

EXPLICIT TEMPERATURE DEPENDENCE OF SPIN HAMILTONIAN PARAMETERS FOR JAHN-TELLER IONS

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The concept of a spin Hamiltonian with temperature-dependent parameters is introduced and the explicit temperature dependence is considered as resulting from electron-lattice coupling. For Jahn-Teller ions with the ground crystal term orbital degeneracy removed by a large axial crystal field component, the effect of temperature-dependent renormalization of the spin Hamiltonian parameters occurs instead of the dynamic or static Jahn-Teller effects known for perfect or almost perfect cubic symmetry. Here, electron-lattice coupling replaces a single orbital state by a family of vibronic states and a single spin Hamiltonian by a family of spin Hamiltonians with slightly different parameters. According to the theory of motional averaging, they can be averaged under specific conditions over the thermal population of vibronic states. The cases of the orbital cubic doublet and triplet are considered separately for the single-ion spin Hamiltonian. The zero point motion correction of the parameters is found to be of the order of 5 p. c. and the temperature effects become observable at temperatures corresponding to the characteristic frequencies of the lattice vibrations. The experimental aspects of the theory are discussed.

1. Introduction

Since electrons localized on paramagnetic ions and complexes do not form an isolated subsystem in the crystal, a description of low-energy magnetic states of the latter in terms of a purely electronic effective Hamiltonian can be no more than approximate. For a more accurate treatment, an extended Hamiltonian containing additional degrees of freedom is necessary. Nevertheless, in many cases, the electronic effective Hamiltonian alone suffices in explaining strictly all the experimental data, provided some alterations as well as a temperature dependence of its parameters are considered.

Phenomenologically, the temperature variation of any quantity A with constant external parameters X_i (e.g. pressure, uniaxial stress, magnetic or electric field) can be written as

$$\left(\frac{\partial A}{\partial T}\right)_{(X_i)} = \left(\frac{\partial A}{\partial T}\right)_{(Y_i)} + \sum_j \left(\frac{\partial A}{\partial Y_j}\right)_{T, (Y_{i \neq j})} \left(\frac{\partial Y_j}{\partial T}\right)_{(X_i)}, \quad (1.1)$$

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where Y_i denote "forces" thermodynamically conjugate to X_i (e.g. volume, structural parameters, magnetization or polarization). After Walsh et al. [1], we refer to the first and second term in Eq. (1.1) as the *explicit* and *implicit* temperature variation, respectively. To obtain the microscopical picture, let us assume that the total renormalization of the effective Hamiltonian parameters results from the coupling of electrons to the lattice degree of freedom, and expand the energy of every magnetic electron localized on a site in a series in normal displacements of ligands from some chosen high-symmetry configuration,

$$U = U_0 + \sum_{\Gamma\gamma} \left(\frac{\partial U}{\partial q_{\Gamma\gamma}} \right)_0 q_{\Gamma\gamma} + \dots \quad (1.2)$$

(Γ and γ denote irreducible representations and their basis vectors, respectively, for the symmetry group of the configuration adopted). Clearly, with regard to both size and symmetry, the assumed configuration need not to be identical to the equilibrium configuration within the whole range of temperatures and it is useful to resolve the normal displacements $q_{\Gamma\gamma}$ into two components,

$$q_{\Gamma\gamma} = Q_{\Gamma\gamma} + R e_{\Gamma\gamma}. \quad (1.3)$$

The $Q_{\Gamma\gamma}$'s denote *dynamical displacements* of ligands from their equilibrium positions and only the coupling to these displacements is commonly termed electron-lattice coupling. Among other possible phenomena, it can lead to the explicit term in (1.1). The second component of $q_{\Gamma\gamma}$ is a *static strain*, and coupling to it leads to the implicit term in (1.1). The static strain tensor $e_{\Gamma\gamma}$ is a thermodynamical quantity and should be determined by minimization of the free energy for the crystal as a whole. Its temperature dependence can result from cooperative phenomena both in the lattice alone (thermal expansion, ferroelectricity) and in the electronic subsystem (spontaneous magnetization combined with magnetostriction, cooperative Jahn-Teller phenomena).

