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Theoretical Equations of Zeeman Energy Levels for Distorted Metal Complexes with $^3T_1$ Ground Terms

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Abstract: The theoretical equations of Zeeman energy levels, including the zero-field energies and the first- and second-order Zeeman coefficients, have been obtained in closed form for nine states of the $^3T_{1(g)}$ ground term, considering the axial ligand-field splitting and the spin-orbit coupling. The equations are expressed as the functions of three independent parameters, Δ, λ, and κ, where Δ is the axial ligand-field splitting parameter, λ is the spin-orbit coupling parameter, and κ is the effective orbital reduction factor, including the admixing. The equations are useful in simulating magnetic properties (magnetic susceptibility and magnetization) of the complexes with $^3T_{1(g)}$ ground terms, e.g., octahedral vanadium(III), octahedral low-spin manganese(III), octahedral low-spin chromium(II), and tetrahedral nickel(II) complexes.

Keywords: Zeeman coefficients; $^3T_{1(g)}$ ground term; axial ligand-field splitting; spin-orbit coupling; magnetic properties

1. Introduction

Magnetic properties of metal complexes with T ground term is difficult to be interpreted because of the spin-orbit coupling. Since the orbital angular momentum depends on the symmetry around the central metal ion, the distortion effect should be considered in addition to the spin-orbit coupling. This paper reports theoretical expression of Zeeman energy levels for distorted metal complexes with $^3T_1$ ground terms for the purpose of simulating the magnetic properties at high speed.

Concerning the T-term magnetism, Figgis successfully simulated the temperature dependence of the effective magnetic moment of the metal complexes with $^2T_2$ ground terms [1], considering both the axial distortion and the spin-orbit coupling. After that magnetic properties were well interpreted for metal complexes with $^4T_1$ [2], $^3T_1$ [3], and $^5T_2$ [4] ground terms. On the other hand, however, the secular matrices were to be solved each time to simulate the magnetic properties. Therefore, it takes more time to optimize multiple parameters. In addition, simulation can be freely performed only by those who can use programs to solve matrix equations, and simulation output can only be performed within the programmed range.

In order to solve the problem, magnetic susceptibility equation was successfully expressed in closed form for distorted metal complexes with the $^4T_1$ ground terms [5]. The closed-form expression is easily handled, and the extension to the dinuclear and higher nuclearity system is possible [5–7]. In fact, the first successful magnetic analysis of dinuclear octahedral high-spin cobalt(II) complexes with slightly distorted cobalt(II) ions was conducted using the closed-form expression [5]. Theoretical closed-form expression for magnetic properties has been reported for $^2T_2$ [8], $^4T_1$ [5], and $^5T_2$ [9] ground terms; however, the expression for the $^3T_1$ term had not been obtained yet. Therefore, in this study, magnetic susceptibility and magnetization equations were obtained for the $^3T_1$ term.

The magnetic susceptibility and magnetization equations for the $^3T_1$ ground term enable us to analyze magnetic data of metal complexes, including octahedral vanadium(III), octahedral low-spin manganese(III), octahedral low-spin chromium(II), and tetrahedral nickel(II) complexes, considering the spin-orbit coupling and the distortion around the central metal ion, without solving the secular matrix each time.

2. Results

2.1. Zero-Field Energies and Zeeman Coefficients

The $^3T_{1(g)}$ term consists of nine states, which can be expressed as linear combinations of nine orthogonal basses. In general, there are two typical types of basis sets for multielectron systems. One is T-term-based, and the other is P-term-based, using the structural isomorphism of ^nT with ^nP [10]. In this study, the latter was chosen, and the basis set is as follows: [$|0,0\rangle$, $|0,\pm1\rangle$, $|\pm1,0\rangle$, $|\pm1,\pm1\rangle$, $|\pm1,\mp1\rangle$] using the $|M_L, M_S\rangle$ notation. The method for obtaining the wave functions were well described by Kahn [11] for the $^4T_{1g}$ term, and the method is also useful for the $^3T_{1(g)}$ term. Considering both the axial distortion and the spin-orbit coupling, the Hamiltonian can be written as $\mathbf{H} = \Delta(\mathbf{L}_z^2 - \frac{2}{3}) - \frac{3}{2}\kappa\lambda\mathbf{L}\cdot\mathbf{S} + \beta(-\frac{3}{2}\kappa\mathbf{L}_u + g_e\mathbf{S}_u)\cdot H_u\ (u = x, y, z)$ for the basis set, where Δ is the axial splitting parameter, λ is the spin-orbit coupling parameter, and κ is the effective orbital reduction factor. It is noted that the axial distortion includes both the tetragonal distortion and the trigonal distortion and that the effective orbital reduction factor includs the admixing of the excited $^3T_{1(g)}(P)$ term. The ground $^3T_{1(g)}$ term can be described by the following nine wave functions, Ψ_1–Ψ_9, including the 13 coefficients, c_1–c_{13}, and the coefficients are obtained by solving a 9×9 secular matrix established on the basis of the Hamiltonian. The matrix can be reduced to three matrices A, B, and C as shown below. The matrices were basically led according to the method of Lines for the $^4T_{1g}$ term [2], using the structural isomorphism of $^nT_1$ with ^nP [10]; however, the treatment of the orbital reduction factor was modified according to Kahn [11].

