

Rotation of the Tetrahedral Ion in an Octahedral Field

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The matrix element is evaluated for the minimum path of the rotational transfer between two orientationally localized states of the tetrahedral ion dispersed in a cubic ionic crystal. The energy levels derived by the other method using free rotator functions are employed in this evaluation. Three types of orientations T_d , D_{2d} , C_{3v} , have the characteristic region on $\beta_4 - \beta_6$ plane and give smaller value of the matrix element.

I. Introduction

The rotational energy levels of NH_4^+ ion in the cubic crystal of alkali halide were computed in terms of so-called \mathcal{D} -functions or free rotator functions.¹⁾ It was revealed that the levels observed from neutron inelastic scattering²⁾ are due to the orientation with C_{3v} symmetry.

Subsequently, the intensity of neutron scattering was calculated for three types of rotational tunneling system on the basis of orientationally localized states or pocket state.³⁾ It was pointed out that new peaks might be found in $E > 3$ meV. (In fact, the existence of additional levels has been verified recently by a new experiment of neutron scattering.⁴⁾

Here, the relation is investigated between the method of free rotator functions and the approach by pocket states to proceed with more quantitative discussion. In this article, the octahedral field from the crystal lattice is expressed by first two terms in the expansion in Section II. It is possible to calculate the rotational energy states made up by free rotator functions. Next, from a different viewpoint, the tunneling ground states are constructed by localized states and the matrix element for rotational transfer is formulated anew in terms of the energy levels

in Section III. The matrix element is estimated as a function of the 4th and 6th field strengths using the energy gained by first method. In Section IV, conclusion is described.

II. Crystal field and orientation symmetry

The isolated tetrahedral unit (ion or molecule) in host ions or molecules feels the field which depends only on its own orientation, that is, the crystal field. It can be expanded into octahedral function $V_n(\omega)$ as

$$V(\omega) = \sum_n \beta_n V_n(\omega), \quad (2.1)$$

where ω denotes the Euler angles $\{\alpha, \beta, \gamma\}$ which give the orientation of a tetrahedron. The coefficient β_n has a non-zero value solely for $n = 4, 6, 8, 10, \dots$ because of the symmetry of tetrahedron and surrounding lattice. It is confined with first two terms since they contribute to the most significant part. The quantum state of hindered rotation under the octahedral field is gained by solving the eigenvalue problem for the Hamiltonian

$$H = K + V(\omega), \quad (2.2)$$

where K is the rotational kinetic energy. The computed energy will be given in the unit of B , the rotational constant. Thus, the rotational states can be studied for both tunneling ground and librational part as a function

of field strengths β_4 and β_6 .

$$a = \langle i | H | j \rangle, \quad (3.1)$$

Next, let us consider the orientation of a tetrahedral unit in the crystal field. There is a group of characteristic orientations that have an equivalent static energy and can be distinguished from the others within the classical-mechanical point of view. The group of fundamental orientations is classified into four "orientation symmetry"⁵⁾: T_d , D_{2d} , C_{3v} , C_{2v} . Figure 2 in reference 3) depicts equivalent orientations whose Euler angles are shown in Table 1 of reference 6). One of T_d type is a standard orientation where four X-H bonds of the tetrahedral unit XH_4 direct to (111), (1-1-1), (-11-1), (-1-1-1) of the cubic lattice.

III. Tunneling ground states

(a) The distinguishable orientation in an octahedral field : d_n

If the crystal field is quite strong, the ground part of rotational energy levels forms tunnel splitting levels. As a basis for such an orientational state, the highly localized state or pocket state d_n is available. Each type of fundamental orientations consists of N_o equivalent orientations. The rotational transfer from one of them to the other produces the matrix element in the pocket state formalism. The shortest path between distinguishable orientations may give the most important part.

Table 1. Number of equivalent orientations of the tetrahedron in an octahedral field and rotational axis and angle for the shortest transfer between two orientations.

type	N_o	xis	smallest angle	a_0/deg	$\cos a_0$
T_d	2	(001)	90.0		1
D_{2d}	6	(ppq)	62.8	$(2s-1)/4$	
C_{3v}	8	(011)	38.9		$7/9$
C_{2v}	12	(ttu)	33.7		$(2s+1)/8$

$$\begin{aligned} p^2 &= (5+2s)/17, & q^2 &= (7-4s)/17, & s &= (2)^{1/2} \\ t^2 &= (5-2s)/17, & u^2 &= (7+4s)/17, \end{aligned}$$

Table 1 shows the axis and angle for such a rotational path as well as the number N_o .

