Analytical Investigations of Spin-Spin, Spin-Other-Orbit and Combined Mechanisms of Zero-Field Splitting for $3d^3$ Ions at Trigonal Symmetry

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A new method of obtaining approximate analytical expressions of zero-field splitting (ZFS) has been proposed. By analyzing the magnetic interaction mechanisms which affect the properties of ZFS of ground $^4A_2$ state for $3d^3$ ions at trigonal symmetry, and comparing with the calculated results of complete diagonalization method, the approximate analytical expressions of the contribution to zero-field splitting of $^4A_2$ state from spin-spin (SS), spin-other-orbit (SOO), and combined mechanisms have been obtained. Also the applicability of these approximate analytical expressions has been analyzed. It is shown that the approximate analytical expressions are suitable in a wide crystal field parameters range.

Key words: $3d^3$ Ions; Approximate Analytical Expression; Complete Diagonalization Method; Magnetic Interactions Mechanisms.

1. Introduction

Decades ago, Macfarlane [1] obtained the third-order approximate formulas for $3d^3$ ions at trigonal symmetry by using perturbation theory method (PTM). Later, using PTM, researchers deduced the high-order perturbation formulas for $3d^N$ ions at various symmetries. These formulas have been widely used in the researches of optical and magnetic properties of transition metal (TM) ions [2 – 8]. Since the method of successive order approximation is used in PTM, the higher the order the more terms should be deduced. This causes a lot of workloads. Generally, only third-order or fourth-order terms can be derived in PTM. In addition, there are many microscopic states for d^N ions. It is very complex to consider all these states in derivation processes. In fact, only partial microscopic states were considered in PTM. Thus, we can not know the effect on the results by the higher-order terms and microscopic states omitted. To calculate exactly, with the development of computing technology, researchers developed the complete diagonalization method (CDM) [9 – 13]. In this method, all the matrix elements of Hamiltonian can be calculated, and then the energies and eigenvectors can be obtained by diagonalizing the matrix. All the microscopic states are considered in CDM, therefore it can be regard as an exact calculation method. The validity of high-order perturbation formulas can be checked by comparing the results calculated by CDM and PTM [11, 12, 14, 15].

In Macfarlane's perturbation loop method, spin-orbit (SO) interaction is taken into account only. The spin-spin (SS), spin-other-orbit (SOO), and orbit-orbit (OO) interactions are neglected. Recently, a series of studies by CDM [11 – 13, 15 – 20] show that the contributions to zero-field splitting (ZFS) of ground state from above mechanisms for TM ions doped crystals can not be neglected. Although the properties of these slight magnetic interactions have been studied systematically, the approximated analytical expressions have not been obtained yet. The most common method used to obtain the approximated analytical expressions is Macfarlane's perturbation loop method. But the workload of perturbation calculations is very large, and the calculation procedure is difficult to be programmed. In the present paper, we propose a simpler method to obtain the approximated analytical expressions. For the ZFS of ground $^4A_2$ state of $3d^3$ ions at trigonal symmetry, the approximated analytical expressions of the contribution to the ZFS from SS mechanism, SOO mechanism, and combined mechanism have been obtained, respectively. The validity of these formulas has been analyzed by CDM.

Crystal	B	C	Dq	ζ	V	V'	M_0	M_2
$Al_2O_3:Cr^{3+}$	650	3120	1810	180	800	680	0.099	0.0078
$Be_3Al_2(SiO_3)_6:Cr^{3+}$	780	2960	1620	225	−2000	2000	0.099	0.0078
$ZnAl_2O_4:Cr^{3+}$	700	3200	1825	250	−200	−1700	0.099	0.0078

Table 1. CF parameters used in calculations [23] (in units of cm^{-1}).

2. The Approximated Analytical Expressions

The CDM has been developed with the development of calculation techniques. The slight magnetic interactions, such as SS, SOO, and OO interactions have been taken into account recently. And the properties of these slight magnetic interactions are studied systematically [11, 12, 15 – 20]. On the basis of it, by analyzing the properties, the approximated analytical expressions can be obtained.

