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Theory of vibronic transitions with strong nonlinear vibronic interaction in solids

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TABLE OF CONTENTS

LIST OF PUBLICATIONS

List of original papers included to the thesis:

   I.   Hizhnyakov V., Boltrushko V., Kaasik H., Sildos I., *Jahn-Teller effect in the excited state: anomalous temperature dependence of the zero-phonon line*, Adv. Quant. Chem. **44**, 135–149 (2003).

  II. Hizhnyakov V., Boltrushko V., Kaasik H., Sildos I., *Phase relaxation in the vicinity of the dynamic instability: anomalous temperature dependence of zero-phonon line*, J. Lumin. **107**, 351–358 (2004).

 III. Hizhnyakov V., Boltrushko V., *Anomalous optical spectra of centers with soft phonon dynamics in excited state*, In: Proc. SPIE – Optical Materials and Applications, **5946**, 192–201 (2005).

 IV. Hizhnyakov V., Boltrushko V., Tehver I., *Optical transitions in the centres with soft dynamics in the final state*, J. Phys.: Conf. Ser. **21**, 161–166 (2005).

  V. Hizhnyakov V., Benedek G., Tehver I., Boltrushko V., *Optical spectra of systems with nearly unstable excited states: modulated lambda-shaped spectra*, J. Noncryst. Solids **352**, 2558–2561 (2006).

 VI. Boltrushko V., Holmar S., Tehver I., Hizhnyakov V., *Vibronic transitions in the vicinity of the dynamical instability of the final state*, J. Mol. Struct. **838**, 164–169 (2007).

List of other publications:

 VII. Hizhnyakov V., Boltrushko V., Kaasik H., I. Sildos, *Strong Jahn-Teller effect in the excited state: anomalous temperature dependence of the zero-phonon line*, J. Chem. Phys. **119**, 6290–6295 (2003).

VIII. Hizhnyakov V., Boltrushko V., Kaasik H., Shelkan A., *Multiphonon processes in impurity centres: non-perturbative theory*, Phys. Stat. Sol. (a) **202**, 228–234 (2005).

 IX. Hizhnyakov V., Boltrushko V., Tehver I., *Soft dynamics of the excited state: Lambda-shaped optical spectra*, J. Lumin. **127**, 13–18 (2007).

List of conference presentations (with abstracts, if available):

  X. Hizhnyakov V., Boltrushko V., Kaasik H., Sildos I., *Phase relaxation in the vicinity of the dynamic instability: anomalous temperature dependence of the zero-phonon line*. Proceedings of the 8th international meeting on hole burning, single molecule, and related spectroscopies: science and applications, Bozeman, Montana (USA), p. 41, 2003.

 XI. Hizhnyakov V., Boltrushko V., *Anomalous optical spectra of centers with soft phonon dynamics in the excited state*. Abstracts of the Fourth Inter-

national Conference on Advanced Optical Materials and Devices (AOMD-4), Tartu, p. 28, 2004. *(Proc. of SPIE, 5946, 192–201, 2005)*

XII. Hizhnyakov V., Benedek G., Tehver I., Boltrushko V., *Electronic transitions between dynamically stable and weakly unstable states: optical spectra of molecules trapped in superfluid ^{4}He droplets*. Abstracts of First Conference on Advances in Optical Materials (AIOM2005), Tucson, Arizona (USA), p. 20, 2005.

XIII. Hizhnyakov V., Boltrushko V., Tehver I., Optical transitions in the centres with soft dynamics in the final state. Abstracts of Second International Conference on Photo-Induced Phase Transitions: cooperative, non-linear and functional properties (PIPT Rennes 2005), Rennes, France, p. 75, 2005. *(J. Phys.: Conf. Ser., 21, 161–166, 2005)*.

XIV. Boltrushko V., Hizhnyakov V., Tehver I., Benedek G., *Pseudo-Jahn-Teller Effect: Vibronic Transitions in the Vicinity of the Dynamical Instability of the Final State.* International Symposium on the Jahn-Teller Effects: Novel Aspects in Orbital Physics and Vibronic Dynamics of Molecules and Crystals, Trieste, Italy, 2006.

XV. Boltrushko V., *Multiphonon Optical Spectra: Instability Case*. DPC 07 16th International Conference on Dynamical Processes in Excited States of Solids, Segovia, Spain, 2007.

Author's contribution:

The author's research has given an essential contribution to all these publications. He participated in development (and verification) of the theoretical methods, in the numerical calculations and in the analysis of the results. The author is also responsible for the development of mathematical software (related to the Fourier analysis and distributed computing schemes). Some routines have been significantly optimized (or completely rewritten), and miscellaneous packages for different computer algebra systems have been created from scratch.

I. INTRODUCTION

A number of basic processes in solids take place as electro-vibrational transitions associated with localized (impurity) centers. Examples are given by diffusion of defect atoms, interstitials, vacancies and self-trapped quasi-particles, photochemical reactions and electronic transitions. The latter transitions are responsible for the defect-induced absorption and emission of light.

