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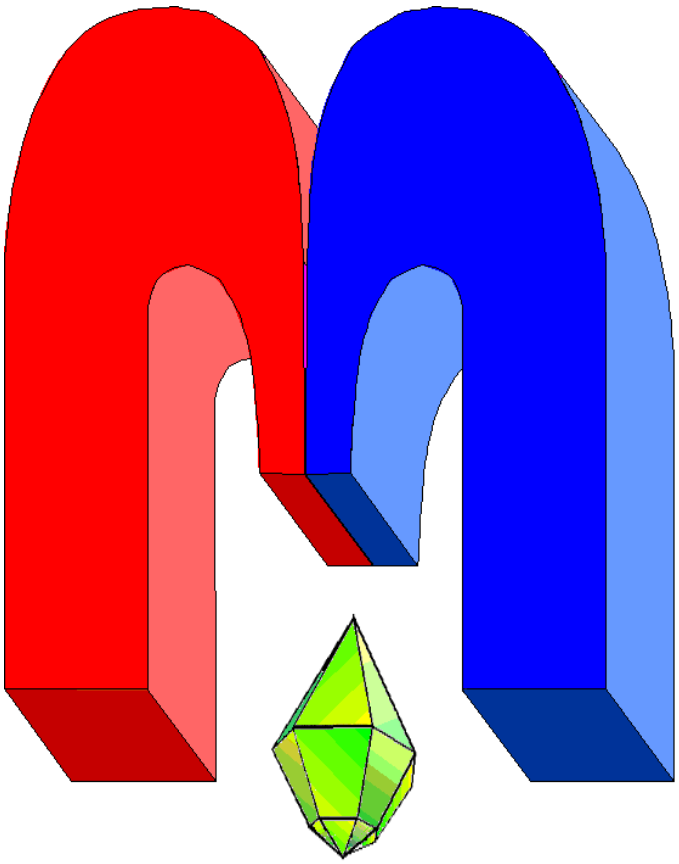

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* Address: "Magnetic Resonance in Solids. Electronic Journal", Kazan Federal University; Kremlevskaya str., 18; Kazan 420008, Russia

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‡ Dedicated to Professor Boris Z. Malkin on the occasion of his 85th birthday

On the theory of spin degeneracy splitting in pairs of Kramers lanthanide ions†

K.K. Pukhov

Moscow Pedagogical State University, Moscow 119435, Russia

E-mail: k_pukhov@mail.ru

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This paper discusses the features of the structure of splitting of energy sublevels of Kramers ion pairs connected by Coulomb interaction. The structure energy sublevels of non-Kramers ion pairs in the presence of a perturbation V is also discussed. Section 2 of this work represent the review of the theoretical part of our previous work [1]. The "Davydov splitting" in cluster composed of two Kramers rare-earth ions was theoretically analyzed for the first time.

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1. Introduction

Ion pair in crystalline matrix is a unique complex for a study of ion-ion interaction, energy transfer, delocalization, upconversion and cross-relaxation processes. Small distance between ions in the ion pair allows strong exchange, magnetic dipole-dipole, and electric multipole ion-ion interactions [1], which can lift degeneracy and split levels of the ion pair [1–5]. As a result of ions coupling, the splitting values, due to different types of interactions, can be varied in wide kHz – GHz frequency interval [4]. Different experimental methods were used to study ion-ion coupling in the pair and quartet centers [1–6]. Electron paramagnetic resonance (EPR) was found to be effective to study spin-spin interaction and splitting in the ground $^4I_{9/2}$ state of Nd^{3+} [6]. Absorption and fluorescence spectroscopy, based, in particular, on narrowband laser excitation, is useful for such a study of the excited states [3, 4, 7]. Coherent ion-ion interaction takes place during the optical dephasing time, hence the photon echo technique is perspective for study of strong coupling in ion pair with very high frequency resolution [8,9]. This study is based on the article [1]. The main goal of this article is to demonstrate the fundamental difference in the nature of the splitting structure of energy sublevels of Kramers ion pair coupled by Coulomb interaction to that of non-Kramers ion pair.

Section 2 of this work represent the review of the theoretical part of the work [1], while Section 3 is a brief revise of the special case of non-Kramers ion pair.