According to the calculations of Table 4 in [11], the contribution to the ZFS of ground state for $3d^3$ ions at trigonal symmetry from OO interaction can be neglected. Thus, the Hamiltonian can be written as

$$H = H_{ee}(B,C) + H_{CF}(Dq,V,V') + H_{SO}(\zeta) + H_{SS}(M_0,M_2) + H_{SOO}(M_0,M_2), \quad (1)$$

where H_{ee}, H_{CF}, H_{SO}, H_{SS}, and H_{SOO} represent, respectively, the electrostatic, the crystal field (CF), the SO interaction, the SS interaction, and the SOO interaction. B and C are Racah parameters, Dq is the cubic CF parameter, V and V' are the trigonal CF parameters, ζ is spin-orbit coupling coefficient, M_0 and M_2 are the Marvin's radial integrals used for representing the SS and SOO interactions [21]. The method of calculations of the matrix elements has been described in [11, 22]. The complete energy matrix can be obtained by substituting the CF parameters to the formulas of matrix elements. Diagnolizing the complete energy matrix, the ZFS of ground $^4A_2$ state for $3d^3$ ions can be obtained. The definition of the ZFS parameter D of $^4A_2$ state is [18]

$$D = \frac{1}{2}[E(|3/2,\pm 3/2\rangle) - E(|3/2,\pm 1/2\rangle)]. \quad (2)$$

According to the studies of [18], there exist combined mechanisms as well as SO, SS, and SOO mechanisms. I. e.

$$D = D_{SO} + D_{SS} + D_{SOO} + D_{SO-SS-SOO}, \quad (3)$$

where the combined mechanism can be expressed as [18]

$$D_{SO-SS-SOO} = D_{SO-SS} + D_{SO-SOO} + D_{SS-SOO}. \quad (4)$$

From the calculations in [20], the order of the magnitude of the contribution to ZFS parameter D from these mechanisms is

$$D_{SO} > D_{SS} > D_{SO-SS-SOO} > D_{SOO}. \quad (5)$$

For D_{SO}, Macfarlane has obtained the approximated analytical expressions by using perturbation loop method. In this section, the approximated analytical expressions of other mechanisms will be obtained in a simpler way.

2.1. The Approximate Analytical Expressions of D_{SS}

First of all, we should know which factors affect the contribution to ZFS of $^4A_2$ state from SS interaction (D_{SS}). The studies in [20] show that, D_{SS} depends on spin quartets only. Thus, we only consider the contributions from spin quartets in the approximate analytical expressions of D_{SS}. In spin quartets excited states $^4T_2$, a^4T_1, and b^4T_1, the b^4T_1 state is the highest one. Its contribution to ZFS of ground $^4A_2$ state can be neglected, as shown in Macfarlane's third-order perturbation formula of D_{SO}. So we also neglect the contribution to D_{SS} from b^4T_1 state, therefor the spin quartets excited states we considered are $^4T_2$ and a^4T_1. The intervals are [23] $D_1 = W(^4T_2) - W(^4A_2) = 10Dq$ and $D_4 = W(a^4T_1) - W(^4A_2) = 10Dq + 12B$, respectively. The studies in [19] refer that the ZFS of $^4A_2$ state at trigonal CF is linear to M_0 and M_2. To study the variations of the contributions to ZFS of $^4A_2$ state from SS mechanism (D_{SS}) with the parameters M_0 and M_2, we calculated D_{SS} by CDM. The parameter M_0 is chosen from 0 to 0.2 cm^{-1}, M_2 is chosen from 0 to 0.016 cm^{-1}, the calculations were performed with the step 0.02 cm^{-1} and 0.002 cm^{-1}, respectively. As values for the parameters were used: $Dq = 1810$ cm^{-1}, $B = 650$ cm^{-1}, $C = 3120$ cm^{-1}, $\zeta = 180$ cm^{-1}, $V = 800$ cm^{-1}, $V' = 680$ cm^{-1}, $M_0 = 0.0990$ cm^{-1}, and $M_2 = 0.0078$ cm^{-1}. The calculated results show that D_{SS} depend in linear way on M_0 and M_2, as shown in Figures 1 and 2. That is to say, in the approximate analytical expressions, M_0 and M_2 should be in the form of a linear term. By calculating the slope of curves, we found that the terms related to M_0 and M_2 should be in the form of $(-M_0 + 3M_2)$.