The shapes of the light absorption and emission spectra of optical centers in condensed matter as well as probability of other mentioned above transitions are determined by the interaction of valence electrons with nuclear vibrations. Due to the collective origin of vibrations a large number of the normal modes, including those of the phonon continuum, give a contribution to the spectrum. In the so-called basic model, when only the linear electron-phonon interaction is considered, all normal modes contribute independently, which allows one to find the spectrum for any number of normal modes. The calculation can be performed by applying standard methods of local vibrational dynamics. This model works well for vast number of systems, allowing one to explain the main features of the spectra. Thus it was successful for explanation of Shpol'skii effect [116, 117] and, in general, quasi-linear spectra [108].

One of the first publications of optical spectra is 1950 paper of Huang and Rhys [59] with quantum-mechanical calculations of the optical absorption in *F*-centers[1], where they considered the linear interaction of the electron with longitudinal optical phonons of a single frequency, resulted in a discrete spectrum due to multi-phonon transitions. Two years later, Lax [79] generalized the Huang-Rhys work to all phonon modes. He also introduced the moments of the absorption (and emission) band, which can be used to determine the values of theoretical parameters from experimental band shapes. In 1953, O'Rourke [97] presented a new approach to the problem of absorption of light by trapped electrons, the method based upon the use of the Slater sum for an oscillator (density matrix). By an assumption that the optical electronic transition accompanies a small change in the lattice vibration frequencies, he showed that absorption maximum shifts with temperature. In 1963, Perlin [105] published the review where he put together the early results of quantum-mechanical theory of vibronic transitions.

If the change of spring constants in the transition is important, then one needs to consider the quadratic electron-phonon interaction which causes the mixing (rotation) of modes (Duschinsky [20] rotation). In the case of small molecules, where the number of the contributing modes is small, the problem can be explicitly solved by applying the method proposed in 1954 by Kubo and Toyozawa [77]. Formally the method applies the adiabatic and harmonic approximations; otherwise it is universal, the theory does not depend on a concrete model of a center being investigated, however, the equations are not

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[1]   an electron trapped in a single negative ion (anion) vacancy

applicable directly to the systems with large number of vibrational degrees of freedom, since one does not know the practically working algorithms allowing to calculate huge number matrix elements of the high-order matrixes contained in the theory. At present as far as we know, there exist applications of this method to the case of two vibronically active modes, - the only non-trivial case, when the method appeared to be really efficient.

In condensed matter, however, one has to consider the mixing of huge (Avogadro number) N of normal modes (phonons), which strongly complicates the solution of the problem. This model enables one to explain, in particular, the temperature shift and broadening of the zero-phonon line (ZPL). The latter effect is of practical importance for application of doped crystals with narrow and intense ZPLs in crystalline lasers and in optical memory devices. It is also of principal importance in the phenomena like photon echo, tunnel and other transitions. The chemical feature of the quadratic vibronic coupling, i.e. the change of the atomic bonds during electronic transition, is essential in consideration of photochemical and other reactions. Very important role plays the quadratic vibronic coupling also in diffusion and other processes where the hopping motion is involved: the braking and reconstitution of atomic bonds at a hopping have strong effect on the temperature dependence of the process [39].

In the case of a weak quadratic interaction with phonons the problem can be solved by applying the time-ordering and cumulant expansion method. Note in this connection the contributions of McCumber [91] and Krivoglaz [75], where the first two cumulants have been considered, which have allowed to describe the temperature shift and temperature broadening of the zero-phonon line (ZPL). A few higher-order cumulants have been calculated by Hsu and Skinner [57, 58]. An important contribution to the problem has been given by Levenson [80], who has found the large time asymptotic of the Fourier transform with consideration of all cumulants (this asymptotic describes ZPL). Some useful properties of this solution have been established by Osad'ko [99]. A new approach has been developed by Hizhnyakov [50], based on algebraic relations between the Fourier transform of the spectrum and the Fourier-amplitudes of one- and two-phonon transitions. This method was successfully used for description of ZPLs in the case of arbitrary quadratic coupling with resonant (pseudolocal) modes [51].

In many cases, however, especially if one is interested in electronic process which involves, p and d electronic states in centers of small radius, the quadratic part of the vibronic interaction is not weak. This especially holds for photochemical reactions. Also diffusion of such defects as vacancies and interstitials is accompanied by strong local change of chemical bonds which correspond to strong quadratic coupling. For a long time there was a shortage of practically working methods which allowed one to perform calculations of vibronic transitions in these cases. Recently the situation has changed: in [VI] it was found that, if the interaction is not weak then the problem still can be solved by applying the method based on the path integrals and Hubbard [63] and Stratonovich [121] identity, which allows one to perform numerical

calculations of the spectral shapes with taking into account arbitrary changes of atomic bonds in crystal at the electronic transition. Some results of calculation by this method are given below and in our publications. However, as far as we know no analytical solutions have been found for the cases when the change of the local phonon dynamics at the transition is not small. Below we present one such a solution.

