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Molecular Mechanics Based Study of Molecular Orbitals of Cobalt(II) Halides

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The quantitative nature of contributions of atomic orbitals in the formation of molecular orbitals with the help of LCAO approximations have been studied using eigenvector values. The contribution of electrons in each occupied molecular orbitals has been calculated by adopting the population analysis method of Mulliken. The overlap population analysis has also been made to identify the bonding, non-bonding and antibonding nature of molecular orbital. The results indicate that in bonding between cobalt and halogens, $3d_{x^2-y^2}$ and $3d_{xy}$ orbitals of cobalt are the main contributors in all the three halides; the next contributors are $3d_{xz}$ and 4*s* orbitals. The 4*p* orbitals have a negligible role in bonding. The nonbonding orbitals in chloride are 9th and 10th, in bromide 7th and 8th and in iodide 6th and 7th molecular orbitasl. The magnitude of splitting of *d* orbital as evaluated by eigenvalues and eigenvector values indicate the following order: $CoCl_2 < CoBr_2 < CoI_2$.

Key Words: Cobalt(II) halides, *sd* Hybridization, Population analysis, Eigenvalue, Eigenvector.

INTRODUCTION

In the last decade, there has been a phenomenal advancement in theoretical inorganic chemistry, much faster computers are available and 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[1, 2]. This is largely due to the successful employment of gradient corrected density functional theory in calculating molecules, particularly of the heavier atoms[3–6] and in the use of small-core relativistic effective core potential[7–9] which set the stage for calculation of geometries, bond energies, and chemical reaction and other important properties of transition metal compounds with impressive accuracy[6, 10, 11]. Application of molecular mechanics to organomettalic and transition metal compounds is growing[12]. Molecular orbital parameters such as eigenvectors, overlap matrix and eigenvalues are well calculated with this method. In this paper we present the calculations of eigenvector, overlap

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matrix and population analysis of cobalt(II) halides, in order to study the extent of contribution of 3*d*, 4*s* and 4*p* orbital in the formation of molecular orbitals. Such a quantitative study will provide correct information about the involvement of 4*p* orbital of cobalt in bonding and will help to resolve the controversy raised by Landis[13–16] and other[17–21] workers.

EXPERIMENTAL

The study materials of this paper are halides of cobalt. The 3D modelling 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 method adopted for various calculations is based on the following principles.

The molecular orbitals are formed by the linear combination of basis functions. Most molecular quantum-mechanical methods (such as SCF, CI etc.) begin the calculation with the choice of a basis function χ_r, which are used to express the MOs ϕ_i as $\phi_i = \Sigma c_{ri}\chi_r$. (c = coefficient of χ, r = number of atomic orbital, i = molecular orbital number). The use of an adequate basis set is an essential requirement for the calculation. The basis functions are usually taken as AOs. Each AO can be represented as a linear combination of one or more Slater-type orbitals (STOs)[12, 22, 23]. Each molecular orbital ϕ_i, is expressed as $\phi_i = \Sigma c_{ri}\chi_r$, where the χ_r's are the STO basis functions. Here we use the STO-6G basis set (which is contracted Gaussian)[24–27] for the SCF calculation.

The coefficients of linear combination for each molecular orbital have been found by the solution of the Roothan equation[28]. The most efficient way to solve the Roothan equation is to use matrix-algebra methods. In matrix-algebra methods, the matrix elements are computed[29] and the secular equation is solved to give the set of orbital energies (*i.e.*, eigenvalues). These orbital energies[30–32] are used to solve Roothan equations for the set of coefficients (*i.e.*, eigenvectors) giving a set of molecular orbitals. The calculations are done using a computer.

By the above calculation, the values of orbital energies (eigenvalues) and coefficients (eigenvectors) have been calculated and are given in Table-6 and Tables 1 (a–c) respectively.

A widely used method to analyze SCF wavefunction is population analysis, introduced by Mulliken[33, 34]. He proposed a method that apportions the electrons of an *n*-electron molecule into net populations n_r in the basis functions χ_r and overlap populations n_{r-s} for all possible pairs of basis functions.

For the set of basis functions $\chi_1, \chi_2, \ldots \chi_b$, each molecular orbital ϕ_i has the form $\phi_i = \Sigma_s c\chi_{si} = c_{1i}\chi_1 + c_{2i}\chi_2 + \ldots + c_{bi}\chi_b$. For simplicity, we shall assume that the c_{si}'s and χ_s's are real. The probability density associated with one electron in ϕ_i is (s and b are the number of the atomic orbital other than r)

$$|\phi_i|^2 = c_{1i}^2\chi_1^2 + c_{2i}^2\chi_2^2 + \ldots + 2c_{1i}c_{2i}\chi_1\chi_2 + 2c_{1i}c_{3i}\chi_1\chi_3 + 2c_{1i}\, c_{3i}\chi_2\chi_3 + \ldots$$

Integrating this equation over three-dimensional space and using the fact that ϕ_i and the χ_s's are normalized, we get

$$1 = c_{1i}^2 + c_{2i}^2 + \ldots + 2c_{1i}c_{2i}S_{12} + 2c_{1i}c_{3i}S_{13} + 2c_{1i}c_{3i}S_{23} + \ldots \qquad (A)$$

where the S's are overlap integrals: $S_{12} = \int \chi_1\chi_2 \, dv_1 dv_2$, etc. Mulliken proposed that the terms in (A) be apportioned as follows. One electron in the molecular orbital ϕ_i contributes c_{1i}^2 to the net population in χ_1, c_{2i}^2 to the net population in χ_2, etc., and contributes $2c_{1i}c_{2i}S_{12}$ to the overlap population between χ_1 and χ_2,, $2c_{1i}c_{3i}S_{13}$ to the overlap population between χ_1 and χ_3 etc.

Let there be n_i electrons in the MO ϕ_i ($n_i = 0, 1, 2$) and $n_{r,\,i}$ and $n_{r-s,\,i}$ electrons in the MO ϕ_i to the net population in χ_r and to the overlap population between χ_r and χ_s, respectively. We have

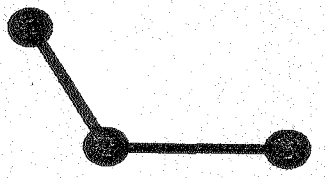
$$n_{r,\,i} = n_i c_{ri}^2$$

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

Based on the above principle, the contributions of electrons in each occupied MO have been calculated with the help of eigenvector values given in Tables 1a–c and the results are presented in Tables 2a–c. The overlap population analysis has also been made with the help of the values of eigenvector and overlap matrix (Tables 3a–c) for distinguishing the bonding, nonbonding and antibonding nature of MO and the results are presented in Table-5.

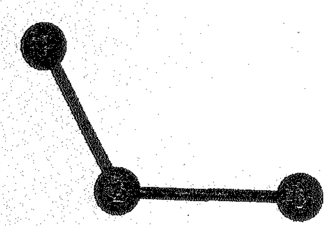
RESULTS AND DISCUSSION

Cobalt(II) halides are triatomic molecule, having the following optimized geometry[35–36] as obtained from molecular mechanics[37–40] method.



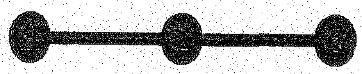
Bond length = 2.450 Å, bond angle = 117.37°

