Application of intermediate-coupling scheme to the kd^6 ($k=4,5$) system

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The generalized intermediate-coupling scheme developed earlier has been applied to the kd^6 ($k=4,5$) system to derive expressions for the energy levels and the magnetic susceptibility. The great simplicity and obvious advantages over the conventional strong-field-coupling scheme have been clearly demonstrated.

I. INTRODUCTION

A generalized intermediate-coupling scheme (ICS) was developed[1] for the many-electron systems of the transition-metal ions under ligand fields with cubic symmetry. In previous publications,[1-3] the scheme was presented for d^2, d^3, d^4, and d^5 systems. In the present paper the d^6 system is treated through this scheme. The usual advantage (in physical interpretation and in consequent simplicity in calculations) of this scheme over the conventional strong-field-coupling scheme is clearly demonstrated in the present context dealing with heavy transition-metal ions with d^6 configurations. The principle of "electron-hole complementarity" (with proper phase relations) between the d^6 and d^4 systems has been established for the present scheme. However, the truncated results for the d^6 system do not follow from those for the d^4 system. Thus, for example, the Hamiltonian matrix for the d^4 system in the ICS (with proper truncation) breaks into A_1, E, T_1, and T_2 blocks of dimensions 2×2, 2×2, 1×1, and 2×2, respectively,[2] whereas, for the d^6 system, we have A_1, A_2, E, T_1, and T_2 blocks of dimensions 2×2, 1×1, 2×2, 3×3, and 3×3, respectively. It is worth noting here that a reasonable truncation of the conventional strong-field-coupling scheme for the d^6 system produces comparatively large blocks, namely A_1, A_2, E, T_1, and T_2 of dimensions 8×8, 4×4, 11×11, 12×12, and 14×14, respectively, which are obviously not convenient in practice when we are interested in the group of low-lying energy levels only, which are associated with the prominent optical spectral lines. In addition, the paramagnetic susceptibility can be easily evaluated by constructing the relevant matrix elements of the magnetic-moment operator with respect to a few wave functions in the truncated ICS.

II. SCHEME AND THE PRINCIPLE OF ELECTRON-HOLE COMPLEMENTARITY

The three single-electron energy levels in the intermediate-coupling scheme[1] are γ_{8l} (fourfold degenerate), γ_7 (doubly degenerate), and γ_{8u} (fourfold degenerate) in order of increasing energy values. We accommodate the six d electrons in these basic levels in various ways, and construct the symmetry-adapted wave functions for each configuration; $\gamma_{8l}^{n_1}\gamma_7^{n_2}\gamma_{8u}^{n_3}$ ($n_1,n_3\le4$; $n_2\le2$; $n_1+n_2+n_3=6$). This task of the construction of determinantal (antisymmetric) wave functions for the different configurations of the d^6 system follows the procedure described in Ref. 1. The next step in the scheme is to express the $\gamma_{8l}^{n_1}\gamma_7^{n_2}\gamma_{8u}^{n_3}$ wave functions in terms of the $\gamma_{8t_2}^{n_1}\gamma_7^{n_2}\gamma_{8e}^{n_3}$ wave functions.[1] These transformations for all the wave functions of the d^6 system are given in matrix form in Appendix A (Ref. 4) [Tables I(1a), I(1b), ..., I(5b), I(5c)]. The final step is to express the $\gamma_{8t_2}^{n_1}\gamma_7^{n_2}\gamma_{8e}^{n_3}$ wave functions in terms of the strong-field-scheme wave functions symmetry adapted to the irreducible representations of the octahedral double group O_h'. These transformations are given in matrix form in Appendix B (Ref. 4) [Tables II(1a), II(1b), ..., II(5c), II(5d)]. The strong-field-scheme wave functions used here are the R forms (for definition, see pp. 250–252 of Ref. 5), so that a direct complementarity relation exists between a state

$$|t_2^m(S_1\Gamma_1)e^n(S_2\Gamma_2)S\Gamma M_S M_\Gamma\rangle$$

of the d^6 system and the corresponding state

$$|t_2^{6-m}(S_1\Gamma_1)e^{4-n}(S_2\Gamma_2)S\Gamma M_S M_\Gamma\rangle$$

of the d^4 system. This enables us to employ the same electrostatic matrices of the d^4 system (Table A29 in Ref. 5) in the present case of the d^6 system by simply adding a constant term $(9A-14B+7C)$ to each diagonal element.

