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Archives of Physics Research, 2011, 2 (2):114-133
(http://scholarsresearchlibrary.com/archive.html)

ISSN 0976-0970
CODEN (USA): APRRC7

Molecular Mechanics Based Study of Molecular Orbitals of Ruthenium Halides

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ABSTRACT

We have studied the molecular orbitals of ruthenium halides, 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 halides 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 halogens, 5s orbital is next and 5p orbitals have a negligible role. There is a difference in energy levels of s and p orbitals of chloride, bromide and iodide are 0.1691, 0.6090 and 0.7472 respectively. The overlap population analysis shows that the nonbonding orbitals are present in 6th and 7th molecular orbitals in both. 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 halides, sd hybridization, population analysis, overlap population analysis, eigenvector, eigenvalues.

INTRODUCTION

In the recent years Landis presented the result of DFT calculation of transition metal hydride [1-3]. 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 [1]. 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 few decades, 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 [4, 5]. This is largely due to the successful employment of gradient corrected density functional theory in calculating molecule; particularly of the heavier atoms [6-9] and in the use of small-core relativistic effective core potential [10-12] which set the stage for calculation of geometries, bond energies, and chemical reaction and other important properties of transition metal compounds with impressive accuracy [9, 13, 14]. Application of molecular mechanics to organometallic and transition metal compounds is growing [15]. Molecular orbital parameters such as eigenvalues, eigenvectors and overlap matrix are well calculated with this method. In this paper we present the comparative study of ruthenium (II) bromide and ruthenium (II) iodide based on eigenvalues, eigenvector, overlap matrix, population analysis and overlap population analysis, 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 halides of ruthenium. The 3D modeling and geometry optimization of the halide 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 and population analysis have been made and discussed.The theory on which various calculations are made is defined elsewhere [16].

RESULTS AND DISCUSSION

Ruthenium (II) halides are triatomic molecule; having the following (Fig. 1.1, 1.2, 1.3) optimized geometry [17–18] as obtained from molecular mechanics [19-22] method.
The MOs of these halides are formed by linear combination of 9 ruthenium orbitals and 4 orbitals from each halogen as detailed below-

Ru-1 = 5s, 5px, 5py, 5pz, $4dx^2-y^2$, $4dz^2$, 4dxy, 4dxz, 4dyz = 9
X-2 = ns, npx, npy, npz = 4
X-3 = ns, npx, npy, npz = 4
Total = 17
where, n = 3 for Cl, n = 4 for Br, and n = 5 for I.

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) halides. The various AOs are represented by χ and MOs by ϕ. χ_1 to χ_9 are 5s, 5px, 5py, 5pz, $4dx^2-y^2$, $4dz^2$, 4dxy, 4dxz, 4dyz, respectively and χ_{10} to χ_{13} and χ_{14} to χ_{17} are ns, npx, npy, npz for X-2 and X-3, respectively are atomic orbitals of halides.

The eigenvalues of 17 MOs (ϕ_1 to ϕ_{17}) of ruthenium (II) chloride are -0.9810, -0.9696, -0.5934, -0.5824, -0.5824, -0.5476, -0.5476, -0.5326, -0.5271, -0.5271, -0.4986, -0.4726, -0.4726, -0.2118, -0.2118, 0.1413 and 0.6063, respectively; 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 and of ruthenium (II) iodide are -0.6884, -0.6679, -0.5565, -0.5565, -0.5560, -0.5476, -0.5476, -0.4843, -0.4811, -0.4700, -0.4700, -0.4521, -0.4521, -0.2336, -0.2336, -0.0681 and 0.2251, respectively. The coefficients of χ are the eigenvector and overlap matrix which has been taken from Table-1.1, 1.2, 1.3 and Table- 2.1, 2.2, 2.3 respectively.

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 (ϕ_1-ϕ_{11}). The summation values of 4dxy, 4dxz, 4dx^2-y^2, 5s, 5px, 5py, and 5pz of ruthenium (II) chloride are 0.9025, 0.8758, 1.7533, 0.6598, 0.2383, 0.1302 and 0.1277, respectively; that of ruthenium (II) bromide are 0.9595, 0.9316, 1.8100, 0.6635, 0.2836, 0.1284 and 0.1254 respectively and of ruthenium (II) iodide are 0.9738, 0.9498, 1.8874, 0.6738, 0.3305, 0.1230 and 0.1199 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 in both halides. In ruthenium (II) chloride the value of 5p orbitals are in the range 0.2383 to 0.1277 which is very low in comparison to d orbitals (dxy, dxz, dx^2-y^2) which is in the range 1.7533 to 0.8758 and the value for 5s is 0.6598; but in ruthenium (II) bromide the value of 5p orbitals are 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. whereas in ruthenium (II) iodide the value of 5p orbitals are between 0.3305 to 0.1199 which is very low in comparison to d orbitals (dxy, dxz, dx^2-y^2) which is in the range 1.8874 to 0.9498. The value for 5s is 0.6738. So the involvement of 5p orbitals is negligible in both in comparison of 4d orbitals. The extent of involvement of 4d, 5s and 5p orbitals of ruthenium in the formation of MOs in the chloride, bromide and iodide 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. The summation values are highest in case of iodide and lowest in chloride. It is perhaps on this account the splitting of d orbitals is maximum in iodide and minimum in chloride.