Effects of explicit temperature dependence or, more generally, renormalization of the effective electronic Hamiltonian parameters caused by electron-lattice coupling depend on the relative strength of the latter and the spin-orbit coupling within the low-energy manifold of states. Three cases can be distinguished:

(a) *strong electron-lattice interaction* (transition metal ions with an orbitally degenerate ground term in the cubic crystal field; we refer to them as Jahn-Teller ions). The electron-lattice coupling is stronger than the spin-orbit coupling. It already enters in the first order of the perturbation procedure and affects the vibrational motion of ligands far more strongly than their interaction with the rest of the lattice, so that the cluster model of the electron-lattice problem can be applied [2, 3]. For a zero or weak lower-symmetry crystal field, in the limit of the dynamical Jahn-Teller effect, the renormalization of effective orbital Hamiltonian parameters is well known as Ham quenching [4]. This quenching can be considered as temperature-dependent [5].

(b) *weak electron-lattice interaction* (rare earth ions, extreme cases of transition metal ions with ground crystal orbital triplet). The spin-orbit coupling is stronger than the electron-lattice coupling. The renormalization effects are formally similar to, but weaker than the

dynamic Jahn–Teller effects by two orders, with crystal orbital multiplets replaced by crystal multiplets corresponding to the resultant angular momentum. Obviously, the cluster approximation ceases to be valid. In this context, temperature-dependent renormalization of parameters for the triplet state has been considered by Mc Mahon and Silsbee [6].

(c) *a very weak electron-lattice interaction* (*S*-state ions, transition metal ions with an orbitally nondegenerate ground term in the high-symmetry crystal field, Kramers ions with a well separated ground doublet state). The orbit-lattice coupling influences low-energy states in high orders of perturbation calculus only, and only in conjunction with other interactions (spin-orbit coupling, magnetic field, interionic interactions). In this case, the effective electronic Hamiltonian reduces to the simple spin Hamiltonian. The temperature-dependent renormalization of its parameters has been discussed for Kramers doublets [7, 8], the 6S term [9–16], the 8S term [17–19] and the A_2 orbital singlet resulting from the F term [20].

The aim of this paper is to consider the temperature-dependent renormalization of the *spin* (in a narrower meaning) Hamiltonian parameters for the case of a *strong* electron-lattice interaction. To remove the orbital degeneracy and make a description of low-energy states in terms of the spin Hamiltonian possible, we consider the lower-symmetry component of the crystal field of the order of orbit-lattice coupling, but not so strong as to affect considerably the cubic symmetry of cluster normal modes. Thus, we are looking for effects quite different from the well known dynamic or static Jahn–Teller effect for perfect or almost perfect high symmetry of the crystal field.

In our case, unlike the cases (b) and (c), the electron-lattice coupling cannot be written in terms of an effective spin-lattice (or resultant angular momentum-lattice) coupling. Conversely, it leads us to replace the single orbital state by a family of vibronic (i.e. orbital-vibrational) states and the single spin Hamiltonian by a direct sum of spin Hamiltonians with slightly different parameters acting in the individual vibronic states,

$$\mathcal{H}^{\text{Spin}} = \sum_i \mathcal{H}_{(i)}^{\text{Spin}} |i\rangle \langle i|. \quad (1.4)$$