In the ICS we find that a state of the $\gamma_{8a}^{n_1}\gamma_7^{n_2}\gamma_{8b}^{n_3}$ configuration of the d^6 system is related (through the principle of electron-hole complementarity) to the corresponding state of the $\gamma_{8a}^{4-n_1}\gamma_7^{2-n_2}\gamma_{8b}^{4-n_3}$ configuration of the d^4 system ($a=l$, $b=u$ or $a=t_2$, $b=e$). A change of sign is involved in each of the following complementarity relations:

$$|\gamma_{8a}^3\gamma_{8b}^3;A_1a_1\rangle\rightarrow-|\gamma_{8a}\gamma_7^2\gamma_{8b};A_1a_1\rangle\ ,$$
$$|\gamma_{8a}^3\gamma_7^2\gamma_{8b};A_1a_1\rangle\rightarrow-|\gamma_{8a}\gamma_{8b}^3;A_1a_1\rangle\ ,$$
$$|\gamma_{8a}^3\gamma_{8b}^3;A_2a_2\rangle\rightarrow-|\gamma_{8a}\gamma_7^2\gamma_{8b};A_2a_2\rangle\ ,$$
$$|\underline{\gamma}_{8a}^3\underline{\gamma}_7(E)\underline{\gamma}_{8b}^2(E);A_2a_2\rangle\rightarrow-|\underline{\gamma}_{8a}\underline{\gamma}_7(E)\underline{\gamma}_{8b}^2(E);A_2a_2\rangle\ ,$$
$$|\underline{\gamma}_{8a}^3\underline{\gamma}_7(E)\underline{\gamma}_{8b}^2(A_1);E\gamma\rangle\rightarrow-|\underline{\gamma}_{8a}\underline{\gamma}_7(E)\underline{\gamma}_{8b}^2(A_1);E\gamma\rangle\ ,$$
$$|\gamma_{8a}^3\gamma_7^2\gamma_{8b};E\gamma\rangle\rightarrow-|\gamma_{8a}\gamma_{8b}^3;E\gamma\rangle\ ,$$

$|\gamma_{8a}^4\gamma_{8b}^2;E\gamma\rangle \rightarrow -|\gamma_7^2\gamma_{8b}^2;E\gamma\rangle$,

$|\gamma_{8a}^2(A_1)\gamma_7^2\gamma_{8b}^2(E);E\gamma\rangle \rightarrow -|\gamma_{8a}^2(A_1)\gamma_{8b}^2(E);E\gamma\rangle$,

$|\gamma_{8a}^3\gamma_{8b}^3;E\gamma\rangle \rightarrow -|\gamma_{8a}\gamma_7^2\gamma_{8b};E\gamma\rangle$,

$|\underline{\gamma}_{8a}^3\underline{\gamma}_7(T_1)\underline{\gamma}_{8b}^2(A_1);T_1\gamma\rangle \rightarrow -|\underline{\gamma}_{8a}\underline{\gamma}_7(T_1)\underline{\gamma}_{8b}^2(A_1);T_1\gamma\rangle$,

$|\gamma_{8a}^3\gamma_{8b}^3;3;T_1\gamma\rangle \rightarrow -|\gamma_{8a}\gamma_7^2\gamma_{8b};3;T_1\gamma\rangle$,

$|\gamma_{8a}^3\gamma_{8b}^3;1;T_1\gamma\rangle \rightarrow -|\gamma_{8a}\gamma_7^2\gamma_{8b};1;T_1\gamma\rangle$,

$|\gamma_{8a}\gamma_7\gamma_{8b}^4;T_1\gamma\rangle \rightarrow -|\gamma_{8a}^3\gamma_7;T_1\gamma\rangle$,

$|\underline{\gamma}_{8a}^3\underline{\gamma}_7(T_2)\underline{\gamma}_{8b}^2(T_2);T_1\gamma\rangle \rightarrow -|\underline{\gamma}_{8a}\underline{\gamma}_7(T_2)\underline{\gamma}_{8b}^2(T_2);T_1\gamma\rangle$,

$|\underline{\gamma}_{8a}^3\underline{\gamma}_7(T_2)\underline{\gamma}_{8b}^2(A_1);T_2\gamma\rangle \rightarrow -|\underline{\gamma}_{8a}\underline{\gamma}_7(T_2)\underline{\gamma}_{8b}^2(A_1);T_2\gamma\rangle$,

$|\gamma_{8a}^3\gamma_7^2\gamma_{8b};2;T_2\gamma\rangle \rightarrow -|\gamma_{8a}\gamma_{8b}^3;2;T_2\gamma\rangle$,

$|\gamma_{8a}^4\gamma_{8b}^2;T_2\gamma\rangle \rightarrow -|\gamma_7^2\gamma_{8b}^2;T_2\gamma\rangle$,

$|\gamma_{8a}^2(T_2)\gamma_7^2\gamma_{8b}^2(A_1);T_2\gamma\rangle \rightarrow -|\gamma_{8a}^2(T_2)\gamma_{8b}^2(A_1);T_2\gamma\rangle$,

$|\gamma_{8a}^3\gamma_{8b}^3;3;T_2\gamma\rangle \rightarrow -|\gamma_{8a}\gamma_7^2\gamma_{8b};3;T_2\gamma\rangle$,

$|\gamma_{8a}^3\gamma_{8b}^3;2;T_2\gamma\rangle \rightarrow -|\gamma_{8a}\gamma_7^2\gamma_{8b};2;T_2\gamma\rangle$.

