# Application of the intermediate-coupling scheme to a $5d^4$ system, $K_2OsCl_6$

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In this paper we have applied the generalized intermediate-coupling scheme, developed by us, to a $5d^4$ system, $K_2OsCl_6$, and have demonstrated very clearly the great convenience and simplicity of this scheme compared to the usual strong-field coupling scheme which was applied earlier in studying this complex. Practically without any labor we have been able to get a very close agreement with experiment for which the conventional approach needed to diagonalize matrices of large dimensions. This shows the distinct advantage of the present model in studying the optical and magnetic properties of the complexes of the palladium and platinum groups.

## I. INTRODUCTION

A generalized intermediate-coupling scheme was developed[1] for the many-electron systems of transition-metal ions under ligand fields with cubic (octahedral or tetrahedral) symmetries. The unperturbed levels in this scheme fully incorporate the crystal field as well as the spin-orbit interaction; the electron-electron Coulomb interaction is treated as a perturbation. Naturally, this scheme is extremely helpful for the complexes of transition-metal ions in the second and third series where the ligand field and the spin-orbit coupling are large compared to the electron-electron Coulomb interaction. The applicability and great simplicity of the scheme was illustrated for the complexes $OsF_6$ ($5d^2$ system)[2,3] and $K_2ReCl_6$ ($5d^3$ system).[1]

In the present paper we shall show the applicability of the scheme for the complex $K_2OsCl_6$ ($5d^4$ system). Rahman[4] studied this complex by using the wave functions in the usual strong-field coupling scheme. He calculated the energy levels by considering the configuration interaction between the $t_2^4$, $t_2^3e$ configurations. Such calculations involve simultaneous diagonalization of the crystal-field, electrostatic, and spin-orbit interactions. Naturally, the matrices encountered in that approach were considerably large in dimension; these were $6\times6$, $8\times8$, $11\times11$, and $12\times12$ for $A_1$, $E$, $T_1$, and $T_2$ levels, respectively. The seven lower-lying levels for this complex $K_2OsCl_6$ can be very easily evaluated by using the intermediate-coupling scheme[1] where, in good approximation, the matrices involved are only $2\times2$, $2\times2$, $1\times1$, and $2\times2$ for $A_1$, $E$, $T_1$, and $T_2$ levels, respectively. For the sake of comparison, we shall employ the same set of values for the parameters $Dq$, $\zeta_d$, $B$, and $C$, as used by Rahman who got good agreement with the experimental results of the optical absorption spectrum and the magnetic susceptibility.

## II. CALCULATION OF ENERGY LEVELS

$Os^{4+}$ in $K_2OsCl_6$ is a $5d^4$ ion situated in the octahedral ligand field. To investigate the ordinary properties of the system we need only a few lower states. So we start with the seven low-lying unperturbed levels constructed in the intermediate-coupling scheme[1]:

$$|\gamma_{8l}^4:A_1\rangle,\ |\gamma_{8l}^2\gamma_7^2:A_1\rangle,\ |\gamma_{8l}^3\gamma_7:E\rangle,\ |\gamma_{8l}^2\gamma_7^2:E\rangle\ ,|\gamma_{8l}^3\gamma_7:T_1\rangle,\ |\gamma_{8l}^3\gamma_7:T_2\rangle,\ |\gamma_{8l}^2\gamma_7^2:T_2\rangle\ .$$

Usually, $\epsilon_0(\gamma_{8u})$ is much greater than $\epsilon_0(\gamma_{8l})$ and $\epsilon_0(\gamma_7)$ so that the states coming from the configurations involving $\gamma_{8u}$ are situated much higher in energy scale and therefore can be omitted. The expressions for these three single-electron energy levels (in terms of the crystal-field parameter $Dq$ and the spin-orbit coupling constant $\zeta_d$) are given in Eqs. (2.3) and (2.6) in Ref. 1. Thus, for the values $Dq=3300$ cm$^{-1}$, $\zeta_d=2575$ cm$^{-1}$ as used by Rahman for $K_2OsCl_6$, we get $\epsilon_0(\gamma_{8l})=-14\,775.2$ cm$^{-1}$, $\epsilon_0(\gamma_7)=-10\,625$ cm$^{-1}$, $\epsilon_0(\gamma_{8u})=20\,087.7$ cm$^{-1}$. Using Tables IIIA and IIIB given in Appendix B of Ref. 1, we express the unperturbed states considered in terms of the strong-field scheme wave functions. Then, using the known electrostatic matrices in the strong-field scheme (see Table A28 in Ref. 5), we can easily construct the required matrix elements of the Hamiltonian with respect to these states of the present scheme. These matrix elements in different blocks are given below.

