PHYSICAL REVIEW B VOLUME 36, NUMBER 1 1 JULY 1987

Calculation of the energy spectrum and eigenfunctions for a model system of interacting $X\mathrm{H}_3$ groups in the low-temperature limit

J. Peternelj and I. Jenčič
Institute "J. Stefan," University E. Kardelj, Ljubljana, Yugoslavia

B. Cvikl
Faculty of Engineering, University of Maribor, Maribor, Yugoslavia
and Institute "J. Stefan," University of E. Kardelj,
Ljubljana, Yugoslavia

M. M. Pintar
Department of Physics, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

(Received 1 July 1986; revised manuscript received 22 January 1987)

A model system of coupled $X\mathrm{H}_3$-type torsional oscillators embedded in a crystal field of a definite symmetry, interacting with an externally applied dc magnetic field and among themselves, is considered. The interaction among the neighboring $X\mathrm{H}_3$ oscillators is approximated by the octupole-octupole term in the general multipole expansion of the electrostatic energy of the two rigid charge distributions. An approximate, reasonably accurate description of the lowest-energy eigenstates is obtained as follows. All classical configurations of the $X\mathrm{H}_3$ groups corresponding to a minimum of the potential energy of the system are found and Gaussian wave packets localized at each of these minima are constructed. The low-temperature limit of the energy spectrum is calculated employing linear superpositions of wave packets as indicated by the symmetry of the problem. Finally, an approach based on the general WKB expansion around classical trajectories corresponding to the real and imaginary time is indicated.

I. INTRODUCTION

The rotational tunneling of atomic groups such as CH_3, NH_4 or CH_4 embedded in solid lattices has been studied extensively by inelastic neutron scattering[1] and NMR.[2] Detailed experimental information and several theoretical calculations have been published. It has been demonstrated that in most situations the ground state of the torsional oscillator CH_3 is split into a symmetric, A, and doubly degenerate antisymmetric state E. A and E denote the irreducible representations of the point group C_3.[3] The energy difference $E_E - E_A \equiv \hbar\omega_T$ has been measured in lattices in which the reorientation of the CH_3 group is hindered strongly so that $\omega_T/2\pi$ is of the order of 10 kHz only. In other lattices with weaker hindering potential $\omega_T/2\pi$ was found to be up to hundreds of GHz.[4] Most of these experimental studies were limited, in NMR measurements by the rf frequency range which could be covered or in the inelastic neutron scattering measurements by the instrumental resolution. The characteristic of the single-particlelike CH_3 ground-state rotational tunneling spectrum as consisting of one frequency has been established. In addition, the phonon-torsion interaction has been examined and the origin of the temperature dependence of ω_T studied.[5] Since the CH_3 ground-state tunneling spectrum has been reported as consisting of a single tunneling frequency, most experiments have been set up to look for just that. However, recent experimental study of the CH_3 tunneling in $\mathrm{Ge(CH_3)_4}$ and $\mathrm{Si(CH_3)_4}$ (Ref. 6) demonstrated that at temperatures around 30 K the CH_3 tunneling spectrum is not as simple as predicted.

It was this experimental observation that stimulated the present calculation of the tunneling spectrum of an ensemble of interacting $X\mathrm{H}_3$ groups embedded in crystal lattices. Because of the lack of proper crystallographic information concerning the structure of $\mathrm{Ge(CH_3)_4}$ or $\mathrm{Si(CH_3)_4}$ and to simplify the calculations we considered a model system where the $X\mathrm{H}_3$ groups form a rectangular lattice. We treat the $X\mathrm{H}_3$ group as a solid body; i.e., with the atoms "rigidly fixed." This means that a single angular variable is needed for the description of such a motion. Likewise, the crystal-field potential at the site of each $X\mathrm{H}_3$ group is defined as a function of a single angle determining the orientation of the group with respect to the lattice and having the usual threefold periodicity.[7]

II. FORMULATION OF THE PROBLEM

The system under consideration is represented as a collection of $X\mathrm{H}_3$ torsional oscillators embedded in a solid matrix. Even as such, the system is far too complex to be treated in all details, and consequently the following approximations are made.

(1) The $X\mathrm{H}_3$ groups are assumed to form a rectangular lattice with the respective lattice constants denoted as l_1, l_2 and l_3.

(2) Only the dynamics of the $X\mathrm{H}_3$ groups is being considered.

(3) The electronic and vibrational degrees of freedom of

the XH$_3$ groups are assumed to be frozen out.

(4) The effect of the rest of the lattice on the motion of the XH$_3$ groups is represented through the introduction of a mean crystal field $V(\mathbf{R}_n;\alpha_n,\beta_n,\gamma_n)$ defined at the site of each group. Here $\mathbf{R}_n$ is the equilibrium position of the n-th group. The Euler angles $(\alpha_n,\beta_n,\gamma_n)$ determine its orientation with respect to the coordinate system fixed in the lattice.

In the spirit of the above approximations and in view of the purpose of our calculation as outlined in the introduction, the relevant Hamiltonian of the system is

$$\mathcal{H}=\mathcal{H}_Z+\mathcal{H}_{0T}+\mathcal{H}_{\mathrm{TT}} . \tag{2.1}$$

The various terms appearing in the above equation are defined as follows:

$$\mathcal{H}_Z=-\hbar\omega_{0L}\sum_{n=1}^{N} I_{zn} , \tag{2.2}$$

where ω_{0L} is the Larmor frequency of the protons in the external magnetic field and I_{zn} is the z component of the total spin operator of the nth group XH$_3$. In what follows, it will be assumed that the external dc magnetic field $\mathbf{H}_0$ is parallel to the z axis of the lattice-fixed coordinate system.

The torsional Hamiltonian is approximated by

$$\mathcal{H}_{0T}=\sum_{n=1}^{N}\left[-\frac{\hbar^2}{2J}\frac{d^2}{d\gamma_n^2}+V_3\{1-\cos[3(\gamma_n-\delta_n)]\}\right], \tag{2.3}$$

where J is the moment of inertia of the XH$_3$ group around its symmetry axis, and δ_n is a constant phase factor which is left unspecified for the time being. The torsion-torsion interaction is defined as a term in the multipole expansion of the electrostatic interaction of two rigid charge distributions. For the purpose of this calculation it is assumed that the XH$_3$ groups are electrically neutral. In particular, for the CH$_3$ groups we take the following point charge distribution

$$q(\mathrm{C})=-3q ,$$

$$q(\mathrm{H1})=q(\mathrm{H2})=q(\mathrm{H3})=q\equiv 0.20\ |e_0| ,$$

where e_0 is the elementary charge, and $\Sigma_x q(x)=0$. The CH$_3$-group–fixed coordinate system shown in Fig. 1 is defined with the parameters given in Table I. Here d is the proton-proton distance (which is approximately 1.7 Å) and the carbon atom is situated in the center of a regular tetrahedron. The value of κ^2 is thus equal to $\frac{1}{24}$. The leading term in the above-mentioned multipole expansion of the electrostatic interaction of two CH$_3$ groups, which depends on the relative orientation of the interacting groups, is the octupole-octupole interaction, resulting in the following expression for the torsion-torsion interaction,

$$\mathcal{H}_{\mathrm{TT}}=\tfrac{1}{2}V_3\sum_{n\neq n'}\{g_{n,n'}^{(+)}(\alpha_n,\beta_n;\alpha_{n'},\beta_{n'})\cos[3(\gamma_n+\gamma_{n'})] + g_{n,n'}^{(-)}(\alpha_n,\beta_n;\alpha_{n'},\beta_{n'})\cos[3(\gamma_n-\gamma_{n'})]\} . \tag{2.4}$$

The coupling constants $g_{n,n'}^{(\pm)}$ are given as

$$g_{n,n'}^{(\pm)}=\mp\tfrac{5}{192}\left[\frac{e^2/R_{n,n'}}{V_3}\right]\left[\frac{d}{R_{n,n'}}\right]^6 \times(A_\pm^3+18A_\pm^2B_\pm+\tfrac{111}{2}A_\pm B_\pm^2+41B_\pm^3) , \tag{2.5}$$

$$A_\pm\equiv(1\mp\cos\beta_n\cos\beta_{n'})\cos(\alpha_n-\alpha_{n'}) +(1\pm\cos\beta_n\cos\beta_{n'})\sin(\alpha_n+\alpha_{n'}) , \tag{2.6a}$$

$$B_\pm\equiv\pm\sin\beta_n\sin\beta_{n'} , \tag{2.6b}$$

and $R_{n,n'}$ is the distance between the centers of the equilateral triangles formed by the protons belonging to nth and the n'th CH$_3$ group, respectively. The Euler angles β_n, $\beta_{n'}$ are measured with respect to the line joining the two interacting groups and we will further illustrate the use of expression (2.4) later on when we discuss specific examples.

TABLE I. Parameters defining the CH$_3$-group–fixed coordinate system shown in Fig. 1.

ρ_i	x	y	z
ρ(C)	0	0	$d\kappa$
ρ(H1)	0	$d\sqrt{3}/3$	0
ρ(H2)	$-d/2$	$-d\sqrt{3}/6$	0
ρ(H3)	$d/2$	$-d\sqrt{3}/6$	0

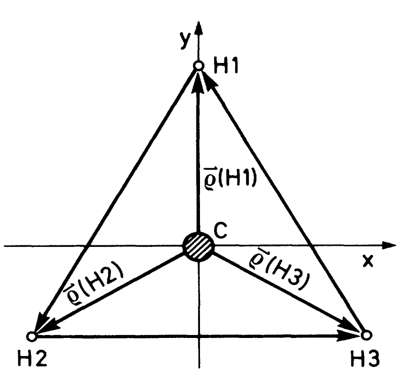

FIG. 1. XH$_3$-group–fixed coordinate system for the calculation of the electrostatic interaction.