(Here, $a=l$, $b=u$; or $a=u$, $b=l$; or $a=t$, $b=e$; or $a=e$, $b=t$.)

Other complementarity relations do not involve any change of phase. Thus, for example, we have

$|\gamma_{8a}^4\gamma_7^2;A_1a_1\rangle \rightarrow |\gamma_{8b}^4;A_1a_1\rangle$,

$|\gamma_{8a}^4\gamma_7\gamma_{8b};E\gamma\rangle \rightarrow |\gamma_7\gamma_{8b}^3;E\gamma\rangle$,

$|\underline{\gamma}_{8a}^3\underline{\gamma}_7(T_1)\underline{\gamma}_{8b}^2(T_2);A_2a_2\rangle \rightarrow |\underline{\gamma}_{8a}\underline{\gamma}_7(T_1)\underline{\gamma}_{8b}^2(T_2);A_2a_2\rangle$,

$|\underline{\gamma}_{8a}^3\underline{\gamma}_7(E)\underline{\gamma}_{8b}^2(T_2);T_1\gamma\rangle \rightarrow |\underline{\gamma}_{8a}\gamma_7(E)\underline{\gamma}_{8b}^2(T_2);T_1\gamma\rangle$,

$|\gamma_{8a}^2(E)\gamma_7^2\gamma_{8b}^2(T_2);T_2\gamma\rangle \rightarrow |\gamma_{8a}^2(E)\gamma_{8b}^2(T_2);T_2\gamma\rangle$.

A comparison of the transformation matrices (in Appendices A and B of Ref. 4) for the d^6 system with those for the d^4 system given in Ref. 1 reveals these complementarity relations.

III. ENERGY MATRICES

The lowest electronic configuration for the d^6 system in the ICS is $\gamma_{8l}^4\gamma_7^2$, giving the nondegenerate state $|\gamma_{8l}^4\gamma_7^2;A_1\rangle$ only. Thus we must consider the next-higher configurations $\gamma_{8l}^4\gamma_7\gamma_{8u}$ and $\gamma_{8l}^3\gamma_7^2\gamma_{8u}$, which give rise to the following energy levels:

$|\gamma_{8l}^4\gamma_7\gamma_{8u};E\rangle$, $|\gamma_{8l}^4\gamma_7\gamma_{8u};T_1\rangle$, $|\gamma_{8l}^4\gamma_7\gamma_{8u};T_2\rangle$,

$|\gamma_{8l}^3\gamma_7^2\gamma_{8u};A_1\rangle$, $|\gamma_{8l}^3\gamma_7^2\gamma_{8u};A_2\rangle$, $|\gamma_{8l}^3\gamma_7^2\gamma_{8u};E\rangle$,

$|\gamma_{8l}^3\gamma_7^2\gamma_{8u};3;T_2\rangle$, $|\gamma_{8l}^3\gamma_7^2\gamma_{8u};2;T_2\rangle$,

$|\gamma_{8l}^3\gamma_7^2\gamma_{8u};3;T_1\rangle$, $|\gamma_{8l}^3\gamma_7^2\gamma_{8u};1;T_1\rangle$.

The determinantal wave functions for these states in the ICS are given in Ref. 4, Appendix C. These 11 unperturbed energy states (coming from the configurations $\gamma_{8l}^4\gamma_7^2$, $\gamma_{8l}^4\gamma_7\gamma_{8u}$, and $\gamma_{8l}^3\gamma_7^2\gamma_{8u}$) can now be treated through the perturbation of the electron-electron Coulomb interaction (in the present scheme,[1] the crystal-field potential and the spin-orbit interaction have already been considered in the unperturbed part of the Hamiltonian). In our case of a heavy transition metal, $\epsilon_0(\gamma_{8u})$ is much greater than $\epsilon_0(\gamma_{8l})$ and $\epsilon_0(\gamma_7)$[1], so that the states coming from the other higher configurations such as $\gamma_{8l}^4\gamma_{8u}^2$, $\gamma_{8l}^3\gamma_7\gamma_{8u}^2$, $\gamma_{8l}^3\gamma_{8u}^3$, etc., are situated much higher (in energy scale) than the 11 states already considered. Then the perturbation will be too weak to cause any significant "mixing" of this group of 11 states with the other higher states. Thus, we truncate our scheme by considering only this group of 11 states and omitting all the other higher states. The matrix elements of the Hamiltonian with respect to these states can be constructed by following the usual procedure,[1] which consists of using the transformation matrices (in appendices A and B of Ref. 4), and then employing the known electrostatic matrices in the strong-field scheme (See Tables A28 in Ref. 5).