$$\Psi_1 = c_1|1,-1\rangle + c_2|0,0\rangle + c_3|-1,1\rangle \tag{1}$$

$$\Psi_2 = c_4|1,0\rangle + c_5|0,1\rangle \tag{2}$$

$$\Psi_3 = c_4|-1,0\rangle + c_5|0,-1\rangle \tag{3}$$

$$\Psi_4 = c_6|1,-1\rangle + c_7|0,0\rangle + c_8|-1,1\rangle \tag{4}$$

$$\Psi_5 = c_9|1,-1\rangle + c_{10}|0,0\rangle + c_{11}|-1,1\rangle \tag{5}$$

$$\Psi_6 = c_{12}|1,0\rangle + c_{13}|0,1\rangle \tag{6}$$

$$\Psi_7 = c_{12}|-1,0\rangle + c_{13}|0,-1\rangle \tag{7}$$

$$\Psi_8 = |1,1\rangle \tag{8}$$

$$\Psi_9 = |-1,-1\rangle \tag{9}$$

Matrix A

$\|1,-1\rangle$	$\|0,0\rangle$	$\|-1,1\rangle$
$\frac{\Delta}{3} + \frac{3}{2}\kappa\lambda$	$-\frac{3}{2}\kappa\lambda$	0
$-\frac{3}{2}\kappa\lambda$	$\frac{-2\Delta}{3}$	$-\frac{3}{2}\kappa\lambda$
0	$-\frac{3}{2}\kappa\lambda$	$\frac{\Delta}{3} + \frac{3}{2}\kappa\lambda$

Matrix B

$\|\pm1,0\rangle$	$\|0,\pm1\rangle$
$\frac{\Delta}{3}$	$-\frac{3}{2}\kappa\lambda$
$-\frac{3}{2}\kappa\lambda$	$\frac{-2\Delta}{3}$

Matrix C
$\lvert \pm 1, \pm 1 \rangle$
$\frac{\Delta}{3} - \frac{3}{2}\kappa\lambda$

By solving the matrices, the coefficients, c_1–c_{13}, are expressed as the functions of v ($= \frac{\Delta}{\kappa\lambda}$) as shown below.

$$c_1 = \frac{d_1}{|d_1|}\sqrt{\frac{d_1^2}{d_1^2 + d_2^2 + d_3^2}} \tag{10}$$

$$c_2 = \frac{d_2}{|d_2|}\sqrt{\frac{d_2^2}{d_1^2 + d_2^2 + d_3^2}} \tag{11}$$

$$c_3 = \frac{d_3}{|d_3|}\sqrt{\frac{d_3^2}{d_1^2 + d_2^2 + d_3^2}} \tag{12}$$

$$c_4 = \frac{d_4}{|d_4|}\sqrt{\frac{d_4^2}{d_4^2 + d_5^2}} \tag{13}$$

$$c_5 = \frac{d_5}{|d_5|}\sqrt{\frac{d_5^2}{d_4^2 + d_5^2}} \tag{14}$$

$$c_6 = \frac{d_6}{|d_6|}\sqrt{\frac{d_6^2}{d_6^2 + d_7^2 + d_8^2}} \tag{15}$$

$$c_7 = \frac{d_7}{|d_7|}\sqrt{\frac{d_7^2}{d_6^2 + d_7^2 + d_8^2}} \tag{16}$$

$$c_8 = \frac{d_8}{|d_8|}\sqrt{\frac{d_8^2}{d_6^2 + d_7^2 + d_8^2}} \tag{17}$$

$$c_9 = \frac{d_9}{|d_9|}\sqrt{\frac{d_9^2}{d_9^2 + d_{10}^2 + d_{11}^2}} \tag{18}$$

$$c_{10} = \frac{d_{10}}{|d_{10}|}\sqrt{\frac{d_{10}^2}{d_9^2 + d_{10}^2 + d_{11}^2}} \tag{19}$$

$$c_{11} = \frac{d_{11}}{|d_{11}|}\sqrt{\frac{d_{11}^2}{d_9^2 + d_{10}^2 + d_{11}^2}} \tag{20}$$

$$c_{12} = \frac{d_{12}}{|d_{12}|}\sqrt{\frac{d_{12}^2}{d_{12}^2 + d_{13}^2}} \tag{21}$$

$$c_{13} = \frac{d_{13}}{|d_{13}|}\sqrt{\frac{d_{13}^2}{d_{12}^2 + d_{13}^2}} \tag{22}$$