Population Analysis:

The contribution of electrons in each occupied MO are calculated by using the population analysis method, introduced by Mulliken [23, 24]. This method apportions the electrons of n-electron molecule into net population n_r in the basis function χ_r.

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

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

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

Equation- 2 has been solved for 22 electrons of 11 molecular orbitals. Two electrons in the Ist MO to 11th 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 1.1, 1.2. The results of solution of equation-1 are included in Table 3.1, 3.2, 3.3 which enlists the contribution of electrons in molecular orbitals under two sections- major and minor. It is evident that major contribution is from 4d and 5s orbital. The p orbitals have negligible contribution. The details of contribution are in Table 3.1, 3.2, 3.3.

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

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

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 halides of ruthenium have been taken from Table-1.1, 1.2, 1.3 and Table-2.1, 2.2, 2.3 respectively and the number of electrons is taken as two for Ist to 11th MOs and zero for 12th to 17th 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 for each halide are constructed, because remaining six which have no electrons are left over. In such a way there will be 33 tables for all the three halides.
Column 1 – number of electron n_i

Column 2, 4 – atomic orbitals of ruthenium and halogen.
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 metal and halogens in each molecular orbital will be 88, as detailed below–
8 overlaps – 4s AO of ruthenium with ns, npx, npy, npz AOs of X-2 and X-3.
8 overlaps – 4px AO of ruthenium with ns, npx, npy, npz AOs of X-2 and X-3.
8 overlaps – 4py AO of ruthenium with ns, npx, npy, npz AOs of X-2 and X-3.
8 overlaps – 4pz AO of ruthenium with ns, npx, npy, npz AOs of X-2 and X-3.
8 overlaps – $3dx^2{-}y^2$ AO of ruthenium with ns, npx, npy, npz AOs of X-2 and X-3.
8 overlaps – $3dz^2$ AO of ruthenium with ns, npx, npy, npz AOs of X-2 and X-3.
8 overlaps – 3dxy AO of ruthenium with ns, npx, npy, npz AOs of X-2 and X-3.

8 overlaps – 3dxz AO of ruthenium with ns, npx, npy, npz AOs of X-2 and X-3.
8 overlaps – 3dyz AO of ruthenium with ns, npx, npy, npz AOs of X-2 and X-3.
4 overlaps – ns AO of X–2 with ns, npx, npy, npz AO of X-3.
4 overlaps – npx AO of X–2 with ns, npx, npy, npz AO of X-3.
4 overlaps – npy AO of X–2 with ns, npx, npy, npz AO of X-3.
4 overlaps – npz AO of X–2 with ns, npx, npy, npz AO of X-3.
Total– 88 overlaps

where,

n = 3 for Cl, n = 4 for Br and n = 5 for I and X = Cl, Br and I.

For the study of overlap population we have to construct eleven table for each halides, each having 88 possible overlaps but while building up the table we have dropped the values of zero eigenvector value (Table 1.1, 1.2, 1.3), 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 I^st^ MO of ruthenium chloride.

Ruthenium chloride.
This table has 31 possible overlaps; out of which 24 provide coefficient values of ruthenium orbitals and 7 for Cl-2, in column 3 that are c_{ri}. Column-5 is for coefficient value c_{si}, for both the chlorines. Up to 24, both the chlorines are involved and for remaining seven only Cl-3. Column-6 is overlapping 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.

Ruthenium bromide
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.

Ruthenium iodide
This table has 29 possible overlaps; out of which 24 provide coefficient values of ruthenium orbitals and 5 for I-2, in column 3 that are c_{ri}. Column-5 is for coefficient value c_{si}, for both the chlorines. Up to 24, both the iodides are involved and for remaining five only I-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 [25, 26]. This hypothesis is the central theme of a recent text book of transition-metal chemistry by Gerloch and Constable [27]. 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 [1-3] has also emphatically denied the involvement of np orbital in hybridization. He has supported sd hybridization and has based his observation on the bond angles. The idealized sd hybridization has been shown to have angles of 90^0 .This is because the energy curves are a function of the bond angles and have two minima one below 90^0 and one above 90^0. The bond angles also 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 $RuCl_2$ is 0.19218 which is positive indicating or supporting the bonding nature of MO.

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

The overlap population analysis as presented in Table 5 shows that the nonbonding electrons are present in 6th and 7th molecular orbitals in both $RuCl_2$ and $RuBr_2$. The non bonding orbital is degenerate in all the cases. The eigenvector analysis as presented in Table-1.1, 1.2 indicates that these orbitals are 4dyz and $4dz^2$.

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.

CONCLUSIONS

1. Eigenvector analysis shows that $4dx^2$-y^2 and 4dxy orbitals of ruthenium play a major role in bonding between ruthenium and halides, 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 halogen are involved in bonding with ruthenium. There is a difference in energy levels of s and p orbitals are 0.1691 in chloride, 0.6090 in bromide and 0.7472 in iodide.
3. The overlap population analysis shows that the nonbonding orbitals are present in 6th and 7th molecular orbitals in both.
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.

