ( $n_i = 0, 1, 2$ ) and let  $n_{r,i}$  symbolize the contribution of electrons in the MO  $\phi_i$  to the net population in  $\chi_r$ . We have

$$n_{r,i} = n_i c_{ri}^2 \quad (1)$$

where,  $c_{ri}$  is the coefficient of atomic orbitals for the  $i^{\text{th}}$  MO ( $r=1-17$ ).

Equation- 1 has been solved for 22 electrons of 11 molecular orbitals. Two electrons in the 1<sup>st</sup> MO to 11<sup>th</sup> MO have been considered. The six molecular orbitals having no electron are left over. The data relating to  $c_{ri}$  have been taken from Table 1. The results of solution of equation-1 are included in Table 3 which enlists the contribution of electrons in molecular orbitals under two sections- major and intermediate. It is evident that major contribution is from 4d and 5s orbital. The p orbitals have negligible contribution. The details of contribution are as shown in Table 3.

Besides contribution of electrons the Mulliken's method is also used for evaluating overlap population, in order to distinguish bonding, nonbonding and anti bonding molecular orbitals. This method allocates proportionally the overlap population  $n_{r-s}$  for all possible pairs of basis functions. This is shown by the equation-2.

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

Where,  $c_{ri}$  = the coefficient of atomic orbitals for one atom.

$c_{si}$  = the coefficient of atomic orbitals for other atom .

and  $S_{rs}$  = the overlap integral between the two AOs (one of an atom and one of other atom ).

It is evident from equation-2 that for overlap population analysis of MOs of a molecule, we need eigenvector values (coefficients), values of overlap matrix (overlap integrals) and number of electrons in each MO. The eigenvector and overlap integral values for bromide of ruthenium have been taken from Table-1 and Table-2 respectively and the number of electrons is taken as two for 1<sup>st</sup> to 11<sup>th</sup> MOs and zero for 12<sup>th</sup> to 17<sup>th</sup> MO. With these values Table 4 is constructed for overlap-population contributions  $n_{r-s,i}$  of one molecular orbital. This table has 7 columns, defined as below. There will be 17 such tables for 17 MO but only 11 tables are constructed, because remaining six which have no electrons are left over. In such a way there will be 11 tables.

Column 1 – number of electron  $n_i$

Column 2, 4 – atomic orbitals of ruthenium and bromide.

Column 3 – coefficients of AOs of one atom ( $c_{ri}$ )

Column 5 – coefficients of AOs of other atom ( $c_{si}$ )

Column 6 – overlap integral between two AOs of different atoms ( $S_{rs}$ )

Column 7 – overlap population contribution  $n_{r-s,i}$  .

The possible overlaps between the various AOs of ruthenium and bromide in each molecular orbital will be 88, as detailed below–

8 overlaps – 5s AO of Ruthenium with 4s, 4px, 4py, 4pz AOs of Br-2 and Br-3.

8 overlaps – 5px AO of Ruthenium with 4s, 4px, 4py, 4pz AOs of Br-2 and Br-3.

8 overlaps – 5py AO of Ruthenium with 4s, 4px, 4py, 4pz AOs of Br-2 and Br-3.

8 overlaps – 5pz AO of Ruthenium with 4s, 4px, 4py, 4pz AOs of Br-2 and Br-3.

8 overlaps –  $4dx^2-y^2$  AO of Ruthenium with 4s, 4px, 4py, 4pz AOs of Br-2 and Br-3.

8 overlaps –  $4dz^2$  AO of Ruthenium with 4s, 4px, 4py, 4pz AOs of Br-2 and Br-3.

8 overlaps – 4dxy AO of Ruthenium with 4s, 4px, 4py, 4pz AOs of Br-2 and Br-3.

8 overlaps – 4dxz AO of Ruthenium with 4s, 4px, 4py, 4pz AOs of Br-2 and Br-3.

8 overlaps – 4dyz AO of Ruthenium with 4s, 4px, 4py, 4pz AOs of Br-2 and Br-3.

4 overlaps – 4s AO of Br-2 with 4s, 4px, 4py, 4pz AO of Br-3.  
 4 overlaps – 4px AO of Br-2 with 4s, 4px, 4py, 4pz AO of Br-3.  
 4 overlaps – 4py AO of Br-2 with 4s, 4px, 4py, 4pz AO of Br-3.  
 4 overlaps – 4pz AO of Br-2 with 4s, 4px, 4py, 4pz AO of Br-3.

Total– 88 overlaps

For the study of overlap population we have to construct eleven tables, Having 88 possible overlaps but while building up the table we have dropped the values of zero eigenvector value (Table 1), hence each table of overlap-population contribution differs in its number of orbitals. For obtaining the values of overlap-population contributions ( $n_{r-s,i}$ ) we have to discuss each table separately, but for brevity we here discuss Table 4 for molecular orbital number 1 of ruthenium bromide which is below:

Table 4. Overlap populations of 1st MO of Ruthenium (II) bromide.						
$n_i$	AOs	$c_{ri}$	AOs	$c_{si}$	$S_{rs}$	$n_{r-s,i} = n_i(2c_{ri}.c_{si}.S_{rs})$
2	5s(Ru 1)	-0.1235	4s(Br 2)	-0.6531	0.1947	0.0628
2	5s(Ru 1)	-0.1235	4px(Br 2)	-0.0020	-0.2872	-0.0002
2	5s(Ru 1)	-0.1235	4s(Br 3)	-0.6531	0.1947	0.0628
2	5s(Ru 1)	-0.1235	4px(Br 3)	0.0020	0.2872	-0.0002
2	4dx <sup>2</sup> -y <sup>2</sup> (Ru 1)	-0.1425	4s(Br 2)	-0.6531	0.0849	0.0316
2	4dx <sup>2</sup> -y <sup>2</sup> (Ru 1)	-0.1425	4px(Br 2)	-0.0020	-0.1261	-0.0001
2	4dx <sup>2</sup> -y <sup>2</sup> (Ru 1)	-0.1425	4s(Br 3)	-0.6531	0.0849	0.0316
2	4dx <sup>2</sup> -y <sup>2</sup> (Ru 1)	-0.1425	4px(Br 3)	0.0020	0.1261	-0.0001
2	4dz <sup>2</sup> (Ru 1)	0.0823	4s(Br 2)	-0.6531	-0.0490	0.0105
2	4dz <sup>2</sup> (Ru 1)	0.0823	4px(Br 2)	-0.0020	0.0728	0.0000
2	4dz <sup>2</sup> (Ru 1)	0.0823	4s(Br 3)	-0.6531	-0.0490	0.0105
2	4dz <sup>2</sup> (Ru 1)	0.0823	4px(Br 3)	0.0020	-0.0728	-0.0000
2	4dxy(Ru 1)	-0.0031	4s(Br 2)	-0.6531	0.0018	0.0000
2	4dxy(Ru 1)	-0.0031	4px(Br 2)	-0.0020	-0.0035	-0.0000
2	4dxy(Ru 1)	-0.0031	4s(Br 3)	-0.6531	0.0018	0.0000
2	4dxy(Ru 1)	-0.0031	4px(Br 3)	0.0020	0.0035	-0.0000
2	4s(Br 2)	-0.6531	4s(Br 3)	-0.6531	0.0001	0.0001
2	4s(Br 2)	-0.6626	4px(Br 3)	0.0020	0.0008	-0.0000
2	4px(Br 2)	-0.0020	4s(Br 3)	-0.6531	-0.0008	0.0000
2	4px(Br 2)	-0.0020	4px(Br 3)	0.0020	-0.0036	0.0000
						$\sum n_{r-s,i} = 0.2095$

This table has 20 possible overlaps; out of which 16 provide coefficient values of ruthenium orbitals and 4 for Br-2, in column 3 that are  $c_{ri}$ . Column-5 is for coefficient value  $c_{si}$ , for both the bromides. Up to 16, both the bromides are involved and for remaining four only Br-3. Column-6, is overlap integral  $S_{rs}$  and exhibits the magnitude of overlap between the AOs represented in column-2 and 4. The values are self explanatory for indicating the magnitude.

The overlap population analysis also shows negligible involvement of 5p orbitals of ruthenium. It has earlier been suggested that much smaller radius of the 4d orbital than the 5s orbital makes the involvement of 5s orbital dominant contribution in the bonding [17,18]. This hypothesis is the central theme of a recent text book of transition-metal chemistry by Gerloch and Constable [17]. 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 results indicate that 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 emphatically denied the involvement of np orbital in hybridization. He has supported sd hybridization and support the Landis concept.

The column-7 of Table 4 enlists the values of overlap population, derived from the equation –2. The sum of the values of overlap-populations decides whether the MO in a covalent molecule is bonding, nonbonding or antibonding. If the sum of this inter atomic overlap population contribution is substantially positive, the MO is bonding; if substantially negative, the MO is antibonding and if zero or near zero, the MO is nonbonding. Table 4 indicates that the sum of overlap- population contribution in first MO of RuBr<sub>2</sub> is 0.19218 which is positive indicating or supporting the bonding nature of MO.

Similarly the sum of overlap population for the 11 MO has been worked out and the results are tabulated in Table 5 below:

MO. No	Sum of overlap population contribution ( $\sum_{n,r,s,l}$ )		Nature of MOs
1	0.2095	Positive	Bonding
2	0.1373	Positive	Bonding
3	0.1679	Positive	Bonding
4	0.1394	Positive	Bonding
5	0.1394	Positive	Bonding
6	0.0000	Zero	Nonbonding
7	0.0000	Zero	Nonbonding
8	0.3308	Positive	Bonding
9	-0.0007	Negative	Antibonding
10	0.0945	Positive	Bonding
11	0.1422	Positive	Bonding

The overlap population analysis as presented in Table 5 shows that the nonbonding orbitals are present in 6<sup>th</sup> and 7<sup>th</sup> molecular orbitals. The difference in positions of nonbonding molecular orbitals prompted us to examine the eigenvalues of ruthenium ion and to compare them with the eigenvalues of the bromide. The eigenvalues of the molecular orbitals of the bromide are described above. The nonbonding orbital is degenerate in all the cases. The eigenvector analysis as presented in Table-1 indicates that these orbitals are 4dyz and 4dz<sup>2</sup>.

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

## CONCLUSION

**1.** Eigenvector analysis shows that 4dx<sup>2</sup>-y<sup>2</sup> and 4dxy orbitals of ruthenium play a major role in bonding between ruthenium and bromide, 5s orbital is next and 4p orbitals have a negligible role. This supports the Landis observation and concept of sd hybridization.

2. s and p orbitals of bromide are involved in bonding with ruthenium. There is a difference in energy levels of s and p orbitals are 0.6090.
3. The overlap population analysis shows that the nonbonding orbitals are present in 6<sup>th</sup> and 7<sup>th</sup> molecular orbitals.
4. No molecular orbital is formed by only two atomic orbitals. All molecular orbitals have contribution from many atomic orbitals; the difference is only in extent of involvement.
5. The sum of overlap population contribution of IV<sup>th</sup> and V<sup>th</sup> MOs are equal.

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