III. MANY-PARTICLE SCHRÖDINGER EQUATION

The Hamiltonian (2.1) can be written as

$$\mathcal{H}=\mathcal{H}_Z-\frac{\hbar^2}{2J}\nabla^2+V(\gamma) , \tag{3.1}$$

where $\boldsymbol{\gamma}$ is the N-dimensional Euclidean vector $(\gamma_1, \gamma_2, \ldots, \gamma_N)$,

$$\nabla \equiv \left[\frac{\partial}{\partial \gamma_1}, \frac{\partial}{\partial \gamma_2}, \ldots, \frac{\partial}{\partial \gamma_N} \right] ,$$

and the potential term $V(\boldsymbol{\gamma})$ is defined by

$$V(\boldsymbol{\gamma}) = \sum_{n=1}^{N} V_3 \{ 1 - \cos[3(\gamma_n - \delta_n)] \} + \mathcal{H}_{\mathrm{TT}}(\boldsymbol{\gamma}) . \tag{3.2}$$

The solutions of the Schrödinger equation corresponding to the Hamiltonian (3.1), can be written as a product of spin functions and functions depending only on the angular variables $\boldsymbol{\gamma}$. Correspondingly, the energy is written as a sum of Zeeman energy and torsional energy E_T. The latter is determined by

$$\left[-\frac{\hbar^2}{2J} \nabla^2 + V(\boldsymbol{\gamma}) \right] \Phi(\boldsymbol{\gamma}) = E_T \Phi(\boldsymbol{\gamma}) . \tag{3.3}$$

In order to analyze the solutions of Eq. (3.3), let us recall that quantum mechanics is essentially a theory of small fluctuations around classical trajectories.[8] Consequently, we expand Eq. (3.3) in terms of small fluctuations $\boldsymbol{\eta}$ around a given periodic classical orbit $\boldsymbol{\gamma}_c(t)$ which is a solution of the classical equations of motion,

$$J \ddot{\boldsymbol{\gamma}}_c = -\nabla V(\boldsymbol{\gamma}_c) , \tag{3.4}$$

where $\dot{\boldsymbol{\gamma}}_c \equiv d\boldsymbol{\gamma}_c / dt$. Applying the formalism presented in Ref. 9. we write

$$\boldsymbol{\gamma} = \boldsymbol{\gamma}_c(t(q)) + \sum_{a=2}^{N} \hat{\mathbf{n}}_a \eta_a . \tag{3.5}$$

We also note that in the quantum-mechanical context the time t is introduced only as a geometrical parameter of the corresponding wave function in configuration space. Therefore, $t(q)$ as introduced in (3.5) is simply a function which determines the parametrization of the curve $\boldsymbol{\gamma}_c$, and the parameter q is appropriately called the collective variable. η_a are the fluctuation variables which describe the deviations from $\boldsymbol{\gamma}_c$ and are assumed to be small. $\hat{\mathbf{n}}_a(t(q))$ is a set of orthonormal unit vectors which are orthogonal to the classical path at q, i.e.,

$$\begin{aligned} \hat{\mathbf{n}}_a \cdot \dot{\boldsymbol{\gamma}}_c &= 0 , \\ \hat{\mathbf{n}}_a \cdot \hat{\mathbf{n}}_b &= \delta_{a,b} , \end{aligned} \tag{3.6}$$

with $a,b = 2.3, \ldots, N$, and they satisfy the completeness relation

$$\frac{(\dot{\boldsymbol{\gamma}}_c)_n (\dot{\boldsymbol{\gamma}}_c)_m}{\dot{\boldsymbol{\gamma}}_c^2} + \sum_{a=2}^{N} (\hat{\mathbf{n}}_a)_n (\hat{\mathbf{n}}_a)_m = \delta_{n,m} , \tag{3.7}$$

with $n,m = 1,2, \ldots, N$. Using the above definitions, a computation shows that

$$-i\hbar\nabla = -i\hbar \left[\frac{\dot{\boldsymbol{\gamma}}_c}{\dot{\boldsymbol{\gamma}}_c^2 - \ddot{\boldsymbol{\gamma}}_c \cdot \boldsymbol{\eta}} \right] \left[\frac{1}{t'} \frac{\partial}{\partial q} - \sum_{a,b} \Gamma_{a,b} \eta_b \frac{\partial}{\partial \eta_a} \right] + \sum_{a=2}^{N} (-i\hbar) \hat{\mathbf{n}}_a \frac{\partial}{\partial \eta_a} , \tag{3.8}$$

where $t' \equiv dt/dq$, $\boldsymbol{\eta} \equiv \sum_{a=2}^{N} \hat{\mathbf{n}}_a \eta_a$, and

$$\Gamma_{a,b} = \hat{\mathbf{n}}_a \cdot \dot{\hat{\mathbf{n}}}_b . \tag{3.9}$$

The torsional Hamiltonian

$$\mathcal{H}_T = -\frac{\hbar^2}{2J} \nabla^2 + V(\boldsymbol{\gamma}) , \tag{3.10}$$

becomes

$$\mathcal{H}_T = -\frac{\hbar^2}{2J} \left[\frac{\dot{\boldsymbol{\gamma}}_c^2}{(\dot{\boldsymbol{\gamma}}_c^2 - \ddot{\boldsymbol{\gamma}}_c \cdot \boldsymbol{\eta})^2} \left[\frac{1}{t'} \frac{\partial}{\partial q} - \sum_{a,b} \Gamma_{a,b} \eta_b \frac{\partial}{\partial \eta_a} \right]^2 + \sum_{a} \frac{\partial^2}{\partial \eta_a^2} \right] + V(\boldsymbol{\gamma}_c + \boldsymbol{\eta}) , \tag{3.11}$$

and the potential term $V(\boldsymbol{\gamma}_c + \boldsymbol{\eta})$, when expanded in powers of η_a, reads

$$V(\boldsymbol{\gamma}_c + \boldsymbol{\eta}) = V(\boldsymbol{\gamma}_c) + \sum_{a=2}^{N} \sum_{n=1}^{N} \left[\frac{\partial V}{\partial \gamma_n} \right]_{\gamma_c} (\hat{\mathbf{n}}_a)_n \eta_a + \tfrac{1}{2} \sum_{a=2}^{N} \sum_{b=2}^{N} \sum_{n=1}^{N} \sum_{m=1}^{N} (\hat{\mathbf{n}}_a)_n \left[\frac{\partial^2 V}{\partial \gamma_n \partial \gamma_m} \right]_{\gamma_c} (\hat{\mathbf{n}}_b)_m \eta_a \eta_b + \cdots . \tag{3.12}$$

The most systematic approach toward solutions of the Schrödinger equation corresponding to the Hamiltonian defined by (3.11) and (3.12) lies within the framework of WKB approximation as described in details in Ref. 9. It turns out, that if one can find all the relevant classical periodic orbits $\boldsymbol{\gamma}_c$ it is possible, by using the procedure outlined above, to obtain the energy spectrum of the torsional Hamiltonian (3.11). This is in general, for the case of nonseparable systems, a difficult problem. For this reason, we will employ, in what follows, a somewhat less elegant approach, and study only the small fluctuations around the time-independent classical solution $\boldsymbol{\gamma}_c$. In this case the Eq. (3.5) simplifies to,

$$\gamma_n = \gamma_{cn} + \eta_n , \quad n = 1,2, \ldots, N \tag{3.13}$$

where $\boldsymbol{\gamma}_c$ is a solution of

$$\frac{\partial V(\boldsymbol{\gamma})}{\partial \gamma_n}=0, \quad n=1,\ldots,N \; . \tag{3.14}$$

The solution $\boldsymbol{\gamma}_c$ will represent a stable local minimum, if the real symmetric matrix

$$U_{n,m}\equiv\frac{1}{J}\left[\frac{\partial^2 V}{\partial\gamma_n\partial\gamma_m}\right]_{\boldsymbol{\gamma}_c} , \tag{3.15}$$

is positive definite. This means that all the eigenvalues ω_α^2 defined by

$$\sum_{n=1}^{N} U_{n,m}u_m^{(\alpha)}=\omega_\alpha^2 u_n^{(\alpha)} , \tag{3.16}$$

are positive, i.e., $\omega_\alpha^2>0$. For the time being we shall assume this to be the case, however, this is not true in general. For example if the Hamiltonian $\mathcal{H}_T$ possesses a continuous symmetry this symmetry is not necessarily shared by the solutions $\boldsymbol{\gamma}_c$. As is well known, with this symmetry breaking there is associated always a zero-frequency mode which tends to restore the original symmetry. In this case, the corresponding normal mode

$$q_\alpha=\sum_{n=1}^{N} u_n^{(\alpha)}\eta_n , \tag{3.17}$$

has to be separated out of the original Schrödinger equation in a manner discussed at the beginning of this section, before the expansion in terms of small fluctuations is performed. However, when we have a discrete lattice such as ours, discreteness causes the pinning of these zero-frequency modes thus making the corresponding ω_α nonvanishing. These pinning effects are associated with the existence of the so-called Peierls-Nabarro barrier.[10]

Assuming all $\omega_\alpha>0$, the analogs of the Eqs. (3.6), (3.7), (3.11), and (3.12) are given respectively as,

$$\hat{\mathbf{u}}^{(\alpha)}\cdot\hat{\mathbf{u}}^{(\beta)}=\delta_{\alpha,\beta}, \quad \alpha,\beta=1,2,\ldots,N \tag{3.18}$$

$$\sum_{\beta=1}^{N} u_n^{(\beta)}u_m^{(\beta)}=\delta_{n,m}, \quad n,m=1,2,\ldots,N \tag{3.19}$$

where $\mathbf{u}^{(\alpha)}\equiv(u_1^{(\alpha)},u_2^{(\alpha)},\ldots,u_N^{(\alpha)})$, and

$$\mathcal{H}_T=\sum_{n=1}^{N}\left[-\frac{\hbar^2}{2J}\frac{\partial^2}{\partial\eta_n^2}\right]+V(\boldsymbol{\gamma}_c+\boldsymbol{\eta}) , \tag{3.20}$$

$$V(\boldsymbol{\gamma}_c+\eta)=V(\boldsymbol{\gamma}_c)+\tfrac{1}{2}J\sum_{n,m}U_{n,m}\eta_n\eta_m+\cdots \; . \tag{3.21}$$

The corresponding ground-state wave function $\phi_0(\boldsymbol{\gamma})$ is,

$$\phi_0(\boldsymbol{\gamma})=\frac{(\det M)^{1/4}}{\pi^{N/4}}\exp[-(1/2)(\boldsymbol{\gamma}-\boldsymbol{\gamma}_c)^T M(\boldsymbol{\gamma}-\boldsymbol{\gamma}_c)] \; . \tag{3.22}$$

The matrix M introduced in (3.22) is defined as

$$M_{n,m}=\sum_{\alpha=1}^{N}\left[\frac{J\omega_\alpha}{\hbar}\right]u_n^{(\alpha)}u_m^{(\alpha)} , \tag{3.23}$$

with the determinant equal to

$$\det M=\prod_{\alpha=1}^{N}(J\omega_\alpha/\hbar), \quad \omega_\alpha>0 \text{ for all } \alpha \; . \tag{3.24}$$

$\mathbf{a}^T$ is the transpose of $\mathbf{a}$ and $\mathbf{a}^T M\mathbf{a}\equiv\sum_{i,j}M_{ij}a_ia_j$.