Acknowledgement
This paper is dedicated to Sri Zaheeruddin Khan, father of corresponding author.

Table 1.1: Eigenvector values of molecular orbitals of Ruthenium (II) chloride.

Atom	**AOs**	**Eigenvector values or coefficients of Atomic Orbitals**																
	(χ)	**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	-0.1029	0.0000	0.0966	-0.0000	0.0000	0.0000	0.0000	-0.0000	-0.0000	0.0000	-0.4603	-0.0000	-0.0000	-0.0000	-0.0000	-1.1218	0.0000
	5px	-0.0000	-0.0688	-0.0000	0.0000	-0.0000	0.0000	0.0000	-0.1681	-0.0014	0.0000	0.0000	-0.0000	-0.0000	0.0111	0.0000	0.0000	1.4554
	5py	0.0000	-0.0007	0.0000	0.0000	-0.0000	-0.0000	-0.0000	-0.0018	0.1271	-0.0006	-0.0000	0.0000	0.0000	-1.0225	-0.0003	0.0000	0.0158
	5pz	-0.0000	-0.0000	-0.0000	0.0000	0.0000	0.0000	-0.0000	0.0000	0.0006	0.1271	-0.0000	-0.0000	0.0000	0.0003	-1.0226	-0.0000	-0.0000
	$4dx^2$-y^2	-0.1049	-0.0000	0.4628	-0.0027	0.0161	-0.0000	-0.4999	0.0000	0.0000	-0.0000	0.6669	0.0003	0.0146	-0.0000	-0.0000	-0.4071	0.0000
	$4dz^2$	0.0606	-0.0000	-0.2673	0.0000	-0.0000	-0.0000	-0.8660	-0.0000	-0.0000	0.0000	-0.3851	-0.0000	-0.0000	0.0000	0.0000	0.2351	-0.0000
	4dxy	-0.0023	0.0000	0.0100	0.1234	-0.7415	-0.0000	-0.0108	-0.0000	-0.0000	0.0000	0.0145	-0.0131	-0.6721	-0.0000	-0.0000	-0.0088	-0.0000
	4dxz	0.0000	-0.0000	-0.0000	0.7416	0.1234	0.0108	-0.0000	-0.0000	-0.0000	-0.0000	0.0000	0.6722	-0.0131	0.0000	-0.0000	-0.0000	0.0000
	4dyz	0.0000	0.0000	0.0000	0.0080	0.0013	-0.9999	0.0000	-0.0000	0.0000	0.0000	-0.0000	0.0073	-0.0001	-0.0000	0.0000	-0.0000	-0.0000
Cl-2	3s	-0.6626	-0.6829	-0.1572	0.0000	-0.0000	-0.0000	-0.0000	0.0675	0.0000	-0.0000	-0.0028	-0.0000	-0.0000	0.0000	0.0000	0.3728	-0.5297
	3px	-0.0142	-0.0187	-0.4916	-0.0007	0.0043	-0.0000	0.0000	0.6403	-0.0074	0.0000	0.2812	-0.0001	-0.0064	-0.0028	-0.0000	-0.6084	0.6516
	3py	-0.0002	-0.0002	-0.0053	0.0660	-0.3966	-0.0000	-0.0000	0.0069	0.6796	-0.0032	0.0030	0.0115	0.5894	0.2616	0.0001	-0.0066	0.0071
	3pz	0.0000	-0.0000	-0.0000	0.3967	0.0660	0.0000	-0.0000	0.0000	0.0032	0.6796	0.0000	-0.5894	0.0115	-0.0001	0.2616	0.0000	-0.0000
Cl-3	3s	-0.6626	0.6829	-0.1572	-0.0000	0.0000	0.0000	-0.0000	-0.0675	0.0000	-0.0000	-0.0028	0.0000	0.0000	0.0000	0.0000	0.3728	0.5297
	3px	0.0142	-0.0187	0.4916	0.0007	-0.0043	-0.0000	0.0000	0.6403	-0.0074	0.0000	-0.2812	0.0001	0.0064	-0.0028	-0.0000	0.6084	0.6516
	3py	0.0002	-0.0002	0.0053	-0.0660	0.3966	-0.0000	-0.0000	0.0069	0.6796	-0.0032	-0.0030	-0.0115	-0.5894	0.2616	0.0001	0.0066	0.0071
	3pz	0.0000	0.0000	-0.0000	-0.3967	-0.0660	0.0000	-0.0000	0.0000	0.0032	0.6796	0.0000	0.5894	-0.0115	-0.0001	0.2616	0.0000	0.0000

Table 1.2: Eigenvector values of molecular orbitals of Ruthenium (II) bromide.

Atom	AOs	Eigenvector values or coefficients of Atomic Orbitals																
	(χ)	**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^2-y^2	-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^2	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 1.3: Eigenvector values of molecular orbitals of Ruthenium (II) Iodide.