The matrix element for the rotational Hamiltonian (2.2) is expressed as

Where $|i\rangle$ or $|j\rangle$ is one of N_o pocket states. By solving the eigenvalue problem, the rather simple structure of orientational levels is gained as shown in Table 2. The level is specified by the symmetry under

Table 2. Orientational levels of the tetrahedral unit.

	type	levels	eigenvalue/a	degeneracy
T_d	E ₁	(A ₁)	1	1
	E ₂	(A ₂)	-1	1
F_{2d}	E ₁	(A ₁)	4	1
	E ₂	(T ₂)	0	3
	E ₃	(E)	-2	2
C_{3v}	E ₁	(A ₁)	3	1
	E ₂	(T ₁)	1	3
	E ₃	(T ₂)	-1	3
	E ₄	(A ₂)	-3	1
C_{2v}	E ₁	(A ₁)	4	1
	E ₂	(T ₁)	2	3
	E ₃	(T ₂)	0	3
	E ₄	(A ₂)	-2	5

group O. It should be noted that C_{3v} and C_{2v} have a very similar level structure. However, the next procedure is necessary because the light proton atoms in XH_4 have a nature of the quantum-mechanical tunneling motion.

(b) The distinguishable orientation in an tetrahedral field : $d(m)$

When four protons in a tetrahedron are labeled, it is possible to construct twelve similar orientations using operations under tetrahedral symmetry. This approach in a tetrahedral field has been introduced initially by Nagamiya⁷⁾ and revised by Hüller et al^{8,9)}. It is quite easy to extend this method to the case of an octahedral field.

Combining the above two categories of localized states d_n and $d(m)$, we can make $12N_o$ states $d_n(m)$ as a basis. The same matrix element as Eq. (3.1) is employed to solve the eigenvalue problem in terms of $d_n(m)$. The energy levels for each type are seen in Tables 3 (a) - (c). The symmetry under OO is given in the second column. The energy difference between the lowest two levels is fixed at the experimental value for the NH_4^+ ion in solid KBr²⁾ and the other energy is also

Table 3. Tunneling levels of the tetrahedral ion in an octahedral field.

(a) T_d ($a = -0.1325$ meV)

levels	eigenvalue/ a	E/meV	degeneracy
$E_1 (\bar{A}_1 A_1)$	6	0.0	5
$E_2 (\bar{T}_1 T_1)$	2	0.530	9
$E_3 (\bar{E} E)$	0	0.795	4
$E_4 (\bar{T}_2 T_2)$	-2	1.060	9
$E_5 (\bar{A}_2 A_2)$	-6	1.590	5

(b) D_{2d} ($a = -0.1840$ meV)

levels	eigenvalue/ a	E/meV	degeneracy
$E_1 (\bar{A}_1 A_1)$	8	0.0	5
$E_2 (\bar{T}_1 T_1)$	$1+c$	0.530	9
$E_3 (\bar{E} E, \bar{T}_2 T_2)$	2	1.105	4,9
$E_4 (\bar{A}_2 T_2, \bar{E} T_2, \bar{T}_2 A_2, \bar{T}_2 E)$	0	1.474	15,6,3,6
$E_5 (\bar{T}_1 T_2, \bar{T}_2 T_1)$	-2	1.842	9,9
$E_6 (\bar{T}_1 T_1)$	$1-c$	2.049	9
$E_7 (\bar{A}_1 E, \bar{E} A_1)$	-4	2.211	10,2

$$c = (17)^{1/2}$$

(c) C_{3v} ($a = -1.2090$ meV)