IV. TUNNELING APPROXIMATION FOR THE CASE OF MULTIPLE MINIMA

Let us suppose that $\boldsymbol{\gamma}_c$ represents a classically stable minimum of the potential $V(\boldsymbol{\gamma})$. Due to the assumed symmetry of the $X\text{H}_3$ groups, $\boldsymbol{\gamma}_c+(2\pi/3)\boldsymbol{\sigma}$, where $\boldsymbol{\sigma}\equiv(\sigma_1,\sigma_2,\ldots,\sigma_N)$, $\sigma_i=0, \pm1$, also represents a minimum of the potential because $V(\boldsymbol{\gamma}_c)=V[\boldsymbol{\gamma}_c+(2\pi/3)\boldsymbol{\sigma}]$. Around each of these minima we can construct a set of harmonic-oscillator states similar to those defined by (3.22). Quantum mechanically, however, the above minima are not absolutely stable, because the system can tunnel from one potential well to another. The ground-state wave function as given by the Eq. (3.22) and which starts out peaked around the minimum $\boldsymbol{\gamma}_c$, will spread into the other wells corresponding to $\boldsymbol{\gamma}_c+(2\pi/3)\boldsymbol{\sigma}$ and cause, in general, splitting of the energy levels. To account for these tunneling effects one can use again the WKB expansion outlined at the beginning of the preceding section and described in detail in Ref. 9. It has been shown [11] that the "classical path" relevant for the description of tunnelling is given as the solution of the Euclidean or imaginary-time version of the classical equation of motion (3.4), which in our case generalizes to

$$J\frac{d^2\gamma_{cn}^{(E)}}{d\tau_n^2}=-\frac{\partial V(\boldsymbol{\gamma}_c^{(E)})}{\partial\gamma_{cn}^{(E)}} , \tag{4.1}$$

where $\tau_n=\epsilon_n t$, $\epsilon_n^2=\pm1$, and $n=1,2,\ldots,N$. The choice of the set $(\epsilon_1,\ldots,\epsilon_N)$ is determined once the minimum $\boldsymbol{\gamma}_c+(2\pi/3)\boldsymbol{\sigma}$ is selected, i.e., $\epsilon_n^2=(-1)^{\sigma_n}$. It is also required that $\gamma_{cn}^{(E)}(t=-\infty)=\gamma_{cn}$, and

$$\gamma_{cn}^{(E)}(t=+\infty)=\gamma_{cn}+\frac{2\pi}{3}\sigma_n ,$$

together with

$$\sum_{n=1}^{N}\left[\frac{1}{2}J\left[\frac{d\gamma_{cn}^{(E)}}{d\tau_n}\right]^2\right]+V(\boldsymbol{\gamma}_c^{(E)})=V(\boldsymbol{\gamma}_c) , \tag{4.2}$$

where $\boldsymbol{\gamma}_c$ is the solution of (3.14) and the superscript E above stands for "Euclidean." Expanding the potential in terms of small fluctuations, we can repeat the analysis outlined earlier and thus obtain the WKB expression for the wave function $\phi(\boldsymbol{\gamma})$ in the classically forbidden region between the minima $\boldsymbol{\gamma}_c$ and $\boldsymbol{\gamma}_c+(2\pi/3)\boldsymbol{\sigma}$, which must be matched then with the harmonic-oscillator-type functions (3.22) centered at $\boldsymbol{\gamma}_c$ and $\boldsymbol{\gamma}_c+(2\pi/3)\boldsymbol{\sigma}$, respectively. In order to perform the above calculation explicitly, one needs the solution of (4.1), which, in general, is difficult to come by. In order to proceed we will assume that in the low-temperature limit, $(\hbar\omega_\alpha)_{\min}\gg kT$, the harmonic-oscillator wave functions (3.22) will yield a reasonable approximation also in the classically forbidden region.

Then, if we denote the ground-state wave function centered around $\boldsymbol{\gamma}_c$ and $\boldsymbol{\gamma}_c+(2\pi/3)\boldsymbol{\sigma}$ by ϕ_0 and $\phi_{0,\sigma}$, respectively, we can calculate the corresponding overlap integral $S_0(\boldsymbol{\sigma})$, which is

$$S_0(\boldsymbol{\sigma})=\langle\phi_0\,|\,\phi_{0,\sigma}\rangle=e^{-(\pi^2/9)\sigma^TM\sigma}\;, \tag{4.3}$$

where the matrix M is given by (3.23). Similarly, the matrix element of $\mathcal{H}_T$ defined by (3.10), is calculated to be

$$\begin{aligned}\langle\phi_0\,|\,\mathcal{H}_T\,|\,\phi_{0,\sigma}\rangle&\equiv S_0(\boldsymbol{\sigma})H(\boldsymbol{\sigma})\\ &=S_0(\boldsymbol{\sigma})\left[\frac{\hbar^2}{2J}\left[\frac{1}{2}\mathrm{Tr}M-\frac{\pi^2}{9}\boldsymbol{\sigma}^TM^2\boldsymbol{\sigma}\right]+\sum_n V_3\{1-(-1)^{\sigma_n}\cos[3(\gamma_{cn}-\delta_n)]e^{-(9/4)M^{-1}_{n,n}}\}\right.\\ &\quad+\tfrac{1}{2}V_3\sum_{n,m}\{g^{(+)}_{n,m}(-1)^{\sigma_n+\sigma_m}\cos[3(\gamma_{cn}+\gamma_{cm})]e^{-(9/4)(M^{-1}_{n,n}+M^{-1}_{m,m}+2M^{-1}_{n,m})}\\ &\quad\left.+g^{(-)}_{n,m}(-1)^{\sigma_n-\sigma_m}\cos[3(\gamma_{cn}-\gamma_{cm})]e^{-(9/4)(M^{-1}_{n,n}+M^{-1}_{m,m}-2M^{-1}_{n,m})}\}\right]\;,\end{aligned} \tag{4.4}$$

and the inverse matrix

$$M^{-1}_{n,m}=\sum_{\alpha=1}^{N}\left[\frac{\hbar}{J\omega_\alpha}\right]u_n^{(\alpha)}u_m^{(\alpha)} \tag{4.5}$$

is well defined provided $\omega_\alpha>0$ for all α.

Considering the symmetry properties of $\mathcal{H}_T$, it seems natural to attempt its diagonalization in the subspace spanned by the functions $\phi_{0,\sigma}$, by forming the following linear combinations

$$\tilde{\phi}_{0,\alpha}=\sum_{\beta}\left[\prod_{i=1}^{N}S_{\alpha_i,\beta_i}\right]\phi_{0,\beta}\;, \tag{4.6}$$

where $\boldsymbol{\alpha}\equiv(\alpha_1,\alpha_2,\ldots,\alpha_N)$, $\boldsymbol{\beta}\equiv(\beta_1,\beta_2,\ldots,\beta_N)$, $\alpha_i,\beta_i=1,2,3$, and there is a one-to-one correspondence between $\boldsymbol{\beta}$ and σ. We introduced this labeling merely to utilize matrix notation. The 3×3 matrix $S_{\alpha,\beta}$ is given by

$$S=\frac{1}{\sqrt{3}}\begin{bmatrix}1&1&1\\1&\epsilon&\epsilon^*\\1&\epsilon^*&\epsilon\end{bmatrix},\quad\alpha,\beta=1,2,3,\quad\epsilon=e^{i2\pi/3}\;. \tag{4.7}$$

It will be noticed that the entries of the matrix $\sqrt{3}S_{\alpha,\beta}$ represent the characters of the irreducible representations of the point group C_3.[3] Using (4.3), a straightforward computation shows that $\tilde{\phi}_{0,\alpha}$ are mutually orthogonal, that is

$$\langle\tilde{\phi}_{0,\alpha}\,|\,\tilde{\phi}_{0,\beta}\rangle=\delta_{\alpha,\beta}\sum_{\sigma}S_0(\boldsymbol{\sigma})\prod_{i=1}^{N}g(\alpha_i,\sigma_i)\;, \tag{4.8}$$

where $\delta_{\alpha,\beta}\equiv\prod_{i=1}^{N}\delta_{\alpha_i,\beta_i}$ and

$$g(\boldsymbol{\alpha},\sigma)=\begin{array}{cc|ccc|} & & & \sigma & \\ & & 1 & 0 & -1\\ & 1 & 1 & 1 & 1\\ \alpha & 2 & \epsilon & 1 & \epsilon^*\\ & 3 & \epsilon^* & 1 & \epsilon\end{array}\;.$$

In the same manner we obtain

$$\langle\tilde{\phi}_{0,\alpha}\,|\,\mathcal{H}_T\,|\,\tilde{\phi}_{0,\beta}\rangle=\delta_{\alpha,\beta}\sum_{\sigma}S_0(\boldsymbol{\sigma})H(\boldsymbol{\sigma})\prod_{j=1}^{N}g(\alpha_j,\sigma_j)\;. \tag{4.9}$$