Note that our consideration is done for the case when electronic states are non-degenerate. If it not so, then one needs to take into account the Jahn-Teller effect. This effect often demands consideration of non-adiabatic effects, which may be very strong (in this connection, see e.g. the book of Perlin and Tsukerblat [104], where these effects are discussed). At present there exist numerical methods (based on the diagonalization of the vibronic Hamiltonian presented in the space of electronic and harmonic oscillators levels), which allow one to describe these effects supposing that the number of active vibrational mode is small. Recently in Institute of Physics, University of Tartu an investigation of strong non-adiabatic effects in optical spectra in case of phonon continuum given by an optical phonon band was performed; however the obtained results are not yet published. Note that zero-phonon lines in case of strong Jahn-Teller effect and strong psedo-Jahn-Teller effect in the final electronic state was studied in author's publications [VII,VIII] and by others.

The general plan of this work is as follows. In Sec. 2 the general theory of absorption line shapes is considered. The description of lattice dynamics in the presence of defect is given within a notion of normal modes. A thorough derivation of line-shape function is given with account of mode-mixing effects.

In Sec. 3 we discuss the influence of mode mixing on optical electronic-vibrational spectra of impurity centers. We provide model calculations for the case of two-mode mixing with various mixing parameters. Computer simulations of optical line shapes are based on common method of spectral estimation in time-domain with a subsequent Fourier analysis. We use Kubo-Toyozawa method of generating function (to account the mode mixing) and the density-matrix method by O'Rourke.

In Sec. 4, we apply the formal method of Fourier amplitudes for the special case of transitions between electronic states with different local lattice dynamics (in this connection see [III] and [V]). In particular, we consider the transition to the vicinity of a flat minimum of the potential energy in the configurational coordinate space. The method takes into account the phonon continuum and describes the behavior of zero-phonon line and phonon sideband.

Section 5 is a generalization of quadratic vibronic interaction theory to the case of interaction picture representation. Using operator calculus, a numerical framework is developed which enables to calculate high-accuracy absorption line shapes by finite discretization techniques. This method (see [IV], [VI]) is used to calculate the spectra of multiphonon transitions caused by quadratic vibronic coupling with phonon continuum.

2. GENERAL THEORY OF ABSORPTION LINE SHAPES IN ADIABATIC APPROXIMATION

2.1. Formulating of the Problem and Basic Assumptions

We consider the optical absorption and emission spectra arising from electronic transition between non-degenerate electronic states of an interacting defect-lattice system.

In the adiabatic approximation the electrons follow the motion of the nuclei adiabatically[2], so the motion of electrons and nuclei is treated separately. Thus, different Hamiltonians are used to describe phonons in different electronic states.

The shape of the absorption band[3] is determined by

$$I_{ab}(E) = \mathrm{Av}_\alpha \sum_\beta \left| \langle a\alpha | M_{ab}(\mathbf{R}) | b\beta \rangle \right|^2 \delta\left(E_{b\beta} - E_{a\alpha} - E\right), \qquad (2.1)$$

where Av_α stands for a thermal average[4] over the initial vibrational states, Σ_β for a sum over final vibrational states, $|a\alpha\rangle$ and $|b\beta\rangle$ are the vibrational wave functions for the ground (*a*) and excited (*b*) electronic states, $\langle a\alpha | M_{ab}(\mathbf{R}) | b\beta \rangle$ is the matrix element of the dipole moment electric operator between the electronic wave functions for the initial (a) and final (b) electronic states of impurity,

$$\langle a\alpha | M_{ab}(\mathbf{R}) | b\beta \rangle = \int \psi_{a\alpha}^*(\mathbf{R}) M_{ab}(\mathbf{R}) \psi_{b\beta}(\mathbf{R}) d\mathbf{R}, \qquad (2.2)$$

$$M_{ab}(\mathbf{R}) = \int \varphi_a^*(\mathbf{r}, \mathbf{R}) \left(\sum_i e\mathbf{r}_i \right) \varphi_b(\mathbf{r}, \mathbf{R}) d\mathbf{r}, \qquad (2.3)$$

The wave functions φ and ψ are the usual Born-Oppenheimer functions for the electrons and lattice, (**R**,**r**) are abbreviations for the nuclear and electronic coordinates. In general, dipole matrix element is a function of the nuclear coordinates. However, it suffices for many purposes to regard it as a constant (the Condon approximation[5]), for simplicity one can normalize it to unity. It

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[2] in other words, electronic states adjusts adiabatically to the slowly varying positions of nuclei

[3] some authors call it the (normalized) "shape function" and its Fourier transform – "characteristic function".