Since the two A_1 states $|\gamma_{8l}^4\gamma_7^2;A_1\rangle$ and $|\gamma_{8l}^3\gamma_7^2\gamma_{8u};A_1\rangle$ are widely separated in energy scale, we can neglect the interaction (through the perturbation) between them. Then, the energy values for the two A_1 levels including perturbation will be

$$\langle\gamma_{8l}^4\gamma_7^2;A_1a_1|\mathscr{H}|\gamma_{8l}^4\gamma_7^2;A_1a_1\rangle=[4\epsilon_0(\gamma_{8l})+2\epsilon_0(\gamma_7)]+15A+B(-30+6C_{04}+8\sqrt{6}C_{13})+C(15-8C_{02}+\tfrac{20}{3}C_{04}) \quad (3.1)$$

and

$$\langle\gamma_{8l}^3\gamma_7^2\gamma_{8u};A_1a_1|\mathscr{H}|\gamma_{8l}^3\gamma_7^2\gamma_{8u};A_1a_1\rangle$$
$$=[3\epsilon_0(\gamma_{8l})+2\epsilon_0(\gamma_7)+\epsilon_0(\gamma_{8u})]+15A+B(-30+6C_{02}-3C_{04}+4\sqrt{6}C_{31})+C(12+\tfrac{8}{3}C_{02}-\tfrac{10}{3}C_{04}) . \quad (3.2)$$

Next, the energy for the only A_2 level is

$$\langle\gamma_{8l}^3\gamma_7^2\gamma_{8u};A_2a_2|\mathscr{H}|\gamma_{8l}^3\gamma_7^2\gamma_{8u};A_2a_2\rangle$$
$$=[3\epsilon_0(\gamma_{8l})+2\epsilon_0(\gamma_7)+\epsilon_0(\gamma_{8u})]+15A+B(-22+10C_{02}-7C_{04}+4\sqrt{6}C_{31})+C(12+\tfrac{4}{3}C_{02}-2C_{04}) . \quad (3.3)$$

Here, we use the same notation as in Ref. 1. Thus we have

$$C_{mn}=\cos^m\theta\sin^n\theta , \quad (3.4)$$

with

$$\tan 2\theta = \frac{\sqrt{6}\zeta'}{10Dq + \frac{1}{2}\zeta} , \tag{3.5}$$

where Dq is the usual crystal-field parameter; ζ,ζ' are the two spin-orbit—interaction parameters (since, as a result of the covalency effects, the radial part of the wave function for a "t_2" electron may be slightly different from that for an "e" electron, two different spin-orbit—interaction parameters may be involved in general[1]).

$\epsilon_0(\gamma_{8l})$, $\epsilon_0(\gamma_7)$, and $\epsilon_0(\gamma_{8u})$ are the three one-electron energies in the ICS.[1] These are expressed in terms of Dq, ζ, and ζ':

$$\begin{aligned}
\epsilon_0(\gamma_{8l}) &= Dq - \tfrac{1}{4}\zeta - \tfrac{1}{2}[(10Dq + \tfrac{1}{2}\zeta)^2 + 6\zeta'^2]^{1/2} , \\
\epsilon_0(\gamma_{8u}) &= Dq - \tfrac{1}{4}\zeta + \tfrac{1}{2}[(10Dq + \tfrac{1}{2}\zeta)^2 + 6\zeta'^2]^{1/2} , \\
\epsilon_0(\gamma_7) &= -4Dq + \zeta .
\end{aligned} \tag{3.6}$$

Furthermore, A, B, and C are the usual Racah parameters appearing in the electrostatic matrices.[5]