Table 2. Calculated results of D_{SS}, D_{SOO}, D_{SO-SS}, and D_{SO-SOO} using CDM and the approximate expressions (App.) of (7) – (10) for three typical crystals (in units of cm^{-1}).

Crystal	Meth.	D_{SS}	D_{SOO}	D_{SO-SS}	D_{SO-SOO}	D_{SM}	D_{SO}	D_{SM}/D_{SO}
$Al_2O_3:Cr^{3+}$	CDM	−0.04561	−0.00012	−0.00026	0.00479	−0.0412	−0.1554	0.265122
	App.	−0.04483	−0.00013	−0.00025	0.00468	−0.04053	−0.145	0.279517
$Be_3Al_2(SiO_3)_6:Cr^{3+}$	CDM	−0.13046	−0.00086	−0.00336	0.03710	−0.09758	−0.8527	0.114436
	App.	−0.13882	−0.00096	−0.00415	0.03724	−0.10669	−0.775	0.137665
$ZnAl_2O_4:Cr^{3+}$	CDM	0.12749	0.00056	0.00226	−0.02824	0.10207	0.8558	0.119269
	App.	0.10977	0.00050	0.00220	−0.02432	0.08815	0.76	0.115987

To illustrate the variations of D_{SS} with V and V', we vary V and V' in the range from -3000 to 3000 cm^{-1}. From the results we learn that the effect to D_{SS} from V is slight. So the effect on D_{SS} from V can be neglected reasonably. The results also show that D_{SS} depend almost in a linear way on V', as shown in Figure 3. Considering D_{SS} in the unit of cm^{-1}, from the dimensional rules one can obtained the approximate analytical expression of D_{SS} as:

$$D_{SS} = (-M_0 + 3M_2)V' \left(\frac{a}{D_1} + \frac{b}{D_4} \right), \qquad (6)$$

where a and b are dimensionless undetermined coefficients. Let $b = 0$, then D_{SS} is related to D_1 only, i. e. the contribution to D_{SS} from $^4T_2$ state is considered. In the case of considering $^4A_2$ and $^4T_2$ only, D_{SS} can be calculated by CDM. The value of D_{SS} in this way should be equal to the calculated result taken from (6) in the case of $b = 0$. From this equality, the value of the coefficient a can be obtained. Then, one can calculate D_{SS} by CDM in the case of considering all the spin quartets. The value of D_{SS} here should be equal to the calculated result taken from (6). From this equality, the value of the coefficient b can be obtained. To simplify the expression, we take the coefficients a and b as integers. Thus, the expression of D_{SS} can be written as:

$$D_{SS} = (-M_0 + 3M_2)V' \left(\frac{6}{D_1} + \frac{14}{D_4} \right). \qquad (7)$$

2.2. The Approximate Analytical Expressions of D_{SOO}

Using the same way as in the last subsection, we can obtain the variations of D_{SOO} with all parameters. The results are: (1) The relations between D_{SOO} and V, V' are approximately linear. By calculating the slope of curves, it is shown that terms related to V and V' should be in the form of $(V - 3V')$. (2) The relation between D_{SOO} and M_0 is not linear, but is a square relation. That is to say, M_0^2 should appear in the approximate expression of D_{SOO}. (3) The value of D_{SOO} is almost invariant with varying the value of M_2, i. e. D_{SOO} is independent of M_2. (4) From the results of [20], D_{SOO} is dependent on spin quartets only, that is to say, energy denominators are only related to D_1 and D_4. According to dimensional rules, energy denominators should be the quadratic term of D_1 and D_4. After detailed calculations, the approximate analytical expression of D_{SOO} can be written as:

$$D_{SOO} = 1450M_0^2(V - 3V') \left(\frac{1}{D_1^2} + \frac{3}{D_4^2} \right). \qquad (8)$$