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*$A_1$ block* $(2\times 2)$:

$$\langle \gamma_{8l}^4:A_1|\mathcal{H}|\gamma_{8l}^4:A_1\rangle = 4\epsilon_0(\gamma_{8l}) + B[-10-12C_{02}+6C_{04}+8\sqrt{6}(-C_{71}-2C_{53}+C_{35})] + C(\tfrac{20}{3}C_{40}+8C_{42}+8C_{06}+16C_{26})+6A \ , \tag{2.1}$$

$$\langle \gamma_{8l}^4:A_1|\mathcal{H}|\gamma_{8l}^2\gamma_7^2:A_1\rangle = B[\sqrt{2}(5C_{40}+7C_{42}+C_{04}+C_{06})+4\sqrt{3}(-C_{31}-C_{33}+C_{15})] + C\left[\frac{\sqrt{2}}{3}(5C_{40}+16C_{42}-C_{24}+3C_{06})\right] \ , \tag{2.2}$$

$$\langle \gamma_{8l}^2\gamma_7^2:A_1|\mathcal{H}|\gamma_{8l}^2\gamma_7^2:A_1\rangle = 2\epsilon_0(\gamma_{8l})+2\epsilon_0(\gamma_7)+B[-5C_{40}+2C_{22}+4C_{04}+4\sqrt{6}(C_{31}+C_{11})] + C\tfrac{1}{3}(13+12C_{20}+10C_{04})+6A \ . \tag{2.3}$$

*$E$ block* $(2\times 2)$:

$$\langle \gamma_{8l}^3\gamma_7:E|\mathcal{H}|\gamma_{8l}^3\gamma_7:E\rangle = 3\epsilon_0(\gamma_{8l})+\epsilon_0(\gamma_7)+B(-11-4C_{02}+3C_{04}+4\sqrt{6}C_{13}) + C\tfrac{1}{3}(19-14C_{02}+10C_{04})+6A \ , \tag{2.4}$$

$$\langle \gamma_{8l}^3\gamma_7:E|\mathcal{H}|\gamma_{8l}^2\gamma_7^2:E\rangle = -2\sqrt{2}B(C_{10}+C_{12})-\frac{2\sqrt{2}}{3}C(C_{30}) \ , \tag{2.5}$$

$$\langle \gamma_{8l}^2\gamma_7^2:E|\mathcal{H}|\gamma_{8l}^2\gamma_7^2:E\rangle = 2\epsilon_0(\gamma_{8l})+2\epsilon_0(\gamma_7)+B(-13+4\sqrt{6}C_{13}+4C_{02}+5C_{04}) + C\tfrac{1}{3}(17-8C_{02}+8C_{04})+6A \ . \tag{2.6}$$

*$T_1$ block* $(1\times 1)$:

$$\langle \gamma_{8l}^3\gamma_7:T_1|\mathcal{H}|\gamma_{8l}^3\gamma_7:T_1\rangle = 3\epsilon_0(\gamma_{8l})+\epsilon_0(\gamma_7)+B(-15+4\sqrt{6}C_{13}+3C_{04}) + C(5-\tfrac{8}{3}C_{02}+\tfrac{10}{3}C_{04})+6A \ . \tag{2.7}$$

*$T_2$ block* $(2\times 2)$:

$$\langle \gamma_{8l}^3\gamma_7:T_2|\mathcal{H}|\gamma_{8l}^3\gamma_7:T_2\rangle = 3\epsilon_0(\gamma_{8l})+\epsilon_0(\gamma_7)+B\left[-11-\tfrac{4}{3}C_{02}+3C_{04}+\frac{4\sqrt{6}}{3}(-2C_{31}+C_{13})\right] + C\tfrac{1}{3}(19-12C_{02}+10C_{04})+6A \ , \tag{2.8}$$

$$\langle \gamma_{8l}^3\gamma_7:T_2|\mathcal{H}|\gamma_{8l}^2\gamma_7^2:T_2\rangle = B\left[\frac{\sqrt{2}}{3}(6C_{10}-14C_{12})+\frac{4}{\sqrt{3}}C_{21}\right]+C\frac{2\sqrt{2}}{3}(C_{30}-C_{12}) \ . \tag{2.9}$$

$$\langle \gamma_{8l}^2\gamma_7^2:T_2|\mathcal{H}|\gamma_{8l}^2\gamma_7^2:T_2\rangle = 2\epsilon_0(\gamma_{8l})+2\epsilon_0(\gamma_7)+B\left[-13+\tfrac{4}{3}C_{02}-\tfrac{1}{3}C_{04}+\frac{4\sqrt{6}}{3}(2C_{11}+C_{13})\right] + C\tfrac{1}{3}(17-4C_{02}-2C_{04})+6A \ . \tag{2.10}$$

In Eqs. (2.1)–(2.10) we have used the same notations as in Ref. 1.