The corresponding eigenvalues $E_T(\boldsymbol{\alpha})$ are

$$E_T(\boldsymbol{\alpha})=\frac{\sum_{\sigma}S_0(\boldsymbol{\sigma})H(\boldsymbol{\sigma})\prod_{j=1}^{N}g(\alpha_j,\sigma_j)}{\sum_{\sigma}S_0(\boldsymbol{\sigma})\prod_{j=1}^{N}g(\alpha_j,\sigma_j)}\;, \tag{4.10}$$

and the ground-state energy corresponding to the symmetric combination (4.6) is

$$\begin{aligned}E_T^0&\equiv E_T(\alpha_i=1,i=1,\ldots,N)\\ &=\sum_{\sigma}S_0(\boldsymbol{\sigma})H(\boldsymbol{\sigma})/\sum_{\sigma}S_0(\boldsymbol{\sigma})\;.\end{aligned}$$

Before examining some particular solutions of the Eq. (3.14), it is instructive to consider the limit $g^{(\pm)}_{n,m}\to0$, of noninteracting $X\mathrm{H}_3$ groups. Here we obtain

$$\begin{aligned}&E_T(\alpha_1,\ldots,\ \alpha_i=2,\ldots,\alpha_N)-E_T(\alpha_1,\ldots,\ \alpha_i=1,\ldots,\alpha_N)\\ &\qquad\equiv\hbar\omega_T=\frac{3}{2}\hbar\omega_0e^{-(\pi^2/9)(J\omega_0/\hbar)}\left[\left[\frac{J\omega_0}{\hbar}\right]\left[\frac{\pi^2}{9}-\frac{4}{9}\right]+1+\cdots\right]\;,\end{aligned} \tag{4.11}$$

where $\omega_0^2=9V_3/J$. If we take $J \doteq 4.7\times 10^{-47}$ kg m^2 and $V_3/k_B \doteq 400$ K, then $\omega_0=3.2\times 10^{13}$ sec^{-1} and the tunnelling frequency ω_T is estimated to be

$$\omega_T \doteq 5\times 10^7 \text{ sec}^{-1}=50 \text{ MHz} .$$

Here we give specific examples.

(i) As a first illustration of the above calculations, let us consider a rectangular lattice of XH$_3$ groups with their symmetry axes parallel with each other. We also assume that the lattice constants perpendicular and parallel to the symmetry axes are $|\boldsymbol{l}_1| = |\boldsymbol{l}_2| \equiv l_\perp$ and $|\boldsymbol{l}_3| \equiv l_\parallel$, respectively. Then, taking into account only the nearest-neighbor interaction and using the Eqs. (2.4) to (2.6), we obtain

$$g_\parallel^{(\pm)}=\begin{cases} 0 \\ \dfrac{5}{24}\left[\dfrac{e^2/l_\parallel}{V_3}\right]\left[\dfrac{d}{l_\parallel}\right]^6 , \end{cases} \tag{4.12}$$

which corresponds to the choice $\alpha_n,\alpha_{n'}$ and $\beta_n,\beta_{n'}=0$. Similarly, taking $\alpha_n,\alpha_{n'}=0$ and $\beta_n=\beta_{n'}=\pi/2$, and considering the two orthogonal directions in the plane defined by the lattice vectors $\boldsymbol{l}_1$ and $\boldsymbol{l}_2$, the Eqs. (2.4) to (2.6) yield,

$$g_\perp^{(+)}=\pm\frac{1155}{384}\,\frac{(e^2/l_\perp)}{V_3}\left[\frac{d}{l_\perp}\right]^6 , \tag{4.13}$$

and $|g_\perp^{(-)}/g_\perp^{(+)}| \doteq 2\times 10^{-2}$. Consequently, neglecting in $V(\gamma)$ the terms containing $g_\perp^{(-)}$, (3.14) has a solution which represents an absolute minimum of the potential energy and is given by

$$\gamma_{c\mathbf{n}}=\delta_{\mathbf{n}} , \tag{4.14}$$

$$\delta_{\mathbf{n}+\hat{\mathbf{e}}_1}+\delta_{\mathbf{n}}=\pm\pi/3 , \tag{4.15a}$$

$$\delta_{\mathbf{n}+\hat{\mathbf{e}}_2}+\delta_{\mathbf{n}}=0 , \tag{4.15b}$$

$$\delta_{\mathbf{n}+\hat{\mathbf{e}}_3}-\delta_{\mathbf{n}}=\pm\pi/3 , \tag{4.15c}$$

where $\mathbf{n}\equiv(n_1,n_2,n_3)$, $n_i=1,\ldots,N_i$, $i=1,2,3$, and $\hat{\mathbf{e}}_i \equiv \boldsymbol{l}_i/|\boldsymbol{l}_i|$. The position vector $\mathbf{R}_n$ of a given XH$_3$ group is $\mathbf{R}_n=n_1\boldsymbol{l}_1+n_2\boldsymbol{l}_2+n_3\boldsymbol{l}_3$ and the arrangement of the XH$_3$ groups in their respective equilibrium orientations is shown in Fig. 2. Imposing the periodic boundary conditions and assuming without a loss of generality that N_1,N_2,N_3 are even numbers the eigenfunctions $u_n^{(\alpha)}$ defined by (3.16) become

$$u_n^{(\mathbf{q})}\equiv\frac{1}{\sqrt{N_1N_2N_3}}e^{i\mathbf{n}\cdot\mathbf{q}} , \tag{4.16}$$

$\mathbf{q}\equiv(q_1,q_2,q_3)$ and the values of q_i are determined by

$$q_i=\frac{2\pi}{N_i}m_i, \quad m_i=0,\pm1,\pm2,\ldots,\pm(\tfrac{1}{2}N_i-1),\tfrac{1}{2}N_i , \qquad i=1,2,3 .$$

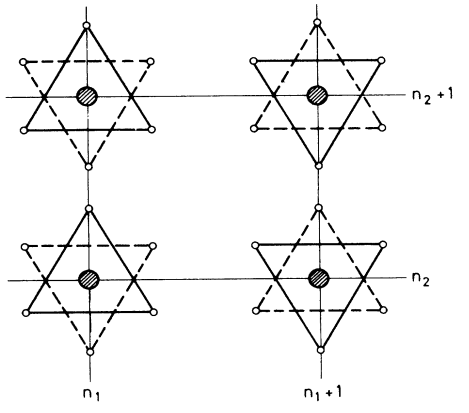

FIG. 2. Equilibrium orientation of the XH$_3$ groups corresponding to the minimum of the potential energy, as defined by the Eq. (4.14). The groups represented by dashed lines lie in the n_3 plane and the groups represented by solid lines are in the n_3+1 plane.

We use the complex notation in (4.16) for convenience. The corresponding normal-mode frequencies $\omega_\alpha^2\equiv\omega^2(\mathbf{q})$, are

$$\omega^2(\mathbf{q})=\omega_0^2\{1+2|g_\perp^{(+)}|[(1+\cos q_1)+(1+\cos q_2)] +2g_\parallel^{(-)}(1-\cos q_3)\} , \tag{4.17}$$

while the matrix $M_{n,m}$ and its inverse are given, respectively, as

$$M_{n,m}=\left[\frac{1}{N_1N_2N_3}\right]\sum_{\mathbf{q}}\left[\frac{J\omega(\mathbf{q})}{\hbar}\right]e^{i\mathbf{q}\cdot(\mathbf{n}-\mathbf{m})} , \tag{4.18}$$

and

$$M_{n,m}^{-1}=\left[\frac{1}{N_1N_2N_3}\right]\sum_{\mathbf{q}}\frac{\hbar}{J\omega(\mathbf{q})}e^{-i\mathbf{q}\cdot(\mathbf{n}-\mathbf{m})} . \tag{4.18a}$$

The ground-state wave function is given by (3.22) and the matrix element $\langle\phi_0|\mathcal{H}_T|\phi_{0,\sigma}\rangle$ can be obtained from the Eq. (4.4). The solution γ_c given above corresponds to the special choice of the phase factors $\delta_{\mathbf{n}}$, which are required to obey the Eqs. (4.15). Alternatively, we can choose $\delta_{\mathbf{n}}=0$, and then (3.14) yields

$$\gamma_{c\mathbf{n}}=\frac{1}{3}(-1)^{n_2+n_3}\cos^{-1}\left[\frac{1}{4}\,\frac{1}{(|g_\perp^{(+)}|+g_\parallel^{(-)})}\right] , \tag{4.19}$$

provided $[1/(|g_\perp^{(+)}|+g_\parallel^{(-)})]<4$. Since the small-oscillation spectrum resulting in this case is qualitatively the same as the one discussed above, we will not repeat the analysis.

(ii) The next example that we will analyze is an isolated X(CH$_3$)$_4$ cluster, a situation which may occur in metal tetramethyl compounds with the relative orientation of the four CH$_3$ groups as shown in Fig. 3. The application of the Eqs. (2.4) to (2.6) to this case yields

$$g^{(\pm)}=\pm\left[\frac{e^2/R}{V_3}\right]\left[\frac{d}{R}\right]^6\times\begin{cases}\frac{8935}{10\,368}\\ \frac{25}{10\,368} .\end{cases} \tag{4.20}$$

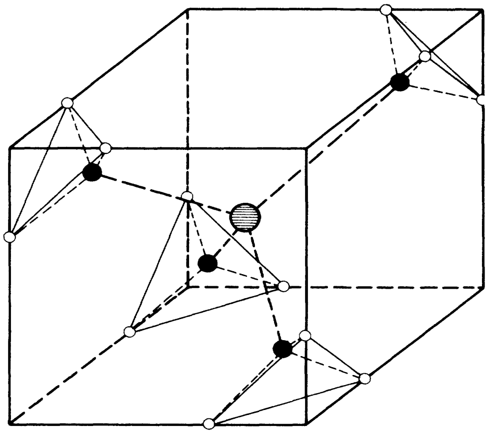

FIG. 3. Schematic representation of the structure of $X(\mathrm{CH}_3)_4$ molecule.