The index i denotes the set of vibronic quantum numbers. Effective Hamiltonians $\mathcal{H}_{(i)}^{\text{Spin}}$ have to be found in the appropriate perturbation procedure and expression (1.4) is meaningful only if this procedure is convergent. If we assume vibronic states as given in the cluster approximation, remaining cluster-lattice interactions have to be considered, together with other neglected interactions, as causing transitions between eigenstates of the Hamiltonian (1.4) with a different vibronic index (“vibronic relaxation”) or spin index (spin-lattice relaxation). In the limit of slow spin-lattice relaxation, a stochastic treatment of the Hamiltonian (1.4) reduces to considering the family of operators $\{|i\rangle \langle i|\}$, only, as a random process. Following the line-shape theory [21, 22], for a sufficiently fast “vibronic” relaxation, an effect of motional averaging and narrowing takes place, which allows one to replace the family of operators $\{\mathcal{H}_{(i)}^{\text{Spin}}\}$ by a single operator with averaged parameters. Since the statistical weights for individual operators depend on temperature according to the population of the vibronic states, the averaged parameters should also depend on temperature. Denoting by ν the frequency corresponding to a transition between spin

states within one vibronic state, by $\Delta\nu$ the difference between ν 's for different vibronic states, by τ_v the vibronic relaxation time and by τ_s the spin-lattice relaxation time (we have always $\tau_v \ll \tau_s$), we can define the range within which the concept of the discussed spin Hamiltonian with temperature dependent parameters is meaningful by way of the following inequalities:

$$\Delta\nu \ll \tau_v^{-1}, \quad \tau_s^{-1} \ll \nu. \quad (1.5)$$

The first inequality expresses the condition of motional averaging whereas the second inequality expresses that of slow spin-lattice relaxation.

To specify the vibronic states, we restrict ourselves to ions having a sixfold coordination of ligands of the cubic symmetry O_h , in a first approximation. The orbit-lattice coupling, the axial crystal field component removing orbital degeneracy, as well as the spin-dependent interactions are weaker than the cubic crystal term separations, and we shall deal with them as expressed by effective Hamiltonians, acting within a single cubic term (Ham [3]; we adopt his notation of orbital states and operators as well as normal modes). For simplicity, we take into account only single ion spin Hamiltonians, though the generalization to Hamiltonians containing interactions between ions is possible (see Kurzyński [23], where the temperature dependence of superexchange between ions was already considered in this spirit). In the following Sections, the cases of cubic orbital doublet and triplet will be considered separately.

2. Cubic orbital doublet

The orbital doublet $E \equiv [|\theta\rangle, |\varepsilon\rangle]$ can be split only by an axial crystal field of tetragonal symmetry, and the only possible linear orbit-lattice coupling within this doublet can be to the E vibrational mode of the cluster. Hence, the vibronic Hamiltonian takes the form

$$\mathcal{H}_{(E)}^{\text{vib}} = \frac{1}{2} \delta \mathcal{U}_0 + V(Q_\theta \mathcal{U}_\theta + Q_\varepsilon \mathcal{U}_\varepsilon) + H^E \mathcal{J}, \quad (2.1)$$

where δ is the value of the tetragonal field splitting, V the coupling parameter, and H^E the Hamiltonian of the E vibrational mode ($\hbar = 1$),

$$H^E = \frac{1}{2\mu} (P_\theta^2 + P_\varepsilon^2) + \frac{1}{2} \mu \omega^2 (Q_\theta^2 + Q_\varepsilon^2). \quad (2.2)$$

On introducing polar coordinates,

$$Q_\theta \equiv \rho \cos \varphi, \quad Q_\varepsilon \equiv \rho \sin \varphi, \quad (2.3)$$

the low-lying vibronic states are found in the adiabatic approximation to be of the form [23]:

$$|gmn\rangle = (\cos \frac{1}{2}\alpha |\theta\rangle - \sin \frac{1}{2}\alpha |\varepsilon\rangle) \otimes |m\rangle \otimes |n\rangle, \quad (2.4)$$

where

$$\tan \alpha \equiv V\rho \sin \varphi / (V\rho \cos \varphi + \frac{1}{2}\delta). \quad (2.5)$$

The states $|m\rangle$ are eigenstates of the radial oscillator with the equilibrium position

$$\varrho_0 \equiv |V|/\mu\omega^2 \quad (2.6)$$

and frequency ω , and $|n\rangle$ are eigenstates of the angular oscillator with equilibrium position $\varphi_0 = 0$, for $V\delta > 0$, or $\varphi_0 = \pi$, for $V\delta < 0$, and the frequency

$$\Omega \equiv [\delta/(\delta + 4\varepsilon)]^{1/2}\omega. \quad (2.7)$$

ε denotes the Jahn-Teller energy

$$\varepsilon \equiv V^2/2\mu\omega^2. \quad (2.8)$$

The approximation (2.4) is valid only for $\varepsilon, \delta \gg \omega$.