$$d_1 = 1/V_1 \tag{23}$$

$$d_2 = -1 \tag{24}$$

$$d_3 = 1/V_1 \tag{25}$$

$$d_4 = -1/V_4 \tag{26}$$

$$d_5 = -1 \tag{27}$$

$$d_6 = 1/V_2 \tag{28}$$

$$d_7 = -1 \tag{29}$$

$$d_8 = 1/V_2 \tag{30}$$

$$d_9 = 1/V_3 \tag{31}$$

$$d_{10} = -1 \tag{32}$$

$$d_{11} = 1/V_3 \tag{33}$$

$$d_{12} = -1/V_5 \tag{34}$$

$$d_{13} = -1 \tag{35}$$

$$V_1 = \frac{1}{6}\left(-2v - 3 + \sqrt{4v^2 + 12v + 81}\right) \tag{36}$$

$$V_2 = \frac{12}{3 + 2v} \tag{37}$$

$$V_3 = \frac{1}{6}\left(-2v - 3 - \sqrt{4v^2 + 12v + 81}\right) \tag{38}$$

$$V_4 = \frac{1}{3}\left(v - \sqrt{v^2 + 9}\right) \tag{39}$$

$$V_5 = \frac{1}{3}\left(v + \sqrt{v^2 + 9}\right) \tag{40}$$

Using the coefficients, c_1–c_{13}, the zero-field energies ($E_n^{(0)}$), the first-order Zeeman coefficients ($E_{n,z}^{(1)}$ and $E_{n,x}^{(1)}$), and the second-order Zeeman coefficients ($E_{n,z}^{(2)}$ and $E_{n,x}^{(2)}$) are expressed as follows, where g_e is the g-factor of the free-electron.

$$E_1^{(0)} = {c_1}^2\left(\frac{\Delta}{3} + \frac{3}{2}\kappa\lambda\right) + {c_2}^2\left(\frac{-2\Delta}{3}\right) + {c_3}^2\left(\frac{\Delta}{3} + \frac{3}{2}\kappa\lambda\right) + 2c_1c_2\left(-\frac{3}{2}\kappa\lambda\right) + 2c_2c_3\left(-\frac{3}{2}\kappa\lambda\right) \tag{41}$$

$$E_2^{(0)} = E_3^{(0)} = {c_4}^2\left(\frac{\Delta}{3}\right) + {c_5}^2\left(\frac{-2\Delta}{3}\right) + 2c_4c_5\left(-\frac{3}{2}\kappa\lambda\right) \tag{42}$$

$$E_4^{(0)} = {c_6}^2\left(\frac{\Delta}{3} + \frac{3}{2}\kappa\lambda\right) + {c_7}^2\left(\frac{-2\Delta}{3}\right) + {c_8}^2\left(\frac{\Delta}{3} + \frac{3}{2}\kappa\lambda\right) + 2c_6c_7\left(-\frac{3}{2}\kappa\lambda\right) + 2c_7c_8\left(-\frac{3}{2}\kappa\lambda\right) \tag{43}$$

$$E_5^{(0)} = {c_9}^2\left(\frac{\Delta}{3} + \frac{3}{2}\kappa\lambda\right) + {c_{10}}^2\left(\frac{-2\Delta}{3}\right) + {c_{11}}^2\left(\frac{\Delta}{3} + \frac{3}{2}\kappa\lambda\right) + 2c_9c_{10}\left(-\frac{3}{2}\kappa\lambda\right) + 2c_{10}c_{11}\left(-\frac{3}{2}\kappa\lambda\right) \tag{44}$$

$$E_6^{(0)} = E_7^{(0)} = {c_{12}}^2\left(\frac{\Delta}{3}\right) + {c_{13}}^2\left(\frac{-2\Delta}{3}\right) + 2c_{12}c_{13}\left(-\frac{3}{2}\kappa\lambda\right) \tag{45}$$

$$E_8^{(0)} = E_9^{(0)} = \frac{\Delta}{3} - \frac{3}{2}\kappa\lambda \tag{46}$$

$$E_{1,z}^{(1)} = (-{c_1}^2 + {c_3}^2)(\frac{3\kappa}{2} + g_e)\beta \tag{47}$$

$$E_{2,z}^{(1)} = -{c_4}^2(\frac{3\kappa}{2})\beta + {c_5}^2 g_e\beta \tag{48}$$

$$E_{3,z}^{(1)} = {c_4}^2(\frac{3\kappa}{2})\beta - {c_5}^2 g_e\beta \tag{49}$$

$$E_{4,z}^{(1)} = (-{c_6}^2 + {c_8}^2)(\frac{3\kappa}{2} + g_e)\beta \tag{50}$$

$$E_{5,z}^{(1)} = (-{c_9}^2 + {c_{11}}^2)(\frac{3\kappa}{2} + g_e)\beta \tag{51}$$

$$E_{6,z}^{(1)} = -{c_{12}}^2(\frac{3\kappa}{2})\beta + {c_{13}}^2 g_e\beta \tag{52}$$

$$E_{7,z}^{(1)} = {c_{12}}^2(\frac{3\kappa}{2})\beta - {c_{13}}^2 g_e\beta \tag{53}$$

$$E_{8,z}^{(1)} = -(\frac{3\kappa}{2})\beta + g_e\beta \tag{54}$$

$$E_{9,z}^{(1)} = (\frac{3\kappa}{2})\beta - g_e\beta \tag{55}$$

$$E_{1,z}^{(2)} = \frac{(-c_1c_6 + c_3c_8)^2(\frac{3\kappa}{2} + g_e)^2\beta^2}{E_1^{(0)} - E_4^{(0)}} + \frac{(-c_1c_9 + c_3c_{11})^2(\frac{3\kappa}{2} + g_e)^2\beta^2}{E_1^{(0)} - E_5^{(0)}} \tag{56}$$

$$E_{2,z}^{(2)} = \frac{(-c_4c_{12}(\frac{3\kappa}{2}) + c_5c_{13}g_e)^2\beta^2}{E_2^{(0)} - E_6^{(0)}} \tag{57}$$