levels	eigenvalue/ a	E/meV	degeneracy
$E_1 (\bar{A}_1 A_1)$	3	0.0	5
$E_2 (\bar{T}_1 T_1)$	$(1+c)/2$	0.530	9
$E_3 (\bar{T}_2 E, \bar{E} T_2)$	2	1.209	6,6
$E_4 (\bar{T}_2 T_2)$	$(-1+c)/2$	1.739	9
$E_5 (\bar{A}_2 T_1, \bar{T}_1 T_2)$	1	2.418	15,3
$E_6 (\bar{T}_1 T_2, \bar{T}_2 T_1, \bar{E} E)$	0	3.626	9,9,4
$E_7 (\bar{A}_1 T_2, \bar{T}_2 A_1)$	-1	4.835	15,3
$E_8 (\bar{T}_1 T_1)$	$(1-c)/2$	5.514	9
$E_9 (\bar{T}_1 E, \bar{E} T_1)$	-2	6.044	6,6
$E_{10} (\bar{T}_2 T_2)$	$(-1-c)/2$	6.723	9
$E_{11} (\bar{A}_2 A_2)$	-3	7.253	5

$$c = (17)^{1/2}$$

evaluated. Symmetry C_{2v} has the same levels as C_{3v} except for the degeneracy of the highest level.

The smallest rotational angle α_0 in Table 1 decreases in the order of $T_d, D_{2d}, C_{3v}, C_{2v}$. This reduction of α_0 corresponds to the increase in N_0 . It seems to be reasonable that the separation of tunneling levels increases in the above order if the potential barrier is the

same for the rotation by angle α_0 . In other words, for the fixed energy difference, the potential barrier enhances in the same order. Therefore, the tetrahedron in C_{3v} or C_{2v} is subjected to the fairly stronger field than in the others.

Now, the eigenstate is formed in terms of localized states. When it is given as

$$|m\rangle = \sum_i s_{i,m} |i\rangle \quad (3.2)$$

the matrix element a in Eq. (3.1) is rewritten as

$$a = \sum_m s_{i,m} s_{j,m}^* E_m, \quad (3.3)$$

Where E_m is the energy of m -th level. The off-diagonal component a as well as the diagonal one b is calculated in terms of the energy E_m . Table 4 gives the explicit expressions.

Table 4. Matrix element given in Eq. (3.3) using the eigenstates of tunneling levels for the off-diagonal part (a) and the diagonal part (b).

T_d	$a : (E_1 - E_5)/24 + (E_2 - E_4)/8$ $b : (E_1 + E_5)/24 + (E_2 + E_4)(3/8) + E_3/6$
D_{2d}	$a : (E_1 - 2E_7)/72 + [(1+c)E_2 - (-1+c)E_6]/64$ $+ E_3(13/288) - E_5/16$ $b : (E_1 + 4E_7)/72 + (E_2 + E_6)/8$ $+ E_3(13/72) + E_5/4 + E_4/4$
C_{3v}	$a : (E_1 - E_{11})/96 + [(1+c)(E_2 - E_{10}) + (-1+c)(E_4 - E_8)]/64$ $+ (E_3 - E_9)/12 + (E_5 - E_7)/48$ $b : (E_1 + E_{11})/96 + (E_2 + E_{10} + E_4 + E_8)(3/32)$ $+ (E_3 + E_9)/8 + (E_5 + E_7)/16 + E_6(11/48)$

$$c = (17)^{1/2}$$

When the energy of tunneling levels in Tables 3 (a) – (c) is used as E_m in Eq. (3.3), the right-hand side of the equation in the table becomes exactly a . Instead of it, the energy computed from Eq. (2.2) is adapted, the matrix element a for the tunneling levels is estimated as a function of β_4 and β_6 . The contour map is calculated with J truncated at 14. (J is a rotational quantum number.) The lower left region in Fig. 1 (a) corresponds to T_d symmetry.¹⁾ It has a quite small negative value as is expected. The T_d type of tunneling split-