2. Theory of Structure energy sublevels of Kramers ion pair coupled by Coulomb interaction

2.1. Structure of energy sublevels of Kramers ion pair coupled by Coulomb interaction

Energy levels of Kramers ions are at least twofold degenerate in absence of a magnetic field. Let us denote states of a Kramers doublet as ξ and $\bar{\xi}$. These states have the following properties

$$\hat{\theta}\xi = \bar{\xi}, \quad \hat{\theta}\bar{\xi} = -\xi, \tag{1}$$

†This paper is dedicated to Professor Boris Z. Malkin, who made a significant contribution to the field of magnetic radio spectroscopy in Kazan University, on the occasion of his 85th birthday.

where $\hat{\theta}$ is the time-reversal operator [2]. Excited energy level of a pair noninteracting a and b ions have eight-fold degeneracy [5] with states

$$\begin{aligned} &\varphi_1 = \xi_{1a}\xi_{2b}, \quad \varphi_2 = \xi_{2a}\xi_{1b}, \quad \varphi_3 = \bar{\xi}_{1a}\bar{\xi}_{2b}, \quad \varphi_4 = \bar{\xi}_{2a}\bar{\xi}_{1b}, \\ &\varphi_5 = \bar{\xi}_{1a}\xi_{2b}, \quad \varphi_6 = \xi_{2a}\bar{\xi}_{1b}, \quad \varphi_7 = \xi_{1a}\bar{\xi}_{2b}, \quad \varphi_8 = \bar{\xi}_{2a}\xi_{1b}. \end{aligned} \tag{2}$$

Here subscripts $1a$ ($1b$) and $2a$ ($2b$) designate ground and excited states of ion a (b), respectively. In states φ_1, φ_3, φ_5, φ_7 (φ_2, φ_4, φ_6, φ_8) the ion b (a) is excited and ion a (b) is nonexcited. In the case under consideration, the ground level is a lowest Stark level of $^4\mathrm{I}_{9/2}$ manifold and excited level is a lowest Stark level of the $^4G_{5/2}$ manifold of Nd^{3+} ion.

Here we examine the splitting of eight-fold degenerate level of similar Kramers ions under Coulomb interionic interaction

$$V = \sum_{i_a, j_b} \frac{e^2}{|\mathbf{r}_{i_a} - \mathbf{r}_{j_b}|} = \sum_{\alpha\beta} G_{\alpha\beta} V_\alpha^{(a)} V_\beta^{(b)}, \tag{3}$$

where $\mathbf{r}_{i_a}$ ($\mathbf{r}_{j_b}$) is radius vector of 4f-electron of ion a (b). Right side of Eq. (3) is expansion of Coulomb interaction V into multipoles. Operators $V_\alpha^{(a)}$ ($V_\beta^{(b)}$) depend on electron coordinates of ion a (b). Operators $V_\alpha^{(a)}$ ($V_\beta^{(b)}$) are time-even. This means that they have property [2] (below the upper indices a and b are omitted for simplicity)

$$\hat{\theta} V_\alpha \hat{\theta}^{-1} = V_\alpha^+, \tag{4}$$

where operator V_α^+ is Hermitian-conjugate with V_α.

From Eqs. (1) and (4) one obtains the following properties of matrix elements [2]

$$\langle \xi_2 | V_\alpha | \bar{\xi}_2 \rangle = \langle \xi_1 | V_\alpha | \bar{\xi}_1 \rangle = 0, \ \langle \bar{\xi}_1 | V_\alpha | \xi_2 \rangle = -\langle \bar{\xi}_2 | V_\alpha | \xi_1^{(1)} \rangle, \ \langle \bar{\xi}_1 | V_\alpha | \bar{\xi}_2 \rangle = \langle \xi_2 | V_\alpha | \xi_1 \rangle. \tag{5}$$

Let us introduce states

$$\begin{aligned} &\psi_1 = (\varphi_1 + \varphi_2 + \varphi_3 + \varphi_4)/2, \quad \psi_5 = (\varphi_1 - \varphi_2 + \varphi_3 - \varphi_4)/2, \\ &\psi_2 = (\varphi_5 + \varphi_6 - \varphi_7 - \varphi_8)/2, \quad \psi_6 = (\varphi_5 - \varphi_6 - \varphi_7 + \varphi_8)/2, \\ &\psi_3 = (\varphi_5 + \varphi_6 + \varphi_7 + \varphi_8)/2, \quad \psi_7 = (\varphi_5 - \varphi_6 + \varphi_7 - \varphi_8)/2, \\ &\psi_4 = (\varphi_1 + \varphi_2 - \varphi_3 - \varphi_4)/2, \quad \psi_8 = (\varphi_1 - \varphi_2 - \varphi_3 + \varphi_4)/2. \end{aligned} \tag{6}$$