As a perturbation with respect to the vibronic Hamiltonian, we consider the spin-orbit coupling

$$\mathcal{H}_{(E)}^{\text{SO}} = -\frac{3\lambda^2}{\Delta} \left[(S_z^2 - \frac{1}{3}S(S+1))\mathcal{U}_\theta + \frac{1}{\sqrt{3}}(S_x^2 - S_y^2)\mathcal{U}_\varepsilon \right] \quad (2.9)$$

together with the Zeeman interaction

$$\begin{aligned} \mathcal{H}_{(E)}^{\text{Z}} = & \left(2 - \frac{4\lambda}{\Delta} \right) \mu_B \mathbf{H} \cdot \mathbf{S} \\ & - \frac{6\lambda}{\Delta} \mu_B \left[(H_z S_z - \frac{1}{3} \mathbf{H} \cdot \mathbf{S}) \mathcal{U}_\theta + \frac{1}{\sqrt{3}} (H_x S_x - H_y S_y) \mathcal{U}_\varepsilon \right] \end{aligned} \quad (2.10)$$

the treatment of spin-spin and hyperfine interactions is similar). Δ is the cubic-field splitting of the term D , from which the doublet E originates in a first approximation, and λ is the spin-orbit coupling parameter within the D term. The projection of $\mathcal{H}_{(E)}^{\text{SO}}$ and $\mathcal{H}_{(E)}^{\text{Z}}$ onto the one-dimensional subspaces of vibronic states $|gmn\rangle$ yields, for $\varepsilon, \delta \gg \omega$, the effective Hamiltonians

$$\begin{aligned} \mathcal{H}_{(mn)}^{\text{SO}} &= D_{(mn)} [S_z^2 - \frac{1}{3}S(S+1)], \\ \mathcal{H}_{(mn)}^{\text{Z}} &= \mu_B [g_{(mn)}^{\parallel} H_z S_z + g_{(mn)}^{\perp} (H_x S_x + H_y S_y)], \end{aligned} \quad (2.11)$$

with

$$\begin{aligned} D_{(mn)} &= \pm \frac{3\lambda^2}{\Delta} K_{(n)}, \\ g_{(mn)}^{\parallel} &= 2 - \frac{4\lambda}{\Delta} (1 \mp K_{(n)}), \quad g_{(mn)}^{\perp} = 2 - \frac{2\lambda}{\Delta} (2 \pm K_{(n)}), \end{aligned} \quad (2.12)$$

where

$$K_{(n)} = 1 - \frac{2\varepsilon\Omega}{(\delta \pm 4\varepsilon)\delta} (2n+1). \quad (2.13)$$

The upper sign corresponds to $\delta > 0$ (the ground state $|\theta\rangle$) and the lower sign to $\delta < 0$ (the ground state $|\varepsilon\rangle$). Let us note that the expression (2.13) is independent of m .

On averaging over the thermal population of the angular oscillator states, we obtain

$$D(T) = \pm \frac{3\lambda^2}{A} K(T),$$

$$g^{\parallel}(T) = 2 - \frac{4\lambda}{A} (1 \mp K(T)), \quad g^{\perp}(T) = 2 - \frac{2\lambda}{A} (2 \pm K(T)), \quad (2.14)$$

where

$$K(T) = 1 - \frac{2\varepsilon\Omega}{(\delta \pm 4\varepsilon)\delta} \coth\left(\frac{\Omega}{2kT}\right). \quad (2.15)$$

The absolute values of the effective parameter D and orbital corrections of the effective g -factors decrease with temperature. This corresponds to dynamical mixing of states $|\theta\rangle$ and $|\varepsilon\rangle$, in which the quantities under discussion differ in sign.