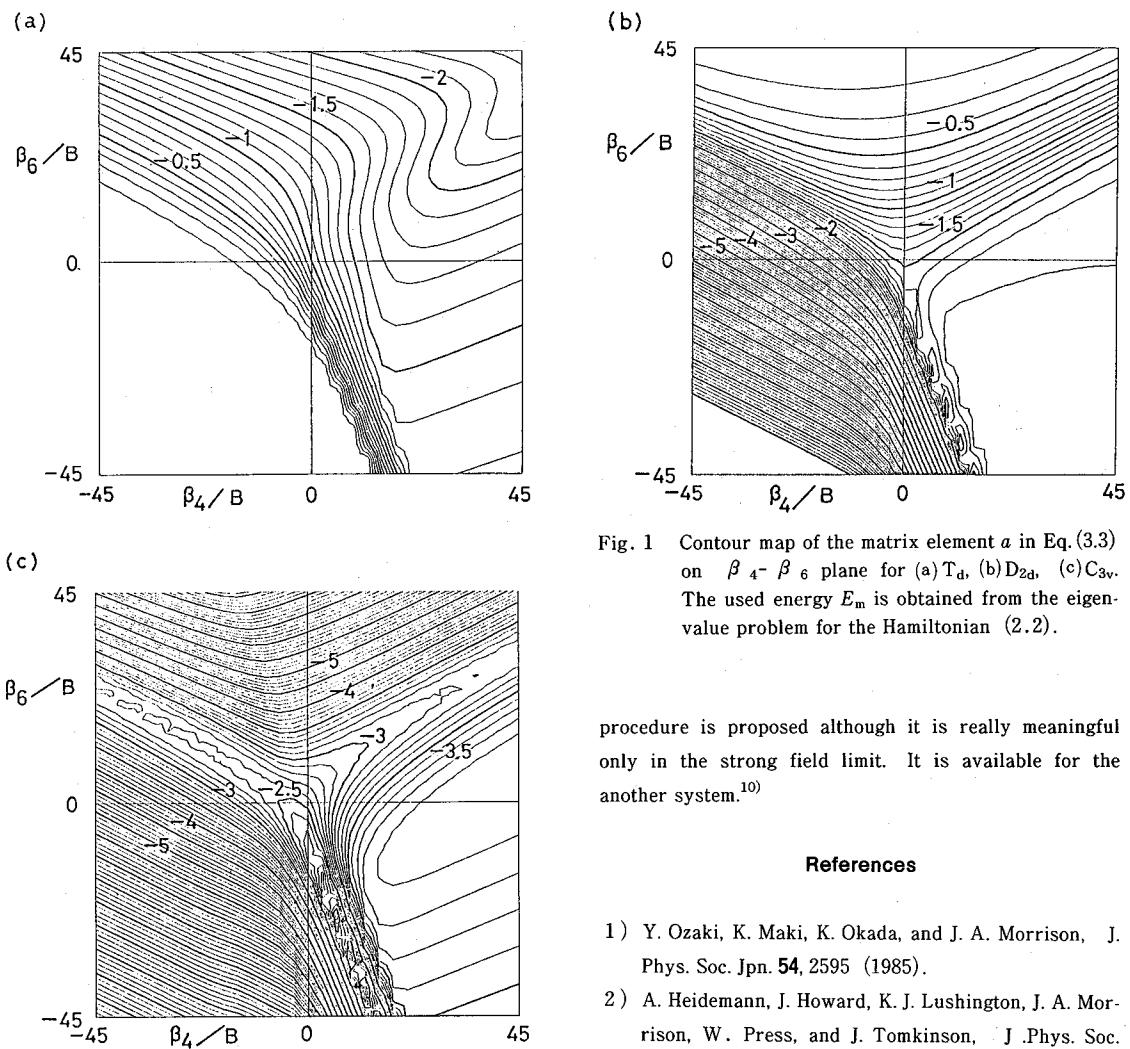


Fig. 1 Contour map of the matrix element a in Eq. (3.3) on $\beta_4/B - \beta_6/B$ plane for (a) T_d , (b) D_{2d} , (c) C_{3v} . The used energy E_m is obtained from the eigenvalue problem for the Hamiltonian (2.2).

procedure is proposed although it is really meaningful only in the strong field limit. It is available for the another system.¹⁰⁾

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ting is realized in that region. In Fig. 1 (b), D_{2d} symmetry yields in upper region and the value becomes small absolutely. The right part of Fig. 1 (c) does not give so large value which forms the tunneling levels with C_{3v} symmetry

IV. Conclusion

The extremely localized state has a tiny width about rotational angles. The matrix element in Eq. (3.1) should be estimated from the pocket state with definite width. However, the overlap is very little between one orientation and an adjacent one. Therefore, the estimate of matrix element is subtle problem and it is hard to derive it with high precision. In this article, an alternative