Fig. 1a. Structure of $CoCl_2$



Bond Length = 2.300 Å, Bond Angle = 120°

Fig. 1b. Structure of $CoBr_2$



Bond length = 2.488 Å, bond angle = 179.84°

Fig. 1c. Structure of CoI_2

TABLE-1a

EIGENVECTOR VALUES OF MOLECULAR ORBITALS OF COBALT(II) CHLORIDE

Atom No.	Atom (χ)	AOs	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
1	Co	$4s$	–0.0774	0.0000	–0.1809	–0.0000	0.0000	0.0003	0.0000	0.0000	–0.0000	–0.0000	0.3504	–0.0000	–0.0000	0.0017	0.0000	1.1361	0.0020
		$4p_x$	0.0000	0.0293	–0.0000	0.0001	–0.0000	–0.0000	0.0064	–0.1238	0.0000	–0.0000	–0.0000	0.0000	–0.0004	0.0006	0.0991	0.0018	–1.3430
		$4p_y$	–0.0000	–0.0029	0.0000	–0.0000	–0.0000	–0.0012	0.0655	0.0121	0.0001	–0.0000	0.0000	0.0001	0.0000	0.0179	1.0168	–0.0002	0.1309
		$4p_z$	0.0000	0.0000	–0.0000	0.0000	0.0000	–0.0658	–0.0012	–0.0001	0.0000	0.0001	0.0000	–0.0000	–0.0001	1.0216	–0.0179	–0.0021	–0.0016
		$3d_{x^2-y^2}$	–0.0653	0.0000	–0.2800	–0.0011	0.0967	–0.0002	0.0000	–0.000	–0.0002	0.4906	–0.7664	0.1684	–0.0020	0.0004	–0.0000	0.3191	0.0006
		$3d_{z^2}$	0.0385	–0.0000	0.1648	–0.0010	–0.0000	0.0012	0.0000	0.0000	0.0000	0.8660	0.4510	–0.0000	–0.0018	–0.0003	0.0000	–0.1878	–0.0004
		$3d_{xy}$	0.0129	–0.0000	0.0551	–0.0087	0.4913	0.0000	0.0001	0.0000	–0.0011	–0.0965	0.1508	0.8559	–0.0152	–0.0001	–0.0001	–0.0628	–0.0001
		$3d_{xz}$	–0.0002	–0.0001	–0.0007	–0.4983	–0.0087	–0.0001	–0.0001	0.0001	0.0970	–0.0012	–0.0018	–0.0151	–0.8682	–0.0001	–0.0000	0.0007	0.0006
		$3d_{yz}$	0.0000	0.0000	0.0001	0.0485	0.0014	0.0000	–0.0010	–0.0000	0.9953	0.0001	0.0002	0.0025	0.0846	0.0000	–0.0001	–0.0001	–0.0001
2	Cl	$3s$	–0.6801	0.6989	0.1120	–0.0001	0.0000	–0.0000	–0.0000	0.0357	–0.0000	–0.0000	0.0348	–0.0000	–0.0001	–0.0002	–0.0000	0.3175	0.4111
		$3p_x$	–0.0122	0.0105	0.5597	–0.0021	0.0558	–0.0015	0.0674	0.6593	0.0001	–0.0000	–0.1684	–0.0406	0.0015	0.0003	–0.0194	0.5695	–0.5751
		$3p_y$	0.0012	–0.0010	–0.0545	–0.0099	0.5722	–0.0121	0.6921	–0.0643	0.0007	–0.0000	0.0164	–0.4171	0.0072	–0.0036	–0.1992	–0.0555	0.0561
		$3p_z$	–0.0000	0.0000	–0.0002	–0.5749	–0.0101	–0.6954	–0.0122	–0.0015	0.0000	0.0007	0.0008	0.0073	0.4190	–0.2002	0.0035	0.0004	0.0001
3	Cl	$3s$	–0.6807	–0.6982	0.1121	0.0001	–0.0000	–0.0000	–0.0000	–0.0357	–0.0000	–0.0000	0.0349	–0.0000	0.0001	–0.0002	–0.0000	–0.3166	–0.4125
		$3p_x$	0.0123	0.0105	–0.5599	–0.0015	–0.0558	0.0007	0.0674	0.6591	0.0001	–0.0000	0.1684	0.0407	0.0010	–0.0005	–0.0194	–0.5681	–0.5771
		$3p_y$	–0.0012	–0.0010	0.0545	0.0103	–0.5729	–0.0123	0.6913	–0.0642	0.0007	–0.0000	–0.0164	0.4174	–0.0075	–0.0035	–0.1995	0.0553	0.5620
		$3p_z$	0.0000	0.0000	–0.0015	0.5756	0.0101	–0.6945	–0.0122	0.0030	0.0000	0.0007	0.0012	–0.0073	–0.4194	–0.2004	0.0035	–0.0010	–0.0014

TABLE-1b
EIGENVECTOR VALUES OF MOLECULAR ORBITALS OF COBALT(II) BROMIDE

Atom No.	Atom (χ)	AOs	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
1	Co	$4s$	0.0925	–0.0000	0.1611	–0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	–0.0000	0.3893	0.0000	–0.0000	–0.0000	–0.0000	–1.0571	0.0010
		$4p_x$	0.0000	0.0410	–0.0000	–0.0000	0.0000	0.1373	0.0000	0.0000	–0.0000	0.0061	0.0000	0.0000	0.0001	–0.0003	–0.0982	0.0009	1.2565
		$4p_y$	–0.0000	–0.0040	0.0000	0.0000	0.0000	–0.0134	–0.0002	0.0000	–0.0009	0.0621	–0.0000	0.0000	–0.0000	–0.0153	–1.0076	–0.0001	–0.1224
		$4p_z$	–0.0000	0.0000	0.0000	0.0000	–0.0000	0.0002	–0.0000	–0.0002	–0.0624	–0.0009	0.0000	–0.0000	–0.0000	–1.0123	0.0152	0.0005	0.0015
		$3dx^2-y^2$	0.0856	–0.0000	0.4147	0.0012	0.1345	–0.0001	–0.0002	0.4906	–0.0019	–0.0001	–0.7048	–0.1395	0.0013	–0.0001	–0.0000	–0.2910	0.0003
		$3d_z{}^2$	–0.0504	0.0000	–0.2440	0.0014	–0.0000	0.0000	0.0000	0.8660	–0.0030	–0.0001	0.4147	0.0000	0.0014	0.0001	–0.0000	0.1712	0.0002
		$3d_{xy}$	–0.0168	0.0000	–0.0816	0.0104	0.6834	0.0000	–0.0011	–0.0965	0.0004	–0.0000	0.1387	–0.7089	0.0108	0.0000	–0.0000	0.0573	–0.0001
		$3d_{xz}$	0.0002	–0.0000	0.0010	0.6933	–0.0104	0.0001	0.0970	–0.0012	0.0000	0.0003	–0.0017	0.0107	0.7191	–0.0000	0.0000	–0.0007	–0.0001
		$3d_{yz}$	–0.0000	0.0000	–0.0001	–0.0675	0.0018	–0.0000	0.9953	0.0001	–0.0001	0.0035	0.0002	–0.0019	–0.0701	0.0000	0.0000	0.0001	0.0000
2	Br	$4s$	0.6772	0.6961	–0.1334	0.0000	0.0000	–0.0405	–0.0000	–0.0000	–0.0000	0.0000	0.0196	0.0000	0.0000	0.0001	0.0000	0.2703	–0.3415
		$4p_x$	0.0063	0.0106	–0.5088	0.0005	0.0453	–0.6524	–0.0002	0.0000	–0.0005	0.0677	–0.2659	0.0519	–0.0005	–0.0001	0.0159	–0.5382	0.5261
		$4p_y$	–0.0006	–0.0010	0.0496	0.0070	0.4647	0.0636	–0.0024	0.0000	–0.0105	0.6946	0.0259	0.5325	–0.0080	0.0025	0.1628	0.0524	–0.0513
		$4p_z$	0.0000	0.0000	–0.0004	0.4669	–0.0070	–0.0003	–0.0000	–0.0025	–0.6979	–0.0105	–0.0000	–0.0081	–0.5350	0.1636	–0.0025	–0.0006	0.0005
3	Br	$4s$	0.6767	–0.6966	–0.1334	–0.0000	–0.0000	0.0405	–0.0000	–0.0000	–0.0000	0.0000	0.0196	–0.0000	–0.0000	0.0001	0.0000	0.2706	0.3408
		$4p_x$	–0.0063	0.106	0.5086	0.0002	–0.0452	–0.6526	–0.0002	0.0000	0.0000	0.0677	0.2659	–0.0519	–0.0002	0.0002	0.0159	0.5388	0.5251
		$4p_y$	0.0006	–0.0010	–0.0496	–0.0071	–0.4643	0.0636	–0.0024	0.0000	–0.0106	0.6951	–0.0259	–0.5322	0.0081	0.0025	0.1627	–0.0525	–0.0512
		$4p_z$	–0.0000	0.0000	0.0007	–0.4665	0.0070	–0.0013	–0.0000	–0.0025	–0.6984	–0.0105	0.0006	0.0080	0.5347	0.1634	–0.0025	0.0007	0.0007