Wave functions ψ_1, ψ_2, ψ_3 and ψ_4 (ψ_5, ψ_6, ψ_7 and ψ_8) are symmetric (antisymmetric) with respect to the ion interchange $a \Leftrightarrow b$. We must note that the interaction V is symmetric with respect to ion interchange $a \Leftrightarrow b$. Consequently, matrix elements

$$V_{ij} \equiv \langle \psi_i | V | \psi_j \rangle = 0, \quad (i = 1, 2, 3, 4; \quad j = 5, 6, 7, 8). \tag{7}$$

Taking into account the Eqs. (5)-(7), we obtain that in the representation ψ_i the operator V is given by the following matrix:

$$\{h_{ij}\} = E_0 + \begin{pmatrix} \hat{F} & 0 \\ 0 & -\hat{F} \end{pmatrix}, \tag{8}$$

where $E_0 = \langle \xi_{1a}\xi_{2b}|V|\xi_{1a}\xi_{2b}\rangle$ and $\hat{F}$ is 4×4 matrix. Matrix elements $F_{ij} = \langle \psi_i|V|\psi_j\rangle$ can be expressed in terms of matrix elements $V_{kl} \equiv \langle \varphi_k|V|\varphi_l\rangle$ as

$$\begin{gathered} F_{11} = V_{12} + (V_{14} + V_{41})/2, \quad F_{12} = -(V_{18} + V_{81})/2 + (V_{16} + V_{61})/2, \\ F_{13} = (V_{18} - V_{81})/2 + (V_{16} + V_{61})/2, \quad F_{14} = -(V_{14} - V_{41})/2, \\ F_{22} = V_{56} - (V_{58} + V_{85})/2, \quad F_{23} = -(V_{58} - V_{85})/2, \\ F_{24} = (V_{18} - V_{81})/2 - (V_{16} - V_{61})/2, \quad F_{33} = V_{56} + (V_{58} + V_{85})/2, \\ F_{34} = (V_{18}V_{81})/2 + (V_{16} + V_{61})/2, \quad F_{44} = V_{12} - (V_{14} + V_{41})/2. \end{gathered} \tag{9}$$

As it follows from Eq. (8), electrostatic coupling V splits the 8-fold degenerate level in general case into 8 sublevels with energies $E_0 \pm E_i$ ($i = 1, 2, 3, 4$), where E_i are eigenvalues of the matrix $\hat{F}$ and E_0 is the overall shift of the sublevels. In other words, for every sublevel with energy $E_0 + E_i$ there is a sublevel with energy $E_0 - E_i$. Notice that in the case when the coupling V is exchange or magnetic interaction, the operators $V^{(a)}$ and $V^{(b)}$ are time-odd operators. As result, the level splitting structure will be different from that caused by electrostatic coupling [5].

2.2. Estimation of the splittings.

In case of dipole-dipole electrostatic interactions ($V^{(dd)}$), the value of the splitting (Δ_{dd}) will be of the order of $d_a d_b/R^3$, where $d_a = |\langle \xi_{1a}|\mathbf{d}_a|\xi_{2a}\rangle|$ and $d_a = e\sum_i \mathbf{r}_{ia}$ is operator of dipole momentum for 4f-electrons, R is ion-ion distance (for M centers in CaF_2, $R = R_{\min} = 0.385\,\text{nm}$). For similar ions, $d_a = d_b$. The value d_a^2 can be estimated as $e^2 S(J, J')/(2J+1)(2J'+1)$, where $S(J, J')$ is the line strength of the induced electric dipole transition from the ground manifold J to the excited manifold J' partially allowed by odd part of crystal field. This leads to

$$\Delta_{dd} \sim \frac{e^2 S(J, J')}{(2J+1)(2J'+1)R_{\min}^3}. \tag{10}$$

For the Nd^{3+} transitions from the $^4I_{9/2}$ ground to other multiplets, the value $S/(2J+1)(2J'+1)$ for crystals is estimated $\sim 10^{-20}\,\text{cm}^2$ or less [10]. Therefore, we obtain $\Delta_{dd} \sim 0.1\,\text{cm}^{-1}$ for excited level splitting due to dipole-dipole coupling in the Nd^{3+}-Nd^{3+} pair in CaF_2. Notice that when the $V^{(dd)}$ interaction gives dominant contribution to the overall splitting, the splitting value must correlate with the line strength $S(J, J')$, which usually has induced electric dipole nature. However, this assumption is not confirmed in our case.

