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Effects of lower-symmetric crystal fields in the intermediate-coupling scheme for the transition-metal complexes

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A generalized intermediate-coupling scheme was developed for the transition-metal ions embedded in cubic (octahedral or tetrahedral) crystal fields. This scheme is useful for the cubic complexes of $4d$ and $5d$ ions and in this context the advantage (in physical interpretation and in consequent simplicity in calculations) of this scheme over the conventional strong-field coupling scheme was clearly demonstrated. In this paper, this new scheme has been further generalized to include a lower-symmetric (tetragonal or trigonal) crystal field, which is essential in dealing with most of the complexes where deviations from the cubic symmetry are considerable. As in previous papers, one can easily find out the obvious advantages of this scheme which allows one to arrive at the useful energy levels and wave functions with the minimum amount of labor in calculations. The truncation in the calculation by using only the group of lower-lying energy states (which, according to the very nature of the scheme, are easily recognizable) is the salient feature of the scheme, and to show in passing the validity of this method, we have, at the end, considered the case of a d^1 system with the tetragonal (D_{4h}) distortion and the results obtained thereby are compared with the corresponding exact results appearing elsewhere.

I. INTRODUCTION

A generalized intermediate-coupling scheme was developed[1] for the many-electron systems of the transition-metal ions under ligand fields with cubic (octahedral or tetrahedral) symmetry. This scheme is extremely helpful for the complexes of the transition-metal ions in the second and third series, where the ligand field and the spin-orbit coupling are large compared to the interelectronic Coulomb interaction.

The applicability and great simplicity of the scheme was illustrated for the perfectly octahedral complexes OsF_6 ($5d^2$ system),[2,3] K_2ReCl_6 ($5d^3$ system),[1] and K_2OsCl_6 ($5d^4$ system).[4] There are, however, a great number of similar complexes which suffer deviations from perfect cubic symmetry. A number of reasons, amongst which are the Jahn-Teller effect and crystal-packing considerations,[2,5–7] may be responsible for the formation of such distorted complexes. The ligand field in such a complex is of lower symmetry,[2,5–7] depending upon the nature of distortion. The cubic part of the ligand field potential is represented by the usual parameter Dq, and to represent the remaining part (which is of lower symmetry) additional parameters are introduced [say, the parameters Ds and Dt for tetragonal (D_{4h}) symmetry].

In the present paper we have extended the intermediate-coupling scheme[1] by including the perturbing lower-symmetric field. The unperturbed states in this scheme fully incorporate the cubic ligand field as well as the spin-orbit interaction; the interelectronic Coulomb interaction together with the lower-symmetric part of the ligand field will be treated as a perturbation. We consider in detail the cases of tetragonal (D_{4h}) and trigonal (D_{3d}) distortions,[2,5–7] which are the most common in the complexes of transition-metal ions. The case of an orthorhombic distortion (with the symmetry group D_2) is just indicated briefly in the following section.

II. SPLITTING OF LEVELS

In the absence of distortions, the terms of the intermediate-coupling scheme[1] correspond to the irreducible representations of the octahedral double group O_h'. These are A_1, A_2, E, T_1, T_2, Γ_6, Γ_7, and Γ_8, in general. 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. Thus some or all of the degenerate levels in the original scheme are split by the lower-symmetric field. The basis functions for the new terms can be given in terms of the original basis functions.

In the presence of the perturbation involving the interelectronic Coulomb potential (V_e) and the lower-symmetric part (V_l) of the ligand field potential, there will be 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. The specific cases of lower-symmetric fields are considered one by one.

A. Tetragonal (D_{4h}) symmetry

We consider the introduction of a tetragonal distortion (along the Z axis, say). The original levels (corresponding to the representations in O_h') will generate new levels (corresponding to the irreducible representations in the tetragonal double group D_{4h}') according to the following scheme[2,8,9]:

$$
\begin{aligned}
&A_1 \rightarrow A_1^T\ ,\\
&A_2 \rightarrow B_1^T\ ,\\
&E \rightarrow A_1^T + B_1^T\ ,\\
&T_1 \rightarrow A_2^T + E^T\ ,\\
&T_2 \rightarrow B_2^T + E^T\ ,\\
&\Gamma_6 \rightarrow \Gamma_6^T\ ,\\
&\Gamma_7 \rightarrow \Gamma_7^T\ ,\\
&\Gamma_8 \rightarrow \Gamma_6^T + \Gamma_7^T\ .
\end{aligned}
\tag{2.1}
$$

Here, the superscript T on each of the transformed terms implies that tetragonal symmetry is involved. The basis functions for these new levels in terms of the original basis functions are as follows[2,8,9]:

$$
\begin{aligned}
&|n;A_1 \rightarrow A_1^T a_1\rangle = |n;A_1 a_1\rangle\ ,\\
&|n;A_2 \rightarrow B_1^T b_1\rangle = |n;A_2 a_2\rangle\ ,\\
&|n;E \rightarrow A_1^T a_1\rangle = |n;E\theta\rangle\ ,\\
&|n;E \rightarrow B_1^T b_1\rangle = |n;E\epsilon\rangle\ ,\\
&|n;T_1 \rightarrow A_2^T a_2\rangle = |n;T_1 0\rangle\ ,\\
&|n;T_1 \rightarrow E^T\theta\rangle = |n;T_1 1\rangle\ ,\\
&|n;T_1 \rightarrow E^T\epsilon\rangle = |n;T_1 -1\rangle\ ,\\
&|n;T_2 \rightarrow B_2^T b_2\rangle = |n;T_2 0\rangle\ ,\\
&|n;T_2 \rightarrow E^T\theta\rangle = |n;T_2 -1\rangle\ ,\\
&|n;T_2 \rightarrow E^T\epsilon\rangle = |n;T_2 1\rangle\ ,\\
&|n;\Gamma_6 \rightarrow \Gamma_6^T a'\rangle = |n;\Gamma_6\alpha'\rangle\ ,\\
&|n;\Gamma_6 \rightarrow \Gamma_6^T b'\rangle = |n;\Gamma_6\beta'\rangle\ ,\\
&|n;\Gamma_7 \rightarrow \Gamma_7^T a''\rangle = |n;\Gamma_7\beta''\rangle\ ,\\
&|n;\Gamma_7 \rightarrow \Gamma_7^T b''\rangle = |n;\Gamma_7\alpha''\rangle\ ,\\
&|n;\Gamma_8 \rightarrow \Gamma_7^T a''\rangle = |n;\Gamma_8\kappa\rangle\ ,\\
&|n;\Gamma_8 \rightarrow \Gamma_7^T b''\rangle = |n;\Gamma_8\nu\rangle\ ,\\
&|n;\Gamma_8 \rightarrow \Gamma_6^T a'\rangle = |n;\Gamma_8\lambda\rangle\ ,\\
&|n;\Gamma_8 \rightarrow \Gamma_6^T b'\rangle = |n;\Gamma_8\mu\rangle\ .
\end{aligned}
\tag{2.2}
$$

Here n denotes a configuration notation similar to $\gamma_{8l}^2\gamma_7^2$.

B. Trigonal (D_{3d}) symmetry

We consider the introduction of a trigonal distortion along the (1,1,1) direction. The original levels (corresponding to the irreducible representations in O_h') will generate new levels (corresponding to the irreducible representations in the trigonal double group D_{3d}') according to the following scheme:

$$
\begin{aligned}
&A_1 \rightarrow A_1^\tau\ ,\\
&A_2 \rightarrow A_2^\tau\ ,\\
&E \rightarrow E^\tau\ ,\\
&T_1 \rightarrow A_2^\tau + E^\tau\ ,\\
&T_2 \rightarrow A_1^\tau + E^\tau\ ,\\
&\Gamma_6 \rightarrow \Gamma_4^\tau\ ,\\
&\Gamma_7 \rightarrow \Gamma_4^\tau\ ,\\
&\Gamma_8 \rightarrow \Gamma_4^\tau + (\Gamma_5^\tau + \Gamma_6^\tau)\ .
\end{aligned}
\tag{2.3}
$$

Here, the pair of new nondegenerate levels $\Gamma_5^\tau, \Gamma_6^\tau$ are Kramers conjugates[2] having the same energy values. The superscript τ on each of the transformed terms implies that trigonal symmetry is involved. The basis functions for these new levels in terms of the original basis functions are as follows:

$$
\begin{aligned}
&|n;A_1 \rightarrow A_1^\tau a_1\rangle = |n;A_1 a_1\rangle\ ,\\
&|n;A_2 \rightarrow A_2^\tau a_2\rangle = |n;A_2 a_2\rangle\ ,\\
&|n;E \rightarrow E^\tau x\rangle = |n;E\theta\rangle\ ,\\
&|n;E \rightarrow E^\tau y\rangle = |n;E\epsilon\rangle\ ,\\
&|n;T_1 \rightarrow A_2^\tau a_2\rangle = \frac{1}{\sqrt{6}}[(1+i)\,|n;T_1 1\rangle + (1-i)\,|n;T_1 -1\rangle - i\sqrt{2}\,|n;T_1 0\rangle]\ ,\\
&|n;T_1 \rightarrow E^\tau x\rangle = \tfrac{1}{2}[(-1+i)\,|n;T_1 1\rangle - (1+i)\,|n;T_1 -1\rangle]\ ,\\
&|n;T_1 \rightarrow E^\tau y\rangle = \frac{1}{2\sqrt{3}}[(1+i)\,|n;T_1 1\rangle + (1-i)\,|n;T_1 -1\rangle + i2\sqrt{2}\,|n;T_1 0\rangle]\ ,\\
&|n;T_2 \rightarrow A_1^\tau a_1\rangle = \frac{1}{\sqrt{6}}[(1+i)\,|n;T_2 1\rangle + (1-i)\,|n;T_2 -1\rangle - i\sqrt{2}\,|n;T_2 0\rangle]\ ,\\
&|n;T_2 \rightarrow E_x^\tau\rangle = -\frac{1}{2\sqrt{3}}[(1+i)\,|n;T_2 1\rangle + (1-i)\,|n;T_2 -1\rangle + i2\sqrt{2}\,|n;T_2 0\rangle]\ ,\\
&|n;T_2 \rightarrow E^\tau y\rangle = \tfrac{1}{2}[(-1+i)\,|n;T_2 1\rangle - (1+i)\,|n;T_2 -1\rangle]\ ,\\
&|n;\Gamma_6 \rightarrow \Gamma_4^\tau a\rangle = |n;\Gamma_6\alpha'\rangle\ ,
\end{aligned}
\tag{2.4}
$$

$$|n;\Gamma_6\rightarrow\Gamma_4^T b\rangle=|n;\Gamma_6\beta'\rangle\ ,$$

$$|n;\Gamma_7\rightarrow\Gamma_4^T a\rangle=\frac{1}{\sqrt{3}}[-i\,|n;\Gamma_7\alpha''\rangle+(1-i)\,|n;\Gamma_7\beta''\rangle]\ ,$$