[4] an average in canonical ensemble

[5] in Condon approximation, the probability of the optical transition is independent on vibronic coordinate

should be mentioned that if the symmetry-restricted transitions take place, this particular approximation is not sufficient, since the element of transition matrix vanishes. To obtain non-zero transition matrix, non-Condon corrections must be applied. In present work we consider the symmetry-allowed transitions only.

Vibrational and electronic wave functions satisfy the following equations:

$$[T_N + V_i(\mathbf{R})]\psi_{i\gamma}(\mathbf{R}) = E_{i\gamma}\psi_{i\gamma}(\mathbf{R}), \tag{2.4}$$

$$[T_E + U_i(\mathbf{r},\mathbf{R})]\varphi_i(\mathbf{r},\mathbf{R}) = V_i(\mathbf{R})\varphi_i(\mathbf{r},\mathbf{R}), \tag{2.5}$$

where T_N is the nuclear kinetic-energy operator, T_E is the electronic kinetic-energy operator, $V_i(\mathbf{R})$ is the adiabatic potential in which the nuclei move, U_i ($\mathbf{r}$,$\mathbf{R}$) stands for all terms in Hamiltonian except the nuclear and electronic kinetic energies, $E_{i\gamma}$ is the energy eigenvalue (the vibrational part) of the adiabatic Hamiltonian [10,69] and $i\gamma$ stands for either $a\alpha$ or $b\beta$.

The adiabatic potential $V_a(\mathbf{R})$ for the ground state can be expanded in a Taylor series about the equilibrium position of nuclear displacements. The dynamics obviously are not affected by the constant term of the expansion, which thus can be discarded. Small displacements about the equilibrium position do not alter the potential energy to the first order, so that the linear term must be identically zero. If we retain the quadratic term neglecting all others, we are dealing with the *harmonic approximation*. Equation (2.4) for the initial state may be written

$$H_a\psi_{a\alpha}(\mathbf{R}) \equiv \sum_n \left[-\frac{\hbar^2}{2m_n}\frac{\partial^2}{\partial u_n^2} + \frac{1}{2}\sum_{n'}V_{nn'}u_nu_{n'} \right]\psi_{a\alpha}(\mathbf{R}) = E_{a\alpha}\psi_{a\alpha}(\mathbf{R}), \tag{2.6}$$

or, introducing mass-dependent[6] (generalized) coordinates $q_n = m^{1/2}u_n$ and the *dynamical matrix* with the elements $W_{nn'} = (m_n m_{n'})^{-1/2}V_{nn'}$, the initial-state Hamiltonian yields

$$H_a = -\frac{\hbar^2}{2}\sum_n \frac{\partial^2}{\partial q_n^2} + \frac{1}{2}\sum_{nn'}W_{nn'}q_nq_{n'}. \tag{2.7}$$

Potential energy is thus the quadratic form in generalized coordinates. This form is diagonalizable with the orthogonal[7] transformation

$$q_n = \sum_i e_{in}x_i, \tag{2.8}$$

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[6] or "mass-weighted"

[7] a transformation which transforms the sum of the squares of one set of coordinates into the sum of the other set is called an *orthogonal* transformation

where x is the normal coordinate, n is the number of degrees of freedom of the system, and $\mathbf{e}_i$ is the normal mode eigenvector[8], which satisfy the conditions of orthonormality and completeness:

$$\sum_i e_{in} e_{in'} = \delta_{nn'} \quad , \quad \sum_n e_{in} e_{i'n} = \delta_{ii'}. \qquad (2.9)$$

One can also prove the inverse transformation, $x_i = \sum_n e_{in} q_n$. Exploiting orthogonality,

$$\sum_n q_n^2 = \sum_k \left(\sum_i e_{ik} x_i \sum_j e_{jk} x_j \right) = \sum_{i,j} \left(\sum_k e_{ik} e_{jk} \right) x_i x_j = \sum_{i,j} \delta_{ij} x_i x_j = \sum_n x_n^2, \quad (2.10)$$

$$\sum_n \frac{\partial^2}{\partial q_n^2} = \sum_k \left(\sum_i \frac{\partial}{\partial x_i} \frac{\partial x_i}{\partial q_k} \sum_j \frac{\partial}{\partial x_j} \frac{\partial x_j}{\partial q_k} \right) = \sum_{i,j} \left(\sum_k e_{ik} e_{jk} \right) \frac{\partial^2}{\partial x_i \partial x_j} = \sum_{i,j} \delta_{ij} \frac{\partial^2}{\partial x_i \partial x_j} = \sum_n \frac{\partial^2}{\partial x_n^2}, \quad (2.11)$$

one can express initial-state Hamiltonian as a collection of normal modes, that is

$$H_a = -\frac{\hbar^2}{2} \sum_n \frac{\partial^2}{\partial x_n^2} + \frac{1}{2} \sum_n \omega_n^2 x_n^2. \qquad (2.12)$$