$$E_{3,z}^{(2)} = \frac{(-c_4c_{12}(\frac{3\kappa}{2}) + c_5c_{13}g_e)^2\beta^2}{E_3^{(0)} - E_7^{(0)}} \tag{58}$$

$$E_{4,z}^{(2)} = \frac{(-c_1c_6 + c_3c_8)^2(\frac{3\kappa}{2} + g_e)^2\beta^2}{E_4^{(0)} - E_1^{(0)}} + \frac{(-c_6c_9 + c_8c_{11})^2(\frac{3\kappa}{2} + g_e)^2\beta^2}{E_4^{(0)} - E_5^{(0)}} \tag{59}$$

$$E_{5,z}^{(2)} = \frac{(-c_6c_9 + c_8c_{11})^2(\frac{3\kappa}{2} + g_e)^2\beta^2}{E_5^{(0)} - E_4^{(0)}} + \frac{(-c_1c_9 + c_3c_{11})^2(\frac{3\kappa}{2} + g_e)^2\beta^2}{E_5^{(0)} - E_1^{(0)}} \tag{60}$$

$$E_{6,z}^{(2)} = \frac{(-c_4c_{12}(\frac{3\kappa}{2}) + c_5c_{13}g_e)^2\beta^2}{E_6^{(0)} - E_2^{(0)}} \tag{61}$$

$$E_{7,z}^{(2)} = \frac{(-c_4c_{12}(\frac{3\kappa}{2}) + c_5c_{13}g_e)^2\beta^2}{E_7^{(0)} - E_3^{(0)}} \tag{62}$$

$$E_{8,z}^{(2)} = E_{9,z}^{(2)} = 0 \tag{63}$$

$$E_{1,x}^{(1)} = E_{2,x}^{(1)} = E_{3,x}^{(1)} = E_{4,x}^{(1)} = E_{5,x}^{(1)} = E_{6,x}^{(1)} = E_{7,x}^{(1)} = E_{8,x}^{(1)} = E_{9,x}^{(1)} = 0 \tag{64}$$

$$\begin{aligned} E_{1,x}^{(2)} = {} & \frac{((c_1c_4+c_2c_5)(\frac{\sqrt{2}}{2}g_e)+(c_2c_4+c_3c_5)(-\frac{3\sqrt{2}}{4}\kappa))^2\beta^2}{E_1^{(0)}-E_2^{(0)}} + \frac{((c_3c_4+c_2c_5)(\frac{\sqrt{2}}{2}g_e)+(c_2c_4+c_1c_5)(-\frac{3\sqrt{2}}{4}\kappa))^2\beta^2}{E_1^{(0)}-E_3^{(0)}} + \\ & \frac{((c_1c_{12}+c_2c_{13})(\frac{\sqrt{2}}{2}g_e)+(c_2c_{12}+c_3c_{13})(-\frac{3\sqrt{2}}{4}\kappa))^2\beta^2}{E_1^{(0)}-E_6^{(0)}} + \frac{((c_3c_{12}+c_2c_{13})(\frac{\sqrt{2}}{2}g_e)+(c_2c_{12}+c_1c_{13})(-\frac{3\sqrt{2}}{4}\kappa))^2\beta^2}{E_1^{(0)}-E_7^{(0)}} \end{aligned} \tag{65}$$

$$\begin{aligned} E_{2,x}^{(2)} = {} & \frac{((c_1c_4+c_2c_5)(\frac{\sqrt{2}}{2}g_e)+(c_2c_4+c_3c_5)(-\frac{3\sqrt{2}}{4}\kappa))^2\beta^2}{E_2^{(0)}-E_1^{(0)}} + \frac{((c_6c_4+c_7c_5)(\frac{\sqrt{2}}{2}g_e)+(c_7c_4+c_8c_5)(-\frac{3\sqrt{2}}{4}\kappa))^2\beta^2}{E_2^{(0)}-E_4^{(0)}} + \\ & \frac{((c_9c_4+c_{10}c_5)(\frac{\sqrt{2}}{2}g_e)+(c_{10}c_4+c_{11}c_5)(-\frac{3\sqrt{2}}{4}\kappa))^2\beta^2}{E_2^{(0)}-E_5^{(0)}} + \frac{(c_4(\frac{\sqrt{2}}{2}g_e)+c_5(-\frac{3\sqrt{2}}{4}\kappa))^2\beta^2}{E_2^{(0)}-E_8^{(0)}} \end{aligned} \tag{66}$$

$$\begin{aligned} E_{3,x}^{(2)} = {} & \frac{((c_3c_4+c_2c_5)(\frac{\sqrt{2}}{2}g_e)+(c_2c_4+c_1c_5)(-\frac{3\sqrt{2}}{4}\kappa))^2\beta^2}{E_3^{(0)}-E_1^{(0)}} + \frac{((c_8c_4+c_7c_5)(\frac{\sqrt{2}}{2}g_e)+(c_7c_4+c_6c_5)(-\frac{3\sqrt{2}}{4}\kappa))^2\beta^2}{E_3^{(0)}-E_4^{(0)}} + \\ & \frac{((c_{11}c_4+c_{10}c_5)(\frac{\sqrt{2}}{2}g_e)+(c_{10}c_4+c_9c_5)(-\frac{3\sqrt{2}}{4}\kappa))^2\beta^2}{E_3^{(0)}-E_5^{(0)}} + \frac{(c_4(\frac{\sqrt{2}}{2}g_e)+c_5(-\frac{3\sqrt{2}}{4}\kappa))^2\beta^2}{E_3^{(0)}-E_9^{(0)}} \end{aligned} \tag{67}$$