We use the same values of the parameters as chosen by Rahman.[4] These are

$$Dq = 3300\ \text{cm}^{-1},$$
$$\zeta_d = 2575\ \text{cm}^{-1} \ ,$$
$$B = 365.5\ \text{cm}^{-1},$$
$$C = 1561\ \text{cm}^{-1} \ .$$

These values of the parameters give rise to the following energy levels easily obtained by diagonalizing the small matrix blocks in our scheme:

$$\begin{aligned} A_1 &\begin{cases} E_1(A_1)=0 \\ E_2(A_1)=18\,595\ \text{cm}^{-1} \ , \end{cases} \\ E &\begin{cases} E_1(E)=4629.4\ \text{cm}^{-1} \\ E_2(E)=10\,173\ \text{cm}^{-1} \ , \end{cases} \\ T_1 &\begin{cases} E_1(T_1)=2681.4\ \text{cm}^{-1} \ , \end{cases} \\ T_2 &\begin{cases} E_1(T_2)=4511.4\ \text{cm}^{-1} \\ E_2(T_2)=10\,314.2\ \text{cm}^{-1} \ , \end{cases} \end{aligned} \tag{2.11}$$

where the positions of the energy levels are given relative to the lowest level $E_1(A_1)$. These relative positions of the low-lying energy levels almost agree with those in Ref. 4.

We note that Rahman's calculations in the strong-field scheme involve the configurations $t_2^4$ and $t_2^3e$ only, omitting the higher states coming from the configurations $t_2^2e^2$, $t_2e^3$, and $e^4$. If all the configurations were included in that scheme the dimensions of the matrix blocks would have been much larger: $14\times14$, $19\times19$, $23\times23$, and $27\times27$ for $A_1$, $E$, $T_1$, and $T_2$ blocks, respectively. That this truncation made by Rahman in the strong-field scheme does not lead to serious errors can be easily checked with the help of our intermediate-coupling scheme. Thus, if we retain in our scheme only these strong-field states which come from the configurations $t_2^4$ and $t_2^3e$, then the relative positions of the energy levels are found to be not very much different from those originally obtained in our scheme and given in (2.11). These new positions of the energy levels are given below and are naturally found to be a little closer to those in Ref. 4.

$$\begin{aligned}
&A_1\begin{cases}E_1(A_1)=0\ \text{cm}^{-1}\\ E_2(A_1)=18\,473.4\ \text{cm}^{-1}\end{cases},\\
&E\begin{cases}E_1(E)=4585.8\ \text{cm}^{-1}\\ E_2(E)=10\,181.9\ \text{cm}^{-1}\end{cases},\\
&T_1\begin{cases}E_1(T_1)=2651.2\ \text{cm}^{-1}\end{cases},\\
&T_2\begin{cases}E_1(T_2)=4490.5\ \text{cm}^{-1}\\ E_2(T_2)=10\,303.5\ \text{cm}^{-1}\end{cases}.
\end{aligned}\tag{2.12}$$

## III. MAGNETIC SUSCEPTIBILITY

As we have seen in Sec. II, the ground level transforms as $A_1$ (in $O_h'$ double group) so that there is only a temperature-independent paramagnetic susceptibility in first-order calculations. The general expression for this susceptibility is given by Eq. (3) in Ref. 4. This is

$$\chi=0.5106\sum_n|\langle\psi_n|KL_z+2S_z|\psi_0\rangle|^2/(E_n-E_0)\ .\tag{3.1}$$

Since the ground state $\psi_0$ transforms as $A_1$ and both $L_z$ and $S_z$ transform as $|T_10\rangle$, the matrix elements in Eq. (3.1) will be nonvanishing only for those excited states which transform as $|T_10\rangle$. There is only one such excited state in the group of low-lying levels considered in the present analysis. This is $|\gamma_{8l}^3\gamma_7;T_10\rangle$.

Diagonalization of the $A_1$ block made earlier yields the following wave function for the ground level:

$$\psi_0\equiv|E_1(A_1)\rangle=\cos\phi|\gamma_{8l}^4;A_1\rangle-\sin\phi|\gamma_{8l}^2\gamma_7^2;A_1\rangle\ ,\tag{3.2}$$

where

$$\cos\phi=0.995\,865\,8,\quad \sin\phi=0.090\,836\,3\ .$$

The matrix element of the magnetic-moment operator ($N_z=KL_z+2S_z$) between the ground state and the excited $|T_10\rangle$ state can now be evaluated by using Appendix A together with Eq. (3.21) in Ref. 1. Thus we find that

$$\langle E_1(A_1)|N_z|\gamma_{8l}^3\gamma_7;T_10\rangle=-\frac{2}{3}\left(\cos\phi+\frac{1}{\sqrt{2}}\sin\phi\right)[(2+K_2)C_{10}-\sqrt{6}K_1C_{01}]\ ,\tag{3.3}$$

where, as in Ref. 1, two different orbital reduction factors ($K_1$ and $K_2$) are introduced. Using Eq. (3.3) and the value of the excitation energy for the $T_1$ level as obtained earlier in (2.11), we find the susceptibility $\chi$ as a simple function of the parameters $k_1$ and $k_2$. The experimental values of susceptibility in literature vary from $860\times10^{-6}$ to $941\times10^{-6}$ and the average value is $908\times10^{-6}$ (see Ref. 4 for details). If we take $k_1=k_2=1$ in our calculation, the value of the susceptibility comes out to be $907\times10^{-6}$. However, Rahman[4] found the value of $\chi$ to be $922\times10^{-6}$ on taking $k_1=k_2=0.7$ (in Ref. 4 the notations $k$ and $k'$ are used in place of $k_2$ and $k_1$, respectively).

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