3. Cubic orbital triplet

In the orbital triplet $T \equiv [|\xi\rangle, |\eta\rangle, |\zeta\rangle]$, linear orbit-lattice coupling to the E as well as to the T_2 vibrational mode is possible. However, for the octahedral coordination, coupling to the E mode is much stronger than to the T_2 mode, so that we neglect the latter. Since the matrix elements of the trigonal crystal field vanish between eigenstates of the orbit- E mode coupling, we restrict ourselves to the case of an axial field of tetragonal symmetry only. Thus, we assume the vibronic Hamiltonian within the orbital triplet to be

$$\mathcal{H}_{(T)}^{\text{vib}} = \frac{2}{3} \delta \mathcal{E}_\theta + V(Q_\theta \mathcal{E}_\theta + Q_\varepsilon \mathcal{E}_\varepsilon) + H^E \mathcal{J}. \quad (3.1)$$

The tetragonal crystal field splits the triplet into the singlet $|\zeta\rangle$ (lower, if $\delta > 0$) and the doublet $[|\eta\rangle, |\xi\rangle]$ distant by δ . The exact eigenstates of $\mathcal{H}_{(T)}^{\text{vib}}$ are of the form

$$\begin{aligned} |\xi mn\rangle &= |\xi\rangle \otimes |-\frac{1}{2} \varrho_0, m\rangle \otimes \left| \frac{\sqrt{3}}{2} \varrho_0, n \right\rangle, \\ |\eta mn\rangle &= |\eta\rangle \otimes |-\frac{1}{2} \varrho_0, m\rangle \otimes \left| -\frac{\sqrt{3}}{2} \varrho_0, n \right\rangle, \\ |\zeta mn\rangle &= |\zeta\rangle \otimes |\varrho_0, m\rangle \otimes |0, n\rangle, \end{aligned} \quad (3.2)$$

where $|R_\theta, m\rangle$ and $|R_\varepsilon, n\rangle$ denote the harmonic oscillator states for coordinates Q_θ and Q_ε with the same frequency ω and equilibrium positions R_θ and R_ε , respectively. ϱ_0 and ε are the same as those determined by Eqs (2.6) and (2.8). For $\delta > 0$, the low lying vibronic states are $|\zeta mn\rangle$.

As perturbation, we assume the spin-orbit coupling

$$\mathcal{H}_{(T)}^{\text{SO}} = \alpha\lambda(S_x\mathcal{L}_x + S_y\mathcal{L}_y + S_z\mathcal{L}_z) \quad (3.3)$$

and Zeeman interaction

$$\mathcal{H}_{(T)}^Z = 2\mu_B\mathbf{H} \cdot \mathbf{S} + \alpha\mu_B(H_x\mathcal{L}_x + H_y\mathcal{L}_y + H_z\mathcal{L}_z) \quad (3.4)$$

(we neglect second-order contributions like (2.9) and (2.10)). The reduced matrix element α is equal to -1 for the triplet T_2 originating, in a first approximation, from the term D , and to $\alpha = -3/2$ for the triplet T_1 originating, in a first approximation, from the term F . We consider the Hamiltonian $\mathcal{H}_{(T)}^{\text{SO}}$ as a perturbation with respect to $\mathcal{H}_{(T)}^{\text{vib}}$ though, differently from the orbital doublet case, this need not be generally the physical situation; in the Introduction, we have mentioned the opposite formulation of the perturbation procedure. The matrix elements of $\mathcal{H}_{(T)}^{\text{SO}}$ and of the orbital part of $\mathcal{H}_{(T)}^Z$ vanish between vibronic states $|\zeta mn\rangle$ and, in the second order of perturbation calculus, we obtain effective Hamiltonians of the form (2.11) with