Atom	**AOs**	**Eigenvector values or coefficients of Atomic Orbitals**																
	(χ)	**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	0.1682	0.0000	-0.0000	-0.0000	0.0083	-0.0000	-0.0000	0.0000	0.4973	-0.0000	0.0000	0.0000	-0.0000	0.0000	0.0000	-1.0160	0.0000
	5px	0.0000	-0.1190	0.0000	0.0000	0.0000	0.0000	-0.0000	0.2102	-0.0000	0.0000	-0.0013	0.0000	-0.0000	-0.0109	-0.0000	0.0000	1.3059
	5py	-0. 0000	-0.0013	0.0000	0.0000	-0.0000	-0.0000	0.0000	0.0023	-0.0000	-0.0005	0.1194	-0.0000	0.0000	1.0072	0.0023	0.0000	0.0142
	5pz	-0.0000	0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.1194	0.0005	-0.0000	-0.0000	0.0023	-1.0073	-0.0000	0.0000
	$4dx^2-y^2$	0.2522	-0.0000	-0.0002	-0.0202	-0.6232	0.0000	0.4999	-0.0000	-0.4917	0.0000	-0.0000	-0.0001	0.0081	0.0000	0.0000	-0.3287	0.0000
	$4dz^2$	-0.1457	-0.0000	-0.0000	-0.0000	-0.3599	0.0000	0.8660	0.0000	0.2839	-0.0000	0.0000	0.0000	-0.0000	-0.0000	-0.0000	0.1898	-0.0000
	4dxy	0.0055	0.0000	0.0079	0.9309	-0.0135	0.0000	0.0108	0.0000	-0.0107	0.0000	-0.0000	0.0037	-0.3745	0.0000	0.0000	-0.0071	-0.0000
	4dxz	0.0000	0.0000	-0.9311	0.0079	-0.0000	0.0108	-0.0000	-0.0000	0.0000	-0.0000	-0.0000	0.3745	0.0037	0.0000	-0.0000	0.0000	0.0000
	4dyz	0.0000	-0.0000	-0.0101	0.0001	0.0000	-0.9999	0.0000	0.0000	-0.0000	0.0000	0.0000	0.0041	0.0000	-0.0000	0.0000	0.0000	0.0000
I-2	5s	0.6043	-0.6703	0.0000	0.0000	0.2911	0.0000	0.0000	-0.1031	-0.0636	0.0000	-0.0000	-0.0000	0.0000	-0.0000	-0.0000	0.3208	-0.4207
	5px	-0.0470	-0.0091	-0.0000	-0.0023	0.3536	0.0000	0.0000	0.6191	-0.4060	0.0000	0.0075	-0.0001	-0.0064	-0.0022	0.0000	-0.5813	0.6031
	5py	-0.0005	-0.0001	0.0018	0.2067	0.0038	0.0000	0.0000	-0.0067	-0.0040	-0.0027	0.6879	-0.0068	0.6787	-0.2026	-0.0005	-0.0063	0.0065
	5pz	-0.0000	-0.0000	-0.2076	0.0018	0.0000	0.0000	0.0000	-0.0000	0.0000	0.6880	0.0027	-0.6787	-0.0068	-0.0005	0.2026	0.0000	-0.0000
I-3	5s	0.6043	0.6703	-0.0000	-0.0000	0.2911	0.0000	0.0000	0.1031	-0.0637	0.0000	-0.0000	0.0000	-0.0000	-0.0000	-0.0000	0.3208	0.4207
	5px	0.4070	-0.0091	0.0000	0.0023	-0.3536	-0.0000	-0.0000	-0.6191	0.4060	0.0000	-0.0075	-0.0001	0.0074	0.0022	0.0000	0.5813	0.6031
	5py	0.0005	-0.0001	-0.0018	-0.2076	-0.0038	0.0000	0.0000	-0.0067	0.0044	-0.0027	-0.6879	0.0068	-0.6787	-0.2026	-0.0005	0.0063	0.0065
	5pz	-0.0000	0.0000	0.2076	-0.0018	0.0000	0.0000	0.0000	0.0000	0.0000	0.6880	0.0027	0.6787	0.0068	-0.0005	0.2026	0.0000	0.0000

Table 2.1: Overlap matrix (Overlap integrals values) of Ruthenium (II) chloride.