2.3. The Approximate Analytical Expressions of the Contribution from Combined Mechanism

In the combined mechanism expressed as (4), D_{SS-SOO} is the smallest term, the ratio $D_{SS-SOO}/D_{SO-SS-SOO}$ is about 0.001. So we can omit it reasonably. Thus, we can just obtain the approximate analytical expressions of D_{SO-SS} and D_{SO-SOO}. The contribution to ZFS of $^4A_2$ state from combined mechanism depends on spin quartets mainly [20]. So here we can consider spin quartets only, i. e. the energy denominators are related only to D_1 and D_4. Using the same way as above, the relations between D_{SO-SS} and D_{SO-SOO} and ζ, M_0, M_2, V and V' are investigated. Finally, the approximate analytical expressions of D_{SO-SS} and D_{SO-SOO} can be written as

$$D_{SO-SS} = 6\zeta(M_0 - 10M_2)(V - 2V') \left(\frac{6}{D_1^2} + \frac{1}{D_4^2} \right), \qquad (9)$$

$$D_{SO-SOO} = 12\zeta(M_0 - M_2)(-2V + 7V') \left(\frac{1}{D_1^2} + \frac{3}{D_4^2} \right). \qquad (10)$$

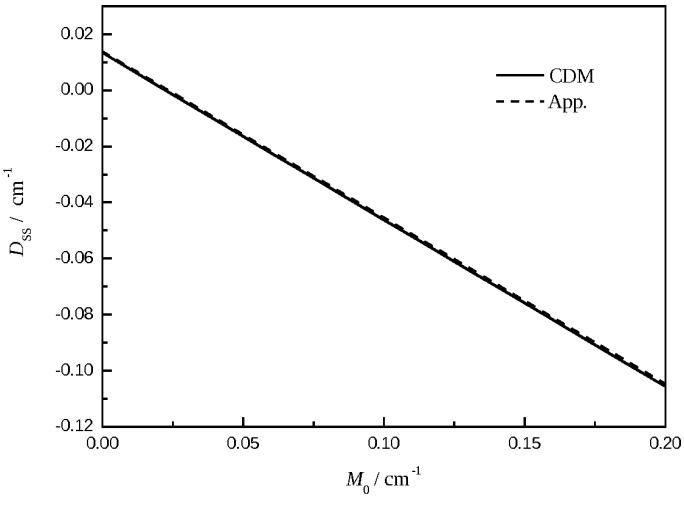

Fig. 1. Contributions to ZFS of $^4A_2$ state from SS mechanism D_{SS} vs. M_0. Solid line: calculated results by CDM; dashed line: calculated results by approximated expressions of this paper.

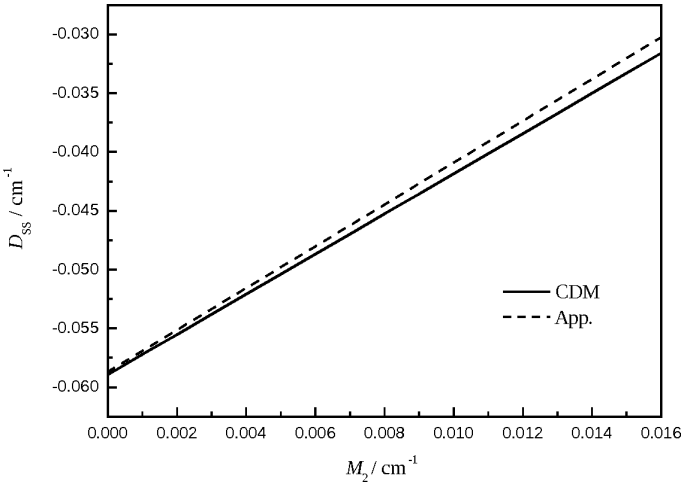

Fig. 2. Contributions to ZFS of $^4A_2$ state from SS mechanism D_{SS} vs. M_2. Solid line: calculated results by CDM; dashed line: calculated results by approximated expressions of this paper.