$$D_{(mn)} = \frac{\alpha^2\lambda^2}{\delta + 3\varepsilon} K_{(mn)},$$

$$g_{(mn)}^{\parallel} = 2, \quad g_{(mn)}^{\perp} = 2 - \frac{\alpha^2\lambda}{\delta + 3\varepsilon} K_{(mn)}, \quad (3.5)$$

where

$$K_{(mn)} = (\delta + 3\varepsilon) \sum_{n'=0}^{\infty} \sum_{m'=0}^{\infty} \frac{|\langle 0, n' | \frac{3}{2} \varrho_0, n \rangle|^2 |\langle 0, m' | \frac{\sqrt{3}}{2} \varrho_0, m \rangle|^2}{\delta + (n' - n + m' - m)\omega}. \quad (3.6)$$

The summation of the series (3.6) is performed in the Appendix and, for $\varepsilon \gg \omega$, we obtain the approximate expression

$$K_{(mn)} = 1 + \frac{3\varepsilon\omega}{4(\delta + 3\varepsilon)^2} [3(2n+1) + (2m+1)]. \quad (3.7)$$

Subsequent to thermal averaging, we obtain

$$D(T) = \frac{\alpha^2\lambda^2}{\delta + 3\varepsilon} K(T), \quad g^{\parallel}(T) = 2, \quad g^{\perp}(T) = 2 - \frac{\alpha^2\lambda^2}{\delta + 3\varepsilon} K(T), \quad (3.8)$$

where

$$K(T) = 1 + \frac{3\varepsilon\omega}{(\delta + 3\varepsilon)^2} \coth\left(\frac{\omega}{2kT}\right). \quad (3.9)$$

In the triplet case, the absolute values of the effective parameter D and orbital corrections to the effective g -factor increase with temperature corresponding to a decrease of the energetic denominators in (3.6) for excited initial vibronic states.

Since the states (3.2) are strict eigenstates of the Hamiltonian (3.1), the validity of the approximation (3.7) does not depend on the value of δ and, for $\delta \rightarrow 0$, Eqs (3.5—3.9) describe a temperature dependent static Jahn–Teller effect. For $\delta = 0$ and $T = 0$ (when only the ground vibronic state with $m = n = 0$ is populated), Eqs (3.7) and (3.9) reduce to the results of Ham [4].

4. Discussion

To evaluate the magnitude of the renormalization effects found, let us insert as reasonable values $\omega = 300 \text{ cm}^{-1}$, $\delta = 1000 \text{ cm}^{-1}$ and $\epsilon = 3000 \text{ cm}^{-1}$ for the orbital doublet, and $\epsilon = 1000 \text{ cm}^{-1}$ for the orbital triplet [3] into Eqs (2.15) and (3.9). We obtain a zero point motion correction of the order of 5 p.c., i.e. a value which cannot be omitted in model calculations of spin Hamiltonian parameters (still stronger effects are to be expected in cases of interionic superexchange interactions [23]). In the case of the orbital doublet, this correction has still to be reduced slightly by the anharmonic and quadratic Jahn–Teller coupling terms omitted, for simplicity, in the vibronic Hamiltonian (2.1). From the static Jahn–Teller effect, it is known that these terms are important, causing three wells on the adiabatic potential vs angle φ diagram of the depth of the order of 200 cm^{-1} . These wells, if added to the large single well caused by the tetragonal field can modify considerably the zero point motion correction that should rather be described by the expression appropriate for the static Jahn–Teller effect [24]. However, they do not affect the high-temperature reduction. With regard to coth behaviour, the temperature corrections should be detectable experimentally at temperatures above ω , or Ω , and are of order kT/δ .

From the above estimations, it follows that effects of renormalization of the spin Hamiltonian parameters have to influence considerably the thermodynamical quantities measured up to very high temperatures such as e. g. magnetic susceptibility and anisotropy constants but, to our knowledge, no such analysis has been performed.