$$\begin{aligned} E_{4,x}^{(2)} = {} & \frac{((c_6c_4+c_2c_5)(\frac{\sqrt{2}}{2}g_e)+(c_7c_4+c_8c_5)(-\frac{3\sqrt{2}}{4}\kappa))^2\beta^2}{E_4^{(0)}-E_2^{(0)}} + \frac{((c_8c_4+c_2c_5)(\frac{\sqrt{2}}{2}g_e)+(c_7c_4+c_6c_5)(-\frac{3\sqrt{2}}{4}\kappa))^2\beta^2}{E_4^{(0)}-E_3^{(0)}} + \\ & \frac{((c_6c_{12}+c_7c_{13})(\frac{\sqrt{2}}{2}g_e)+(c_7c_{12}+c_8c_{13})(-\frac{3\sqrt{2}}{4}\kappa))^2\beta^2}{E_4^{(0)}-E_6^{(0)}} + \frac{((c_8c_{12}+c_7c_{13})(\frac{\sqrt{2}}{2}g_e)+(c_7c_{12}+c_6c_{13})(-\frac{3\sqrt{2}}{4}\kappa))^2\beta^2}{E_4^{(0)}-E_7^{(0)}} \end{aligned} \tag{68}$$

$$E_{5,x}^{(2)} = \frac{((c_9c_4+c_{10}c_5)(\frac{\sqrt{2}}{2}g_e)+(c_{10}c_4+c_{11}c_5)(-\frac{3\sqrt{2}}{4}\kappa))^2\beta^2}{E_5^{(0)}-E_2^{(0)}} + \frac{((c_{11}c_4+c_{10}c_5)(\frac{\sqrt{2}}{2}g_e)+(c_{10}c_4+c_9c_5)(-\frac{3\sqrt{2}}{4}\kappa))^2\beta^2}{E_5^{(0)}-E_3^{(0)}} + \frac{((c_9c_{12}+c_{10}c_{13})(\frac{\sqrt{2}}{2}g_e)+(c_{10}c_{12}+c_{11}c_{13})(-\frac{3\sqrt{2}}{4}\kappa))^2\beta^2}{E_5^{(0)}-E_6^{(0)}} + \frac{((c_{11}c_{12}+c_{10}c_{13})(\frac{\sqrt{2}}{2}g_e)+(c_{10}c_{12}+c_9c_{13})(-\frac{3\sqrt{2}}{4}\kappa))^2\beta^2}{E_5^{(0)}-E_7^{(0)}} \quad (69)$$

$$E_{6,x}^{(2)} = \frac{((c_1c_{12}+c_2c_{13})(\frac{\sqrt{2}}{2}g_e)+(c_2c_{12}+c_3c_{13})(-\frac{3\sqrt{2}}{4}\kappa))^2\beta^2}{E_6^{(0)}-E_1^{(0)}} + \frac{((c_6c_{12}+c_7c_{13})(\frac{\sqrt{2}}{2}g_e)+(c_7c_{12}+c_8c_{13})(-\frac{3\sqrt{2}}{4}\kappa))^2\beta^2}{E_6^{(0)}-E_4^{(0)}} + \frac{((c_9c_{12}+c_{10}c_{13})(\frac{\sqrt{2}}{2}g_e)+(c_{10}c_{12}+c_{11}c_{13})(-\frac{3\sqrt{2}}{4}\kappa))^2\beta^2}{E_6^{(0)}-E_5^{(0)}} + \frac{(c_{12}(\frac{\sqrt{2}}{2}g_e)+c_{13}(-\frac{3\sqrt{2}}{4}\kappa))^2\beta^2}{E_6^{(0)}-E_8^{(0)}} \quad (70)$$

$$E_{7,x}^{(2)} = \frac{((c_3c_{12}+c_2c_{13})(\frac{\sqrt{2}}{2}g_e)+(c_2c_{12}+c_1c_{13})(-\frac{3\sqrt{2}}{4}\kappa))^2\beta^2}{E_7^{(0)}-E_1^{(0)}} + \frac{((c_8c_{12}+c_7c_{13})(\frac{\sqrt{2}}{2}g_e)+(c_7c_{12}+c_6c_{13})(-\frac{3\sqrt{2}}{4}\kappa))^2\beta^2}{E_7^{(0)}-E_4^{(0)}} + \frac{((c_{11}c_{12}+c_{10}c_{13})(\frac{\sqrt{2}}{2}g_e)+(c_{10}c_{12}+c_9c_{13})(-\frac{3\sqrt{2}}{4}\kappa))^2\beta^2}{E_7^{(0)}-E_5^{(0)}} + \frac{(c_{12}(\frac{\sqrt{2}}{2}g_e)+c_{13}(-\frac{3\sqrt{2}}{4}\kappa))^2\beta^2}{E_7^{(0)}-E_9^{(0)}} \quad (71)$$

$$E_{8,x}^{(2)} = \frac{(c_4(\frac{\sqrt{2}}{2}g_e)+c_5(-\frac{3\sqrt{2}}{4}\kappa))^2\beta^2}{E_8^{(0)}-E_2^{(0)}} + \frac{(c_{12}(\frac{\sqrt{2}}{2}g_e)+c_{13}(-\frac{3\sqrt{2}}{4}\kappa))^2\beta^2}{E_8^{(0)}-E_6^{(0)}} \quad (72)$$

$$E_{9,x}^{(2)} = \frac{(c_4(\frac{\sqrt{2}}{2}g_e)+c_5(-\frac{3\sqrt{2}}{4}\kappa))^2\beta^2}{E_9^{(0)}-E_3^{(0)}} + \frac{(c_{12}(\frac{\sqrt{2}}{2}g_e)+c_{13}(-\frac{3\sqrt{2}}{4}\kappa))^2\beta^2}{E_9^{(0)}-E_7^{(0)}} \quad (73)$$