Since $|g^{(-)}/g^{(+)}| = 2.8\times 10^{-3}$ we shall, in what follows, retain only the $g^{(+)}$ term in (3.2) corresponding to the present example. To obtain an estimate of the order of magnitude of $g^{(+)}$ let us take $d = 1.7$ Å, $e^2 = 0.04 e_0^2$, $R = 3$ Å, and $(V_3/k_B) = 400$ K. This yields $g^{(+)} = 0.16 < \frac{1}{6}$. However, if we choose $R = 2.5$ Å, we obtain $g^{(+)} = 0.58 > \frac{1}{6}$. Looking for a symmetric solution, Eq. (3.14) with $\delta_n = 0$ yields,

$$\gamma_c = \begin{cases} 0 \ \text{ if } g^{(+)} < \frac{1}{6} \\ \pm\frac{1}{3}\cos^{-1}(1/6g^{(+)}) \ \text{ if } g^{(+)} > \frac{1}{6}\ . \end{cases} \tag{4.21}$$

$V(\gamma_c)$, where γ_c is subjected to constraint $\gamma_{c1} = \gamma_{c2} = \gamma_{c3} = \gamma_{c4} \equiv \gamma_c$, and for several values of the coupling parameter $g^{(+)}$ is shown in Fig. 4.

Using (3.15) and (4.21) we have

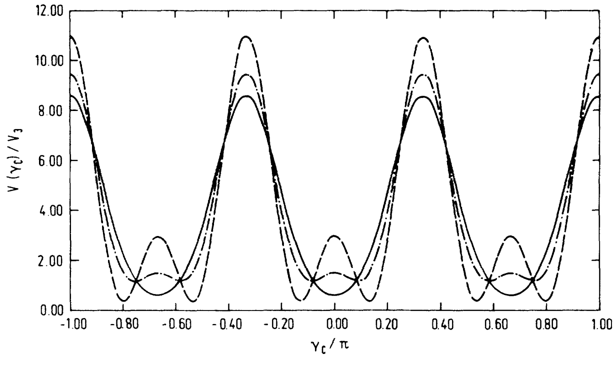

FIG. 4. Angular dependence of the potential $V(\gamma)$, when all four CH_3 groups have identical orientation. The solid line corresponds to $g^{(+)} = 1/10$, the dotted line to $g^{(+)} = 1/4$ and the dashed line to $g^{(+)} = 1/2$.

$$\omega_1^2 = \omega_2^2 = \omega_3^2 \neq \omega_4^2\ ,$$

where

$$\omega_1^2 = \begin{cases} \omega_0^2 \ \text{ if } g^{(+)} < \frac{1}{6} \\ \omega_0^2/6g^{(+)} \ \text{ if } g^{(+)} > \frac{1}{6} \end{cases} \tag{4.22}$$

and

$$\omega_4^2 = \begin{cases} \omega_0^2(1-4g^{(+)}) \ \text{ if } g^{(+)} < \frac{1}{6} \\ \omega_0^2 \left[4g^{(+)} - \dfrac{1}{18g^{(+)}}\right] \ \text{ if } g^{(+)} > \frac{1}{6} \end{cases} \tag{4.23}$$

Similarly, we can calculate also the eigenvectors $\hat{\mathbf{u}}^{(\alpha)}$ and subsequently by using (3.23) we obtain,

$$M_{n,m} = \left[\frac{J\omega_1}{\hbar}\right]\delta_{n,m} + \frac{1}{4}\frac{J}{\hbar}(\omega_4 - \omega_1) l_{n,m}\ , \tag{4.24}$$

together with

$$M_{n,m}^{-1} = \left[\frac{\hbar}{J\omega_1}\right]\delta_{n,m} + \frac{1}{4}\frac{\hbar}{J}\left[\frac{1}{\omega_4} - \frac{1}{\omega_1}\right] l_{n,m}\ . \tag{4.25}$$

where $\delta_{n,m}$ is as the Kronecker δ function and $l_{n,m} \equiv 1$ for all values of the subscripts.

V. SYMMETRIZATION OF THE WAVE FUNCTIONS ACCORDING TO THE PAULI EXCLUSION PRINCIPLE

According to Pauli principle, the states of a system containing N identical particles are necessarily all symmetrical or all antisymmetrical with respect to the permutations of the particles, depending on whether the particles have integer or half-integer spin, respectively.[12,13] In practical calculations, however, it is not always necessary to symmetrize the wave function with respect to the full permutation group. In the present case, it follows, that it is sufficient for the purpose of our calculation, if the wave function describing the dynamical state of the whole system has the correct symmetry properties only with respect to the subgroup of even permutations A_3, for each group of the three protons separately. Because A_3 is isomorphic with the point group C_3 of real rotations of $X\mathrm{H}_3$ group around its symmetry axis, we conclude that the Pauli exclusion principle will be satisfied within the framework of our approximations, if it is required that the wave function $\Psi(\gamma,\{I,m\})$, describing the system of N interacting $X\mathrm{H}_3$ groups is invariant with respect to the symmetry transformations of the direct product group $C_3^{(N)} = (C_3)_1 \otimes \cdots \otimes (C_3)_N$. Therefore we can write

$$\Psi(\gamma,\{I,m\}) = \tilde{\phi}_{0,\alpha}\chi_{\alpha_c}(\{I_{\alpha_n}, m_{\alpha_n}\})\ , \tag{5.1}$$

where $\{I,m\} \equiv (I_I, m_I; \ldots; I_N, m_N)$, and I_n, m_n are the total spin quantum number and its z component of the nth group, respectively.

The spatial component $\tilde{\phi}_{0,\alpha}$ is given by the Eq. (4.6) and the spin component χ_{α_c} is

$$\chi_{\alpha_c}(\{I_{\alpha_n}, m_{\alpha_n}\}) = \left[\frac{1}{\sqrt{3}}\right]^{\mathcal{S}} \sum_{\beta} \prod_{n=1}^{N} S^{*}_{\alpha_n,\beta_n} \chi_{\beta_n}(s_{n_1}, s_{n_2}, s_{n_3}) , \tag{5.2}$$

where $\mathcal{S} = \sum_{n=1}^{N} \delta_{s_n, s_n'}$. The following notation has been employed:

$$\begin{aligned} \chi_{1n}(s_{n_1}, s_{n_2}, s_{n_3}) &\equiv \chi_n^{(1)}(s_n')\chi_n^{(2)}(s_n)\chi_n^{(3)}(s_n) , \\ \chi_{2n}(s_{n_1}, s_{n_2}, s_{n_3}) &\equiv \chi_n^{(1)}(s_n)\chi_n^{(2)}(s_n')\chi_n^{(3)}(s_n) , \\ \chi_{3n}(s_{n_1}, s_{n_2}, s_{n_3}) &\equiv \chi_n^{(1)}(s_n)\chi_n^{(2)}(s_n)\chi_n^{(3)}(s_n') , \end{aligned} \tag{5.3}$$

where $s_n, s_n' = \pm\frac{1}{2}$, and $S^{*}_{\alpha,\beta}$ is the complex conjugate of the matrix $S_{\alpha,\beta}$. The function $\chi_n^{(j)}(s_n)$ represents the spin function of the jth proton belonging to the nth $X\mathrm{H}_3$ group with the z component of its spin equal to s_n. It is also easy to see that

$$I_{\alpha_n} = \begin{cases} \frac{3}{2} & \text{if } \alpha_n = 1 \\ \frac{1}{2} & \text{if } \alpha_n = 2,3 \end{cases}$$

together with $-I_{\alpha_n} \le m_{\alpha_n} \le I_{\alpha_n}$.

VI. DISCUSSION AND CONCLUSIONS

Since the purpose of this calculation has been to investigate the effect of coupling among $X\mathrm{H}_3$ groups on the tunneling spectrum, we will examine the content of Eq. (4.10) in greater detail. To start with, let us define $\boldsymbol{\alpha}_c$ as a conjugate of $\boldsymbol{\alpha}$, by changing all the α_n's equal to 2 into 3 and vice versa. Then using the properties $S_0(\boldsymbol{\sigma}) = S_0(-\boldsymbol{\sigma})$, $H(\boldsymbol{\sigma}) = H(-\boldsymbol{\sigma})$ and $g(\alpha_j, \sigma_j) = g(\alpha_{jc}, -\sigma_j)$, it is easy to see that $E_T(\boldsymbol{\alpha}) = E_T(\boldsymbol{\alpha}_c)$, which implies that the degeneracy connected with the E-symmetry-type levels of the noninteracting $X\mathrm{H}_3$ groups is not removed completely by the introduction of the torsional-torsional interaction as given by the Eq. (2.4). As already mentioned, the ground-state energy corresponding to an absolute minimum $(\boldsymbol{\gamma}_c)_{\mathrm{AM}}$, of the potential $V(\boldsymbol{\gamma})$ is $E_T^0 \equiv E_T(\boldsymbol{\alpha} \equiv 1)$. If $\boldsymbol{\gamma}_c$ represents only a local minimum $(\boldsymbol{\gamma}_c)_{\mathrm{LM}}$, then the physically meaningful quantity is $E_T^0[(\boldsymbol{\gamma}_c)_{\mathrm{LM}}] - E_T^0[(\boldsymbol{\gamma}_c)_{\mathrm{AM}}]$, which represents the energy associated with the static excitation $(\boldsymbol{\gamma}_c)_{\mathrm{LM}}$ of the lattice. To simplify the following discussion, let us assume that $\boldsymbol{\gamma}_c$ represents either an absolute minimum of $V(\boldsymbol{\gamma})$ or a local minimum, which, however, is sufficiently stable quantum mechanically, so that the result (4.10) is applicable. In this case the first "excited state" is defined by,

$$E_T(\alpha_i = 1, i = 1, \ldots, N, \alpha_k = 2,3, i \neq k) \equiv E_T(\alpha_k = 2,3) = \frac{\sum_{\sigma} S_0(\boldsymbol{\sigma}) H(\boldsymbol{\sigma}) g(\alpha_k, \sigma_k)}{\sum_{\sigma} S_0(\boldsymbol{\sigma}) g(\alpha_k, \sigma_k)} , \quad k = 1, \ldots, N , \tag{6.1}$$

and the energy difference between this level and the corresponding "ground state" is

$$E_T(\alpha_k = 2,3) - E_T^0 = \frac{E_T^0 + \dfrac{\sum_{\sigma} S_0(\boldsymbol{\sigma}) H(\boldsymbol{\sigma})[g(\alpha_k, \sigma_k) - 1]}{\sum_{\sigma} S_0(\boldsymbol{\sigma})}}{1 + \dfrac{\sum_{\sigma} S_0(\boldsymbol{\sigma})[g(\alpha_k, \sigma_k) - 1]}{\sum_{\sigma} S_0(\boldsymbol{\sigma})}} - E_T^0 , \tag{6.2}$$

which is, to first order in the overlap integral, equal to,

$$\begin{aligned} E_T(\alpha_k = 2,3) - E_T^0 = 3e^{-(\pi^2/9)M_{k,k}} \Bigg[& \frac{\hbar^2}{2J} \frac{\pi^2}{9} (M^2)_{k,k} - \tfrac{2}{9} J\omega_0^2 \cos[3(\gamma_{ck} - \delta_k)] e^{-(9/4)M^{-1}_{k,k}} \\ & + 2V_3 \sum_{m} \{ g_{k,m}^{(+)} \cos[3(\gamma_{ck} + \gamma_{cm})] e^{-(9/4)(M^{-1}_{k,k} + M^{-1}_{m,m} + 2M^{-1}_{k,m})} \\ & + g_{k,m}^{(-)} \cos[3(\gamma_{ck} - \gamma_{cm}] e^{-(9/4)(M^{-1}_{k,k} + M^{-1}_{m,m} - 2M^{-1}_{k,m})} \} \Bigg] + \cdots . \end{aligned} \tag{6.3}$$

This energy difference reduces to (4.11) in the zero coupling limit.