For quadrupole-quadrupole interaction

$$\Delta_{qq} \sim \frac{e^2 \left\langle r^2 \right\rangle^2}{R^5} \left| \left\langle J \left| U^{(2)} \right| J' \right\rangle \right|^2, \tag{11}$$

where $\langle r^2 \rangle$ is the mean value of square of the 4f-electron radius averaged over the 4f-wave-function, $\langle J|U^{(2)}|J'\rangle$ is second-rank reduced matrix element for transition from ground manifold $^{2S+1}L_J$ to exited manifold $^{2S'+1}L'_{J'}$. Substituting $\langle r^2 \rangle = 1.001$ a.u. [11] and $\left|\langle {}^4I_{9/2}|U^{(2)}|{}^4G_{5/2}\rangle\right|^2 = 0.8779$ [12] in Eq. (11) leads to very high quadrupole-quadrupole splitting $\Delta_{qq} \sim 10\,\text{cm}^{-1}$ for Nd^{3+}-Nd^{3+} pair.

Note that the experimental 1-5 cm^{-1} level splittings occur specifically for $^4I_{9/2} \rightarrow {}^4G_{5/2}$ transitions, where the square of reduced matrix element $\langle {}^4I_{9/2}|U^{(2)}|{}^4G_{5/2}\rangle^2$ is one of the highest for different transitions in Nd^{3+} ion and equal to 0.8779, whereas these are less than 0.1 for all other Nd^{3+} transitions [12].

The magnetic dipole-dipole and exchange spin-spin interactions cause splittings of the order $0.1\,\text{cm}^{-1}$ for ground $^4I_{9/2} \times {}^4I_{9/2}$ state level of coupled Nd^{3+}-Nd^{3+} pair [6,13]. There is no good

reason to assume that these interactions will cause higher-order splittings for excited ${}^4I_{9/2}\times{}^4G_{5/2}$ manifold.

2.3. Quadrupole-quadrupole splitting.

Above rough estimations give support to an expectation that quadrupole-quadrupole interaction dominates in the excited state fine level splitting of strongly coupled Nd^{3+}- Nd^{3+} ion pair. Let us investigate the quadrupole-quadrupole interaction in detail. Using the expression [14,15] for the expansion of Coulomb potential in spherical harmonics, the quadrupole-quadrupole interaction ($V^{(qq)}$) between a pair of similar rare-earth ions can be written as

$$V^{(qq)} = C_{qq} \sum_{m=-2}^{2} G_m V_m^{(a)} V_{-m}^{(b)}. \tag{12}$$

Here

$$C_{qq} = \frac{e^2\langle r^2\rangle}{R^5} \left|\langle L_1 S_1 J_1 | U^{(2)} | L_2 S_2 J_2\rangle\right|^2 \tag{13}$$

is the constant of quadrupole-quadrupole interaction; $G_m = G_{-m} = 7\times 32/[(2+m)!(2-m)!5]$; matrix elements of operators V_m in the $|JM\rangle$ representation are directly proportional to $3j$-symbol:

$$\langle JM|V_m|J'M'\rangle = (-1)^{J_{\max}-M} \begin{pmatrix} J & 2 & J' \\ -M & m & M' \end{pmatrix}; \tag{14}$$

the z-axis for a and b ions are taken to be parallel to the line joining RE ions in pair. In general case, the states ξ and $\bar{\xi}$ are of the form [2]

$$|\xi\rangle = \sum_M C_{JM}|J,M\rangle, \quad |\bar{\xi}\rangle = \sum MC_{JM}^*(-1)^{J-M}|J,-M\rangle. \tag{15}$$

The point symmetry at the Nd^{3+} ions consisting M-center is C_{2v}. In this case, the values of magnetic quantum number M in (15) differ by at least two units because of binary symmetry [2]:

$$\begin{gathered} |\xi_1\rangle = a_1|9/2\rangle + a_2|5/2\rangle + a_3|1/2\rangle + a_4|-3/2\rangle + a_5|-7/2\rangle, \quad (J=9/2), \\ |\bar{\xi}_1\rangle = a_5^*|7/2\rangle + a_4^*|3/2\rangle + a_3^*|-1/2\rangle + a_2^*|-5/2\rangle + a_1^*|-9/2\rangle, \quad (J=9/2), \\ |\xi_2\rangle = b_1|5/2\rangle + b_2|1/2\rangle + b_3|-3/2\rangle, \quad (J=5/2), \\ |\bar{\xi}_2\rangle = b_3^*|3/2\rangle + b_2^*|-1/2\rangle + b_1^*|-5/2\rangle, \quad (J=5/2). \end{gathered} \tag{17}$$