TABLE-1c
EIGENVECTOR VALUES OF MOLECULAR ORBITALS OF COBALT(II) IODIDE

Atom No.	Atom (χ)	AOs	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
1	Co	$4s$	–0.1307	–0.0000	0.1454	–0.0000	–0.0000	–0.0000	0.0000	–0.0001	–0.0001	–0.0000	–0.3913	–0.0000	–0.0000	–0.0004	–0.0000	1.0347	0.0027
		$4p_x$	–0.0001	0.0597	–0.0000	–0.0000	–0.0000	0.0000	0.0000	–0.1452	0.0001	–0.0056	–0.0000	–0.0000	0.0001	–0.0013	–0.0978	–0.0025	1.2165
		$4p_y$	0.0000	–0.0058	0.0000	0.0000	–0.0000	0.0000	0.0000	0.0142	0.0014	–0.0571	0.0000	–0.0001	–0.0000	–0.0249	–1.0037	0.0002	–0.1185
		$4p_z$	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	–0.0000	–0.0002	0.0574	0.0014	–0.0000	0.0000	–0.0001	–1.0084	0.0249	0.0004	0.0014
		$3d_{x^2-y^2}$	–0.1377	–0.0000	0.4617	0.0029	–0.1537	0.0002	0.4906	0.0003	0.0003	0.0000	0.6734	0.1175	0.0022	–0.0001	–0.0000	0.2582	0.0008
		$3d_{z^2}$	0.0810	0.0000	–0.2717	0.0016	0.0000	–0.0000	0.8660	–0.0002	0.0001	0.0000	–0.3962	–0.0000	0.0012	0.0001	–0.0000	–0.1519	–0.0005
		$3d_{xy}$	0.0271	0.0000	–0.0908	0.0195	–0.7813	0.0011	–0.0965	–0.0001	–0.0001	0.0001	–0.1325	0.5971	0.0149	0.0000	–0.0001	–0.0508	–0.0002
		$3d_{xz}$	–0.0003	–0.0000	0.0011	0.7925	0.0195	–0.0970	–0.0012	–0.0001	–0.0001	–0.0000	–0.0160	–0.0149	0.6057	–0.0001	0.0000	0.0006	–0.0001
		$3d_{yz}$	0.0000	0.0000	–0.0001	–0.772	–0.0028	–0.9953	0.0001	0.0000	0.0000	–0.0002	0.0002	0.0022	–0.590	0.0000	0.0000	–0.0001	0.0000
2	I	$5s$	–0.6586	0.6915	–0.1902	0.0000	–0.0000	0.0000	–0.0000	0.0478	0.0000	0.0000	–0.0140	–0.0000	0.0000	0.0001	0.0000	–0.2683	–0.3179
		$5p_x$	0.0194	0.0099	–0.4821	0.0007	–0.0378	0.0000	0.0000	0.6500	0.0011	–0.0678	0.3065	–0.0575	–0.0010	0.0000	0.0138	0.5244	0.5025
		$5p_y$	–0.0019	–0.0010	0.0470	0.0096	–0.3880	0.0001	0.0000	–0.0633	0.0172	–0.6958	–0.0299	–0.5901	–0.0146	0.0035	0.1416	–0.0511	–0.4090
		$5p_z$	0.0000	0.0000	–0.0005	0.3899	0.0096	0.0000	–0.0001	0.0004	0.6991	0.0173	0.0001	0.0146	–0.5928	0.1423	–0.0035	0.0006	0.0005
3	I	$5s$	–0.6571	–0.6931	–0.1899	–0.0000	0.0000	0.0000	–0.0000	–0.0478	0.0000	0.0000	–0.0140	0.0000	–0.0000	0.0001	0.0000	–0.2691	0.3161
		$5p_x$	–0.0194	0.0099	0.4815	–0.0003	0.0377	0.0000	0.0000	0.6505	0.0007	–0.0680	–0.3067	0.0574	0.0005	0.0003	0.0138	–0.5259	0.4996
		$5p_y$	0.0019	–0.0010	–0.0469	–0.0096	0.3871	0.0001	0.0000	–0.0634	0.0173	–0.6973	0.0299	0.5888	0.0146	0.0035	0.1413	0.0512	–0.0487
		$5p_z$	0.0000	0.0000	0.0007	–0.3889	–0.0096	0.0000	–0.0001	0.0011	0.7006	0.0173	0.0006	–0.0146	0.5916	0.1419	–0.0035	–0.0006	0.0007

TABLE-1d

COEFFICIENT VALUES OF $3dxy$, $3dxz$, $3d_{x^2-y^2}$, $4s$, $4p_x$, $4p_y$, $4p_z$ ORBITALS

MOs	Cobalt halides	$3d_{xy}$	$3d_{xz}$	$3d_{x^2-y^2}$	$4s$	$4p_x$	$4p_y$	$4p_z$
ϕ_1	Cobalt chloride	0.0129	0.0002	0.653	0.0774	0.0000	0.0000	0.0000
	Cobalt bromide	0.0168	0.0002	0.0856	0.0925	0.0000	0.0000	0.0000
	Cobalt iodided	0.0271	0.0003	0.1377	0.1307	0.0001	0.0000	0.0000
ϕ_2	Cobalt chloride	0.0000	0.0001	0.0000	0.0000	0.0293	0.0029	0.0000
	Cobalt bromide	0.0000	0.0000	0.0000	0.0000	0.0410	0.0040	0.0000
	Cobaltiodide	0.0000	0.0000	0.0000	0.0000	0.0597	0.0058	0.0001
ϕ_3	Cobalt chloride	0.0551	0.0007	0.2800	0.1809	0.0000	0.0000	0.0000
	Cobalt bromide	0.0816	0.0010	0.4147	0.1611	0.0000	0.0000	0.0000
	Cobalt iodide	0.0908	0.0011	0.4617	0.1454	0.0000	0.0000	0.0000
ϕ_4	Cobalt chloride	0.0087	0.4983	0.0011	0.0000	0.0001	0.0000	0.0000
	Cobalt bromide	0.0104	0.6933	0.0012	0.0000	0.0000	0.0000	0.0000
	Cobalt iodide	0.0195	0.7925	0.0029	0.0000	0.0000	0.0000	0.0000
ϕ_5	Cobalt chloride	0.4913	0.0087	0.0967	0.0000	0.0000	0.0000	0.0000
	Cobalt bromide	0.6834	0.0104	0.1345	0.0000	0.0000	0.0000	0.0000
	Cobalt iodide	0.7813	0.195	0.1537	0.0000	0.0000	0.0000	0.0000
ϕ_6	Cobalt chloride	0.0000	0.0001	0.0002	0.0003	0.0000	0.0012	0.0658
	Cobalt bromide	0.0000	0.0001	0.0001	0.0000	0.1373	0.0134	0.0002
	Cobalt iodide	0.0011	0.0970	0.0002	0.0000	0.0000	0.0000	0.0000
ϕ_7	Cobalt chloride	0.0001	0.0001	0.0000	0.0000	0.0064	0.0655	0.0012
	Cobalt bromide	0.0011	0.0970	0.0002	0.0000	0.0000	0.0002	0.0000
	Cobalt iodide	0.0965	0.0012	0.4906	0.0000	0.0000	0.0000	0.0000
ϕ_8	Cobalt chloride	0.0000	0.0001	0.0000	0.0000	0.1238	0.0121	0.0001
	Cobalt bromide	0.0965	0.0012	0.4906	0.0000	0.0000	0.0000	0.0002
	Cobalt iodide	0.0001	0.0001	0.0003	0.0001	0.1452	0.0142	0.0002
ϕ_9	Cobalt chloride	0.0011	0.0970	0.0002	0.0000	0.0000	0.0001	0.0000
	Cobalt bromide	0.0004	0.0000	0.0019	0.0001	0.0000	0.0009	0.0624
	Cobalt iodide	0.0001	0.0001	0.0003	0.0001	0.0001	0.0014	0.0574
ϕ_{10}	Cobalt chloride	0.0965	0.0012	0.4906	0.0000	0.0000	0.0000	0.0001
	Cobalt bromide	0.0000	0.0003	0.0001	0.0000	0.0061	0.0621	0.0009
	Cobalt iodide	0.0001	0.0000	0.0000	0.0000	0.0056	0.0571	0.0014
ϕ_{11}	Cobalt chloride	0.1508	0.0018	0.7664	0.3504	0.0000	0.0000	0.0000
	Cobalt bromide	0.1387	0.0017	0.7048	0.3893	0.0000	0.0000	0.0000
	Cobalt iodide	0.1325	0.0160	0.6734	0.3913	0.0000	0.0000	0.0000
ϕ_{12}	Cobalt chloride	0.8559	0.0151	0.1684	0.0000	0.0000	0.0001	0.0000
	Cobalt bromide	0.7089	0.0107	0.1395	0.0000	0.0000	0.0000	0.0000
	Cobalt iodide	0.5971	0.0149	0.1175	0.0000	0.0000	0.0001	0.0000
Summation								
	Cobalt chloride	1.6724	0.6234	1.8689	0.6090	0.1596	0.0819	0.0672
	Cobalt bromide	1.7378	0.8159	1.9732	0.6430	0.1844	0.0806	0.0637
	Cobalt iodide	1.7462	0.9427	2.0383	0.6676	0.2107	0.0786	0.0591