AOs	**5s (Ru-1)**	**5px (Ru-1)**	**5py (Ru-1)**	**5pz (Ru-1)**	**4dx^2-y^2 (Ru-1)**	**4dz^2 (Ru-1)**	**4dxy (Ru-1)**	**4dxz (Ru-1)**	**4dyz (Ru-1)**	**3s (Cl-2)**	**3px (Cl-2)**	**3py (Cl-2)**	**3pz (Cl-2)**	**3s (Cl-3)**	**3px (Cl-3)**	**3py (Cl-3)**	**3pz (Cl-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^2-y^2 (Ru -1)	0.0000	0.0000	-0.0000	0.0000	1.0000												
4dz^2 (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								
3s (Cl-2)	0.2270	0.3406	0.0037	0.0000	0.0994	-0.0574	0.0022	0.0000	0.0000	1.0000							
3px (Cl-2)	-0.3205	-0.3862	-0.0060	0.0000	-0.1310	0.0757	-0.0038	0.0000	0.0000	-0.0000	1.0000						
3py (Cl-2)	-0.0035	-0.0060	0.1707	0.0000	-0.0034	0.0008	0.0923	0.0000	0.0000	-0.0000	0.0000	1.0000					
3pz (Cl-2)	0.0000	0.0000	0.0000	0.1708	0.0000	0.0000	0.0000	0.0923	0.0010	0.0000	0.0000	0.0000	1.0000				
3s (Cl-3)	0.2270	-0.3406	-0.0037	0.0000	0.0994	-0.0574	0.0022	0.0000	0.0000	0.0004	-0.0027	-0.0000	0.0000	1.0000			
3px (Cl-3)	0.3205	-0.3862	-0.0060	0.0000	0.1310	-0.0757	0.0038	0.0000	0.0000	0.0027	-0.0108	-0.0001	0.0000	0.0000	1.0000		
3py (Cl-3)	0.0035	-0.0060	0.1707	0.0000	0.0034	-0.0008	-0.0923	0.0000	0.0000	0.0000	-0.0001	0.0011	0.0000	-0.0000	-0.0000	1.0000	
3pz (Cl-3)	0.0000	0.0000	0.0000	0.1708	0.0000	0.0000	0.0000	-0.0923	-0.0010	0.0000	0.0000	0.0000	0.0011	0.0000	0.0000	0.0000	1.0000

Table 2.2: Overlap matrix (Overlap integrals values) of Ruthenium (II) bromide.

AOs	**5s (Ru-1)**	**5px (Ru-1)**	**5py (Ru-1)**	**5pz (Ru-1)**	**4dx^{2}-y^{2} (Ru-1)**	**4dz^{2} (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^{2}-y^{2} (Ru -1)	0.0000	0.0000	-0.0000	0.0000	1.0000												
4dz^{2} (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

Table 2.3: Overlap matrix (Overlap integrals values) of Ruthenium (II) Iodide.

AOs	5s	5px	5py	5pz	4dx^2-y^2	4dz^2	4dxy	4dxz	4dyz	5s	5px	5py	5pz	5s	5px	5py	5pz
	(Ru-1)	(Ru-1)	(Ru-1)	(Ru-1)	(Ru-1)	(Ru-1)	(Ru-1)	(Ru-1)	(Ru-1)	(I-2)	(I-2)	(I-2)	(I-2)	(I-3)	(I-3)	(I-3)	(I-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^2-y^2 (Ru -1)	0.0000	0.0000	-0.0000	0.0000	1.0000												
4dz^2 (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								
5s (I-2)	0.1844	0.2783	0.0030	0.0000	0.0748	-0.0432	0.0016	0.0000	0.0000	1.0000							
5px (I-2)	-0.2793	-0.3722	-0.0053	0.0000	-0.1156	0.0667	-0.0032	-0.0000	-0.0000	-0.0000	1.0000						
5py (I-2)	-0.0030	-0.0053	0.1185	0.0000	-0.0026	0.0007	0.0605	-0.0000	0.0000	-0.0000	0.0000	1.0000					
5pz (I-2)	0.0000	0.0000	0.0000	0.1185	0.0000	0.0000	0.0000	0.0605	0.0007	0.0000	0.0000	0.0000	1.0000				
5s (I-3)	0.1844	-0.2783	-0.0030	0.0000	0.0748	-0.0432	0.0016	0.0000	0.0000	0.0001	-0.0006	-0.0000	0.0000	1.0000			
5px (I-3)	0.2793	-0.3722	-0.0053	0.0000	0.1156	-0.0667	0.0032	-0.0000	-0.0000	0.0006	-0.0024	-0.0000	0.0000	0.0000	1.0000		
5py (I-3)	0.0030	-0.0053	0.1185	0.0000	0.0026	-0.0007	-0.0605	-0.0000	0.0000	0.0000	-0.0000	0.0002	0.0000	-0.0000	-0.0000	1.0000	
5pz (I-3)	0.0000	0.0000	0.0000	0.1185	0.0000	0.0000	0.0000	-0.0605	-0.0007	0.0000	0.0000	0.0000	0.0002	0.0000	0.0000	0.0000	1.0000

Table 3.1: Contribution of electrons in MO of Ruthenium (II) chloride.