The result (6.3) shows that the set of the first excited states (corresponding to different values of k), in general forms a band of N doubly degenerate levels. The width of this band is determined by the strength of the torsional-torsional interaction and what is more interesting, also by the type of the classical minimum $\boldsymbol{\gamma}_c$. For example, if the crystal field is such that either (4.14) and (4.15) or (4.19) is realized, then the Eq. (6.3) shows, that to first order in the exponential factors $e^{-(\pi^2/9)M_{k,k}}$, the first excited state as defined above is $2N$-fold degenerate and thus corresponds to a single tunneling splitting. We also note that those minima $\boldsymbol{\gamma}_c$ which more or less preserve the original translational symmetry of the lattice, such as (4.14) and (4.15) and (4.19), will support energy spectra with very narrow bands. On the other hand, if the classical solution $\boldsymbol{\gamma}_c$ breaks the translational symmetry of the Hamiltonian, then the result (6.3) shows that we obtain a nonvanishing bandwidth already in first order in the exponential $e^{-(\pi^2/9)M_{k,k}}$.

Similarly, the second excited state is defined as,

$$E_T(\alpha_k,\alpha_l=2,3)-E_T^0$$

$$=\frac{E_T^0+\dfrac{\sum\limits_{\sigma} S_0(\boldsymbol{\sigma})H(\boldsymbol{\sigma})\{[g(\alpha_k,\sigma_k)-1]+[g(\alpha_l,\sigma_l)-1]\}}{\sum\limits_{\sigma} S_0(\boldsymbol{\sigma})}+\dfrac{\sum\limits_{\sigma} S_0(\boldsymbol{\sigma})H(\boldsymbol{\sigma})[g(\alpha_k,\sigma_k)-1][g(\alpha_l,\sigma_l)-1]}{\sum\limits_{\sigma} S_0(\boldsymbol{\sigma})}}{1+\dfrac{\sum\limits_{\sigma} S_0(\boldsymbol{\sigma})\{[g(\alpha_k,\sigma_k)-1]+[g(\alpha_l,\sigma_l)-1]\}}{\sum\limits_{\sigma} S_0(\boldsymbol{\sigma})}+\dfrac{\sum\limits_{\sigma} S_0(\boldsymbol{\sigma})[g(\alpha_k,\sigma_k)-1][g(\alpha_l,\sigma_l)-1]}{\sum\limits_{\sigma} S_0(\boldsymbol{\sigma})}}-E_T^0\ ,$$

$$k,l=1,2,\ldots,N,\ k\neq l\ , \qquad (6.4)$$

where we notice again, by comparing (6.2) and (6.4), that a similar band structure appears at least to first order in the exponential factors $e^{-(\pi^2/9)M_{k,k}}$.

Analogous situation occurs also in the case of isolated $X(\mathrm{CH}_3)_4$ clusters if the coupling constant $g^{(+)}$ is less than $\frac{1}{6}$. The tunneling spectrum is in this case single-particle-like and using Eqs. (6.3) and (4.21) to (4.25), we can calculate the energy difference between the ground state defined by $\boldsymbol{\alpha}=1$, $\alpha_n=1$, $n=1,2,3,4$, and the eightfold degenerate first excited state defined by (6.1). The result is,

$$E_T(\alpha_k=2,3)-E_T^0=\frac{3}{2}\hbar\omega_0\exp-\frac{\pi^2}{9}\left[\frac{J\omega_0}{\hbar}\right]\left[\frac{3}{4}+\frac{1}{4}(1-4g^{(+)})^{1/2}\right]$$

$$\times\left[\left[\frac{J\omega_0}{\hbar}\right]\frac{\pi^2}{9}(1-g^{(+)})-\frac{4}{9}\left[\frac{J\omega_0}{\hbar}\right]\exp-\frac{9}{4}\left[\frac{\hbar}{J\omega_0}\right]\left[\frac{3}{4}+\frac{1}{4}\frac{1}{(1-4g^{(+)})^{1/2}}\right]\right.$$

$$\left.+\frac{12}{9}\left[\frac{J\omega_0}{\hbar}g^{(+)}\exp-\frac{9}{4}\left[\frac{\hbar}{J\omega_0}\right]\left[1+\frac{1}{(1-4g^{(+)})^{1/2}}\right]\right]\right]+\cdots\ . \qquad (6.5)$$

If we take $(J\omega_0/\hbar)=15$, $g^{(+)}=\frac{1}{8}$, (6.5) yields $\omega_T\doteq 127$ MHz which is equivalent to 38.6 MHz in the limit $g^{(+)}\to 0$ (we have assumed $J=4.7\times 10^{-47}\ \mathrm{kg\,m^2}$).

In the above discussion it was assumed that $\boldsymbol{\gamma}_c$ represents a local minimum of the potential $V(\boldsymbol{\gamma})$, which is sufficiently stable and consequently only tunneling between those minima which are related through a C_3 symmetry transformations, namely $\boldsymbol{\gamma}_c\leftrightarrow\boldsymbol{\gamma}_c+(2\pi/3)\boldsymbol{\sigma}$, needs to be considered. It is evident, however, that Eq. (3.14) can have several distinct solutions $\boldsymbol{\gamma}_c$, $\boldsymbol{\gamma}_c{}'$, etc. Now we distinguish among the following possibilities, $V(\boldsymbol{\gamma}_c)\gtrless V(\boldsymbol{\gamma}_c')$. If $V(\boldsymbol{\gamma}_c)>V(\boldsymbol{\gamma}_c')$, then the system initially belonging to a state constructed around the minima $\boldsymbol{\gamma}_c+(2\pi/3)\boldsymbol{\sigma}$, can in principle decay to a lower lying state representing a linear superposition of pocket states centered around the minima defined by $\boldsymbol{\gamma}_c'+(2\pi/3)\boldsymbol{\sigma}$. The rate of this process and the resulting life-time broadening of the corresponding levels depends, of course, on the height and the width of the potential barrier separating the minima $\boldsymbol{\gamma}_c$ and $\boldsymbol{\gamma}_c'$. Although we will not consider this possibility at this time, the formalism discussed briefly at the beginning of Sec. IV, can be used to deal with this as well. What we wish to examine instead, is the case $V(\boldsymbol{\gamma}_c)=V(\boldsymbol{\gamma}_c')$ which occurred in the example (ii) of Sec. IV, as seen from the result (4.21) with the value of the coupling constant $g^{(+)}$ larger than $\frac{1}{6}$. In this case we have to account also for tunneling $\boldsymbol{\gamma}_c\leftrightarrow\boldsymbol{\gamma}_c+(2\pi/3)\boldsymbol{\sigma}'$. For this purpose, let us introduce

$$\gamma_{cn}^{(\pm)}=\pm\gamma_c+\frac{2\pi}{3}\sigma_n\ , \qquad (6.6)$$

where γ_c is given by (4.21). In analogy with (3.22) we then define,

$$\phi_{0,\beta}^{(\pm)}=\frac{(\det\mathrm{M})^{1/4}}{\pi}\exp[-(1/2)(\boldsymbol{\gamma}-\boldsymbol{\gamma}_c^{(\pm)})^T\boldsymbol{M}(\boldsymbol{\gamma}-\boldsymbol{\gamma}_c^{(\pm)}]\ , \qquad (6.7)$$

and in accordance with (4.6) we also introduce the corresponding linear combinations $\tilde{\phi}_{0,\boldsymbol{\alpha}}^{(\pm)}$. Consequently, $\langle\tilde{\phi}_{0,\boldsymbol{\alpha}}^{(\pm)}\,|\,\tilde{\phi}_{0,\boldsymbol{\beta}}^{(\pm)}\rangle$ and $\langle\tilde{\phi}_{0,\boldsymbol{\alpha}}^{(\pm)}\,|\,\mathcal{H}_T\,|\,\tilde{\phi}_{0,\boldsymbol{\beta}}^{(\pm)}\rangle$ are given by (4.8) and (4.9), respectively, with the help of Eqs. (4.3), (4.4), and (4.21) to (4.25). However, in addition to the above, we have to consider also the following matrix elements $\langle\tilde{\phi}_{0,\boldsymbol{\alpha}}^{(\pm)}\,|\,\tilde{\phi}_{0,\boldsymbol{\beta}}^{(\mp)}\rangle$ and $\langle\tilde{\phi}_{0,\boldsymbol{\alpha}}^{(\pm)}\,|\,\mathcal{H}_T\,|\,\tilde{\phi}_{0,\boldsymbol{\beta}}^{(\mp)}\rangle$. A short calculation yields

$$\langle \tilde{\phi}^{(+)}_{0,\alpha} \mid \tilde{\phi}^{(-)}_{0,\beta} \rangle = \delta_{\alpha,\beta} \sum_{\sigma} \exp\left[- \left[\gamma_c + \frac{\pi}{3}\sigma \right]^T M \left[\gamma_c + \frac{\pi}{3}\sigma \right] \right] \left[\prod_{i=1}^{4} g^*(\alpha_i,\sigma_i) \right] , \tag{6.8}$$

with $\gamma_{c1}=\gamma_{c2}=\gamma_{c3}=\gamma_{c4}=\gamma_c$ and

$$\begin{aligned} \langle \tilde{\phi}^{(+)}_{0,\alpha} \mid \mathcal{H}_T \mid \tilde{\phi}^{(-)}_{0,\beta} \rangle = \delta_{\alpha,\beta} \sum_{\sigma} \prod_{i=1}^{4} g^*(\alpha_i,\sigma_i) \exp\left[- \left[\gamma_c + \frac{\pi}{3}\sigma \right]^T M \left[\gamma_c + \frac{\pi}{3}\sigma \right] \right] \\ \times \left[\frac{\hbar^2}{2J}[\tfrac{1}{2}\mathrm{Tr} M - (\gamma_c + \frac{\pi}{3}\sigma)^T M^2 (\gamma_c + \frac{\pi}{3}\sigma)] + V_3 \sum_{n} [1-(-1)^{\sigma_n} e^{-9/4M^{-1}_{n,n}}] \right. \\ \left. + \tfrac{1}{2} V_3 g^{(+)} \sum_{n \neq m} (-1)^{\sigma_n + \sigma_m} e^{-9/4(M^{-1}_{n,n} + M^{-1}_{m,m} + 2M^{-1}_{n,m})} \right] . \end{aligned} \tag{6.9}$$