We must take into account the interaction between the two E states. Then we have a 2×2 E block for the Hamiltonian matrix. Diagonalization of this block will give the energies of the two perturbed E levels and the corresponding wave functions. The matrix elements for this block are given below:

$$\begin{aligned}
&\langle \gamma_{8l}^3\gamma_7^2\gamma_{8u}; E\gamma \,|\, \mathscr{H} \,|\, \gamma_{8l}^3\gamma_7^2\gamma_{8u}; E\gamma \rangle \\
&\qquad = [3\epsilon_0(\gamma_{8l}) + 2\epsilon_0(\gamma_7) + \epsilon_0(\gamma_{8u})] + 15A + B(-26 + 2C_{02} + C_{04} + 4\sqrt{3}C_{13}) + C(12 + 2C_{02} - \tfrac{8}{3}C_{04}) ,
\end{aligned} \tag{3.7a}$$

$$\langle \gamma_{8l}^3\gamma_7^2\gamma_{8u}; E\gamma \,|\, \mathscr{H} \,|\, \gamma_{8l}^4\gamma_7\gamma_{8u}; E\gamma \rangle = B(-4C_{10} + \tfrac{4}{3}C_{12} - \tfrac{10}{3}C_{14}) + \tfrac{2}{3}C(C_{12}) , \tag{3.7b}$$

$$\begin{aligned}
&\langle \gamma_{8l}^4\gamma_7\gamma_{8u}; E\gamma \,|\, \mathscr{H} \,|\, \gamma_{8l}^4\gamma_7\gamma_{8u}; E\gamma \rangle \\
&\qquad = [4\epsilon_0(\gamma_{8l}) + \epsilon_0(\gamma_7) + \epsilon_0(\gamma_{8u})] + 15A + B(-26 - 2C_{02} + 3C_{04} - 4\sqrt{6}C_{31}) + C(12 - 2C_{02} + \tfrac{10}{3}C_{04}) .
\end{aligned} \tag{3.7c}$$

Here, $\gamma = \theta$ or ϵ.

Similarly, the three T_1 states give rise to a 3×3 T_1 block for the Hamiltonian matrix. The associated matrix elements are as follows:

$$\begin{aligned}
&\langle \gamma_{8l}^4\gamma_7\gamma_{8u}; T_1\gamma \,|\, \mathscr{H} \,|\, \gamma_{8l}^4\gamma_7\gamma_{8u}; T_1\gamma \rangle \\
&\quad = [4\epsilon_0(\gamma_{8l}) + \epsilon_0(\gamma_7) + \epsilon_0(\gamma_{8u})] + 15A + B[-26 + 14C_{02} - 29C_{04} + 12C_{06} - 2\sqrt{6}(C_{31} + 2C_{33})] \\
&\qquad + \tfrac{1}{3}C(38 - 12C_{02} + 10C_{04}) ,
\end{aligned} \tag{3.8a}$$

$$\begin{aligned}
&\langle \gamma_{8l}^4\gamma_7\gamma_{8u}; T_1\gamma \,|\, \mathscr{H} \,|\, \gamma_{8l}^3\gamma_7^2\gamma_{8u}; 3; T_1\gamma \rangle \\
&\qquad = B\left[-\sqrt{5}(\tfrac{4}{5}C_{50} + 2C_{32} + \tfrac{22}{9}C_{14}) + \frac{3\sqrt{6}}{\sqrt{5}}(3C_{41} + C_{23})\right] - \frac{1}{3\sqrt{5}}C(2C_{10} + 14C_{12}) ,
\end{aligned} \tag{3.8b}$$

$$\begin{aligned}
&\langle \gamma_{8l}^4\gamma_7\gamma_{8u}; T_1\gamma \,|\, \mathscr{H} \,|\, \gamma_{8l}^3\gamma_7^2\gamma_{8u}; 1; T_1\gamma \rangle \\
&\qquad = B\left[\frac{2}{3\sqrt{5}}(-12C_{10} + 23C_{12} - 10C_{14}) + \frac{2\sqrt{2}}{\sqrt{15}}(2C_{01} - 3C_{03} + 2C_{05})\right] \frac{+2}{3\sqrt{5}}C(3C_{10} - 4C_{12} + 5C_{14}) ,
\end{aligned} \tag{3.8c}$$

$$\begin{aligned}
&\langle \gamma_{8l}^3\gamma_7^2\gamma_{8u}; 3; T_1\gamma \,|\, \mathscr{H} \,|\, \gamma_{8l}^3\gamma_7^2\gamma_{8u}; 3; T_1\gamma \rangle \\
&\quad = [3\epsilon_0(\gamma_{8l}) + 2\epsilon_0(\gamma_7) + \epsilon_0(\gamma_{8u})] + 15A + \tfrac{1}{5}B[-146 + 2C_{02} + 13C_{04} + 4\sqrt{6}(2C_{11} + C_{13})] + \tfrac{1}{15}C(182 - 70C_{02} + 60C_{04}) ,
\end{aligned} \tag{3.8d}$$