TABLE-2a

CONTRIBUTION OF ELECTRONS IN MO OF $CoCl_2$

MO No. (i)	n_i	Major contribution		Minor contribution	
		Basis functions (χ_r)	$n_{r,i} = n_i c_{ri}^2$	Basis functions (χ_r)	$n_{r,i} = n_i c_{ri}^2$
1	2	$4s$ (Co1)	0.0119	$3d_{x^2-y^2}$ (Co1)	0.0085
		—	—	$3d_{z^2}$ (Co1)	0.0029
		$3s$ (Cl2)	0.9250	—	—
		$3s$ (Cl3)	0.9250	—	—
2	2	$4p_x$ (Co1)	0.0017	—	—
		$3s$ (Cl2)	0.9769	—	—
		$3s$ (Cl3)	0.9749	—	—
3	2	$3d_{x^2-y^2}$ (Co1)	0.1568	$4s$ (Co1)	0.0654
		—	—	$3d_{z^2}$ (Co1)	0.0543
		—	—	$3d_{xy}$ (Co1)	0.0060
		$3p_x$ (Cl2)	0.6265	$3s$ (Cl2)	0.0250
		$3p_x$ (Cl3)	0.6269	$3s$ (Cl3)	0.0250
		—	—	$3p_y$ (Cl2)	0.0059
		—	—	$3p_y$ (Cl3)	0.0059
4	2	$3d_{xz}$ (Co1)	0.4966	$3p_{yz}$ (Co1)	0.0047
		$3p_z$ (Cl2)	0.6610	—	—
		$3p_z$ (Cl3)	0.6626	—	—
5	2	$3d_{xz}$ (Co1)	0.4827	$3d_{x^2-y^2}$ (Co1)	0.0187
		$3p_y$ (Cl2)	0.6548	$3p_x$ (Cl2)	0.0062
		$3p_y$ (Cl3)	0.6564	$3p_x$ (Cl3)	0.0062
6	2	$4p_z$ (Co1)	0.0086	—	—
		$3p_z$ (Cl2)	0.9671	—	—
		$3p_z$ (Cl3)	0.9646	—	—
7	2	$4p_y$ (Co1)	0.0085	—	—
		$3p_y$ (Cl2)	0.9580	$3p_x$ (Cl2)	0.0090
		$3p_y$ (Cl3)	0.9557	$3p_x$ (Cl3)	0.0090
8	2	$4p_x$ (Co1)	0.0306	—	—
		$3p_x$ (Cl2)	0.8693	$3p_y$ (Cl2)	0.0082
		$3p_x$ (Cl3)	0.8683	$3p_y$ (Cl3)	0.0082
		—	—	$3s$ (Cl2)	0.0025
		—	—	$3s$ (Cl3)	0.0025
9	2	$3d_{yz}$ (Co1)	1.9812	$3d_{xz}$ (Co1)	0.0188
10	2	$4d_{z^2}$ (Co1)	1.4999	$3d_{x^2-y^2}$ (Co1)	0.4813
		—	—	$3d_{xy}$ (Co1)	0.0186
11	2	$3d_{x^2-y^2}$ (Co1)	1.1747	$3d_{z^2}$ (Co1)	0.4068
		—	—	4s (Co1}	0.2455
		—	—	$3d_{xy}$ (Co1)	0.0454
		$3p_x$ (Cl2)	0.0567	$3s$ (Cl2)	0.0024
		$3p_x$ (Cl3)	0.0567	$3s$ (Cl3)	0.0024
12	1	$3d_{xy}$ (Co1)	0.7325	$3d_{x^2-y^2}$ (Co1)	0.0283
		$3p_y$ (Cl2)	0.1739	$3p_x$ (Cl2)	0.0016
		$3p_y$ (Cl3)	0.1742	$3p_x$ (Cl3)	0.0016

TABLE-2b

CONTRIBUTION OF ELECTRONS IN MO OF $CoBr_2$

MO No. (i)	n_i	Major contribution		Minor contribution	
		Basis functions (χ_r)	$n_{r,i} = n_i c_{ri}^2$	Basis functions (χ_r)	$n_{r,i} = n_i c_{ri}^2$
1	2	$4s$ (Co1)	0.0171	$3d_{x^2-y^2}$ (Co1)	0.0147
		—	—	$3d_{z^2}$ (Co1)	0.0051
		$4s$ (Br2)	0.9172	—	—
		$4s$ (Br3)	0.9158	—	—
2	2	$4p_x$ (Co1)	0.0034	—	—
		4s (Br2)	0.9635	—	—
		4s (Br3)	0.9705	—	—
3	2	$3d_{x^2-y^2}$ (Co1)	0.3440	$3d_{z^2}$ (Co1)	0.1191
		—	—	$4s$ (Co1)	0.0524
		—	—	$3d_{xy}$ (Co1)	0.0133
		$4p_x$ (Br2)	0.5178	$4s$ (Br2)	0.0356
		$4p_x$(Br3)	0.5173	$4s$ (Br3)	0.0356
		—	—	$4p_y$ (Br2)	0.0049
		—	—	$4p_y$(Br3)	0.0049
4	2	$3d_{xz}$ (Col)	0.9613	$3d_{yz}$ (Co1)	0.0091
		$4p_z$ (Br2)	0.4360	—	—
		$4p_z$ (Br3)	0.4352	—	—
5	2	$3d_{xy}$ (Co1)	0.9341	$3d_{x^2-y^2}$ (Co1)	0.0362
		$4p_y$ (Br2)	0.4319	$4p_x$ (Br2)	0.0041
		$4p_y$ (Br3)	0.4311	$4p_x$ (Br3)	0.0041
6	2	$4p_x$ (Co1)	0.0377	—	—
		$4p_x$ (Br2)	0.8513	$4p_y$ (Br2)	0.0081
		$4p_x$ (Br3)	0.8518	$4p_y$ (Br3)	0.0081
		—	—	$4s$ (Br2)	0.0033
		—	—	$4s$ (Br3)	0.0033
7	2	$3d_{yz}$ (Co1)	1.9812	$3d_{xz}$ (Co1)	0.0188
8	2	$3d_{z^2}$ (Co1)	1.4999	$3d_{x^2-y^2}$ (Col)	0.4814
		—	—	$3d_{xy}$ (Col)	0.0186
9	2	$4p_z$ (Col)	0.0078	—	—
		$4p_z$ (Br2)	0.9741	—	—
		$4p_z$ (Br3)	0.9755	—	—
10	2	$4p_y$ (Col)	0.0077	—	—
		$4p_y$ (Br2)	0.9649	$4p_x$ (Br2)	0.0092
		$4p_y$ (Br3)	0.9663	$4p_x$ (Br3)	0.0092
11	2	$3d_{x^2-y^2}$ (Co1)	0.9935	$3d_{z^2}$ (Co1)	0.3440
		—	—	$4s$ (Col)	0.3031
		—	—	$3d_{xy}$ (Col)	0.0385
		$4p_x$ (Br2)	0.1414	$4p_y$ (Br2)	0.0013
		$4p_x$ (Br3)	0.1414	$4p_y$ (Br3)	0.0013
12	1	$3d_{xy}$ (Col)	0.5025	$3d_{x^2-y^2}$ (Col)	0.0195
		$4p_y$ (Br2)	0.2836	$4p_x$ (Br2)	0.0027
		$4p_y$ (Br3)	0.2832	$4p_x$ (Br3)	0.0027

TABLE-2c
CONTRIBUTION OF ELECTRONS IN MO OF CoI_2

MO No. (i)	n_i	Major contribution		Minor contribution	
		Basis functions (χ_r)	$n_{r,i} = n_i c_{ri}^2$	Basis functions (χ_r)	$n_{r,i} = n_i c_{ri}^2$
1	2	$3d_{x^2-y^2}$ (Co1)	0.0379	$4s$ (Co1)	0.0342
		—	—	$3d_{z^2}$ (Co1)	0.0131
		—	—	$3d_{xy}$ (Co1)	0.0015
		$5s$ (I2)	0.8675	Sp_x(I2)	0.0008
		$5s$ (I3)	0.8636	Sp_x (I3)	0.0008
2	2	$4p_x$(Co1)	0.0071	—	—
		$5s$ (I2)	0.9563	—	—
		$5s$ (I3)	0.9608	—	—
3	2	$3d_{x^2-y^2}$(Co1)	0.4263	$3d_{z^2}$ (Co1)	0.1476
		—	—	$4s$ (Co1)	0.0423
		—	—	$3d_{xy}$(Co1)	0.0165
		Sp_x (12)	0.4648	$5s$ (12)	0.0724
		Sp_x (I3)	0.4637	$5s$ (I3)	0.0721
		—	—	Sp_y (I2)	0.0044
		—	—	Sp_y (I3)	0.0044
4	2	$3d_{xz}$ (Co1)	1.2561	$3d_{yz}$ (Co1)	0.0119
		$5p_z$ (I2)	0.3040	—	—
		$5p_z$ (I3)	0.3025	—	—
5	2	$3d_{xy}$(Co1)	1.2209	$3d_{x^2-y^2}$ (Co1)	0.0472
		Sp_y (I2)	0.3011	Sp_x (I2)	0.0029
		Sp_y (13)	0.2997	Sp_x (13)	0.0028
6	2	$3d_{yz}$(Co1)	1.9812	$3d_{xz}$ (Co1)	0.0188
7	2	$3d_{z^2}$ (Co1)	1.4999	$3d_{x^2-y^2}$ (Co1)	0.4814
		—	—	$3d_{xy}$(Co1)	0.0186
8	2	$4p_x$ (Co1)	0.0422	—	—
		Sp_x (I2)	0.8450	Sp_y (I2)	0.0080
		Sp_x (I3)	0.8463	Sp_y (I3)	0.0080
		—	—	$5s$ (I2)	0.0046
		—	—	$5s$ (I3)	0.0046
9	2	$4p_z$ (Co1)	0.0066	—	—
		$5p_z$ (I2)	0.9775	$5p_z$ (I3)	0.9817
		—	—		
10	2	$4p_y$ (Co1)	0.0065	—	—
		Sp_y (I2)	0.9683	Sp_x (I2)	0.0092
		Sp_y (I3)	0.9725	Sp_x (I3)	0.0092
11	2	$3d_{x^2-y^2}$ (Co1)	0.9069	$3d_{z^2}$ (Co1)	0.3139
		—	—	$4s$ (Co1)	0.3062
		—	—	$3d_{xy}$ (Co1)	0.0351
		Sp_x (I2)	0.1879	Sp_y (I2)	0.0018
		Sp_x (I3)	0.1881	Sp_y (I3)	0.0018
12	1	$3d_{xy}$ (Co1)	0.3565	$3d_{x^2-y^2}$ (Co1)	0.0138
		$5p_y$ (I2)	0.3482	Sp_x (I2)	0.0033
		Sp_y (I3)	0.3467	Sp_x (I3)	0.0033