Using the above zero-field energy equations, the v ($= \frac{\Delta}{\kappa\lambda}$) dependence of the nine levels are calculated as shown in Figure 1. When Δ is zero, the $^3T_{1(g)}$ term splits into three states: a singlet state (Ψ_1), a triplet state (Ψ_2, Ψ_3, Ψ_4), and a quintet state (Ψ_5, Ψ_6, Ψ_7, Ψ_8, Ψ_9). When Δ is not zero, the $^3T_{1(g)}$ term splits into three doublet states [(Ψ_2, Ψ_3), (Ψ_6, Ψ_7), and (Ψ_8, Ψ_9)] and three singlet states [Ψ_1, Ψ_4, and Ψ_5]. When the λ value is positive, the Ψ_1 state is the highest, but when the λ value is negative, the Ψ_1 state is the lowest.

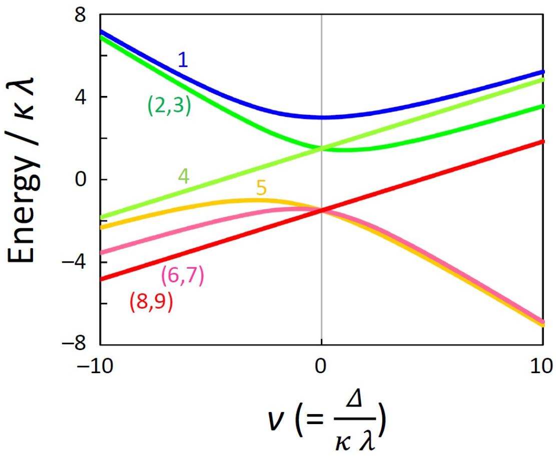

Figure 1. Energy diagram of the nine states of the $^3T_{1(g)}$ term (λ = 100 cm^{-1}, κ = 1).

2.2. Magnetic Susceptibility and Magnetization Equations

The temperature dependence of the magnetic susceptibility χ can be obtained by the Van Vleck formula [12], using the above energy equations and the Zeeman coefficients, where k represents the Boltzmann constatnt. This is a zero-field susuceptibility equation.

$$\chi = \frac{\chi_z + 2\chi_x}{3} \quad (74)$$

$$\chi_{z(x)} = \frac{N\sum_{i=1}^{9}\left(\frac{E^{(1)}_{i,z(x)}{}^{2}}{kT} - 2E^{(2)}_{i,z(x)}\right)\exp\left(\frac{-E^{(0)}_{i}}{kT}\right)}{\sum_{i=1}^{9}\exp\left(\frac{-E^{(0)}_{i}}{kT}\right)} \tag{75}$$

The field-dependent magnetic susceptibility equation can be expressed as follows, where $H_{z(x)}$ represents the magnetic field. This equation is valid when the magnetic field is not so large.

$$\chi_{z(x)} = \frac{N\sum_{i=1}^{9}\left(-\frac{E^{(1)}_{i,z(x)}}{H_{z(x)}} - 2E^{(2)}_{i,z(x)}\right)\exp\left(\frac{-E_{i,z(x)}}{kT}\right)}{\sum_{i=1}^{9}\exp\left(\frac{-E_{i,z(x)}}{kT}\right)} \tag{76}$$

$$E_{i,z(x)} = E^{(0)}_{i} + E^{(1)}_{i,z(x)}H_{z(x)} + E^{(2)}_{i,z(x)}H^{2}_{z(x)} \tag{77}$$

The magnetization for the z and x directions, M_z and M_x, are expressed as follows, where $H_{z(x)}$ represents the magnetic field.

$$M_{z(x)} = \frac{N\sum_{i=1}^{9}\left(-E^{(1)}_{i,z(x)} - 2E^{(2)}_{i,z(x)}H_{z(x)}\right)\exp\left(\frac{-E_{i,z(x)}}{kT}\right)}{\sum_{i=1}^{9}\exp\left(\frac{-E_{i,z(x)}}{kT}\right)} \tag{78}$$

$$E_{i,z(x)} = E^{(0)}_{i} + E^{(1)}_{i,z(x)}H_{z(x)} + E^{(2)}_{i,z(x)}H^{2}_{z(x)} \tag{79}$$

The powder average of the magnetization is generally expressed by the following equation.

$$M_{av} = (4\pi)^{-1}\int_{0}^{2\pi}\int_{0}^{\pi} M(\theta,\phi)\sin\theta d\theta d\phi \tag{80}$$

When the symmetry is axial ($x = y$), the above equation can be expanded by calculating the integrals to obtain the following powder average equation.