$$|n;\Gamma_7\rightarrow\Gamma_4^T b\rangle=\frac{1}{\sqrt{3}}[-(1+i)\,|n;\Gamma_7\alpha''\rangle+i\,|n;\Gamma_7\beta''\rangle]\ ,$$

$$|n;\Gamma_8\rightarrow\Gamma_4^T a\rangle=\frac{1}{2\sqrt{3}}[(-1+i)\,|n;\Gamma_8\kappa\rangle+\sqrt{3}(1+i)\,|n;\Gamma_8\mu\rangle+i2\,|n;\Gamma_8\nu\rangle]\ ,$$

$$|n;\Gamma_8\rightarrow\Gamma_4^T b\rangle=\frac{1}{2\sqrt{3}}[i2\,|n;\Gamma_8\kappa\rangle+\sqrt{3}(1-i)\,|n;\Gamma_8\lambda\rangle-(1+i)\,|n;\Gamma_8\nu\rangle]\ ,$$

$$|n;\Gamma_8\rightarrow\Gamma_5^T a'\rangle=\frac{1}{\sqrt{6}}[i\sqrt{3}\,|n;\Gamma_8\kappa\rangle-(1-i)\,|n;\Gamma_8\lambda\rangle-|n;\Gamma_8\mu\rangle]\ ,$$

$$|n;\Gamma_8\rightarrow\Gamma_6^T b'\rangle=\frac{1}{\sqrt{6}}[i\,|n;\Gamma_8\lambda\rangle+(1-i)\,|n;\Gamma_8\mu\rangle-\sqrt{3}\,|n;\Gamma_8\nu\rangle]\ .$$

C. Orthorhombic (D_2) symmetry

We consider the introduction of an orthorhombic distortion (unequal distortions along the cubic axes). The original levels will generate new levels (corresponding to the irreducible representations in the orthorhombic double group D_2' considered) according to the following scheme:

$$\begin{aligned}
&A_1\rightarrow A_1^{\mathrm{OR}}\ ,\\
&A_2\rightarrow A_1^{\mathrm{OR}}\ ,\\
&E\rightarrow A_1^{\mathrm{OR}}+A_1^{\mathrm{OR}}\ ,\\
&T_1\rightarrow B_1^{\mathrm{OR}}+B_2^{\mathrm{OR}}+B_3^{\mathrm{OR}}\ ,\\
&T_2\rightarrow B_1^{\mathrm{OR}}+B_2^{\mathrm{OR}}+B_3^{\mathrm{OR}}\ ,\\
&\Gamma_6\rightarrow\Gamma_5^{\mathrm{OR}}\ ,\\
&\Gamma_7\rightarrow\Gamma_5^{\mathrm{OR}}\ ,\\
&\Gamma_8\rightarrow\Gamma_5^{\mathrm{OR}}+\Gamma_5^{\mathrm{OR}}\ .
\end{aligned}\tag{2.5}$$

Here, the superscript OR on each of the transformed terms implies that the orthorhombic double group (D_2') is involved. The basis functions for these new levels in terms of the original basis functions are as follows:

$$\begin{aligned}
&|n;A_1\rightarrow A_1^{\mathrm{OR}}a_1\rangle=|n;A_1a_1\rangle\ ,\\
&|n;A_2\rightarrow A_1^{\mathrm{OR}}a_1\rangle=|n;A_2a_2\rangle\ ,\\
&|n;E\rightarrow A_1^{\mathrm{OR}}a_1\rangle_1=|n;E\theta\rangle\ ,\\
&|n;E\rightarrow A_1^{\mathrm{OR}}a_1\rangle_2=|n;E\epsilon\rangle\ ,\\
&|n;T_1\rightarrow B_1^{\mathrm{OR}}b_1\rangle=|n;T_10\rangle\ ,\\
&|n;T_1\rightarrow B_2^{\mathrm{OR}}b_2\rangle=\frac{1}{\sqrt{2}}(|n;T_11\rangle+|n;T_1-1\rangle)\ ,\\
&|n;T_1\rightarrow B_3^{\mathrm{OR}}b_3\rangle=\frac{1}{\sqrt{2}}(|n;T_11\rangle-|n;T_1-1\rangle)\ ,\\
&|n;T_2\rightarrow B_1^{\mathrm{OR}}b_1\rangle=|n;T_20\rangle\ ,\\
&|n;T_2\rightarrow B_2^{\mathrm{OR}}b_2\rangle=\frac{1}{\sqrt{2}}(|n;T_21\rangle+|n;T_2-1\rangle)\ ,\\
&|n;T_2\rightarrow B_3^{\mathrm{OR}}b_3\rangle=\frac{1}{\sqrt{2}}(|n;T_21\rangle-|n;T_2-1\rangle)\ ,\\
&|n;\Gamma_6\rightarrow\Gamma_5^{\mathrm{OR}}\alpha\rangle=|n;\Gamma_6\alpha'\rangle\ ,\\
&|n;\Gamma_6\rightarrow\Gamma_5^{\mathrm{OR}}\beta\rangle=|n;\Gamma_6\beta'\rangle\ ,\\
&|n;\Gamma_8\rightarrow\Gamma_5^{\mathrm{OR}}\alpha\rangle_1=|n;\Gamma_8\kappa\rangle\ ,\\
&|n;\Gamma_8\rightarrow\Gamma_5^{\mathrm{OR}}\beta\rangle_1=|n;\Gamma_8\nu\rangle\ ,\\
&|n;\Gamma_8\rightarrow\Gamma_5^{\mathrm{OR}}\alpha\rangle_2=|n;\Gamma_8\lambda\rangle\ ,\\
&|n;\Gamma_8\rightarrow\Gamma_5^{\mathrm{OR}}\beta\rangle_2=|n;\Gamma_8\mu\rangle\ .
\end{aligned}\tag{2.6}$$

III. d^1 SYSTEM

The intermediate-coupling scheme[1] involves three basic one-electron energy levels: γ_{8l} (fourfold degenerate), γ_7 (twofold degenerate), and γ_{8u} (fourfold degenerate) in the order of increasing energy values. The second level corresponds to the irreducible representation Γ_7 and each of the remaining levels corresponds to the irreducible representation Γ_8.