TABLE-3a
OVERLAP MATRIX (OVERLAP INTEGRALS VALUES) OF $CoCl_2$

AOs		4s	$4p_x$	$4p_y$	$4p_z$	$3d_{x^2-y^2}$	$3d_{z^2}$	$3d_{xy}$	$3d_{xz}$	$3d_{yz}$	3s	$3p_x$	$3p_y$	$3p_z$	3s	$3p_x$	$3p_y$	$3p_z$
		(Co-1)	(Co-1)	(Co-1)	(Co-1)	(Co-1)	(Co-1)	(Co-1)	(Co-1)	(Co-1)	(Cl-2)	(Cl-2)	(Cl-2)	(Cl-2)	(Cl-3)	(Cl-3)	(Cl-3)	(Cl-3)
s	(Co-1)	1.0000																
p_x	(Co-1)	–0.0000	1.0000															
p_y	(Co-1)	–0.0000	–0.0000	1.0000														
p_z	(Co-1)	0.0000	0.0000	0.0000	1.0000													
$d_{x^2-y^2}$	(Co-1)	0.0000	0.0000	–0.0000	0.0000	1.0000												
d_{z^2}	(Co-1)	–0.0000	–0.0000	–0.0000	0.0000	–0.0000	1.0000											
d_{xy}	(Co-1)	0.0000	0.0000	–0.0000	0.0000	0.0000	0.0000	1.0000										
d_{xz}	(Co-1)	0.0000	0.0000	0.0000	–0.0000	0.0000	–0.0000	0.0000	1.0000									
d_{yz}	(Co-1)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	–0.0000	1.0000								
s	(Cl-2)	0.2075	0.2905	–0.0283	0.0000	0.0789	–0.0465	–0.0155	0.0000	–0.0000	1.0000							
p_x	(Cl-2)	–0.3267	–0.3684	0.0507	–0.0001	–0.1001	0.0597	0.0273	–0.0000	0.0000	–0.0000	1.0000						
p_y	(Cl-2)	0.0318	0.0507	0.1469	0.0000	0.0246	–0.0058	0.0729	0.0000	1.0000	0.0000	0.0000	0.0000					
p_z	(Cl-2)	–0.0001	–0.0001	0.0000	0.1518	–0.0000	0.0000	0.0000	0.0762	–0.0074	0.0000	0.0000	0.0000	1.0000				
s	(Cl-3)	0.2076	–0.2907	0.0283	–0.0006	0.0790	–0.0465	–0.0155	0.0003	–0.0000	0.0006	–0.0040	0.0004	–0.0000	1.0000			
p_x	(Cl-3)	0.3269	–0.3685	0.0507	–0.0011	0.1001	–0.0598	–0.0273	0.0006	–0.0001	0.0040	–0.0153	0.0017	–0.0000	–0.0000	1.0000		
p_y	(Cl-3)	–0.0318	0.0507	0.1470	0.0001	–0.0246	0.0058	–0.0729	–0.0001	–0.0002	–0.0004	0.0017	0.0016	0.0000	–0.0000	0.0000	1.0000	
p_z	(Cl-3)	0.0007	–0.0011	0.0001	0.1520	0.0004	–0.0004	–0.0001	–0.0763	0.0074	0.0000	–0.0000	0.0000	0.0017	0.0000	0.0000	0.0000	1.0000

TABLE-3b

OVERLAP MATRIX (OVERLAP INTEGRALS VALUES) OF $CoBr_2$

AOs		4s	$4p_x$	$4p_y$	$4p_z$	$3d_{x^2-y^2}$	$3d_{z^2}$	$3d_{xy}$	$3d_{xz}$	$3d_{yz}$	4s	$4p_x$	$4p_y$	$4p_z$	4s	$4p_x$	$4p_y$	$4p_z$
		(Co-1)	(Co-1)	(Co-1)	(Co-1)	(Co-1)	(Co-1)	(Co-1)	(Co-1)	(Co-1)	(Br-2)	(Br-2)	(Cl-2)	(Br-2)	(Br-3)	(Br-3)	(Br-3)	(Br-3)
s	(Co-1)	1.0000																
p_x	(Co-1)	0.0000	1.0000															
p_y	(Co-1)	–0.0000	0.0000	1.0000														
p_z	(Co-1)	0.0000	0.0000	0.0000	1.0000													
$d_{x^2-y^2}$	(Co-1)	0.0000	0.0000	–0.0000	0.0000	1.0000												
d_{z^2}	(Co-1)	–0.0000	–0.0000	–0.0000	0.0000	0.0000	1.0000											
d_{xy}	(Co-1)	0.0000	0.0000	–0.0000	0.0000	0.0000	0.0000	1.0000										
d_{xz}	(Co-1)	0.0000	0.0000	0.0000	–0.0000	0.0000	–0.0000	0.0000	1.0000									
d_{yz}	(Co-1)	0.0000	0.0000	0.0000	0.0000	0.0000	–0.0000	0.0000	–0.0000	1.0000								
s	(Br-2)	0.1747	0.2508	–0.0244	0.0002	0.0675	–0.0397	–0.0133	0.0001	–0.0000	1.0000							
p_x	(Br-2)	–0.2851	–0.3505	0.0457	–0.0005	–0.0973	0.0579	0.0252	–0.0003	0.0000	–0.0000	1.0000						
p_y	(Br-2)	0.0278	0.0457	0.1142	0.0000	0.0213	–0.0056	0.0576	0.0000	0.0001	–0.0000	–0.0000	1.0000					
p_z	(Br-2)	–0.0003	–0.0005	0.0000	0.1187	–0.0002	0.0002	0.0000	0.0606	–0.0059	0.0000	0.0000	0.0000	1.0000				
	(Br-3)	0.1746	–0.2507	0.0244	–0.0003	0.0675	–0.0397	–0.0133	0.0002	–0.0000	0.0002	–0.0013	0.0001	–0.0000	1.0000			
p_x	(Br-3)	0.2850	–0.3504	0.0457	–0.0006	0.0972	–0.0579	–0.0251	0.0003	–0.0000	0.0013	–0.0055	0.0006	–0.0000	–0.0000	1.0000		
p_y	(Br-3)	–0.0278	0.0457	0.1141	0.0001	–0.0213	0.0056	–0.0576	–0.0000	–0.0001	–0.0001	0.0006	0.0004	0.0000	–0.0000	–0.0000	1.0000	
p_z	(Br-3)	0.0004	–0.0006	0.0001	0.1186	0.0002	–0.0002	–0.0000	–0.0606	0.0059	0.0000	–0.0000	0.0000	0.0005	0.0000	0.0000	0.0000	1.0000

TABLE-3c

OVERLAP MATRIX (OVERLAP INTEGRALS VALUES) OF CoI_2

AOs		4s	$4p_x$	$4p_y$	$4p_z$	$3d_{x^2-y^2}$	$3d_{z^2}$	$3d_{xy}$	$3d_{xz}$	$3d_{yz}$	5s	$5p_x$	$5p_y$	$5p_z$	5s	$5p_x$	$5p_y$	$5p_z$
		(Co-1)	(Co-1)	(Co-1)	(Co-1)	(Co-1)	(Co-1)	(Co-1)	(Co-1)	(Co-1)	(I-2)	(I-2)	(I-2)	(I-2)	(I-3)	(I-3)	(I-3)	(I-3)
s	(Co-1)	1.0000																
p_x	(Co-1)	0.0000	1.0000															
p_y	(Co-1)	–0.0000	–0.0000	1.0000														
p_z	(Co-1)	0.0000	0.0000	0.0000	1.0000													
$d_{x^2-y^2}$	(Co-1)	0.0000	0.0000	–0.0000	0.0000	1.0000												
d_{z^2}	(Co-1)	–0.0000	–0.0000	–0.0000	0.0000	–0.0000	1.0000											
d_{xy}	(Co-1)	–0.0000	–0.0000	–0.0000	0.0000	–0.0000	–0.0000	1.0000										
d_{xz}	(Co-1)	0.0000	0.0000	0.0000	–0.0000	0.0000	0.0000	0.0000	1.0000									
d_{yz}	(Co-1)	0.0000	0.0000	0.0000	–0.0000	0.0000	–0.0000	0.0000	–0.0000	1.0000								
s	(I-2)	0.1645	0.2311	–0.0225	0.0002	0.0591	–0.0348	–0.0116	0.0001	–0.0000	1.0000							
p_x	(I-2)	–0.2707	–0.3372	0.0427	–0.0005	–0.0888	0.0528	0.0224	–0.0002	0.0000	–0.0000	1.0000						
p_y	(I-2)	0.0264	0.0427	0.0971	0.0000	0.0184	–0.0051	0.0473	0.0000	0.0000	–0.0000	–0.0000	1.0000					
p_z	(I-2)	–0.0003	–0.0005	0.0000	0.1013	–0.0001	0.0001	0.0000	0.0500	–0.0049	0.0000	0.0000	0.0000	1.0000				
s	(I-3)	0.1642	–0.2307	0.0225	–0.0003	0.0590	–0.0347	–0.0116	0.0002	–0.0000	0.0002	–0.0010	0.0001	–0.0000	1.0000			
p_x	(I-3)	0.2703	–0.3368	0.0427	–0.0006	0.0887	–0.0528	–0.0224	0.0003	–0.0000	0.0010	–0.0038	0.0004	–0.0000	0.0000	1.0000		
p_y	(I-3)	–0.0263	0.0427	0.0969	0.0001	–0.0184	0.0051	–0.0472	–0.0000	–0.0001	–0.0001	0.0004	0.0003	0.0000	–0.0000	–0.0000	1.0000	
p_z	(I-3)	0.0003	–0.0006	0.0001	0.1010	0.0002	–0.0002	–0.0000	–0.0498	0.0049	0.0000	–0.0000	0.0000	0.0003	0.0000	0.0000	0.0000	1.0000