$$\langle \gamma_{8l}^3\gamma_7^2\gamma_{8u}; 3; T_1\gamma \,|\, \mathscr{H} \,|\, \gamma_{8l}^3\gamma_7^2\gamma_{8u}; 1; T_1\gamma \rangle = \tfrac{1}{15}B[68C_{22} + 2\sqrt{6}(4C_{31} - 7C_{13})] + \tfrac{2}{15}C(-3C_{20} + 7C_{22}) , \tag{3.8e}$$

$$\begin{aligned}
&\langle \gamma_{8l}^3\gamma_7^2\gamma_{8u}; 1; T_1\gamma \,|\, \mathscr{H} \,|\, \gamma_{8l}^3\gamma_7^2\gamma_{8u}; 1; T_1\gamma \rangle \\
&\quad = [3\epsilon_0(\gamma_{8l}) + 2\epsilon_0(\gamma_7) + \epsilon_0(\gamma_{8u})] + 15A + B[-\tfrac{1}{5}(134 - 22C_{02} - 3C_{04}) + 4\sqrt{6}(\tfrac{3}{5}C_{31} + C_{13})] \\
&\qquad + \tfrac{1}{15}C(198 - 40C_{02} + 216C_{04}) .
\end{aligned} \tag{3.8f}$$

Here, $\gamma = 1$, or 0, or -1.

Finally, we have three T_2 states which give rise to a 3×3 T_2 block for the Hamiltonian matrix. The associated matrix elements are as follows:

$$\langle \gamma_{8l}^4\gamma_7\gamma_{8u};T_2\gamma \,|\, \mathscr{H} \,|\, \gamma_{8l}^4\gamma_7\gamma_{8u};T_2\gamma\rangle$$
$$=[4\epsilon_0(\gamma_{8l})+\epsilon_0(\gamma_7)+\epsilon_0(\gamma_{8u})]+15A+\tfrac{1}{3}B[-70-14C_{02}+9C_{04}+4\sqrt{6}(-C_{31}+2C_{13})]+\tfrac{1}{3}C(38-8C_{02}+10C_{04}) , \tag{3.9a}$$

$$\langle \gamma_{8l}^4\gamma_7\gamma_{8u};T_2\gamma \,|\, \mathscr{H} \,|\, \gamma_{8l}^3\gamma_7^2\gamma_{8u};3;T_2\gamma\rangle=\tfrac{2}{3}B[10C_{30}+\sqrt{6}(4C_{01}-C_{03})]+\tfrac{2}{3}C(C_{30}) , \tag{3.9b}$$

$$\langle \gamma_{8l}^4\gamma_7\gamma_{8u};T_2\gamma \,|\, \mathscr{H} \,|\, \gamma_{8l}^3\gamma_7^2\gamma_{8u};2;T_2\gamma\rangle=\tfrac{2}{3}B[4C_{10}-C_{12}-6C_{14}+\sqrt{6}(-6C_{01}+13C_{03}-10C_{05})]+\tfrac{2}{3}C(C_{10}-2C_{14}) , \tag{3.9c}$$

$$\langle \gamma_{8l}^3\gamma_7^2\gamma_{8u};3;T_2\gamma \,|\, \mathscr{H} \,|\, \gamma_{8l}^3\gamma_7^2\gamma_{8u};3;t_2\gamma\rangle$$
$$=[3\epsilon_0(\gamma_{8l})+2\epsilon_0(\gamma_7)+\epsilon_0(\gamma_{8u})]+15A+\tfrac{1}{3}B[-70+14C_{02}-5C_{04}+4\sqrt{6}(C_{31}+C_{11})]+\tfrac{1}{3}C(38-6C_{02}+16C_{04}) , \tag{3.9d}$$

$$\langle \gamma_{8l}^3\gamma_7^2\gamma_{8u};3;T_2\gamma \,|\, \mathscr{H} \,|\, \gamma_{8l}^3\gamma_7^2\gamma_{8u};2;T_2\gamma\rangle=\tfrac{2}{3}(C_{20}-C_{02})(4B+C) , \tag{3.9e}$$

$$\langle \gamma_{8l}^3\gamma_7^2\gamma_{8u};2;T_2\gamma \,|\, \mathscr{H} \,|\, \gamma_{8l}^3\gamma_7^2\gamma_{8u};2;T_2\gamma\rangle$$
$$=[3\epsilon_0(\gamma_{8l})+2\epsilon_0(\gamma_7)+\epsilon_0(\gamma_{8u})]+15A-\tfrac{1}{3}B[58+10C_{02}-19C_{04}+8\sqrt{6}(C_{31}-C_{13})]+\tfrac{1}{3}C(38-4C_{02}+2C_{04}) . \tag{3.9f}$$

Here, $\gamma=1$, or 0, or -1.