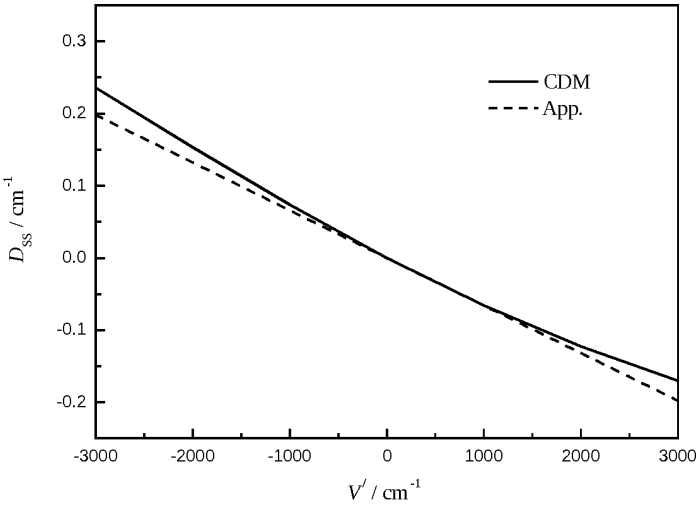

Fig. 3. Contributions to ZFS of $^4A_2$ state from SS mechanism D_{SS} vs. V'. Solid line: calculated results by CDM; dashed line: calculated results by approximated expressions of this paper.

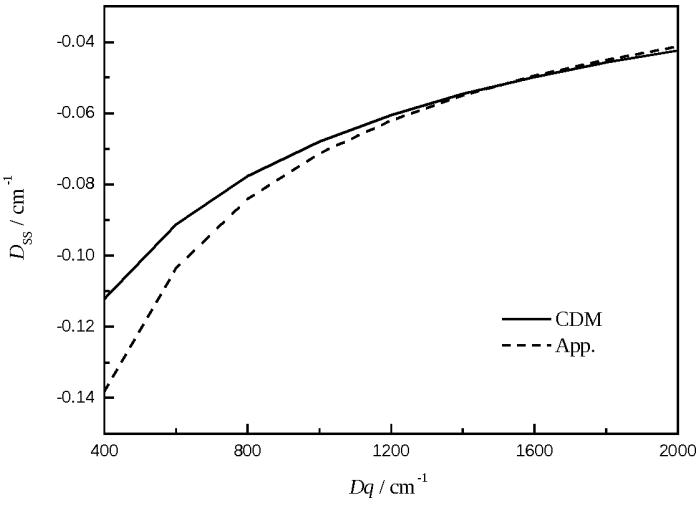

Fig. 4. Contributions to ZFS of $^4A_2$ state from SS mechanism D_{SS} vs. Dq. Solid line: calculated results by CDM; dashed line: calculated results by approximated expressions of this paper.