The MOs of these halides are formed by linear combination of 9 cobalt orbitals and 4 orbitals from each halogen. In total 17 AOs are involved in the formation of MO. The details of the valence orbitals involved in the formation of MO are as detailed below.

Co-1 = $4s$, $4p_x$, $4p_y$, $4p_z$, $3d_{x^2-y^2}$, $3d_{z^2}$, $3d_{xy}$, $3d_{xz}$, $3d_{yz}$ = 9
X-2 = ns, np_x, np_y, np_z = 4
X-3 = ns, np_x, np_y, np_z = 4
Total = 17

where, $n = 3$ 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 cobalt(II) halides. The various AOs are represented by χ and MOs by ϕ. 1–9 χ are atomic orbitals of cobalt and 10–17 χ are atomic orbitals of halogens ($\chi_1 = 4s$, $\chi_2 = 4p_x$, $\chi_3 = 4p_y$, $\chi_4 = 4p_z$, $\chi_5 = 3d_{x^2-y^2}$, $\chi_6 = 3d_{z^2}$, $\chi_7 = 3d_{xy}$, $\chi_8 = 3d_{xz}$, $\chi_9 = 3d_{yz}$, $\chi_{10} = ns$, $\chi_{11} = np_x$, $\chi_{12} = np_y$, $\chi_{13} = np_z$ for X-2 and $\chi_{14} = ns$, $\chi_{15} = np_x$, $\chi_{16} = np_y$, $\chi_{17} = np_z$ for X-3).

The forms of the 17 MOs, that is the magnitude of contribution of various AOs in the formation of MO of the halides are demonstrated in Tables 1a–c. In these tables the coefficients of χ is the eigenvector.

In order to examine the extent of involvement of $3d$, $4s$, $4p$ orbitals in the formation of molecular orbitals the values of coefficient of these orbitals have been separately tabulated for each molecular orbital and are given in Table 1d. The nonbonding orbitals $3d_{z^2}$ and $3d_{yz}$ are excluded. The coefficient values of each orbital have been added to see the total involvement in all the molecular orbitals ($\phi_1 - \phi_{12}$). The summation values are placed at the bottom of the table. It is clearly indicated that the maximum involvement is of $3d_{x^2-y^2}$ orbital and the minimum of $4p_z$ orbital. The involvement of p orbital is negligible. The value of coefficient is between 0.2107 and 0.0591, which is very low in comparison to d orbitals (d_{xy}, d_{xz}, $d_{x^2-y^2}$) which is in the range 2.0383–0.6234. The value for $4s$ is in the range 0.6676–0.6090. The extent of involvement of various cobalt orbitals in the formation of MO in $CoCl_2$, $CoBr_2$ and CoI_2 is very well demonstrated by the values given in the following table and also by the graphs (Figs. 2, 3, 4) drawn between the orbitals and the summation values of their coefficients or eigenvector. It is clear that the involvement of p orbitals is negligible. The summations of coefficient values of various orbitals are highest in case of iodide and lowest in chloride. It is perhaps on this account the splitting of d orbitals as discussed later is maximum in iodide and minimum in chloride.

Orbitals	Summation of coefficient values of orbitals		
	$CoCl_2$	$CoBr_2$	CoI_2
$3d_{xy}$	1.6724	1.7378	1.7462
$3d_{xz}$	0.6234	0.8159	0.9427
$3d_{x^2-y^2}$	1.8689	1.9732	2.0383
$4s$	0.6090	0.6430	0.6676
$4p_x$	0.1596	0.1844	0.2107
$4p_y$	0.0819	0.0806	0.0786
$4p_z$	0.0672	0.0637	0.0591

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

$$n_{r,i} = n_i c_{ri}^2 \tag{1}$$

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

Equation (1) has been solved for 23 electrons of 12 molecular orbitals. Two electrons in the 1st MO to 11th MO and one electron in 12th MO have been considered. The five molecular orbitals having no electron are left over. The data relating to c_{ri} have been taken from Tables 1a–c. The results of solution of eqn. (1) are included in Tables 2a–c which enlist the contribution of electrons in molecular orbitals under two sections: major and minor. It is evident that major contribution is from 3*d* and 4*s* orbital. The *p* orbitals have negligible contribution.

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 eqn. (2).

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

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 integrals between the two AOs (one of an atom and one of the other atom).

It is evident from eqn. (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 cobalt have been taken from Tables 1a–c and Tables 3a–c respectively and the number of electrons is taken as two for 1st to 11th MOs, one for 12th MO and zero for 13th 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 12 tables for each halide are constructed, because remaining five which have no electrons are left over. In such a way there will be 36 tables for all the three halides.

Column 1—number of electrons (n_i)
Columns 2, 4—atomic orbitals of cobalt 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—4*s* AO of cobalt with *ns*, np_x, np_y, np_z AOs of both halogen.
8 overlaps—$4p_x$ AO of cobalt with *ns*, np_x, np_y, np_z AOs of both halogen.
8 overlaps—$4p_y$ AO of cobalt with *ns*, np_x, np_y, np_z AOs of both halogen.
8 overlaps—$4p_z$ AO of cobalt with *ns*, np_x, np_y, np_z AOs of both halogen.
8 overlaps—$3d_{x^2-y^2}$ AO of cobalt with *ns*, np_x, np_y, np_z AOs of both halogen.
8 overlaps—$3d_{z^2}$ AO of cobalt with *ns*, np_x, np_y, np_z AOs of both halogen.

8 overlaps—$3d_{xy}$ AO of cobalt with *ns*, np_x, np_y, np_z AOs of both halogen.
8 overlaps—$3d_{xz}$ AO of cobalt with *ns*, np_x, np_y, np_z AOs of both halogen.
8 overlaps—$3d_{yz}$ AO of cobalt with *ns*, np_x, np_y, np_z AOs of both halogens.
4 overlaps—*ns* AO of X-2 with *ns*, np_x, np_y, np_z AOs of X-3.
4 overlaps—np_x AO of X-2 with *ns*, np_x, np_y, np_z AOs of X-3.
4 overlaps—np_y AO of X-2 with *ns*, np_x, np_y, np_z AOs of X-3.
4 overlaps—np_z AO of X-2 with *ns*, np_x, np_y, np_z AOs of X-3.
Total—88 overlaps.

For the study of overlap population we have to construct twelve tables for each halide, each having 88 possible overlaps, but while building up the table we have dropped the values of zero eigenvector value [Tables 1 (a–c)], 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 cobalt chloride only.

This table has 39 possible overlaps, out of which 30 provide coefficient values of cobalt orbitals and 9 for Cl-2 in column 3, *i.e.*, c_{ri}. Column 5 is the coefficient value c_{si} for both the chlorines. Up to 30, both the chlorines are involved and for the remaining nine only Cl-3. Column 6 is overlap integral S_{rs} and exhibits the magnitude of overlap between the AOs represented in columns 2 and 4. The values are self-explanatory for indicating the magnitude.

The overlap population analysis also shows negligible involvement of 4*p* orbitals of cobalt. It has earlier been suggested that much smaller radius of the 3*d* orbital than the 4*s* orbital makes the involvement of 4*s* orbital dominant contribution in the bonding[41, 42]. This hypothesis is the central theme of a recent text book of transition metal chemistry by Gerloch and Constable[42]. 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[13–16] 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°.This is because the energy curves are a function of the bond angles and have two minima one below 90° and one above 90°. The bond angles as presented in Fig. 1 also support the Landis concept.