A. Tetragonal (D_{4h}) symmetry

In the presence of a tetragonal distortion, the three original levels $|\gamma_{8l};\Gamma_8\rangle$, $|\gamma_7;\Gamma_7\rangle$, and $|\gamma_{8u};\Gamma_8\rangle$ will generate new levels according to the scheme given in Sec. II. The perturbing part (V_T) of the ligand field potential can be represented in terms of two parameters Ds and Dt.[2,7] This tetragonal perturbation leads to a mixing of $|\gamma_{8l};\Gamma_8\rightarrow\Gamma_7^T\rangle$, $|\gamma_7;\Gamma_7\rightarrow\Gamma_7^T\rangle$, $|\gamma_{8u};\Gamma_8\rightarrow\Gamma_7^T\rangle$ and of $|\gamma_{8l};\Gamma_8\rightarrow\Gamma_6^T\rangle$, $|\gamma_{8u};\Gamma_8\rightarrow\Gamma_6^T\rangle$. Thus there are two conjugate 3×3 Γ_7^T blocks and two conjugate 2×2 Γ_6^T blocks for the Hamiltonian matrix. The matrix elements for these blocks can be easily calculated. These are as follows: For the conjugate Γ_7^T blocks ($\delta=a''$ or b'')

$$\langle\gamma_{8l};\Gamma_8\to\Gamma_7^T\delta\,|\,\mathscr{H}\,|\,\gamma_{8l};\Gamma_8\to\Gamma_7^T\delta\rangle = \epsilon_0(\gamma_{8l})+(1+C_{02})Ds+(\tfrac{2}{3}-\tfrac{5}{3}C_{02})Dt\ ,$$

$$\langle\gamma_{8l}:\Gamma_8\to\Gamma_7^T\delta\,|\,\mathscr{H}\,|\,\gamma_7:\Gamma_7\to\Gamma_7^T\delta\rangle = \pm C_{10}\left[\sqrt{2}Ds-\frac{5\sqrt{2}}{3}Dt\right]$$

(+ and − signs are for $\delta=a''$ and b'', respectively),

$$\langle\gamma_{8l};\Gamma_8\to\Gamma_7^T\delta\,|\,\mathscr{H}\,|\,\gamma_{8u};\Gamma_8\to\Gamma_7^T\delta\rangle = C_{11}(-Ds+\tfrac{5}{3}Dt)\ ,$$

$$\langle\gamma_7;\Gamma_7\to\Gamma_7^T\delta\,|\,\mathscr{H}\,|\,\gamma_7;\Gamma_7\to\Gamma_7^T\delta\rangle = \epsilon_0(\gamma_7)+\tfrac{7}{3}Dt\ ,$$

$$\langle\gamma_7;\Gamma_7\to\Gamma_7^T\delta\,|\,\mathscr{H}\,|\,\gamma_{8u};\Gamma_8\to\Gamma_7^T\delta\rangle = \pm C_{01}\left[\sqrt{2}Ds-\frac{5\sqrt{2}}{3}Dt\right]$$

(+ and − signs are for $\delta=a''$ and b'', respectively),

$$\langle\gamma_{8u};\Gamma_8\to\Gamma_7^T\delta\,|\,\mathscr{H}\,|\,\gamma_{8u};\Gamma_8\to\Gamma_7^T\delta\rangle = \epsilon_0(\gamma_{8u})+(2-C_{02})Ds+(-1+\tfrac{5}{3}C_{02})Dt\ . \tag{3.1}$$

For the conjugate Γ_6^T blocks ($\delta=a'$ or b')

$$\langle\gamma_{8l};\Gamma_8\to\Gamma_6^T\delta\,|\,\mathscr{H}\,|\,\gamma_{8l};\Gamma_8\to\Gamma_6^T\delta\rangle = \epsilon_0(\gamma_{81})-(1+C_{02})Ds+(4-10C_{02})Dt\ ,$$

$$\langle\gamma_{8l};\Gamma_8\to\Gamma_6^T\delta\,|\,\mathscr{H}\,|\,\gamma_{8u};\Gamma_8\to\Gamma_6^T\delta\rangle = C_{11}(Ds+10Dt)\ ,$$

$$\langle\gamma_{8u};\Gamma_8\to\Gamma_6^T\delta\,|\,\mathscr{H}\,|\,\gamma_{8u};\Gamma_8\to\Gamma_6^T\delta\rangle = \epsilon_0(\gamma_{8u})+(-2+C_{02})Ds+(-6+10C_{02})Dt\ . \tag{3.2}$$