IV. MAGNETIC SUSCEPTIBILITY

As we have seen in Sec. III, the ground state transforms as A_1 (in the octahedral double group O_h'), so that there is only a temperature-independent paramagnetic susceptibility in first-order calculations. The general expression for this susceptibility is given by[5,6]

$$\chi=\tfrac{2}{3}N\beta^2\sum_n |\langle\psi_n|(kL_z+2S_z)|\psi_0\rangle|^2/(E_n-E_0) , \tag{4.1}$$

where N is Avogadro's number, β is the Bohr magneton, $|\psi_0\rangle$ is the wave function for the ground state with the energy E_0, and $|\psi_n\rangle$ is the wave function for an excited state with the energy E_n. Because of the cubic symmetry the three components of the susceptibility will be the same, and only the z component is expressed in Eq. (4.1) involving the z component of the magnetic-moment operator $\vec{\mu}=k\vec{L}+2\vec{S}$, where $\vec{L}$ is the total orbital angular momentum, $\vec{S}$ is the total spin, and k is a suitable orbital reduction factor[1,6] which originates from the covalency effects.

Since the ground state ψ_0 transforms as A_1, and both L_z and S_z transform as $|T_10\rangle$, the matrix elements in Eq. (4.1) will be nonvanishing only for those excited states which transform as $|T_10\rangle$. There are three such states with the wave functions which, upon diagonalization of the T_1 block (given in Sec. III), are expressed as linear combinations of the three unperturbed $|T_10\rangle$ wave functions:

$$|i;T_10\rangle=\alpha_i|\gamma_{8l}^4\gamma_7\gamma_{8u};T_10\rangle+\beta_i|\gamma_{8l}^3\gamma_7^2\gamma_{8u};3;T_10\rangle+\gamma_i|\gamma_{8l}^3\gamma_7^2\gamma_{8u};1;T_10\rangle, \quad i=1,2,3 \tag{4.2}$$

where $(\alpha_i,\beta_i,\alpha_i)$ are the three sets of combining coefficients. The matrix element of the magnetic-moment operator (μ_z) between the ground state and each state can now be evaluated:

$$\langle \gamma_{8l}^4\gamma_7^2;A_1a_1|\mu_z|i;T_10\rangle=\alpha_i\langle\gamma_{8l}^4\gamma_7^2;A_1a_1|\mu_z|\gamma_{8l}^4\gamma_7\gamma_{8u};T_10\rangle+\beta_i\langle\gamma_{8l}^4\gamma_7^2;A_1a_1|\mu_z|\gamma_{8l}^3\gamma_7^2\gamma_{8u};3;T_10\rangle$$
$$+\gamma_i\langle\gamma_{8l}^4\gamma_7^2;A_1a_1|\mu_z|\gamma_{8l}^3\gamma_7^2\gamma_{8u};1;T_10\rangle , \tag{4.3}$$

where the matrix elements with respect to the unperturbed states can be easily obtained by using the determinantal expressions for the unperturbed wave functions given in Ref. 4, Appendix C. Thus we obtain

$$\langle \gamma_{8l}^4\gamma_7^2;A_1a_1|\mu_z|\gamma_{8l}^4\gamma_7\gamma_{8u};T_10\rangle=-\left[\tfrac{2}{3}(K_2+2)C_{01}+\frac{2\sqrt{2}}{\sqrt{3}}K_1C_{10}\right] , \tag{4.4a}$$

$$\langle \gamma_{8l}^4\gamma_7^2;A_1a_1|\mu_z|\gamma_{8l}^3\gamma_7^2\gamma_{8u};3;T_10\rangle=\frac{4}{3\sqrt{5}}(2K_2-5)C_{11}+\frac{2\sqrt{2}}{\sqrt{15}}K_1(C_{20}-C_{02}) , \tag{4.4b}$$

and

$$\langle \gamma_{8l}^4\gamma_7^2;A_1a_1|\mu_z|\gamma_{8l}^3\gamma_7^2\gamma_{8u};1;T_10\rangle=-\frac{2}{\sqrt{5}}K_2C_{11}+\frac{2\sqrt{6}}{\sqrt{5}}K_1(C_{20}-C_{02}) . \tag{4.4c}$$

Here, as in Ref. 1, we have used two different orbital reduction factors to take into account any inequivalence (resulting from covalency effects) of the dt_2 and de orbitals: we have set $k=k_1$ when μ_z has nonvanishing matrix elements between a t_2 orbital and an e orbital, and $k=k_2$ when μ_z has nonvanishing matrix elements between two t_2 orbitals.