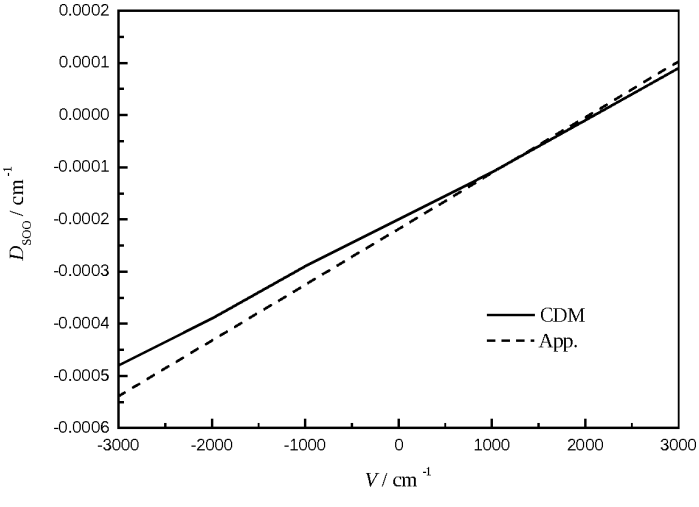

Fig. 5. The contributions to ZFS of $^4A_2$ state from SOO mechanism D_{SOO} vs. V. Solid line: calculated results by CDM; dashed line: calculated results by approximated expressions of this paper.

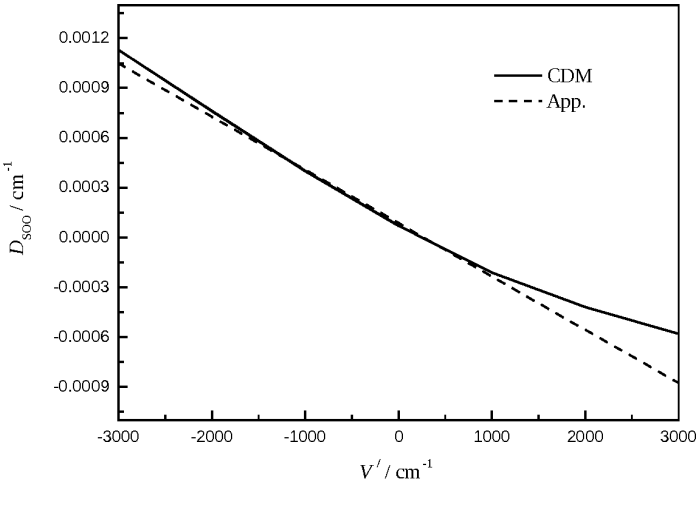

Fig. 6. Contributions to ZFS of $^4A_2$ state from SOO mechanism D_{SOO} vs. V'. Solid line: calculated results by CDM; dashed line: calculated results by approximated expressions of this paper.

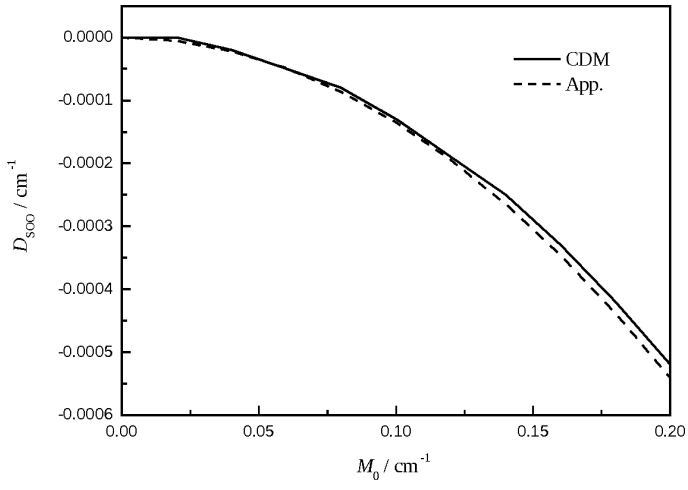

Fig. 7. Contributions to ZFS of $^4A_2$ state from SOO mechanism D_{SOO} vs. M_0. Solid line: calculated results by CDM, dashed line: calculated results by approximated expressions of this paper.