MO. No	n_i	Major contribution		Minor contribution	
		Basis function (χ_r)	$n_{r,i} = n_i c^2_{ri}$	Basis function (χ_r)	$n_{r,i} = n_i c^2_{ri}$
1	2	5s (Ru 1)	0.0211	$4dz^2$ (Ru 1)	0.0073
		$4dx^2$-y^2 (Ru 1)	0.0220		
		3s (Cl 2)	0.8780		
		3s (Cl 3)	0.8780		
2	2	3s (Cl 2)	0.9327	5px (Ru 1)	0.0094
		3s (Cl 3)	0.9327		
3	2	$4dx^2$-y^2 (Ru 1)	0.4283	5s (Ru 1)	0.0186
		$4dz^2$ (Ru 1)	0.1428	3s (Cl 2)	0.0494
		3px (Cl 2)	0.4833	3s (Cl 3)	0.0494
		3px (Cl 3)	0.4833		
4	2	4dxz (Ru 1)	1.0999	4dxy (Ru 1)	0.0304
		3pz (Cl 2)	0.3147	4py (Cl 2)	0.0087
		3pz (Cl 3)	0.3147	4py (Cl 3)	0.0087
5	2	4dxy (Ru 1)	1.0996	4dxz (Ru 1)	0.0304
		3py (Cl 2)	0.3145	3pz (Cl 2)	0.0087
		3py (Cl 3)	0.3145	3pz (Cl 3)	0.0087
6	2	4dyz (Ru 1)	1.9996		
7	2	$4dx^2$-y^2 (Ru 1)	0.4998		
		$4dz^2$ (Ru 1)	1.4999		
8	2	5px (Ru 1)	0.0565	3s (Cl 2)	0.0091
		3px (Cl 2)	0.8199	3s (Cl 3)	0.0091
		3px (Cl 3)	0.8199		
9	2	5py (Ru 1)	0.0323		
		3py (Cl 2)	0.9237		
		3py (Cl 3)	0.9237		
10	2	5pz (Ru 1)	0.0323		
		3pz (Cl 2)	0.9237		
		3pz (Cl 3)	0.9237		
11	2	5s (Ru 1)	0.4237		
		$4dx^2$-y^2 (Ru 1)	0.8895		
		$4dz^2$ (Ru 1)	0.2866		
		3px (Cl 2)	0.1581		
		3px (Cl 3)	0.1581		

Table 3.2: Contribution of electrons in MO of Ruthenium (II) bromide.

MO. No	n_i	Major contribution		Minor contribution	
		Basis function (χ_r)	$n_{r,i} = n_i c^2_{ri}$	Basis function (χ_r)	$n_{r,i} = n_i c^2_{ri}$
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
7	2	$4dx^2-y^2$ (Ru 1)	0.4998	4dxy (Ru 1)	0.0002
		$4dz^2$ (Ru 1)	1.4999		
8	2	5px (Ru 1)	0.0760		
		4s (Br 2)	0.0126		
		4px (Br 2)	0.7865		
		4s (Br 3)	0.0126		
		4px (Br 3)	0.7865		
9	2	5py (Ru 1)	0.0314		
		4py (Br 2)	0.9370		
		4py (Br 3)	0.9370		
10	2	5pz (Ru 1)	0.0314		
		4pz (Br 2)	0.9373		
		4pz (Br 3)	0.9373		
11	2	5s (Ru 1)	0.4976	4dxy (Ru 1)	0.0002
		$4dx^2-y^2$ (Ru 1)	0.6036	4s (Br 2)	0.0021
		$4dz^2$ (Ru 1)	0.2013		
		4px (Br 2)	0.2746		
		4px (Br 3)	0.2746		

Table 3.3: Contribution of electrons in MO of Ruthenium (II) Iodide.

MO. No	n_i	Major contribution		Minor contribution	
		Basis function (χ_r)	$n_{r,i} = n_i c^2_{ri}$	Basis function (χ_r)	$n_{r,i} = n_i c^2_{ri}$
1	2	5s (Ru 1)	0.0565	5px (I 2)	0.0044
		$4dx^2-y^2$ (Ru 1)	0.1272	5px (I 3)	0.0044
		$4dz^2$ (Ru 1)	0.0424		
		5s (I 2)	0.7303		
		5s (I 3)	0.7303		
2	2	5px (Ru 1)	0.0283		
		5s (I 2)	0.8986		
		5s (I 3)	0.8986		
3	2	4dxz (Ru 1)	1.7338		
		5pz (I 2)	0.0861		
		5pz (I 3)	0.0861		
4	2	4dxz (Ru 1)	1.7331	$4dx^2-y^2$ (Ru 1)	0.0008
		5py (I 2)	0.0861		
		5py (I 3)	0.0861		
5	2	$4dx^2-y^2$ (Ru 1)	0.7767	4dxy (Ru 1)	0.0003
		$4dz^2$ (Ru 1)	0.2590		
		5s (I 2)	0.1699		
		5px (I 2)	0.2500		
		5s (I 3)	0.1699		
		5px (I 3)	0.2500		
6	2	4dyz (Ru 1)	1.9996	4dxz (Ru 1)	0.0002
7	2	$4dx^2-y^2$ (Ru 1)	0.4998	4dxy (Ru 1)	0.0002
		$4dz^2$ (Ru 1)	1.4999		
8	2	5px (Ru 1)	0.0883		
		5s (I 2)	0.0212		
		5px (I 2)	0.7665		
		5s (I 3)	0.0212		
		5px (I 3)	0.7665		
9	2	5s (Ru 1)	0.4946	4dxy (Ru 1)	0.0002
		$4dx^2-y^2$ (Ru 1)	0.4835	5s (I 2)	0.0080
		$4dz^2$ (Ru 1)	0.1611	5s (I 3)	0.0080
		5px (I 2)	0.3296		
		5px (I 3)	0.3296		
10	2	5pz (Ru 1)	0.0285		
		5pz (I 2)	0.9466		
		5pz (I 3)	0.9466		
11	2	5py (Ru 1)	0.0285		
		5py (I 2)	0.9464		
		5py (I 3)	0.9464		

Table 4. Overlap populations of Ist MO of Ruthenium (II) chloride.