V. EFFECTS OF LOWER-SYMMETRIC FIELDS

As discussed in Ref. 3, there are complexes which suffer deviations from perfect cubic symmetries. The cases of tetragonal (D_{4h}) and trigonal (D_{3d}) distortions are the most common. In such a case, the interelectronic Coulomb interaction together with the lower-symmetric part of the ligand field will be treated as a perturbation. In the absence of distortions, the terms of the d^6 system correspond to the irreducible representations A_1, A_2, E, T_1, and T_2 of the octahedral double group O_h'. When a lower-symmetric ligand field (associated with the distortion) is introduced, these original terms generate new terms corresponding to the irreducible representations of the associated lower-symmetry group. The basis functions for the new terms can be given in terms of the original basis functions. The general scheme for these transformations is given in Ref. 3. The perturbation involving the interelectronic Coulomb potential (V_e) and the lower-symmetric part (V_l) of the ligand field potential causes mixing in each set of levels corresponding to the same irreducible representation of the associated lower-symmetry group. Thus there will be a Hamiltonian matrix block for each of these irreducible representations.

According to the general scheme,[3] we have, for the d^6 system in the presence of a tetragonal distortion, one 3×3 B_1^T block, one 4×4 A_1^T block, one 3×3 A_2^T block, one 3×3 B_2^T block, and two conjugate 6×6 E^T blocks. Similarly, in the presence of a trigonal distortion, there will be one 5×5 A_1^τ block, one 4×4 A_2^τ block, and two conjugate 8×8 E^τ blocks. The matrix elements for these blocks will involve two additional parameters representing the lower symmetry in the ligand field (these are, as usual, Ds,Dt for D_{4h} symmetry and $D\sigma,D\tau$ for D_{3d} symmetry). These matrix elements can be evaluated by using the determinantal wave functions (given in Ref. 4, Appendix C) through the general scheme.[3]

VI. CONCLUDING REMARKS

If we treat the d^6 system through the conventional strong-field-coupling scheme and truncate by considering the configurations t_2^6 and t_2^5e only, we get the unperturbed terms, $|t_2^6;{}^1A_1\rangle$, $|t_2^5e;{}^3T_1\rangle$, $|t_2^5e;{}^1T_2\rangle$, $|t_2^5e;{}^1T_1\rangle$, and $|t_2^5e;{}^3T_2\rangle$. These are split by the spin-orbit interaction and generate the terms

$$|t_2^6;{}^1A_1\rightarrow A_1\rangle,\quad |t_2^5e;{}^3T_1\rightarrow A_1\rangle,\quad |t_2^5e;{}^3T_1\rightarrow E\rangle,$$
$$|t_2^5e;{}^3T_1\rightarrow T_1\rangle,\quad |t_2^5e;{}^3T_1\rightarrow T_2\rangle,\quad |t_2^5e;{}^1T_2\rightarrow T_2\rangle,$$
$$|t_2^5e;{}^1T_1\rightarrow T_1\rangle,\quad |t_2^5e;{}^3T_2\rightarrow A_2\rangle,\quad |t_2^5e;{}^3T_2\rightarrow E\rangle,$$
$$|t_2^5e;{}^3T_2\rightarrow T_1\rangle,\quad |t_2^5e;{}^3T_2\rightarrow T_2\rangle.$$

Thus, a group of 11 terms is obtained in this case also. However, for heavy transition metals the spin-orbit interaction is quite large. Thus the perturbation involving the spin-orbit energy and the interelectronic Coulomb energy would cause a considerable mixing of these 11 levels with the upper levels. If we neglect this mixing altogether, we are bound to obtain erroneous results. Hence, the influence of the states coming from at least the next-higher configuration, $t_2^4e^2$, should be considered. This configuration gives six A_1 states, three A_2 states, nine E states, nine T_1 states, and eleven T_2 states. Then we have Hamiltonian matrix blocks of large dimensions, namely A_1, A_2, E, T_1, and T_2 blocks of dimensions 8×8, 4×4, 11×11, 12×12, and 14×14, respectively. This shows the advantage of the intermediate-coupling scheme (over the strong-field-coupling scheme) in the present case of a heavy transition-metal ion with the d^6 configuration: the truncation in the intermediate-coupling scheme produces matrix blocks of much smaller dimensions, giving useful results very easily and neatly.

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[4]See AIP Document No. PAPS PRBMBO-31-850-36 for fourteen pages of Appendix A, eighteen pages of Appendix B, and four pages of Appendix C. Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 335 East 45th Street, New York, N.Y. 10017. The price is $1.50 for a microfiche or $5.00 for a photocopy. Airmail additional. Make checks payable to the American Institute of Physics.
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