Available on line www.jocpr.com

Journal of Chemical and Pharmaceutical Research

ISSN No: 0975-7384
CODEN(USA): JCPRC5

J. Chem. Pharm. Res., 2011, 3(2):264-273

Molecular Mechanics Based Study of Molecular Orbitals of Ruthenium (II) Iodide

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ABSTRACT

We have studied the molecular orbitals of ruthenium (II) iodide, 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) iodide 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 iodide, 5s orbital is next and 4p orbitals have a negligible role. There is a difference in energy levels of s and p orbitals of iodide are 0.0.7472 eV. The overlap population analysis shows that the nonbonding orbitals are present in 6^{th} and 7^{th} 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) iodide, 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) iodide, 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.

EXPERIMENTAL SECTION

The study materials of this paper are ruthenium (II) iodide. The 3D modeling and geometry optimization of the ruthenium (II) iodide 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) iodide is triatomic molecule, having the following optimized geometry [11-12] as obtained from molecular mechanics [13–16] method.

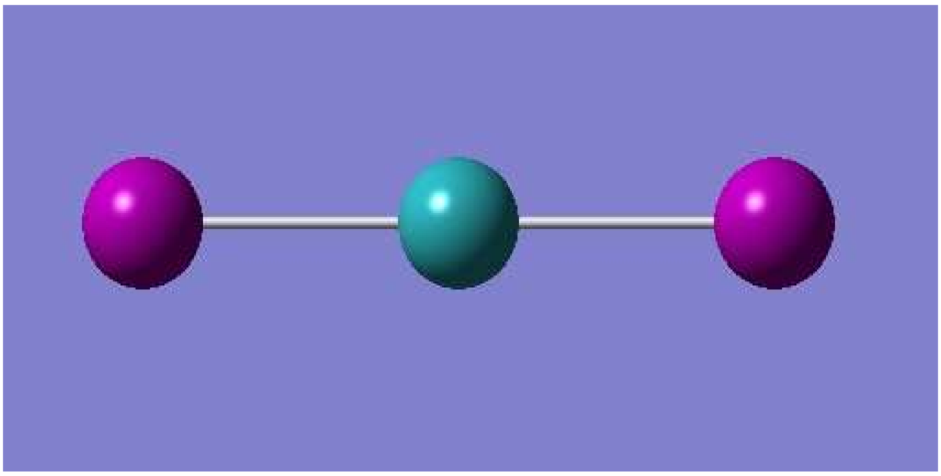

Figure.1 Optimized geometry of ruthenium (II) iodide.

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

Ru-1 = 5s, 5px, 5py, 5pz, $4dx^2-y^2$, $4dz^2$, 4dxy, 4dxz, 4dyz = 9
I-2 = 5s, 5px, 5py, 5pz = 4
I-3 = 5s, 5px, 5py, 5pz = 4
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 give LCAO approximations to the 17 MOs of ruthenium (II) iodide. 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 are atomic orbitals of ruthenium and χ_{10} to χ_{13} are 5s, 5px, 5py, 5pz for I-2; χ_{14} to χ_{17} are 5s, 5px, 5py, 5pz for I-3, respectively are atomic orbitals of iodide.

The eigenvalues of 17 MOs (ϕ_1 to ϕ_{17}) 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 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 0.9738, 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. The involvement of p orbital is negligible. The value of coefficient is 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. The extent of involvement of 4d, 5s and 5p orbitals of ruthenium in the formation of MOs in the 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.