$$M_{av} = \lim_{m\to\infty}\sum_{j=1}^{m} M\left(\frac{\left(j - \frac{45}{m}\right)\pi}{180}\right)\left[\cos\frac{(j-1)\pi}{180} - \cos\frac{j\pi}{180}\right] \tag{81}$$

$$M(\theta) = \frac{N\sum_{i=1}^{9}\left(-E^{(1)}_{i,\theta} - 2E^{(2)}_{i,\theta}H_{\theta}\right)\exp\left(\frac{-E_{i,\theta}}{kT}\right)}{\sum_{i=1}^{9}\exp\left(\frac{-E_{i,\theta}}{kT}\right)} \tag{82}$$

Practically, the following equation, with Equation (82), is good enough to calculate the powder average of magnetization, if m is large enough.

$$M_{av} = \sum_{j=1}^{m} M\left(\frac{\left(j - \frac{45}{m}\right)\pi}{180}\right)\left[\cos\frac{(j-1)\pi}{180} - \cos\frac{j\pi}{180}\right] \tag{83}$$

2.3. Magnetic Simulation

Using the closed-form equations for zero-field energies and Zeeman coefficients, magnetic simulation is possible. Such simulation was performed for the ${}^{4}T_{1g}$-ground-term complexes [5–7], and is expected to be possible also for the ${}^{3}T_{1(g)}$-ground-term complexes if the equations derived in this study are used. Two of the examples are going to shown here. The first one is for a tetrahedral nickekel(II) complex, possessing ${}^{3}T_{1}$ ground term (Figure 2). Such simulation and analysis were conducted earlier [3], and the present simulation was consistent with the earlier ones. Since the nickel(II) ion has a d^8 electronic configuration, the λ has a negative value. In this simulation, the λ and κ were fixed to the often observed values. When the tetrahedral coordination geometry around nickel(II) ion is distorted, the v generally takes the negative values, but the simulation was also performed for the positive v values. With the variation of v, the χT curves systematically change. That is because the ground state is Ψ_1 and unchanged.

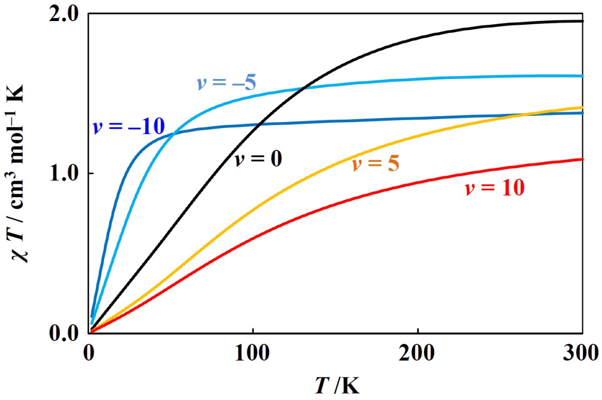

Figure 2. Theoretical χT *versus* T plot for tetrahedral nickel(II) complexes ($\lambda = -100$ cm^{-1}, $\kappa = 0.9$, $v = -10, -5, 0, 5,$ and 10).

The other simulation example is for the positive λ case (Figure 3). This case corresponds to the octahedral vanadium(III) complexes with d^2 electronic configuraions and octahedral low-spin manganese(III) and octahedral low-spin chromium(II) complexes with d^4 electronic configurations. In these cases, λ takes positive values, since the metal ion has less than five d-electrons. With the variation of v, the χT curves drastically change. This is because the ground state changes from a doubly degenerate (Ψ_8, Ψ_9) state ($v < 0$) to a non-degenerate Ψ_5 state ($v > 0$).

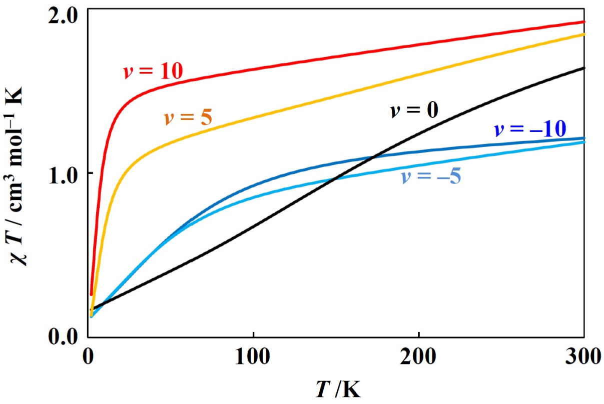

Figure 3. Theoretical χT *versus* T plot for octahedral low-spin manganese(III) complexes ($\lambda = 100$ cm^{-1}, $\kappa = 0.9$, $v = -10, -5, 0, 5,$ and 10).

3. Discussion

In order to obtain magnetic susceptibility and magnetization equations for the metal complexes with $^3T_{1(g)}$ ground terms, the zero-field energies and Zeeman coefficients were obtained in closed form by solving the secular matrices. Fortunately, the resulting equations do not contain the imaginary part. Therefore, the equations can be easily handled, and anyone who wants to obtain Zeeman energy values and so on can calculate them without any specific programs. Using the equations, magnetic susceptibility and magnetization can be calculated simply by substituting the values of the parameters into the equations.