Column 7 of Table-4 enlists the values of overlap population, derived from eqn. (2). The sum of the values of overlap populations decides the nature of MO in a covalent molecule. If the sum of this interatomic overlap population contribution 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 $CoCl_2$ is 0.1238. Similarly the sum of overlap population contribution has been worked out for $CoBr_2$ and CoI_2 and the values are 0.1292 and 0.0623 respectively, which are positive indicating or supporting the bonding nature of MO.

Similarly the sum of overlap population for the 12 MOs in all the halides has been worked out and the results are tabulated in Table-5.

TABLE-4
OVERLAP POPULATION CONTRIBUTIONS OF Ist MOLECULAR ORBITAL OF $CoCl_2$

n_i	AOs	c_{ri}	AOs	c_{si}	S_{rs}	$n_{r-s,\,i} = n_i\,(2c_{ri}\cdot c_{si}\cdot S_{rs})$
2	$4s$ (Co1)	–0.0774	$3s$ (Cl2)	–0.6801	0.2075	0.0437
2	$4s$ (Co1)	–0.0774	$3p_x$ (Cl2)	–0.0122	–0.3267	–0.0012
2	$4s$ (Co1)	–0.0774	$3p_y$ (Cl2)	0.0012	0.0381	0.0000
2	$4s$ (Co1)	–0.0774	3s (Cl3)	–0.6807	0.2076	0.0438
2	$4s$ (Co1)	–0.0774	$3p_x$ (Cl3)	0.0123	0.3269	–0.0012
2	$4s$ (Co1)	–0.0774	$3p_y$ (Cl3)	–0.0012	–0.0318	0.0000
2	$3d_{x^2-y^2}$ (Co1)	–0.0653	3s (Cl2)	–0.6801	0.0789	0.0140
2	$3d_{x^2-y^2}$ (Co1)	–0.0653	$3p_x$ (Cl2)	–0.0122	–0.1001	–0.0003
2	$3d_{x^2-y^2}$ (Co1)	–0.0653	$3p_y$ (Cl2)	0.0012	0.0246	0.0000
2	$3d_{x^2-y^2}$ (Co1)	–0.0653	$3s$ (Cl3)	–0.6807	0.0790	0.0140
2	$3d_{x^2-y^2}$ (Co1)	–0.0653	$3p_x$ (Cl3)	0.0123	0.1001	–0.0003
2	$3d_{x^2-y^2}$ (Co1)	–0.0653	$3p_y$ (Cl3)	–0.0012	–0.0246	0.0000
2	$3d_{z^2}$ (Co1)	0.0385	$3s$ (Cl2)	–0.6801	–0.0465	0.0049
2	$3d_{z^2}$(Co1)	0.0385	$3p_x$ (Cl2)	–0.0122	0.0597	–0.0001
2	$3d_{z^2}$ (Co1)	0.0385	$3p_y$(Cl2)	0.0012	–0.0058	0.0000
2	$3d_{z^2}$ (Co1)	0.0385	$3s$ (Cl3)	–0.6807	–0.0465	0.0049
2	$3d_{z^2}$ (Co1)	0.0385	$3p_x$ (Cl3)	0.0123	–0.0598	–0.0001
2	$3d_{z^2}$ (Co1)	0.0385	$3p_y$ (Cl3)	–0.0012	0.0058	0.0000
2	$3d_{xy}$ (Co1)	0.0129	$3s$ (Cl2)	–0.6801	–0.0155	0.0005
2	$3d_{xy}$ (Co1)	0.0129	$3p_x$ (Cl2)	–0.0122	0.0273	0.0000
2	$3d_{xy}$ (Co1)	0.0129	$3p_y$ (Cl2)	0.0012	0.7290	0.0000
2	$3d_{xy}$ (Co1)	0.0129	$3s$ (Cl3)	–0.6807	–0.0155	0.0005
2	$3d_{xy}$ (Co1)	0.0129	$3p_x$ (Cl3)	0.0123	–0.0273	0.0000
2	$3d_{xy}$ (Co1)	0.0129	$3p_y$ (Cl3)	–0.0012	–0.0729	0.0000
2	$3d_{xz}$ (Co1)	–0.0002	$3s$ (Cl2)	–0.6801	0.0000	0.0000
2	$3d_{xz}$ (Co1)	–0.0002	$3p_x$ (Cl2)	–0.0122	0.0000	0.0000
2	$3d_{xz}$ (Co1)	–0.0002	$3p_y$ (Cl2)	0.0012	0.0000	0.0000
2	$3d_{xz}$ (Co1)	–0.0002	$3s$ (Cl3)	–0.6807	0.0003	0.0000
2	$3d_{xz}$ (Co1)	–0.0002	$3p_x$ (Cl3)	0.0123	0.0006	0.0000
2	$3d_{xz}$ (Co1)	–0.0002	$3p_y$ (Cl3)	–0.0012	–0.0001	0.0000
2	$3s$ (Cl2)	–0.6801	$3s$ (Cl3)	–0.6807	0.0006	0.0011
2	$3s$ (Cl2)	–0.6801	$3p_x$ (Cl3)	0.0123	0.0040	–0.0001
2	$3s$ (Cl2)	–0.6801	$3p_y$ (Cl3)	–0.0012	–0.0004	0.0000
2	$3p_x$ (Cl2)	0.0122	$3s$ (Cl3)	–0.6807	–0.0040	–0.0001
2	$3p_x$ (Cl2)	–0.0122	$3p_x$ (Cl3)	0.0123	–0.0153	0.0000
2	$3p_x$ (Cl2)	–0.0122	$3p_y$ (Cl3)	–0.0012	0.0017	0.0000
2	$3p_y$ (Cl2)	0.0012	$3s$ (Cl3)	–0.6807	0.0004	0.0000
2	$3p_y$ (C12)	0.0012	$3p_x$ (Cl3)	0.0123	0.0017	0.0000
2	$3p_y$ (Cl2)	0.0012	$3p_y$ (Cl3)	–0.0012	0.0016	0.0000
						$\Sigma n_{r-s,\,i} = 0.1238$

TABLE-5
NATURE OF OCCUPIED MOs

MO No.	Sum of overlap-population contribution ($\Sigma n_{r-s,\,i}$)		Nature of MOs
	COBALT(II) CHLORIDE		
1	0.1238	(Positive)	Bonding
2	0.0461	(Positive)	Bonding
3	0.4744	(Positive)	Bonding
4	0.3976	(Positive)	Bonding
5	0.2197	(Positive)	Bonding
6	0.0588	(Positive)	Bonding
7	0.0590	(Positive)	Bonding
8	0.2095	(Positive)	Bonding
9	0.0000	(zero)	Nonbonding
10	0.0000	(zero)	Nonbonding
11	0.0079	(Positive)	Bonding
12	-0.1127	(Negative)	Antibonding
	COBALT(II) BROMIDE		
1	0.1292	(Positive)	Bonding
2	0.0563	(Positive)	Bonding
3	0.3553	(Positive)	Bonding
4	0.1579	(Positive)	Bonding
5	0.1814	(Positive)	Bonding
6	0.2362	(Positive)	Bonding
7	0.0000	(zero)	Nonbonding
8	0.0000	(zero)	Nonbonding
9	0.0423	(Positive)	Bonding
10	0.0418	(Positive)	Bonding
11	0.0340	(Positive)	Bonding
12	-0.0472	(Negative)	Antibonding
	COBALT(II) IODIDE		
1	0.181	(Positive)	Bonding
2	0.0751	(Positive)	Bonding
3	0.2857	(Positive)	Bonding
4	0.1243	(Positive)	Bonding
5	0.1243	(Positive)	Bonding
6	0.0000	(zero)	Nonbonding
7	0.0000	(zero)	Nonbonding
8	0.2409	(Positive)	Bonding
9	0.0331	(Positive)	Bonding
10	0.0332	(Positive)	Bonding
11	0.0577	(Positive)	Bonding
12	0.0727	(Negative)	Antibonding

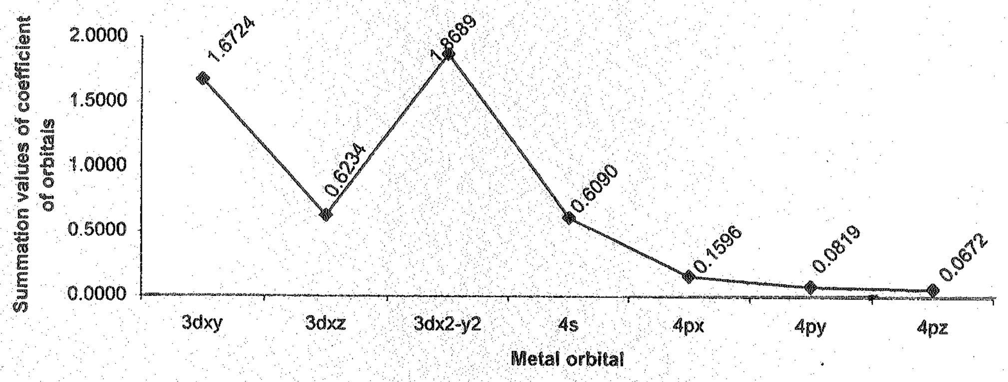


Fig. 2. Extent of involvement of metal orbital in the formation of MOs of $CoCl_2$