From the above results we can see, that within the subspace of functions $\tilde{\phi}^{(\pm)}_{0,\alpha}$, the torsional Hamiltonian $\mathcal{H}_T$ has a block-diagonal from, where each block represents a 2×2 matrix. Consequently, the eigenvalues and the corresponding eigenstates in the low-temperature limit can be calculated easily, and are

$$E_T^{(\pm)}(\alpha) = \frac{[a_\alpha b_\alpha - \mathrm{Re}(c_\alpha d_\alpha^*)] \pm \{ \mid a_\alpha d_\alpha - c_\alpha b_\alpha \mid^2 - [\mathrm{Im}(c_\alpha d_\alpha^*)]^2 \}^{1/2}}{b_\alpha^2 - d_\alpha d_\alpha^*} , \tag{6.10}$$

where

$$a_\alpha \equiv \langle \tilde{\phi}^{(+)}_{0,\alpha} \mid \mathcal{H}_T \mid \tilde{\phi}^{(+)}_{0,\alpha} \rangle , \quad b_\alpha \equiv \langle \tilde{\phi}^{(+)}_{0,\alpha} \mid \tilde{\phi}^{(+)}_{0,\alpha} \rangle ,$$

$$c_\alpha \equiv \langle \tilde{\phi}^{(+)}_{0,\alpha} \mid \mathcal{H}_T \mid \tilde{\phi}^{(-)}_{0,\alpha} \rangle , \quad d_\alpha \equiv \langle \tilde{\phi}^{(+)}_{0,\alpha} \mid \tilde{\phi}^{(-)}_{0,\alpha} \rangle ,$$

and

$$\chi^{(\pm)}_{0,\alpha} = N^{(\pm)}_\alpha (\tilde{\phi}^{(+)}_{0,\alpha} + C^{(\pm)}_\alpha \tilde{\phi}^{(-)}_{0,\alpha}) , \tag{6.11}$$

where $N^{(\pm)}_\alpha$ are suitable normalization factors, while the coefficients $C^{(\pm)}_\alpha$ are given as

$$C^{(\pm)}_\alpha = \frac{i \mathrm{Im}(c_\alpha d_\alpha^*) \mp \{ \mid a_\alpha d_\alpha - c_\alpha b_\alpha \mid^2 - [\mathrm{Im}(c_\alpha d_\alpha^*)]^2 \}^{1/2}}{a_\alpha d_\alpha - c_\alpha b_\alpha} . \tag{6.12}$$

When $\alpha = 1$, it follows from (6.12) that

$$C^{(\pm)}_1 = \mp \frac{\mid a_1 d_1 - c_1 b_1 \mid}{(a_1 d_1 - c_1 b_1)} .$$

Before continuing we should emphasize that two distinct pocket states $\phi^{(\pm)}_{0,\beta}$ as defined by (6.7), exist only for sufficiently strong couplings $g^{(+)}$. As a suitable criterion to determine whether (6.7) is justified, we choose

$$\Delta = V(\gamma = 0) - \left[V(\gamma_c) + \tfrac{1}{2} \sum_{\alpha=1}^{4} \hbar\omega_\alpha \right] , \tag{6.13}$$

which represents the difference between the value of the potential energy at $\gamma = 0$, and the zero-point energy of the normal modes localized in the minimum $\pm\gamma_c$ (see Fig. 4). Using the Eqs. (4.21) to (4.23), we can write Δ as a function of $g^{(+)}$, namely

$$\frac{\Delta(g^{(+)})}{\hbar\omega_0} = \frac{1}{9} \left[\frac{J\omega_0}{\hbar} \right] 6g^{(+)} - \left\{ \frac{1}{2} \left[\frac{3}{(6g^{(+)})^{1/2}} + \left[\frac{2}{3} 6g^{(+)} - \frac{1}{3} \frac{1}{6g^{(+)}} \right]^{1/2} \right] + \frac{1}{9} \left[\frac{J\omega_0}{\hbar} \right] \left[4 - 6g^{(+)} - 2\frac{1}{6g^{(+)}} \right] \right\} , \tag{6.14}$$

and which is also shown in Fig. 5. For (6.7) to make sense, we require that $\mid E_T^{(+)}(\alpha=1) - E_T^{(-)}(\alpha=1) \mid / \Delta \ll 1$. From Figs. 5 and 7, we can see that this condition is satisfied for all values of $(J\omega_0/\hbar)$ considered, provided $g^{(+)}$ is somewhat larger than $\frac{1}{3}$. For the range $\frac{1}{6} < g^{(+)} < \frac{1}{3}$ the above approximation breaks down and a numerical calculation is needed. However, the resulting tunneling spectrum should be somewhere in between the energy level schemes as described by the Eqs. (6.5) and (6.10), respectively.

To illustrate the tunneling spectrum as determined by the Eq. (6.10), let us choose $g^{(+)} = \frac{5}{12} > \frac{1}{3}$, and $(J\omega_0/\hbar) = 15$. The resulting energy-level scheme is shown in Fig. 6. In agreement with the statement made at the

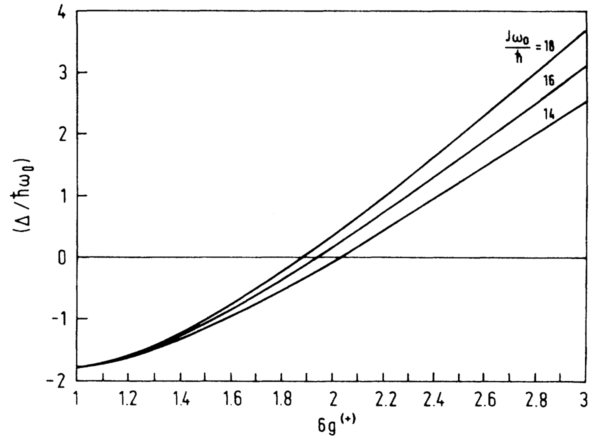

FIG. 5. Difference between the zero-point energy of the normal modes localized at $\pm\gamma_c$ and $V(\gamma=0)$ in units of $\hbar\omega_0$.

beginning of this section, namely $E_T(\alpha)=E_T(\alpha_c)$, this holds true also in the present case. In order to make the comparison with the single-particle spectrum easier, we reinstated the labeling according to the irreducible representations of the point group C_3,[3] i.e., $\alpha_i \equiv (1,2,3) \leftrightarrow (A,E_a,E_b)$, $i=1,2,3,4$. The corresponding numerical values, which can be calculated from the expressions given in the appendix, are for this particular choice of the parameters $g^{(+)}$ and $(J\omega_0/\hbar)$ as follows: $\Delta_1=68.63$ GHz, $\Delta_1^{(-)}=11.94$ GHz, $\Delta_1^{(+)}=10.66$ GHz, $\Delta_2^{(-)}=18.77$ GHz, $\Delta_2^{(+)}=16.18$ GHz, $\Delta_3^{(-)}=25.43$ GHz, $\Delta_3^{(+)}=22.84$ GHz, $\Delta_4^{(-)}=16.62$ GHz, $\Delta_4^{(+)}=12.72$ GHz, $\Delta_5^{(-)}=29.71$ GHz, $\Delta_5^{(+)}=25.81$ GHz, $\Delta_6^{(-)}=8.81$ GHz, $\Delta_6^{(+)}=3.63$ GHz, $\Delta_7^{(-)}=19.64$ GHz, $\Delta_7^{(+)}=14.46$ Ghz, $\Delta_8^{(-)}=25.29$ GHz, $\Delta_8^{(+)}=20.11$ GHz. The quantities Δ_1 and $\Delta_i^{(\pm)}$, $i=1,\ldots,8$, are defined in Fig. 6 and in the Appendix. To further illustrate the range spanned by these splittings, we show in Fig. 7, $E_T^{(+)}(\alpha=1) - E_T^{(-)}(\alpha=1) \equiv \Delta_1$ in units of $\hbar\omega_0$ as a function of $(J\omega_0/\hbar)$ for several values of the coupling constant $g^{(+)}$.

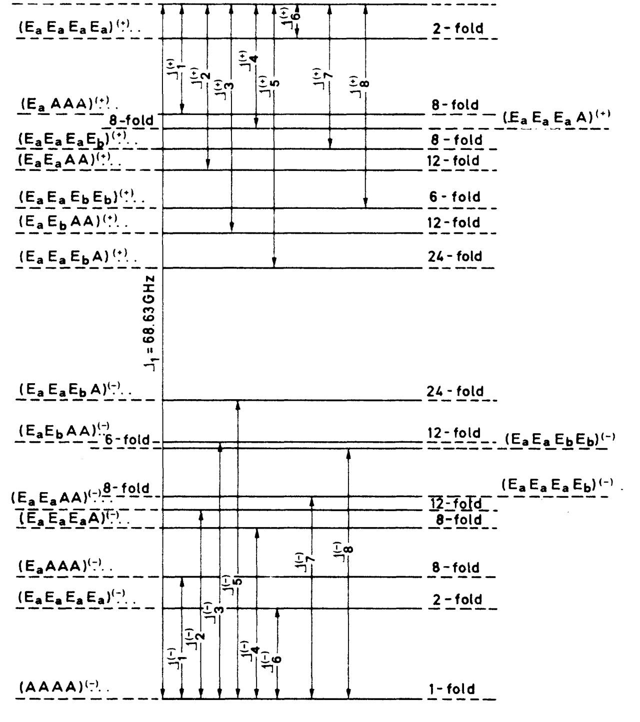

FIG. 6. Energy-level scheme as resulting from the Eq. (6.10) for $6g^{(+)}=2.5$, and $(J\omega_0/\hbar)=15$. It has been assumed that all four CH_3 groups in the $X(CH_3)_4$ cluster are equivalent.