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)	-0.1029	3s(Cl 2)	-0.6626	0.2270	0.06190
2	5s(Ru 1)	-0.1029	3px(Cl 2)	-0.0142	-0.3205	-0.00187
2	5s(Ru 1)	-0.1029	3py(Cl 2)	-0.0002	-0.0035	0.00000
2	5s(Ru 1)	-0.1029	3s(Cl 3)	-0.6626	0.2270	0.06190
2	5s(Ru 1)	-0.1029	3px(Cl 3)	0.0142	0.3205	-0.00187
2	5s(Ru 1)	-0.1029	3py(Cl 3)	0.0002	0.0035	0.00000
2	4dx^2-y^2(Ru 1)	-0.1049	3s(Cl 2)	-0.6626	0.0994	0.02763
2	4dx^2-y^2(Ru 1)	-0.1049	3px(Cl 2)	-0.0142	-0.1310	-0.00078
2	4dx^2-y^2(Ru 1)	-0.1049	3py(Cl 2)	-0.0002	-0.0034	0.00000
2	4dx^2-y^2(Ru 1)	-0.1049	3s(Cl 3)	-0.6626	0.0994	0.02763
2	4dx^2-y^2(Ru 1)	-0.1049	3px(Cl 3)	0.0142	0.1310	-0.00078
2	4dx^2-y^2(Ru 1)	-0.1049	3py(Cl 3)	0.0002	0.0034	0.00000
2	4dz^2(Ru 1)	0.0606	3s(Cl 2)	-0.6626	-0.0574	0.00921
2	4dz^2(Ru 1)	0.0606	3px(Cl 2)	-0.0142	0.0757	-0.00026
2	4dz^2(Ru 1)	0.0606	3py(Cl 2)	-0.0002	0.0008	0.00000
2	4dz^2(Ru 1)	0.0606	3s(Cl 3)	-0.6626	-0.0574	0.00921
2	4dz^2(Ru 1)	0.0606	3px(Cl 3)	0.0142	-0.0757	-0.00026
2	4dz^2(Ru 1)	0.0606	3py(Cl 3)	0.0002	-0.0008	0.00000
2	4dxy(Ru 1)	-0.0023	3s(Cl 2)	-0.6626	0.0022	0.00001
2	4dxy(Ru 1)	-0.0023	3px(Cl 2)	-0.0142	-0.0038	0.00000
2	4dxy(Ru 1)	-0.0023	3py(Cl 2)	-0.0002	0.0923	0.00000
2	4dxy(Ru 1)	-0.0023	3s(Cl 3)	-0.6626	0.0022	0.00001
2	4dxy(Ru 1)	-0.0023	3px(Cl 3)	0.0142	0.0038	0.00000
2	4dxy(Ru 1)	-0.0023	3py(Cl 3)	0.0002	-0.0923	0.00000
2	3s(Cl 2)	-0.6626	3s(Cl 3)	-0.6626	0.0004	0.00070
2	3s(Cl 2)	-0.6626	3px(Cl 3)	0.0142	0.0027	-0.00010
2	3px(Cl 2)	-0.0142	3s(Cl 3)	-0.6626	-0.0027	-0.00010
2	3px(Cl 2)	-0.0142	3px(Cl 3)	0.0142	-0.0108	0.00000
2	3px(Cl 2)	-0.0142	3py(Cl 3)	0.0002	-0.0001	0.00000
2	3py(Cl 2)	-0.0002	3px(Cl 3)	0.0142	-0.0001	0.00000
2	3py(Cl 2)	-0.0002	3py(Cl 3)	0.0002	0.0011	0.00000

$\sum n_{r-s,i} = 0.19218$

Table 5

Nature of occupied MOs of $RuCl_2$

MO. No	Sum of overlap population contribution ($\sum n_{r\text{-}s,I}$)		Nature of MOs
1	0.19218	Positive	Bonding
2	0.12479	Positive	Bonding
3	0.22345	Positive	Bonding
4	0.22263	Positive	Bonding
5	-0.21482	Negative	Antibonding
6	0.00000	Zero	Nonbonding
7	0.00000	Zero	Nonbonding
8	0.28493	Positive	Bonding
9	0.06038	Positive	Bonding
10	0.12005	Positive	Bonding
11	0.07327	Positive	Bonding
Nature of occupied MOs of $RuBr_2$			
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
Nature of occupied MOs of RuI_2			
1	0.3033	Positive	Bonding
2	0.0888	Positive	Bonding
3	0.0934	Positive	Bonding
4	0.0934	Positive	Bonding
5	0.1329	Positive	Bonding
6	0.00000	Zero	Nonbonding
7	0.00000	Zero	Nonbonding
8	0.3358	Positive	Bonding
9	0.3062	Positive	Bonding
10	0.0781	Positive	Bonding
11	0.0781	Positive	Bonding