The metal complexes with $^3T_{1(g)}$ ground terms include octahedral vanadium(III) complexes with d^2 electronic configurations, octahedral low-spin manganese(III) and chromium(II) complexes with

d^4 electronic configurations, and tetrahedral nickel(II) complexes with d^8 electronic configurations. Although any new data were not analyzed in this study, the equations obtained in this study are expected to be useful in analyzing the magnetic data of the $^3T_{1(g)}$ complexes, as well as the the $^4T_{1g}$ expressions utilized in magnetic analyses [5–7].

The magnetic susceptibility and magnetization equations require three independent parameters, the axial splitting parameter, Δ, the spin-orbit coupling parameter, λ, and the effective orbital reduction factor, κ. These three parameters are important in considering T-term magnetism. On the other hand, when the zero-field splitting is treated, the zero-field splitting parameter, D, is used. Since the normal zero-field splitting occurs as the result of the spin-spin interaction in the $S \geq 1$ system, this interaction is different from the spin-orbit interaction. Therefore, the different parameter system was used in this study. Of course, $[\lambda, \kappa, v\ (= \frac{\Delta}{\kappa\lambda})]$ is also a good parameter set for the T-term magnetism.

4. Materials and Methods

The procedure of handling the wave functions of the $^4T_{1g}$ term was well described by Kahn [11] to obtain zero-field energies and Zeeman coefficients. His method was basically used for the $^3T_{1(g)}$ term in this study, obtaining zero-field energies and Zeeman coefficients. Therefore, the detailed method is described in reference [11]. The only difference is the definition of "v". That is, Kahn defined $v = \Delta/|\lambda|$, while v was defined as $\frac{\Delta}{\kappa\lambda}$ in this study. Fortunately, there was no difficulty in solving the matrices in closed form. The code including the obtained equations was written on REALbasic software [13]. Calculations were conducted by MagSaki(3T1) ver.0.0.1 software developed using REALbasic software [13].

5. Conclusions

The zero-field energies and Zeeman coefficients were obtained in closed form for the distorted metal complexes with $^3T_{1(g)}$ ground term. The magnetic susceptibility and magnetization equations were also obtained. Using the equations, magnetic susceptibility and magnetization can be calculated simply by substituting the values of the parameters into the equations. The equations are useful for $^3T_{1(g)}$-ground-term complexes, including octahedral vanadium(III), octahedral low-spin manganese(III), octahedral low-spin chromium(II), and tetrahedral nickel(II) complexes.

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References

1. Figgis, B.N. The magnetic properties of transition metal ions in asymmetric ligand fields. Part 2.—Cubic field $^3T_2$ terms. *Trans. Faraday Soc.* **1961**, *57*, 198–203. [CrossRef]
2. Lines, M.E. Magnetic Properties of $CoCl_2$ and $NiCl_2$. *Phys. Rev.* **1963**, *131*, 546–555. [CrossRef]
3. Figgis, B.N.; Lewis, J.; Mabbs, F.E.; Webb, G.A. The magnetic behaviour of cubic field $^3T_{1g}$ terms. *J. Chem. Soc. A* **1966**, 1411–1421. [CrossRef]
4. Figgis, B.N.; Lewis, J.; Mabbs, F.E.; Webb, G.A. The magnetic behaviour of cubic field $^5T_{2g}$ terms in lower symmetry. *J. Chem. Soc. A* **1967**, 442–447. [CrossRef]
5. Sakiyama, H.; Ito, R.; Kumagai, H.; Inoue, K.; Sakamoto, M.; Nishida, Y.; Yamasaki, M. Dinuclear Cobalt(II) Complexes of an Acyclic Phenol-Based Dinucleating Ligand with Four Methoxyethyl Chelating Arms—First Magnetic Analyses in an Axially Distorted Octahedral Field. *Eur. J. Inorg. Chem.* **2001**, *2001*, 2027–2032. [CrossRef]
6. Sakiyama, H.; Adams, H.; Fenton, D.E.; Cummings, L.R.; McHugh, P.E.; Ōkawa, H. Magnetic analyses of isosceles tricobalt(II) complexes containing two types of octahedral high-spin cobalt(II) ions. *Open J. Inorg. Chem.* **2011**, *1*, 33–38. [CrossRef]

7. Sakiyama, H.; Powell, A.K. Magnetic analysis of a tetranuclear octahedral high-spin cobalt(II) complex based on a newly derived magnetic susceptibility equation. *Dalton Trans.* **2014**, *43*, 14542–14545. [CrossRef] [PubMed]
8. Mabbs, F.E.; Machin, D.J. *Magnetism and Transition Metal Complexes*; Chapman and Hall: London, UK, 1973; pp. 165–167.
9. Sakiyama, H. Theoretical equations of Zeeman energy levels for distorted metal complexes with ${}^5T_{2g}$ ground terms. *J. Math. Chem.* **2018**. [CrossRef]
10. Griffith J.S. *The Theory of Transition-Metal Ions*; Cambridge University Press: Cambridge, UK, 1961; pp. 340–374.
11. Kahn, O. *Molecular Magnetism*; VCH: New York, NY, USA, 1993; pp. 38–43.
12. Van Vleck, J.H. *Theory of Electric and Magnetic Susceptibilities*; Oxford University Press: Oxford, UK, 1932; pp. 181–202.
13. REAL Software, Inc. 1996–2006. Available online: http://www.realsoftware.com/ (accessed on 25 February 2019).

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