Transition-metal ions with an orbitally nondegenerate ground state are the traditional objects of electron paramagnetic resonance spectroscopy, which almost directly determines the values of their spin Hamiltonian parameters. From the EPR point of view, the explicit temperature dependence of these parameters can be resolved from the implicit dependence due to their different functional character or by having recourse to simultaneous variations of external parameters [1]. Unfortunately, to our knowledge, apart from cases of structural transitions where the implicit component is large, no EPR data over a wide range of temperatures is available for ions with a ground orbital state originating in a cubic doublet or triplet. This follows surely from the shortness of the spin-lattice relaxation time. However, usually, the latter is not so short as to render the second of the inequalities (1.5) unfulfilled, and measurements of the temperature variations of the parameters would be possible providing data as valuable as those obtained from the Jahn–Teller effect.

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APPENDIX

To carry out the summations in the expression

$$K_{(m,n)} = (\delta + 3\varepsilon) \sum_{n'=0}^{\infty} \sum_{m'=0}^{\infty} \frac{|\langle 0, n' | \frac{3}{2} \varrho_0, n \rangle|^2 |\langle 0, m' | \frac{\sqrt{3}}{2} \varrho_0, m \rangle|^2}{\delta + (n' - n + m' - m)\omega}, \quad (\text{A.1})$$

it is convenient to introduce its Fourier transform according to the formula

$$\frac{1}{x} = \text{Re} \left[-i \int_0^{\infty} dt e^{i(x+i0)t} \right], \quad (\text{A.2})$$

valid for $x \neq 0$. In this way, with regard to the completeness of the system $(|0, n\rangle)$ of oscillator states, we obtain

$$K_{(m,n)} = (\delta + 3\varepsilon) \text{Re} \left[-i \int_0^{\infty} dt e^{i(\delta+i0)t} \right. \\ \left. \times \left\langle \frac{3}{2} \varrho_0, n \left| e^{i\omega(a^*a-n)t} \right| \frac{3}{2} \varrho_0, n \right\rangle \left\langle \frac{\sqrt{3}}{2} \varrho_0, m \left| e^{i\omega(a^*a-m)t} \right| \frac{\sqrt{3}}{2} \varrho_0, m \right\rangle \right], \quad (\text{A.3})$$

where a^* and a are the creation and annihilation operators of the states $|0, n\rangle$. To calculate the matrix elements occurring in (A.3), let us note that

$$\langle R, n | e^{i\omega(a^*a-n)t} | R, n \rangle = \langle R, n | \exp \left\{ \frac{i}{2} \mu \omega^2 [Q^2 - (Q-R)^2] t \right\} | R, n \rangle \\ = \exp \left(\frac{i}{2} \mu \omega^2 R^2 t \right) \langle 0, n | \exp [i\omega \sqrt{\mu \omega R^2 / 2} t (a^* + a)] | 0, n \rangle.$$

Applying the properties of oscillator operators, we find

$$\langle R, n | e^{i\omega(a^*a-n)t} | R, n \rangle = e^{ixt} e^{-\omega xt^2/2} L_n(\omega xt^2), \quad (\text{A.4})$$

where $x \equiv \mu \omega^2 R^2 / 2$ and L_n are Laguerre polynomials. Finally, we obtain the exact formula

$$K_{(mn)} = (\delta + 3\varepsilon) \text{Re} \left[-i \int_0^{\infty} dt e^{i(\delta+3\varepsilon+i0)t} e^{-\frac{3}{2}\omega \varepsilon t^2} L_n\left(\frac{3}{4}\omega \varepsilon t^2\right) L_m\left(\frac{3}{4}\omega \varepsilon t^2\right) \right]. \quad (\text{A.5})$$

For $\varepsilon \gg \omega$, the first exponential in (A.5) oscillates very rapidly as compared to the variation of the remaining expression under the integral. The latter variations are largest for small values of t and only this range of t gives the main contribution to the value of the integral. Hence it follows that, in the limit discussed, both the second exponential and the Laguerre polynomials can be expanded in a power series with respect to $\omega \varepsilon t^2$. Restricting ourselves to linear terms, we obtain the approximate expression (3.7).

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