Here we have used the same notations as in Ref. 1, i.e.,

$$C_{mn}=\cos^m\theta\sin^n\theta\ ,$$

where

$$\tan2\theta=\frac{\sqrt{2}\zeta_d'}{10Dq+\frac{1}{2}\zeta_d}\ .$$

ζ_d and ζ_d' are two spin-orbit interaction parameters.[1] $\epsilon_0(\gamma_{8l})$, $\epsilon_0(\gamma_{8u})$, and $\epsilon_0(\gamma_7)$ are three different unperturbed one-electron energy values and their expressions (in terms of Dq, ζ_d, ζ_d') are given in Eqs. (2.3) and (2.6) of Ref. 1. The present relations in Eqs. (3.1) and (3.2) have been obtained by using the expressions for $\kappa_l\equiv|\gamma_{8l};\Gamma_8\kappa\rangle$, $\lambda_l\equiv|\gamma_{8l};\Gamma_8\lambda\rangle$, etc. [see Eqs. (2.2) and (2.5) in Ref. 1], together with the following matrix elements of V_T with respect to the usual strong-field bases $(\xi,\eta,\zeta;\theta,\epsilon)$ (Refs. 2 and 7):

$$\langle\xi\,|\,V_T\,|\,\xi\rangle=\langle\eta\,|\,V_T\,|\,\eta\rangle=-Ds+4Dt\ ,$$

$$\langle\zeta\,|\,V_T\,|\,\zeta\rangle=2Ds-Dt\ ,$$

$$\langle\theta\,|\,V_T\,|\,\theta\rangle=-2Ds-6Dt\ ,$$

$$\langle\epsilon\,|\,V_T\,|\,\epsilon\rangle=2Ds-Dt\ .$$

B. Trigonal (D_{3d}) symmetry

The perturbing trigonal part (V_τ) of the ligand field potential can be represented in terms of two parameters $D\sigma$ and $D\tau$.[2,7] This perturbation leads to a mixing of $|\gamma_{8l};\Gamma_8\to\Gamma_4^\tau\rangle$, $|\gamma_7;\Gamma_7\to\Gamma_4^\tau\rangle$, $|\gamma_{8u};\Gamma_8\to\Gamma_4^\tau\rangle$, and of $|\gamma_{8l};\Gamma_8\to\Gamma_5^\tau(\Gamma_6^\tau)\rangle$, $|\gamma_{8u};\Gamma_8\to\Gamma_5^\tau(\Gamma_6^\tau)\rangle$. Thus there are two conjugate 3×3 Γ_4^τ blocks and two conjugate 2×2 $\Gamma_5^\tau(\Gamma_6^\tau)$ blocks for the Hamiltonian matrix. The matrix elements for these blocks are as follows: For the conjugate Γ_4^τ blocks ($\delta=a$ or b)

$$\langle\gamma_{8l};\Gamma_8\to\Gamma_4^\tau\delta\,|\,\mathscr{H}\,|\,\gamma_{8l};\Gamma_8\to\Gamma_4^\tau\delta\rangle=\epsilon_0(\gamma_{8l})-C_{20}(D\sigma+\tfrac{34}{9}D\tau)-\frac{2\sqrt{2}}{\sqrt{3}}C_{11}(D\sigma-\tfrac{5}{3}D\tau)+\tfrac{28}{27}C_{02}(D\tau)\ ,$$

$$\langle\gamma_{8l};\Gamma_8\to\Gamma_4^\tau\delta\,|\,\mathscr{H}\,|\,\gamma_7;\Gamma_7\to\Gamma_4^\tau\delta\rangle=-\sqrt{2}C_{10}(D\sigma+\tfrac{20}{9}D\tau)+\frac{2}{\sqrt{3}}C_{01}(D\sigma-\tfrac{5}{3}D\tau)\ ,$$

$$\langle\gamma_{8l};\Gamma_8\to\Gamma_4^\tau\delta\,|\,\mathscr{H}\,|\,\gamma_{8u};\Gamma_8\to\Gamma_4^\tau\delta\rangle=\frac{\sqrt{2}}{\sqrt{3}}(C_{20}-C_{02})(D\sigma-\tfrac{5}{3}D\tau)-C_{11}(D\sigma+\tfrac{55}{9}D\tau)\ ,$$

$$\langle\gamma_7;\Gamma_7\to\Gamma_4^\tau\delta\,|\,\mathscr{H}\,|\,\gamma_7;\Gamma_7\to\Gamma_4^\tau\delta\rangle=\epsilon_0(\gamma_7)-\tfrac{14}{9}D\tau\ , \tag{3.3}$$

$$\langle\gamma_7;\Gamma_7-\Gamma_4^\tau\delta\,|\,\mathscr{H}\,|\,\gamma_{8u};\Gamma_8\to\Gamma_4^\tau\delta\rangle=-\frac{2}{\sqrt{3}}C_{10}(D\sigma-\tfrac{5}{3}D\tau)-\sqrt{2}C_{01}(D\sigma+\tfrac{20}{9}D\tau)\ ,$$

$$\langle\gamma_{8u};\Gamma_8\to\Gamma_4^\tau\delta\,|\,\mathscr{H}\,|\,\gamma_{8u};\Gamma_8\to\Gamma_4^\tau\delta\rangle=\epsilon_0(\gamma_{8u})+\tfrac{7}{3}C_{20}(D\tau)+\frac{2\sqrt{2}}{\sqrt{3}}C_{11}(D\sigma-\tfrac{5}{3}D\tau)-C_{02}(D\sigma+\tfrac{34}{9}D\tau)\ .$$