Here ω_n are the frequencies of normal modes, that is the solutions of the eigenvalue problem

$$\sum_{nn'} W_{nn'} e_{in} e_{i'n'} = \omega_i^2 \delta_{ii'} \quad \text{or} \quad \mathbf{e}_i^T \mathbf{W} \mathbf{e}_{i'} = \omega_i^2 \delta_{ii'}. \qquad (2.13)$$

The adiabatic potential in the final state differs from that in the initial state. Thus, we may expand the Hamiltonian for the final state (b) in the normal mode coordinates for the initial state

$$H_b = H_a + V, \qquad (2.14)$$

where interaction Hamiltonian can be written in generalized coordinates as

$$V = \hbar \omega_0 + \sum_n a_n q_n + \frac{1}{2} \sum_{nn'} b_{nn'} q_n q_{n'} \equiv V_0 + aq + \frac{1}{2} q^T b q, \qquad (2.15)$$

or, according to (2.8), in normal coordinates as

$$V = \hbar \omega_0 + \sum_i \bar{a}_i x_i + \frac{1}{2} \sum_{ii'} \bar{b}_{ii'} x_i x_{i'}, \qquad (2.16)$$

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[8] Other definitions used are the *displacement vector* or the polarization vector. It should be noted that within the harmonic approximation the displacement vector is independent of the mode amplitude.

$$\bar{a}_i = \sum_n a_n e_{in}; \quad \bar{b}_{ii'} = \sum_{nn'} \bar{b}_{nn'} e_{in} e_{i'n'}. \tag{2.17}$$

Here ω_0 is the frequency of a pure electronic transition, a, b are vector and tensor parameters of the electron-phonon interaction (the phenomenological constants) and q is the configurational coordinate vector depending on the normal coordinates as follows:

$$q = \sum_j e_{1j} x_j = \sum_k e_{2k} \left(y_k - y_{0k} \right) = \sum_k e_{2k} y_k - q_0, \tag{2.18}$$

The excited-state Hamiltonian is also composed of N normal modes, but with different coordinate, momenta and displacements,

$$H_b = -\frac{\hbar^2}{2} \sum_k \frac{\partial^2}{\partial y_k^2} + \frac{1}{2} \sum_k \Omega_k^2 y_k^2 + \bar{\omega}_0, \tag{2.19}$$

the exact expression for $\bar{\omega}_0$ will be given further in the text. Here we have fully neglected anharmonic effects. If these effects are small then anharmonic corrections can be found by applying temperature-ordered expansion. Small anharmonic effects, which result in broadening and shift of vibronic lines in the spectra have been considered by Krivoglaz [75], Hizhnyakov [52], and also by Lubchenko [83].

2.2. Mode Mixing

One can establish the correspondence between coordinates of vibrational modes in initial and final states. The final-state normal coordinates can be regarded as transformed initial-state coordinates; mathematically this can be accomplished by an orthogonal transformation (rotation in a space of normal coordinates)

$$\begin{cases} y_k = \sum_j S_{jk}(x_k + x_{0j}) \equiv \sum_j S_{jk} x_k + y_{0k} \\ x_j = \sum_k S_{jk}(y_k - y_{0k}) \equiv \sum_k S_{jk} y_k - x_{0j} \end{cases}, \quad \begin{cases} y = \mathbf{S}x + y_0 \\ x = \mathbf{S}y - x_0 \end{cases}, \tag{2.20}$$

where x_0, y_0 are the vectors of relative displacements of corresponding coordinates and $\mathbf{S}$ is the orthogonal Duschinsky rotation [20] matrix with the elements [55]

$$S_{jk} = b e_{1j} e_{2k} \left(\Omega_k^2 - \omega_j^2 \right)^{-1}, \tag{2.21}$$

e_{1j} and e_{2k} are the components of the vector q in the space of normal coordinates, which satisfy the conditions

$$e_{2k} = \sum_j S_{jk} e_{1j}, \qquad \sum_j e_{1j}^2 = \sum_k e_{2k}^2 = 1. \tag{2.22}$$

Inserting (2.21) into (2.22) yields

$$\sum_j S_{jk} e_{1j} = b \sum_j \frac{e_{1j}^2 e_{2k}}{\Omega_k^2 - \omega_j^2}. \tag{2.23}$$

Hence it follows that

$$\sum_j \frac{e_{1j}^2}{\Omega_k^2 - \omega_j^2} = \sum_k \frac{e_{2k}^2}{\Omega_k^2 - \omega_j^2} = b^{-1}. \tag{2.24}$$

Relative displacements can be written as the functions of electron-phonon interaction parameters:

$$x_{0j} = (a - bq_0) e_{1j} \omega_j^{-2}, \quad y_{0k} = a e_{2k} \Omega_k^{-2}. \tag{2.25}$$