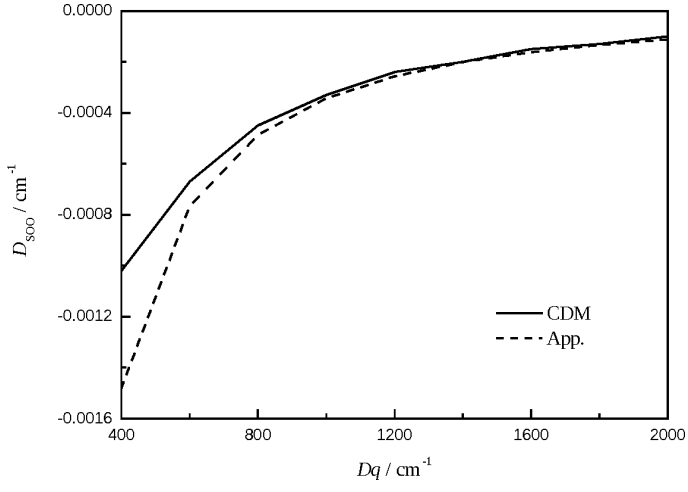

Fig. 8. Contributions to ZFS of $^4A_2$ state from SOO mechanism D_{SOO} vs. Dq. Solid line: calculated results by CDM, dashed line: calculated results by approximated expressions of this paper.

3. The Validity of the Approximate Analytical Expressions

Equations (7)–(10) are obtained by using special CF parameters. Although they are general formulas, it is a problem to research them. To study them, the D_{SS}, D_{SOO}, D_{SO-SS}, and D_{SO-SOO} of three typical crystals, Al_2O_3:Cr^{3+}, $Be_3Al_2(SiO_3)_6$:Cr^{3+}, and $ZnAl_2O_4$:Cr^{3+} have been calculated by CDM and (7)–(10), respectively. The parameters used in the calculations are listed in Table 1. The calculated results are shown in Table 2. From Table 2, one can see that the calculated results obtained by these two ways are in good agreement with each other. Macfarlane calculated the ZFS of $^4A_2$ state of these three crystals by considering the SO mechanism only [23]. We use the notation "D_{SM}" to represent the total contribution from slight magnetic mechanisms, i. e.

$$D_{SM} = D_{SO} + D_{SS} + D_{SO-SS} + D_{SO-SOO}. \quad (11)$$

The calculated results of D_{SM}, D_{SO}, and the ratio D_{SM}/D_{SO} are also listed in Table 2. From the results, one can see that the contribution to the ZFS of $^4A_2$ state from the slight magnetic mechanisms can not be neglected in the calculations.

To study the validity of these expressions further, we compared the calculations by using the two approaches in a wide range of CF parameters. The ranges of M_0, M_2, and Dq are $0 \sim 0.2$ cm^{-1}, $0 \sim 0.016$ cm^{-1}, and $400 \sim 2000$ cm^{-1}, respectively, and that of V and V' is $-3000 \sim 3000$ cm^{-1}. The calculated results are shown in Figures 1–8. In these figures, the solid lines represent the calculated results by CDM and the

dashed lines represent the calculated results by (7)–(10). From these figures one can see that, the results calculated by CDM and the approximate analytical expressions agree well with each other in a wide range of CF parameters. This shows that the approximate analytical expressions obtained in the present paper can be used generally. Due to length limitations of the paper, only the curves of D_{SS} and D_{SOO} versus CF parameters are given. The curves of D_{SO-SS} and D_{SO-SOO} versus CF parameters are omitted. The detailed calculations show that the results calculated by approximate analytical expressions of D_{SO-SS} and D_{SO-SOO} ((9) and (10)) are also in good agreement with those by CDM in a wide range of CF parameters.

4. Summary

By analyzing the characteristics of magnetic interaction mechanisms, the approximate expressions with undetermined coefficients are obtained. Then the coefficients are determined by comparing the calculated results of CDM and the approximate expressions. Thus, we obtained approximate analytical expressions of ZFS of $^4A_2$ ground state from SS, SOO, and the combined mechanisms for $3d^3$ ions at trigonal symmetry with avoiding the complex derivation process of perturbation formulas. By applying the above approximate expressions to some trigonal $3d^3$ systems, the calculated results by CDM and our approximate expressions are in good agreement with each other. The agreement between the two methods show that the method proposed in this paper is reasonable and reliable.

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