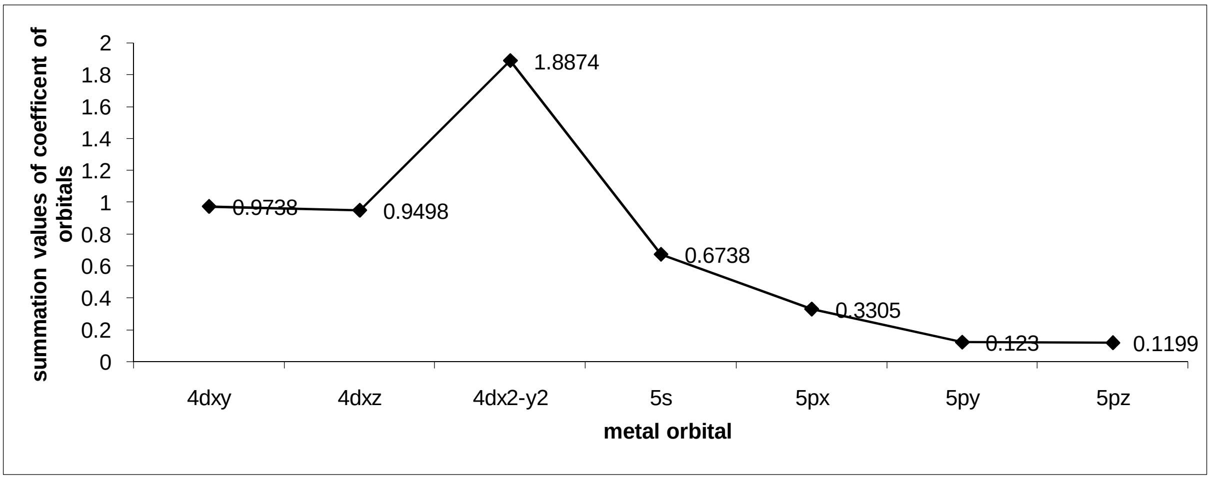

Figure.2 Trend of extent of involvement of metal orbital in the formation of MOs of RuI_2

Table 1. 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. Overlap matrix (Overlap integrals values) of Ruthenium (II) Iodide.

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)**	**5s (I-2)**	**5px (I-2)**	**5py (I-2)**	**5pz (I-2)**	**5s (I-3)**	**5px (I-3)**	**5py (I-3)**	**5pz (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

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 χ_r.

Table 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		

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 i^{th} MO (r =1–17).

Equation- 1 has been solved for 22 electrons of 11 molecular orbitals. Two electrons in the I^{st} MO to 11^{th} 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 above.

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.

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

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 iodide of ruthenium have been taken from Table-1 and Table-2 respectively and the number of electrons is taken as two for I^{st} to 11^{th} MOs and zero for 12^{th} to 17^{th} 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 iodide.
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 iodide in each molecular orbital will be 88, as detailed below–

8 overlaps – 5s AO of Ruthenium with 5s, 5px, 5py, 5pz AOs of I-2 and I-3.
8 overlaps – 5px AO of Ruthenium with 5s, 5px, 5py, 5pz AOs of I-2 and I-3.
8 overlaps – 5py AO of Ruthenium with 5s, 5px, 5py, 5pz AOs of I-2 and I-3.
8 overlaps – 5pz AO of Ruthenium with 5s, 5px, 5py, 5pz AOs of I-2 and I-3.
8 overlaps – $4dx^2–y^2$ AO of Ruthenium with 5s, 5px, 5py, 5pz AOs of I-2 and I-3.
8 overlaps – $4dz^2$ AO of Ruthenium with 5s, 5px, 5py, 5pz AOs of I-2 and I-3.

8 overlaps – 4dxy AO of Ruthenium with 5s, 5px, 5py, 5pz AOs of I-2 and I-3.
8 overlaps – 4dxz AO of Ruthenium with 5s, 5px, 5py, 5pz AOs of I-2 and I-3.
8 overlaps – 4dyz AO of Ruthenium with 5s, 5px, 5py, 5pz AOs of I-2 and I-3.
4 overlaps – 5s AO of I–2 with 5s, 5px, 5py, 5pz AO of I-3.
4 overlaps – 5px AO of I–2 with 5s, 5px, 5py, 5pz AO of I-3.
4 overlaps – 5py AO of I–2 with 5s, 5px, 5py, 5pz AO of I-3.
4 overlaps – 5pz AO of I–2 with 5s, 5px, 5py, 5pz AO of I-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 iodide, which is below:

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

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)	0.1682	5s(I 2)	0.6043	0.1844	0.0749
2	5s(Ru 1)	0.1682	5px(I 2)	-0.0470	-0.2793	0.0088
2	5s(Ru 1)	0.1682	5py(I 2)	-0.0005	-0.0030	0.0000
2	5s(Ru 1)	0.1682	5s(I 3)	0.6043	0.1844	0.0749
2	5s(Ru 1)	0.1682	5px(I 3)	0.0470	0.2793	0.0088
2	5s(Ru 1)	0.1682	5py(I 3)	0.0005	0.0030	0.0000
2	$4dx^2$-y^2(Ru 1)	0.2522	5s(I 2)	0.6043	0.0748	0.0455
2	$4dx^2$-y^2(Ru 1)	0.2522	5px(I 2)	-0.0470	-0.1156	0.0054
2	$4dx^2$-y^2(Ru 1)	0.2522	5py(I 2)	-0.0005	-0.0026	0.0000
2	$4dx^2$-y^2(Ru 1)	0.2522	5s(I 3)	0.6043	0.0748	0.0455
2	$4dx^2$-y^2(Ru 1)	0.2522	5px(I 3)	0.0470	0.1156	0.0054
2	$4dx^2$-y^2(Ru 1)	0.2522	5py(I 3)	0.0005	0.0026	0.0000
2	$4dz^2$(Ru 1)	-0.1457	5s(I 2)	0.6043	-0.0432	0.0152
2	$4dz^2$(Ru 1)	-0.1457	5px(I 2)	-0.0470	0.0667	0.0018
2	$4dz^2$(Ru 1)	-0.1457	5py(I 2)	-0.0005	0.0007	0.0000
2	$4dz^2$(Ru 1)	-0.1457	5s(I 3)	0.6043	-0.0432	0.0152
2	$4dz^2$(Ru 1)	-0.1457	5px(I 3)	0.0470	-0.0667	0.0018
2	$4dz^2$(Ru 1)	-0.1457	5py(I 3)	0.0005	-0.0007	0.0000
2	4dxy(Ru 1)	0.0055	5s(I 2)	0.6043	0.0016	0.0000
2	4dxy(Ru 1)	0.0055	5px(I 2)	-0.0470	-0.0032	0.0000
2	4dxy(Ru 1)	0.0055	5py(I 2)	-0.0005	0.0605	0.0000
2	4dxy(Ru 1)	0.0055	5s(I 3)	0.6043	0.0016	0.0000
2	4dxy(Ru 1)	0.0055	5px(I 3)	0.0470	0.0032	0.0000
2	4dxy(Ru 1)	0.0055	5py(I 3)	0.0005	-0.0605	0.0000
2	5s(I 2)	0.6043	5s(I 3)	0.6043	0.0001	0.0001
2	5s(I 2)	0.6043	5px(I 3)	0.0470	0.0006	0.0000
2	5px(I 2)	-0.0470	5s(I 3)	0.6043	-0.0006	0.0000
2	5px(I 2)	-0.0470	5px(I 3)	0.0470	-0.0024	0.0000
2	5py(I 2)	-0.0005	5py(I 3)	0.0005	0.0002	0.0000
				$\sum n_{r-s,i} =$ 0.3033		

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 [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 RuI_2 is 0.3033 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.

Table 5. Nature of occupied MOs

MO. No	Sum of overlap population contribution ($\sum n_{r-s,I}$)		Nature of MOs
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

The overlap population analysis as presented in Table 5 shows that the nonbonding orbitals are present in 6^{th} and 7^{th} 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 iodide. The eigenvalues of the molecular orbitals of the iodide 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 $4dz^2$.

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.

CONCLUSION

1. Eigen vector analysis shows that $4dx^2$-y^2 and 4dxy orbitals of ruthenium play a major role in bonding between ruthenium and iodide, 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 iodide are involved in bonding with ruthenium. There is a difference in energy levels of s and p orbitals are 0.7472 eV.

3. The overlap population analysis shows that the nonbonding orbitals are present in 6^{th} and 7^{th} 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 3^{rd} and 4^{th}, and 10^{th} and 11^{th} MOs are equal.

Acknowledgement
This paper is dedicated to the father of corresponding author. I am thankful to Dr. Gayasuddin Khan for valuable suggestions.

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