For this reason, $F_{12} = F_{13} = F_{21} = F_{24} = F_{31} = F_{34} = F_{42} = F_{43} = 0$. Besides, all the C_{JM} in (15) can be chosen to be real. This assumption leads to $F_{14} = F_{23} = F_{32} = F_{41} = 0$. As a result, we obtain that states ψ_i are "correct" zero-order eigenstates with eigenvalues $E_0 + \Delta_i$, where

$$\begin{gathered} \Delta_1 = V_{12}^{(qq)} + V_{14}^{(qq)}, \quad \Delta_2 = V_{56}^{(qq)} - V_{58}^{(qq)}, \\ \Delta_3 = V_{56}^{(qq)} + V_{58}^{(qq)}, \quad \Delta_4 = V_{12}^{(qq)} - V_{14}^{(qq)}, \\ \Delta_5 = -\Delta_1, \quad \Delta_6 = -\Delta_2, \quad \Delta_7 = -\Delta_3, \quad \Delta_8 = -\Delta_4. \end{gathered} \tag{18}$$

The quadrupole-quadrupole constant C_{qq} in Eq. (13) is equal to $9.68\,\mathrm{cm}^{-1}$ for Nd^{3+}- Nd^{3+} pair M-centers. We calculated the values of overall splitting (Δ_{qq}) for a variety of wave functions ξ_1 and ξ_2. The calculated values Δ_{qq} lie between zero (for example, for $|\xi_1\rangle = |9/2, 9/2\rangle$ and $|\xi_2\rangle = |5/2, 5/2\rangle$) and $14.92\,\mathrm{cm}^{-1}$ (for $|\xi_1\rangle = |9/2, 1/2\rangle$ and $|\xi_2\rangle = |5/2, 1/2\rangle$). To be specific, we need to know coefficients a_i and b_i in Eqs. (17). Some restrictions on the coefficient a_i

impose the experimental values of g-factor ($g_{xx} = 2.05$, $g_{yy} = 3.35$, $g_{zz} = 2.05$ [6]). Within this restriction, a wide array of coefficients a_i and b_i was looked over for calculation Δ_{qq}. After this treatment, corresponding values Δ_{qq} for examined cases were found to be varied in the smaller region 1–7 cm^{-1}.

3. Theory of the structure of the energy sublevels of non-Kramers ion pairs

The non-Kramers states do not possess the property (1). For them

$$\hat{\theta}\xi = \xi \tag{19}$$

The theory of the structure of the energy sublevels of non-Kramers ion pairs in this work is based on the course of Theoretical Physics of L.D. Landau and E. M. Lifshitz [16]. Let us consider a pair of identical non-Kramers ions a and b located in the crystal at distance R_{ab} from each other.

The ground $|a\rangle$ and the excited $|a'\rangle$ states of the ion (a) are separated by energy E_0, similarly for ion b. The pair has four states: a lower state $|a\rangle|b\rangle \equiv |ab\rangle$ with energy 0, two degenerate states $|a'\rangle|b\rangle \equiv |a'b\rangle$ and $|a\rangle|b'\rangle \equiv |ab'\rangle$ with energy E_0 and an upper state $|a'\rangle|b'\rangle \equiv |a'b'\rangle$ with energy $2E_0$.

In the general case, in the presence of a perturbation V, eigenfunctions and eigenvalues are determined by the secular equation (20) [16]

$$\begin{vmatrix} E_0 + V_{11} - \lambda & V_{12} \\ V_{21} & E_0 + V_{22} - \lambda \end{vmatrix} = 0. \tag{20}$$

Perturbation V removes the degeneracy. The correct functions in the zeroth approximation and the eigenvalues in the first approximation are given by expressions [16]

$$\begin{aligned} |+\rangle &= \frac{1}{\sqrt{2}}\left(1 + \frac{V_{11} - V_{22}}{\Delta}\right)^{1/2}|1\rangle + \frac{1}{\sqrt{2}}\frac{V_{21}}{|V_{21}|}\left(1 - \frac{V_{11} - V_{22}}{\Delta}\right)^{1/2}|2\rangle, \\ |-\rangle &= \frac{1}{\sqrt{2}}\frac{V_{12}}{|V_{12}|}\left(1 - \frac{V_{11} - V_{22}}{\Delta}\right)^{1/2}|1\rangle - \frac{1}{\sqrt{2}}\left(1 + \frac{V_{11} - V_{22}}{\Delta}\right)^{1/2}|2\rangle, \\ E_+ &= E_0 + \frac{1}{2}(V_{11} + V_{22} + \Delta), \\ E_- &= E_0 + \frac{1}{2}(V_{11} + V_{22} - \Delta), \end{aligned} \tag{21}$$

with the splitting

$$\Delta = \sqrt{(V_{11} - V_{22})^2 + 4|V_{12}|^2}. \tag{22}$$

Conclusion.

This work shows that the splitting structure of energy sublevels of non-Kramers ion pairs differs significantly from that of Kramers ion pairs connected by Coulomb interaction.

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