For the conjugate $\Gamma_5^\tau(\Gamma_6^\tau)$ blocks

$$\langle\gamma_{8l};\Gamma_8\to\Gamma_5^\tau(\Gamma_6^\tau)a'(b')\,|\,\mathscr{H}\,|\,\gamma_{8l};\Gamma_8\to\Gamma_5^\tau(\Gamma_6^\tau)a'(b')\rangle=\epsilon_0(\gamma_{8l})+C_{20}(D\sigma+\tfrac{2}{3}D\tau)+\frac{2\sqrt{2}}{\sqrt{3}}C_{11}(D\sigma-\tfrac{5}{3}D\tau)+\tfrac{7}{3}C_{02}(D\tau)\ ,$$

$$\langle\gamma_{8l};\Gamma_8\to\Gamma_5^\tau(\Gamma_6^\tau)a'(b')\,|\,\mathscr{H}\,|\,\gamma_{8u};\Gamma_8\to\Gamma_5^\tau(\Gamma_6^\tau)a'(b')\rangle=\left[C_{11}-\frac{\sqrt{2}}{\sqrt{3}}(C_{20}-C_{02})\right](D\sigma-\tfrac{5}{3}D\tau)\ , \tag{3.4}$$

$$\langle\gamma_{8u};\Gamma_8\to\Gamma_5^\tau(\Gamma_6^\tau)a'(b')\,|\,\mathscr{H}\,|\,\gamma_{8u};\Gamma_8\to\Gamma_5^\tau(\Gamma_6^\tau)a'(b')\rangle=\epsilon_0(\gamma_{8u})+\tfrac{7}{3}C_{20}(D\tau)-\frac{2\sqrt{2}}{\sqrt{3}}C_{11}(D\sigma-\tfrac{5}{3}D\tau)+C_{02}(D\sigma+\tfrac{2}{3}D\tau)\ .$$

These relations in Eqs. (3.3) and (3.4) have been obtained by using the following matrix elements of V_τ with respect to the usual strong-field bases[2,7]:

$$\langle\xi|V_\tau|\xi\rangle=\langle\eta|V_\tau|\eta\rangle=\langle\zeta|V_\tau|\zeta\rangle=-\tfrac{14}{9}D\tau\ ,$$

$$\langle\xi|V_\tau|\eta\rangle=\langle\eta|V_\tau|\zeta\rangle=\langle\zeta|V_\tau|\xi\rangle=-(D\sigma+\tfrac{20}{9}D\tau)\ ,$$

$$-\sqrt{3}\langle\xi|V_\tau|\theta\rangle=\langle\xi|V_\tau|\epsilon\rangle=-\sqrt{3}\langle\eta|V_\tau|\theta\rangle$$

$$=\frac{\sqrt{3}}{2}\langle\zeta|V_\tau|\theta\rangle=-\langle\eta|V_\tau|\epsilon\rangle$$

$$=D\sigma-\tfrac{5}{3}D\tau\ ,$$

$$\langle\theta|V_\tau|\theta\rangle=\langle\epsilon|V_\tau|\epsilon\rangle=\tfrac{7}{3}D\tau\ .$$

IV. d^2 SYSTEM

The low-lying unperturbed levels for the d^2 system in the intermediate-coupling scheme are[1]

$$|\gamma_{8l}^2;A_1\rangle,\ |\gamma_7^2;A_1\rangle\ ,$$

$$|\gamma_{8l}^2;E\rangle,\ |\gamma_{8l}\gamma_7;E\rangle\ ,$$

$$|\gamma_{8l}\gamma_7;T_1\rangle\ ,$$

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

In the first approximation we can neglect the mixing of these lower levels (through the perturbations of the electron-electron Coulomb interaction and the lower-symmetric part of the ligand field) with the much higher levels of configurations involving γ_{8u}. This is because, for the complexes of the transition-metal ions in the second and third series, $\epsilon_0(\gamma_{8u})$ is usually much higher than $\epsilon_0(\gamma_{8l})$ and $\epsilon_0(\gamma_7)$.[1] Then, in the presence of a tetragonal distortion, we have a 4×4 A_1^T block, a 2×2 B_1^T block, a 1×1 A_2^T block, a 2×2 B_2^T block, and two conjugate 3×3 E^T blocks. The matrix elements for these blocks are given in Appendix A. Similarly, in the presence of a trigonal distortion, we have one 4×4 A_1^τ block, one 1×1 A_2^τ block, and two conjugate 5×5 E^τ blocks. The matrix elements for these blocks are given in Ref. 10.

V. d^3 SYSTEM

The low-lying unperturbed levels for the d^3 system in the intermediate-coupling scheme are[1]

$$|\gamma_{8l}^3;\Gamma_8\rangle,\ |\gamma_{8l}^2(E)\gamma_7;\Gamma_8\rangle\ ,$$

$$|\gamma_{8l}^2(T_2)\gamma_7;\Gamma_8\rangle,\ |\gamma_{8l}\gamma_7^2;\Gamma_8\rangle\ ,$$

$$|\gamma_{8l}^2(A_1)\gamma_7;\Gamma_7\rangle\ ,$$

$$|\gamma_{8l}^2(T_2)\gamma_7;\Gamma_6\rangle\ .$$

As usual, we omit the much higher levels of configurations involving γ_{8u}.

In the presence of a tetragonal distortion, we have now two conjugate 5×5 Γ_6^T blocks and two conjugate 5×5 Γ_7^T blocks. The matrix elements for these blocks are given in Ref. 10.

In the presence of a trigonal distortion, we have two conjugate 6×6 Γ_4^τ blocks and two conjugate 4×4 Γ_5^τ (Γ_6^τ) blocks. The matrix elements for these blocks are given in Ref. 10.

VI. d^4 SYSTEM

The low-lying unperturbed levels for the d^4 system in the intermediate-coupling scheme are[1]

$$|\gamma_{8l}^4;A_1\rangle,\ |\gamma_{8l}^2\gamma_7^2;A_1\rangle\ ,$$

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

$$|\gamma_{8l}^3\gamma_7;T_1\rangle\ ,$$

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

In the presence of a tetragonal distortion we get one 4×4 A_1^T block, one 2×2 B_1^T block, one 1×1 A_2^T block, one 2×2 B_2^T block, and two conjugate 3×3 E^T blocks. The matrix elements for these blocks are given in Ref. 10.