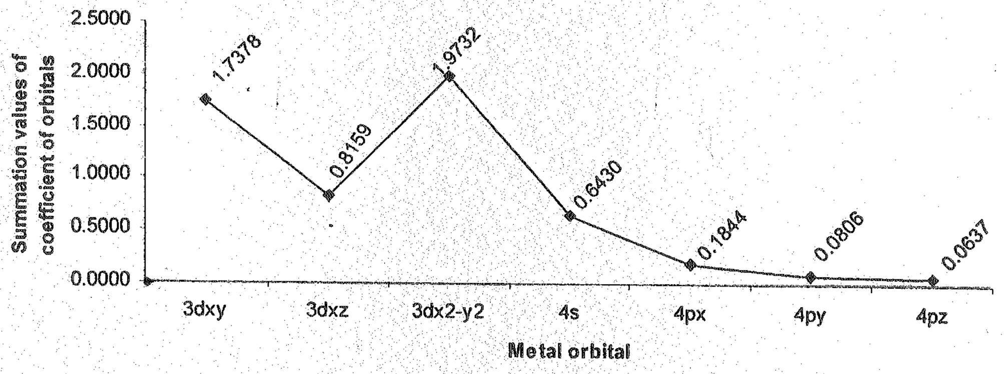


Fig. 3. Extent of involvement of metal orbital in the formation of MOs of $CoBr_2$

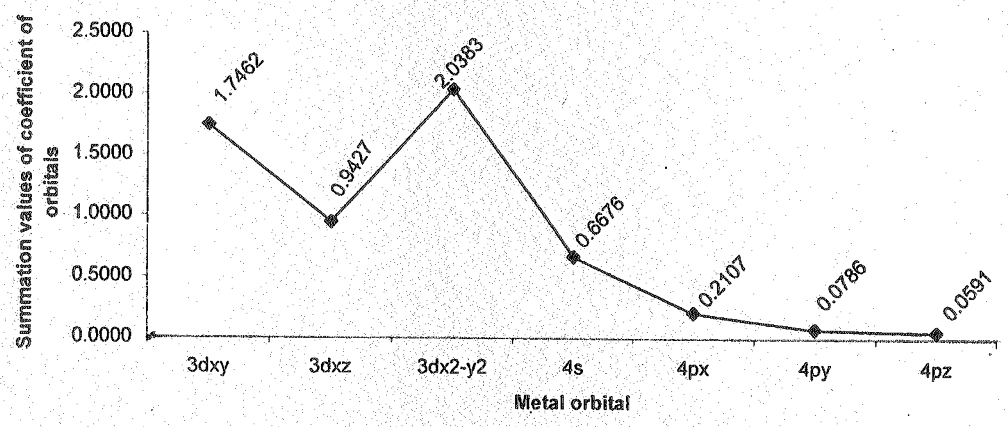


Fig. 4. Extent of involvement of metal orbital in the formation of MOs of CoI_2

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.

The population analysis as presented in Table-5 shows that the nonbonding electrons are present in 9th and 10th molecular orbitals in $CoCl_2$, 7th and 8th molecular orbitals in $CoBr_2$ and 6th and 7th molecular orbitals in CoI_2. The difference in position of nonbonding molecular orbital prompted us to examine the eigenvalues of cobalt ion and to compare them with the eigenvalues of the halides. The eigenvalues of the molecular orbitals of the halides are included in Table-6. The nonbonding orbitals are degenerate in all the cases. The eigenvector analysis as presented in Tables 1a–c indicates that these orbitals are $3d_{yz}$ and $3d_{z^2}$. The energies of these orbitals in cobalt ion and in its three halides are demonstrated in Table-7.

TABLE-6

EIGENVALUES OF ALL THE 17 MOs OF COBALT(II) HALIDES

MO No.	$CoCl_2$	$CoBr_2$	CoI_2
1	–0.9740	–0.8193	–0.6738
2	–0.9667	–0.8119	–0.6631
3	–0.5680	–0.5341	–0.5199
4	–0.5437	–0.5116	–0.5006
5	–0.5437	–0.5116	–0.5006
6	–0.5240	–0.4873	–0.4843
7	–0.5240	–0.4843	–0.4843
8	–0.5232	–0.4843	–0.4734
9	–0.4843	–0.4827	–0.4677
10	–0.4843	–0.4827	–0.4677
11	–0.4596	–0.4524	–0.4516
12	–0.4528	–0.4486	–0.4467
13	–0.4528	–0.4486	–0.4467
14	–0.1670	–0.1786	–0.1831
15	–0.1670	–0.1786	–0.1831
16	0.0767	–0.0620	–0.1075
17	0.3738	0.1780	0.0973

From Table-7, it is clear that all the *d* orbitals in ion are degenerate and their energy is –0.4843 eV. The energy of $3d_{yz}$ and $3d_{z^2}$ orbitals in all the halides is also –0.4843 eV. In case of chloride the energy of $3d_{x^2-y^2}$ is –0.4596 and in bromide and iodide –0.4524 and –0.4516 eV respectively. The $3d_{xy}$ and $3d_{xz}$ are degenerate in all the cases but their energies differ, being –0.4528 eV in chloride, –0.4486 eV in bromide and –0.4467 eV in iodide. If the magnitude of splitting, *i.e.*, difference in energies of two nonbonding degenerate orbitals ($3d_{yz}$, $3d_{z^2}$) and $3d_{x^2-y^2}$ or $3d_{xy}$, $3d_{xz}$ is evaluated, the highest value is in iodide and lowest in chloride.

TABLE-7

SPLITTING OF d ORBITALS IN COBALT(II) HALIDES

Energy	Co^{++}	$CoCl_2$	$CoBr_2$	CoI_2
–0.4843	$3d_{x^2-y^2}$, $3d_{z^2}$, $3d_{xy}$, $3d_{xz}$, $3d_{yz}$	$3d_{yz}$, $3d_{z^2}$	$3d_{yz}$, $3d_{z^2}$	$3d_{yz}$, $3d_{z^2}$
–0.4596	—	$3d_{x^2-y^2}$	—	—
–0.4528	—	$3d_{xy}$, $3d_{xz}$	—	—
–0.4524	—	—	$3d_{x^2-y^2}$	—
–0.4516	—	—	—	$3d_{x^2-y^2}$
–0.4486	—	—	$3d_{xy}$, $3d_{xz}$	—
–0.4467	—	—	—	$3d_{xy}$, $3d_{xz}$

The halogens enter into bonding through their *s* and *p* orbitals. The two orbitals differ in energy significantly. It is worth noticing that energy difference in *s* and *p* orbitals of the chloride, bromide and iodide are not the same. In chloride it is –0.9665 (*s*) and –0.5218 (*p*), in bromide it is –0.8110 (*s*) and –0.4814 (*p*) and in iodide –0.6615 (*s*) and –0.4667 (*p*). The difference between energy levels of *s* and *p* orbitals in chloride is –0.4447, in bromide –0.3296 and in iodide –0.1948. The order is chloride > bromide > iodide. In other words, the *s* and *p* orbitals in iodide are close as compared to *s* and *p* orbitals in bromide and chloride. The splitting of *d* orbitals in the three halides as discussed can be related with the energy levels of *s* and *p* orbitals of the halogens. The iodide in which the *s* and *p* orbitals are very close, cause greater splitting in *d* orbitals or they have greater overlap with *d* orbitals of cobalt. It is perhaps on this account the splitting of *d* orbitals in iodide is more than chloride or bromide.

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

Conclusions

1. Eigenvector analysis shows that $3d_{x^2-y^2}$ and $3d_{xy}$ orbitals of cobalt play a major role in bonding between cobalt and halogen, 4*s* orbital is next and 4*p* orbitals have a negligible role. This supports the Landis observation and concept of *sd* hybridization. The bond angles are also in the range prescribed for *sd* hybridization.
2. *s* and *p* orbitals of halogen are involved in bonding with cobalt. There is a difference in the energy levels of *s* and *p* orbitals in the three halides. The difference in chloride is 0.4447, in bromide 0.3296 and in iodide 0.1948. The closeness in the energy levels of *s* and *p* in iodide makes it more effective for overlap with orbitals of cobalt.
3. The overlap population analysis shows that nonbonding orbitals in chloride are 9th and 10th, in bromide 7th and 8th and in iodide 6th and 7th molecular orbitals. The energy of these orbitals in all the cases is –0.4843 eV. The degenerate *d* orbitals of Co^{2+} has also the same energy.
4. The magnitude of splitting of *d* orbitals as evaluated by eigen values and eigenvectors indicates the following order: $CoCl_2 < CoBr_2 < CoI_2$.
5. No molecular orbital is formed by two atomic orbitals only. All MOs have contribution from many atomic orbitals, the difference is only in extent of involvement.

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