2.3. Normal Modes as Harmonic Oscillators

To gain insight into the properties of solids that are due to lattice vibrations, the quantum mechanics of harmonic oscillators has to be recalled. Imposing the requirement of square integrability[9], the eigenvalues of Hamiltonian are expressed in terms of the Hermite polynomials. Written in normal coordinates (hereafter we use atomic units $e = \hbar = m_e = 1$), the eigenfunctions normalized to unity are

$$\psi_n(x) = (\omega/\pi)^{1/4} (2^n n!)^{-1/2} H_n(\omega^{1/2} x) e^{-\omega x^2/2}, \tag{2.26}$$

and the energy eigenvalue of the state of quantum number n is

$$\varepsilon_n = \omega(n + 1/2). \tag{2.27}$$

The wavefunction of the ground state is a Gaussian of finite width,

$$\psi_0(x) = (\omega/\pi)^{1/4} e^{-\omega x^2/2}. \tag{2.28}$$

The solution of the eigenvalue problem is determined in terms of the Hermitian operators of position and momentum, which satisfy canonical commutation relations. An easier alternative is offered by writing the Hamiltonian in terms of the non-Hermitian operator

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[9] the wavefunction vanishes sufficiently rapidly at infinity

$$a = (\omega/2)^{1/2}(x + ip\omega^{-1}) \qquad (2.29)$$

and its adjoint. Using the new operators, x and p are expressed as

$$x = (2\omega)^{-1/2}(a + a^{\dagger}), \quad p \equiv -i\frac{d}{dx} = (2\omega)^{-1/2}(a - a^{\dagger}). \qquad (2.30)$$

Making use of the canonical commutation relation between position and momentum operators, it is immediately established that $[a, a^{\dagger}] = 1$.

According to (2.20), the normal coordinates can be expressed as

$$x_j = (2\omega_j)^{-1/2}(a_j + a_j^{\dagger}) = -x_{0j} + \sum_k c_{jk}(2\Omega_k)^{-1/2}(A_k + A_k^{\dagger}), \qquad (2.31)$$

$$y_k = (2\Omega_k)^{-1/2}(A_k + A_k^{\dagger}) = y_{0k} + \sum_j c_{jk}(2\omega_j)^{-1/2}(a_k + a_k^{\dagger}), \qquad (2.32)$$

where

$$a_j = -(\omega_j/2)^{1/2}x_{0j} + 1/2\sum_k c_{jk}(\omega_j\Omega_k)^{-1/2}\left[(\omega_j + \Omega_k)A_k + (\omega_j - \Omega_k)A_k^{\dagger}\right], \qquad (2.33)$$

$$A_k = (\Omega_k/2)^{1/2}y_{0k} + 1/2\sum_k c_{jk}(\omega_j\Omega_k)^{-1/2}\left[(\omega_j + \Omega_k)a_j + (\Omega_k - \omega_j)a_j^{\dagger}\right], (2.34)$$

and corresponding (adjoint) raising operators are obtained by Hermitian conjugation. These equations take into account the mixing of the normal coordinates when the electronic transition occurs. Then Hamiltonians of the initial and final states acquire the form

$$H_a = \sum_j \omega_j\left(a_j^{\dagger}a_j + 1/2\right), \qquad (2.35)$$

$$H_b = \bar{\omega}_0 + \sum_k \Omega_k\left(A_k^{\dagger}A_k + 1/2\right), \qquad (2.36)$$

where $a, a^{\dagger}$ (and their alter-egos for the excited state) are the annihilation and creation operators. The corresponding formalism is known as *secondary quantization*.

2.4. Fourier Analysis of Optical Spectra

Introducing the integral (spectral) representation of Dirac's delta function

$$\delta(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} dt,$$

and replacing energies by the corresponding Hamiltonian operators H_a and H_b in order to permit the closure sum over final vibrational states, the expression for the absorption function (2.1) reduces to

$$I_{ab}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i(\omega-\omega_0)t} g_{ab}(t) dt, \tag{2.37}$$

with characteristic function

$$g_{ab}(t) = \text{Av}_\alpha \sum_\beta \langle a\alpha | b\beta \rangle \langle b\beta | e^{iH_b t} e^{-iH_a t} | a\alpha \rangle = \text{Av}_\alpha \langle a\alpha | e^{iH_b t} e^{-iH_a t} | a\alpha \rangle. \tag{2.38}$$

One can perform the Boltzmann averaging by inserting an exponential factor $e^{-H_a/kT}$, and the previous expression written in terms of traces becomes

$$g_{ab}(t) = Tr\left[e^{iH_b t} e^{-iH_a t} e^{-H_a/kT} \right] \Big/ Tr\left[e^{-H_a/kT} \right]. \tag{2.39}$$

Hereafter we omit subscripts for simplicity and make a replacement for distinct electronic states. Thus our concern is to calculate the spectral function

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i(\omega-\omega_0)t - \gamma_0|t|} g(t) dt, \tag{2.40}$$

where

$$g(t) = \text{Av}\left[e^{iH_2 t} e^{-iH_1 t} \right], \tag{2.41}$$

H_2 stands for the excited state Hamiltonian, H_1 for the ground state Hamiltonian, and we introduced the damping factor γ_0 for the natural line width ($\tau = \frac{1}{2}\gamma_0$ is radiation lifetime).