In the presence of a trigonal distortion we get one 4×4 A_1^τ block, one 1×1 A_2^τ block, and two conjugate 5×5 E^τ blocks. The matrix elements for these blocks are given in Ref. 10.

VII. d^5 SYSTEM

There are two low-lying unperturbed levels for the d^5 system in the intermediate-coupling scheme[1]:

$$|\gamma_{8l}^4\gamma_7;\Gamma_7\rangle$$

and

$$|\gamma_{8l}^3\gamma_7^2;\Gamma_8\rangle\ .$$

In the case of a tetragonal distortion we get two conjugate 2×2 Γ_7^T blocks and two conjugate 1×1 Γ_6^T blocks. In the case of a trigonal distortion, we get two conjugate 2×2 Γ_4^τ blocks and two conjugate 1×1 Γ_5^τ (Γ_6^τ) blocks. The matrix elements for these blocks are given in Ref. 10.

VIII. CONCLUDING REMARKS

In the intermediate-coupling scheme, the truncation that can be made by omitting the higher-lying states involving the orbital γ_{8u} is of utmost importance[1]—it makes the calculations very simple and at the same time produces useful results[1–4] which are very close to the exact results obtainable through much more laborious and time-consuming numerical calculations. Even such an exact calculation may be preceded by the short-cut calculations through the truncated intermediate-coupling scheme so that preliminary assignments of the various parameters may be made very quickly. We shall make ready reference to the results given here while applying the intermediate-coupling scheme to $4d^n$ and $5d^n$ complexes having deviations from cubic symmetry.

To show, in passing, the validity of the truncation in the

case of a distorted system, let us consider the case of the d^1 system with the tetragonal (D_{4h}) distortion. Magnetic properties of several such complexes were studied, through exact calculations, by De, Desai, and Chakravarty.[8] The exact calculation for such a d^1 system involves one 2×2 Γ_6^T block and one 3×3 Γ_7^T block,[8] whereas, the truncated intermediate-coupling scheme for this system involves one 1×1 Γ_6^T block and one 2×2 Γ_7^T block (see Sec. II). Here, for the sake of comparison, we employ the same values of the parameters as used in Ref. 8 and see that the results obtained here through the truncated calculations are quite close to the exact results there. The two sets of results (truncated and exact) for the complexes $CsMoF_6$, $NaMoF_6$, $RbMoF_6$, and $KMoF_6$ are given in Table I. For these complexes we have assumed (as in Ref. 8) $Dq=2500$ cm^{-1}, $\zeta=800$ cm^{-1}, $k(k_1=k_2)=0.85$.

The matrix elements of the x and z components of the magnetic moment operator, $\vec{n}=k\vec{l}+2\vec{s}$, with respect to the one-electron orbitals in the intermediate-coupling scheme are given in Appendix B. These results together with those in Sec. II were used to obtain the magnetic properties (given in Table I) by the usual procedure.[2,5,8]

APPENDIX A

The original wave functions for the low-lying unperturbed levels of a d^n ($n=2,3,4,5$) system are used to construct sets of basis functions symmetry adapted to the irreducible representations of the lower-symmetric (tetragonal or trigonal) double group (see the scheme in Sec. II). The Hamiltonian matrix with respect to these basis functions separates into blocks corresponding to the irreducible representations of the lower-symmetric double group. The matrix elements for these blocks in each d^n system ($n=2,3,4,5$) are given in Ref. 10 (Appendix C 1). These blocks are diagonal in the Hamiltonian's unperturbed part H_0 containing the cubic ligand field and the spin-orbit interaction: The diagonal elements of H_0 appear in terms of $\epsilon_0(\gamma_{8l})$, $\epsilon_0(\gamma_7)$. The part V_e (electron-electron Coulomb potential) of the Hamiltonian can give a nonvanishing matrix element only between states originating from the same irreducible representation in O_h'. The lower symmetric potential, V_T or V_τ, in the Hamiltonian gives matrix elements in terms of the pair of additional parameters Ds,Dt or $D\sigma$,$D\tau$. To make the above points clear, we give here only three examples of Hamiltonian matrix elements:

$$\langle\gamma_{8l}\gamma_7;E\rightarrow B_1^T b_1\,|\,\mathscr{H}\,|\,\gamma_{8l}\gamma_7;E\rightarrow B_1^T b_1\rangle=\epsilon_0(\gamma_{8l})+\epsilon_0(\gamma_7)+\langle\gamma_{8l}\gamma_7;E\,|\,V_e\,|\,\gamma_{8l}\gamma_7;E\rangle$$
$$-(1+C_{02})Ds+(\tfrac{19}{3}-10C_{02})Dt\ ,$$

$$\langle\gamma_{8l}^3;\Gamma_8\rightarrow\Gamma_5^\tau a'\,|\,\mathscr{H}\,|\,\gamma_{8l}^2(T_2)\gamma_7;\Gamma_8\rightarrow\Gamma_5^\tau a'\rangle=\langle\gamma_{8l}^3;\Gamma_8\,|\,V_e\,|\,\gamma_{8l}^2(T_2)\gamma_7;\Gamma_8\rangle-\frac{\sqrt{2}}{\sqrt{3}}C_{10}(D\sigma+\tfrac{20}{9}D\tau)$$
$$+\tfrac{2}{3}C_{01}(D\sigma-\tfrac{5}{3}D\tau)\ ,$$

$$\langle\gamma_{8l}^2(T_2)\gamma_7;\Gamma_6\rightarrow\Gamma_4^\tau a\,|\,\mathscr{H}\,|\,\gamma_{8l}^2(A_1)\gamma_7;\Gamma_7\rightarrow\Gamma_4^\tau a\rangle=-\frac{2}{\sqrt{3}}C_{20}(D\sigma+\tfrac{20}{9}D\tau)-\frac{4\sqrt{2}}{3}C_{11}(D\sigma-\tfrac{5}{3}D\tau)\ .$$

TABLE I. Comparison of the truncated and exact results for some $4d^1$ compounds. $Dq=2500$ cm^{-1}, $\zeta=800$ cm^{-1}, and $k=0.85$. The results in parentheses are the exact results collected from Ref. 8.