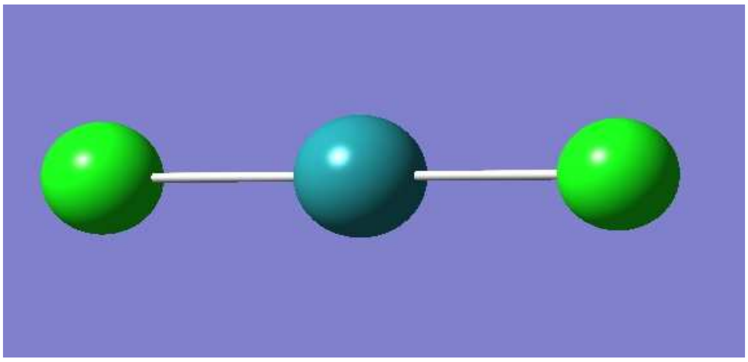

Fig.1.1: Optimized geometry of ruthenium (II) chloride.

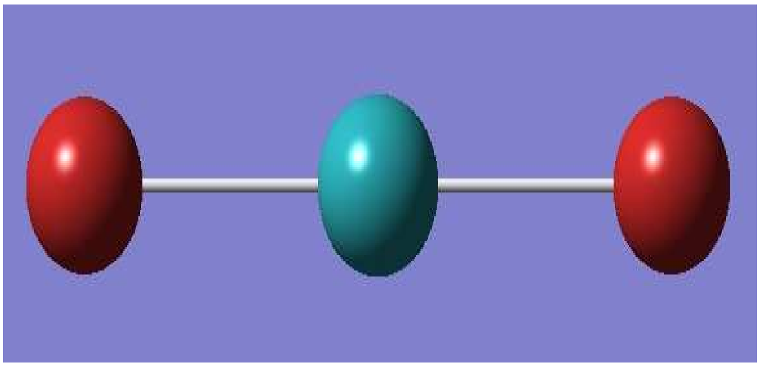

Fig.1.2: Optimized geometry of ruthenium (II) bromide.

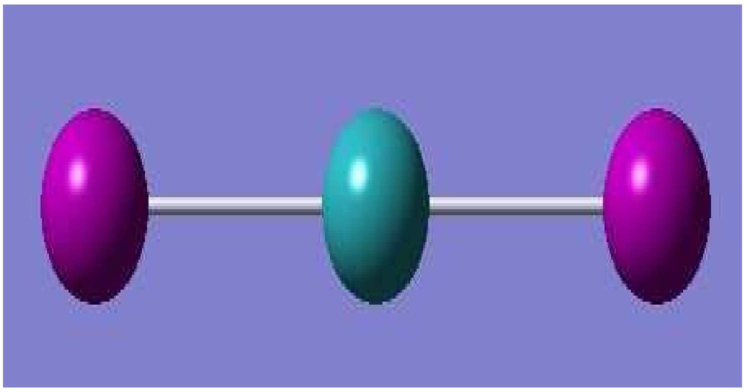

Fig.1.3: Optimized geometry of ruthenium (II) iodide.

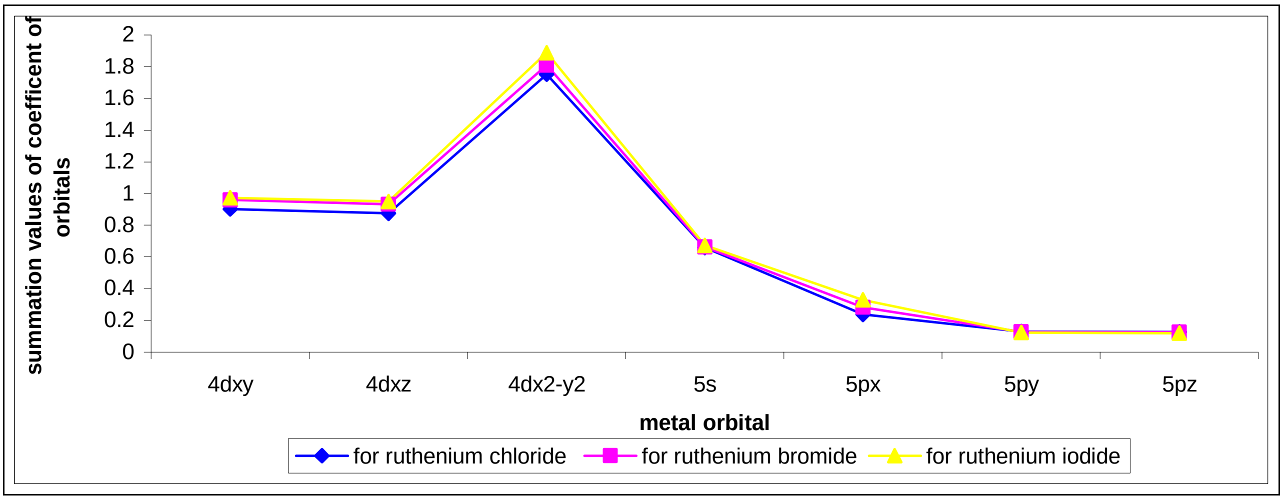

Figure.2 Trend of extent of involvement of metal orbital in the formation of MOs of ruthenium halides

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