3. EFFECTS OF MODE MIXING: A DENSITY MATRIX APPROACH

In this chapter we apply a formal density matrix framework to a selected problem of the optical spectroscopy of solids (with impurities); namely, influence of the mode mixing on electronic-vibrational spectra with arbitrary electron-lattice coupling parameters. We consider exact account of two-mode mixing in the case of zero temperature as well as finite temperatures.

3.1. Slater Sum of Harmonic Oscillators

From Eq.(2.41) it follows that the characteristic function is the average of two exponential operators. Statistical average (with Boltzmann factor, for the single state n) can be written by the means of traces algebra as follows:

$$\text{Av}\left[e^{itH_2} e^{-itH_1} \right] = Tr\left(\rho e^{itH_2} e^{-itH_1} \right) = Z^{-1} \sum_n \langle n | e^{itH_2} e^{-itH_1} e^{-H_1/kT} | n \rangle =$$
$$= Z^{-1} \sum_n \langle n | e^{itH_2} | n \rangle e^{-(it+1/kT)E_n} \tag{3.1}$$

When the adiabatic and Condon approximations are made and the system is described by normal modes with Hamiltonian (2.12), the characteristic function reads

$$g(t) = \sum_{m_j, n_j} \left(e^{-\sum_{j=1}^{N}\left[(n_j+1/2)\beta\omega_j - it(m_j-n_j)\omega_j\right]} \prod_{j=1}^{N} \left| \langle bm_j | an_j \rangle \right|^2 \right) \left(\prod_{j=1}^{N} \sum_{n_j} e^{-(n_j+1/2)\beta\omega_j} \right)^{-1} = \tag{3.2}$$
$$= \prod_{j=1}^{N} g_j,$$

where

$$g_j = Z_j^{-1} \sum_{m_j, n_j} e^{-(m_j+1/2)\mu\omega_j - (n_j+1/2)\lambda\omega_j} \left| \langle bm_j | an_j \rangle \right|^2 = \tag{3.3}$$
$$= Z_j^{-1} \iint dx\,dx' \rho(x_j, x'_j; \mu\omega_j)\rho(x_j, x'_j; \lambda\omega_j),$$

$$\beta = (kT)^{-1}, \quad \mu = -it, \quad \lambda = \beta + it, \tag{3.4}$$

and off-diagonal generalization of the Slater sum $\rho(x, x'; \beta)$ has been used, namely

$$\rho(x, x'; \eta\omega) = \left(\frac{\omega}{2\pi \sinh(\eta\omega)} \right)^{1/2} \exp\left\{ -\frac{\omega}{4}\left[(x+x')^2 \tanh\left(\frac{\eta\omega}{2}\right) + (x-x')^2 \coth\left(\frac{\eta\omega}{2}\right) \right] \right\}. \tag{3.5}$$

Depending on context, the last expression can define the canonical density matrix or the Feynman propagator. In expressions above, the partition function yields

$$Z_j^{-1} = \left(\sum_{n_j} e^{-(n_j+1/2)\beta\omega_j} \right)^{-1} = \frac{1 - e^{-\beta\omega_j}}{e^{-\beta\omega_j/2}} = 2\sinh\left(\beta\omega_j/2\right). \qquad (3.6)$$

3.2. Absorption Spectrum of Two Vibrational Modes

Consider the system described by two normal coordinates. Then Hamiltonians of the system in the initial (1) and final (2) states is given by quadratic forms in the normal coordinates

$$H_1 = T + \frac{1}{2}\sum_{n=1}^{2}\omega_n^2 x_n^2, \quad H_2 = T + \frac{1}{2}\sum_{n=1}^{2}\Omega_n^2 y_n^2, \qquad (3.7)$$

where T is the kinetic energy of the nuclear motion, (x,y) are normal mode coordinates and (ω,Ω) are the frequencies corresponding to the normal modes. The normal coordinates are related by the orthogonal transformation (which is a simple coordinate rotation in a plane plus arbitrary linear shift):

$$\begin{pmatrix} y_1 \\ y_2 \end{pmatrix} = \begin{pmatrix} \cos\varphi & \sin\varphi \\ -\sin\varphi & \cos\varphi \end{pmatrix}\begin{pmatrix} x_1 \\ x_2 \end{pmatrix} + \begin{pmatrix} y_{01} \\ y_{02} \end{pmatrix}, \quad y_k = \sum_{n=1}^{2} S_{nk}x_n + y_{0k}, \quad y = \mathbf{S}x + y_0. \ (3.8)$$