As a final illustration let us consider again the example (i) discussed in Sec. IV and assume that the interaction of the XH_3 groups in the planes perpendicular to their symmetry axes is negligible. In this case we are dealing with a linear chain of coupled XH_3 groups having their symmetry axes parallel to the direction of the chain. The Eqs. (3.14) and (4.12) then show that in addition to the solutions of the type (4.15) and (4.19), there exist other kinds of static excitations which are not accessible by perturbing around the minima given by (4.14) or (4.19). For example, if $g_{\parallel}^{(-)} \geq 3.674$, then Eqs. (3.14) admits also the kink-like solutions γ_c, similar to the kinks of the familiar Sine-Gordon equation .[14]

On the basis of the above results we conclude that torsion-torsion interaction does have, in general, a significant effect on the structure of the rotational tunneling spectrum. Unfortunately the introduction of this interaction into the corresponding Hamiltonian generates an N-dimensional problem, and as such it is difficult to solve analytically. Consequently one has to adopt various approximation schemes in order to test different dynamical models against the experimental data. In this paper we described a simple calculational procedure which yields, with reasonable accuracy, analytical results for the energy levels and the corresponding eigenstates of the tunneling system.

The theoretical results obtained above will be used to analyze the large amount of experimental data concerning

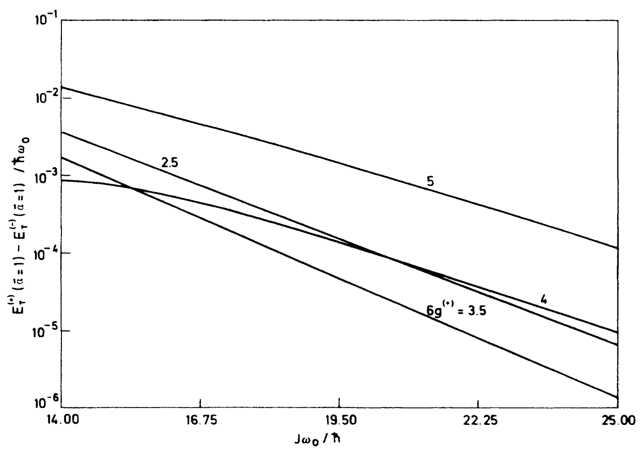

FIG. 7. $E_T^{(+)}(\alpha=1)-E_T^{(-)}(\alpha=1)$ as a function of $(J\omega_0/\hbar)$, for several values of the coupling constant $g^{(+)}$.

the tunneling spectra of metal tetramethyl $Si(CH_3)_4$ and $Ge(CH_3)_4$ at various temperatures.[6] This analysis, since it requires the inclusion of the dipole-dipole interaction[15] and the temperature variation of the tunnel splittings, will be published in a separate paper. In particular, regarding the temperature dependence, the influence of the phonon bath on the methyl group tunneling has yet to be examined. It is known,[16] that in the case of translational tunneling the interaction with phonons tends to suppress the tunneling. This does not occur if we are dealing with rotational tunneling of the type $\gamma_c \leftrightarrow \gamma_c + (2\pi/3)\sigma$, as discussed earlier. However it is not obvious what would be the effect of phonons on the tunneling between the states $\phi_{0,\beta}^{(\pm)}$ defined by the Eq. (6.7), and which according to our analysis occurs in metal tetramethyl compounds.

APPENDIX

Using the Eqs. (4.3) to (4.9), (4.21) to (4.25), and the Eq. (6.10), we can derive approximate expressions for the calculation of the numerical values of the tunneling splittings corresponding to the energy level scheme shown in Fig. 6. The results are:

$$\frac{E_T^{(+)}(\alpha=1)-E_T^{(-)}(\alpha=1)}{\hbar\omega_0} \equiv \Delta_1 = 2F_3\,|\,B+4E+6F+\cdots\,|\;, \tag{A1}$$

$$\frac{E_T^{(\pm)}(\alpha')-E_T^{(\pm)}(1)}{\hbar\omega_0} = \left\{ \begin{array}{l} 3F_4A \pm \{F_3[(B+\frac{5}{2}E+\frac{3}{2}F)^2+\frac{3}{4}(E+3F)^2]^{1/2}-\frac{1}{2}\Delta_1\}, \quad \alpha'=(2111),(3111),\ldots \\ 6AF_4 \pm \left\{ \begin{array}{l} \{F_3[(B+E-\frac{3}{2}F)^2+\frac{3}{4}(2E+3F)^2]^{1/2}-\frac{1}{2}\Delta_1\}, \quad \alpha'=(2211),(3311),\ldots \\ (F_3\,|\,B+E\,|-\frac{1}{2}\Delta_1), \quad \alpha'=(2311),(3211),\ldots \end{array} \right. \\ 9AF_4 \pm \left\{ \begin{array}{l} \{F_3[(B-\frac{1}{2}E-3F)^2+\frac{27}{4}E^2]^{1/2}-\frac{1}{2}\Delta_1\}, \quad \alpha'=(2221),(3331),\ldots \\ \{F_3[(B-\frac{1}{2}E)^2+\frac{3}{4}E^2]^{1/2}-\frac{1}{2}\Delta_1\}, \quad \alpha'=(2231),(3321),\ldots \end{array} \right. \\ 12AF_4 \pm \left\{ \begin{array}{l} \{F_3[(B-2E-3F)^2+\frac{3}{4}(4E-6F)^2]^{1/2}-\frac{1}{2}\Delta_1\}, \quad \alpha'=(2222),(3333),\ldots \\ \{F_3[(B-2E+\frac{3}{2}F)^2+\frac{3}{4}(2E-3F)^2]^{1/2}-\frac{1}{2}\Delta_1\}, \quad \alpha'=(2223),(3332),\ldots \\ (F_3\,|\,B-2E+3F\,|-\frac{1}{2}\Delta_1), \quad \alpha'=(2233),(3322),\ldots \end{array} \right. \end{array} \right. \tag{A2}$$

where the quantities introduced above are defined as follows:

$$A=\frac{1}{9}x_1\left[\frac{\pi^2}{12}\left(x_2+\frac{4}{x_2}\right)+\left(\frac{2}{x_2}-x_2\right)F_2-\frac{2}{x_2}F_1\right]\;, \tag{A3}$$

$$B=\frac{1}{9}x_1\left[18\gamma_c^2\left(\frac{2}{3}x_2-\frac{1}{3x_2}\right)+4\left(1-\frac{1}{x_2}\right)F_1+2\left(\frac{1}{x_2}-x_2\right)F_2\right]\;, \tag{A4}$$

$$C=\frac{1}{9}x_1\left[18\pi^2\left(\frac{\gamma_c^2}{\pi^2}-\frac{\gamma_c}{6\pi}\right)\left(\frac{2}{3}x_2-\frac{1}{3x_2}\right)+\frac{\pi^2}{12}\left(x_2+\frac{4}{x_2}\right)+\left(\frac{2}{x_2}-x_2\right)F_2+2\left(1-\frac{2}{x_2}\right)F_1\right]\;, \tag{A5}$$

$$D=\frac{1}{9}x_1\left[18\pi^2\left(\frac{\gamma_c^2}{\pi^2}-\frac{\gamma_c}{3\pi}\right)\left(\frac{2}{3}x_2-\frac{1}{3x_2}\right)+\frac{\pi^2}{3}\left(x_2+\frac{1}{x_2}\right)-\frac{4}{x_2}F_1+\left(\frac{2}{x_2}-\frac{2}{3}x_2\right)F_2\right]\;, \tag{A6}$$

$$E=C(F_4F_5)\;, \tag{A7}$$

$$F=D\left[\frac{F_4F_5}{F_6}\right]^2\;, \tag{A8}$$

and γ_c is given by the Eq. (4.21). Also,

$$F_1=\exp-\frac{9}{4}\frac{1}{x_1}\left[\frac{3}{4}(x_2)^{1/2}+\frac{1}{4}\frac{1}{\left(\frac{2}{3}x_2-\frac{1}{3x_2}\right)^{1/2}}\right]\;, \tag{A9}$$

$$F_2 = \exp - \frac{9}{4}\frac{1}{x_1}\left[(x_2)^{1/2} + \frac{1}{\left[\frac{2}{3}x_2 - \frac{1}{3x_2} \right]^{1/2}} \right] , \tag{A10}$$

$$F_3 = \exp - 4\gamma_c^2 x_1 \left[\frac{2}{3}x_2 - \frac{1}{3x_2} \right]^{1/2} , \tag{A11}$$

$$F_4 = \exp - \frac{\pi^2}{9} x_1 \left[\frac{3}{4}\frac{1}{(x_2)^{1/2}} + \frac{1}{4}\left[\frac{2}{3}x_2 - \frac{1}{3x_2} \right]^{1/2} \right] , \tag{A12}$$

$$F_5 = \exp \frac{2\pi}{3}\gamma_c x_1 \left[\frac{2}{3}x_2 - \frac{1}{3x_2} \right]^{1/2} , \tag{A13}$$

$$F_6 = \exp \frac{\pi^2}{36} x_1 \left[\left[\frac{2}{3}x_2 - \frac{1}{3x_2} \right]^{1/2} - \frac{1}{(x_2)^{1/2}} \right] , \tag{A14}$$

and $x_1 \equiv (J\omega_0/\hbar)$, $x_2 \equiv 6g^{(+)}$.

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