Compounds	Temperature (K)	Ds (cm^{-1})	Dt (cm^{-1})	Splitting of the lowest Γ_8 (cm^{-1})	Effective no. of Bohr magnetons
$CsMoF_6$	100	230	300	627	0.927
				(620)	(0.950)
$NaMoF_6$	300	430	560	1252	1.262
				(1240)	(1.285)
$RbMoF_6$	100	340	450	997	1.089
				(970)	(1.110)
	300	800	1040	2474	1.392
				(2460)	(1.440)
$KMoF_6$	100	430	560	1252	1.169
				(1240)	(1.185)
	300	600	780	1804	1.362
				(1800)	(1.385)

The electrostatic matrix elements,

$$\langle \gamma_{8l}\gamma_7;E \mid V_e \mid \gamma_{8l}\gamma_7;E \rangle ,$$

etc., appearing in the Hamiltonian matrix elements are expressed in terms of the usual Racah parameters A, B, and C. These electrostatic matrices in the intermediate-coupling scheme can be constructed through the following steps. At first the Tables IA—IVA and IB—IVB given in Ref. 27 of Ref. 1 are used to express the unperturbed states of the intermediate-coupling scheme in terms of the strong-field scheme wave functions. Then, using the known electrostatic matrices in the strong-field scheme, we can easily construct the required electrostatic matrix elements in the intermediate-coupling scheme. For the electrostatic matrices in the strong-field scheme we use Table A28 of Ref. 5 where the matrix elements are given in terms of three Racah parameters A, B, and C. The useful electrostatic matrix elements with respect to the lower-lying states in the intermediate-coupling scheme are given in Ref. 10 (Appendix C 2).

APPENDIX B

The nonvanishing matrix elements of the x and z components of the one-electron magnetic moment operator $\vec{n}=k\vec{l}+2\vec{s}$ with respect to the basic one-electron wave functions in the intermediate-coupling scheme are given below:

$$\langle \kappa_l \mid n_x \mid \lambda_l \rangle = -\frac{1}{\sqrt{3}}(1-k_2)C_{20}+\sqrt{2}k_1C_{11} ,$$

$$\langle \kappa_l \mid n_x \mid \nu_l \rangle = \tfrac{2}{3}(1-k_2)C_{20}+\frac{\sqrt{2}}{\sqrt{3}}k_1C_{11}-C_{02} ,$$

$$\langle \kappa_l \mid n_x \mid \alpha'' \rangle = -\frac{1}{3\sqrt{2}}(2+k_2)C_{10}+\frac{1}{\sqrt{3}}k_1C_{01} ,$$

$$\langle \lambda_l \mid n_x \mid \mu_l \rangle = \sqrt{6}k_1C_{11}-C_{02} ,$$

$$\langle \lambda_l \mid n_x \mid \beta'' \rangle = \frac{1}{\sqrt{6}}(2+k_2)C_{10}-k_1C_{01} ,$$

$$\langle \mu_l \mid n_x \mid \nu_l \rangle = -\frac{1}{\sqrt{3}}(1-k_2)C_{20}+\sqrt{2}k_1C_{11} ,$$

$$\langle \mu_l \mid n_x \mid \alpha'' \rangle = -\frac{1}{\sqrt{6}}(2+k_2)C_{10}+k_1C_{01} ,$$

$$\langle \nu_l \mid n_x \mid \beta'' \rangle = \frac{1}{3\sqrt{2}}(2+k_2)C_{10}-\frac{1}{\sqrt{3}}k_1C_{01} ,$$

$$\langle \alpha'' \mid n_x \mid \beta'' \rangle = -\tfrac{1}{3}(2k_2+1) ,$$

$$\langle \kappa_l \mid n_z \mid \kappa_l \rangle = -\langle \nu_l \mid n_z \mid \nu_l \rangle = -\tfrac{1}{3}(1-k_2)C_{20}+\frac{4\sqrt{2}}{\sqrt{3}}k_1C_{11}-C_{02} ,$$

$$\langle \lambda_l \mid n_z \mid \lambda_l \rangle = -\langle \mu_l \mid n_z \mid \mu_l \rangle = -(1-k_2)C_{20}+C_{02} ,$$

$$\langle \kappa_l \mid n_z \mid \beta'' \rangle = \langle \nu_l \mid n_z \mid \alpha'' \rangle = -\frac{\sqrt{2}}{3}(2+k_2)C_{10}+\frac{2}{\sqrt{3}}k_1C_{01} ,$$

$$\langle \alpha'' \mid n_z \mid \alpha'' \rangle = -\langle \beta'' \mid n_z \mid \beta'' \rangle = -\tfrac{1}{3}(2k_2+1) .$$

Here, in view of the inequivalence of the t_2 and the e orbitals we have used two different orbital reduction factors[1]—we have put $\kappa=k_1$ when we consider matrix elements between a t_2 orbital and an e orbital, and $\kappa=k_2$ while considering matrix elements between two t_2 orbitals.

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