Here φ is the rotation angle (mixing parameter) and y_0, x_0 are the linear translation vectors. In order to decouple the normal coordinates, one should diagonalize the rotation matrix. By orthogonality ($\mathbf{S}^T = \mathbf{S}^{-1}$), it follows that

$$x = \mathbf{S}^{-1}y - \mathbf{S}^{-1}y_0 \equiv \mathbf{S}^T y + x_0, \qquad (3.9)$$

$$x_0 = -\mathbf{S}^T y_0 \quad \Leftrightarrow \quad y_0 = -\mathbf{S}x_0. \qquad (3.10)$$

One can introduce a shorter notation for used hyperbolic functions, such as

$$s_j = \sinh(\lambda\omega_j), \quad c_j = \cosh(\lambda\omega_j), \quad S_j = \sinh(\mu\Omega_j), \quad C_j = \cosh(\mu\Omega_j), \quad (3.11)$$

and recall the identity

$$\tanh\frac{z}{2} = \frac{\sinh z}{\cosh z + 1} = \frac{\cosh z - 1}{\sinh z} \equiv \left(\coth\frac{z}{2} \right)^{-1}. \qquad (3.12)$$

At this point, the preparation process is complete and one can proceed the direct calculation. The single-coordinate characteristic function (3.3) reads

$$g_j = Z_j^{-1} \iint dx_j dx_j' \rho(y_j, y_j'; \mu\Omega_j)\rho(x_j, x_j'; \lambda\omega_j) =$$

$$= \pi^{-1} \sinh\left(\beta\omega_j/2\right)\left(\Omega_j\omega_j / S_j s_j\right)^{1/2} \times \tag{3.13}$$

$$\times \iint dx_j dx_j' e^{-\left[(y_j^2 + y_j'^2)C_j - 2y_j y_j'\right]\Omega_j/2S_j} e^{-\left[(x_j^2 + x_j'^2)c_j - 2x_j x_j'\right]\omega_j/2s_j}$$

Making use of coordinate transformation (3.8), excited-state coordinates (y) can be written as the functions of the ground-state coordinates (x). In such a case the two-mode characteristic function is a quadratic form in y-coordinates. Introducing a new set of variables, one can transform the quadratic form in (3.13) into a form in which there is no cross-product terms[10]. Changing the basis with a new coordinate system,

$$z_j = (2)^{-1/2}\left(x_j + x_j'\right), \quad z_j' = (2)^{-1/2}\left(x_j - x_j'\right), \quad j = 1, 2, \tag{3.14}$$

the quadratic form in the exponential of the characteristic function becomes decoupled in primed and unprimed normal mode coordinates. It follows that

$$g(t) = \pi^{-2}\sinh\left(\tfrac{1}{2}\beta\omega_1\right)\sinh\left(\tfrac{1}{2}\beta\omega_2\right)\left(\frac{\Omega_1\Omega_2\omega_1\omega_2}{S_1 S_2 s_1 s_2}\right)^{1/2} e^{-\Omega_1 y_{01}^2(C_1 - 1)S_1^{-1} - \Omega_2 y_{02}^2(C_2 - 1)S_2^{-1}} \times \tag{3.15}$$

$$\times \int d\mathbf{z}\, e^{-\frac{1}{2}\mathbf{z}^T \mathbf{A}_- \mathbf{z} + \mathbf{b}} \int d\mathbf{z}'\, e^{-\frac{1}{2}\mathbf{z}'^T \mathbf{A}_+ \mathbf{z}'}$$

with

$$\mathbf{A}_{\mp} = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}, \quad \begin{cases} a_{11} = \Omega_1 \cos^2\varphi(C_1 \mp 1)S_1^{-1} + \Omega_2 \sin^2\varphi(C_2 \mp 1)S_2^{-1} + \omega_1(c_1 \mp 1)s_1^{-1} \\ a_{22} = \Omega_1 \sin^2\varphi(C_1 \mp 1)S_1^{-1} + \Omega_2 \cos^2\varphi(C_2 \mp 1)S_2^{-1} + \omega_2(c_2 \mp 1)s_2^{-1} \\ a_{12} = \Omega_1 \sin 2\varphi(C_1 \mp 1)S_1^{-1} \\ a_{21} = -\Omega_2 \sin 2\varphi(C_2 \mp 1)S_2^{-1} \end{cases}, \tag{3.16}$$

$$\mathbf{b} = \begin{pmatrix} b_1 \\ b_2 \end{pmatrix}, \quad \text{where} \quad \begin{cases} b_1 = \sqrt{2}\left(\Omega_1 y_{01}\cos\varphi(C_1 - 1)S_1^{-1} - \Omega_2 y_{02}\sin\varphi(C_2 - 1)S_2^{-1}\right) \\ b_2 = \sqrt{2}\left(\Omega_1 y_{01}\sin\varphi(C_1 - 1)S_1^{-1} + \Omega_2 y_{02}\cos\varphi(C_2 - 1)S_2^{-1}\right) \end{cases}, \tag{3.17}$$

and y_0 defined in (3.10). Integrals in (3.15) are well-known Gaussian integrals,

$$\int d\mathbf{z}\, e^{-\frac{1}{2}\mathbf{z}^T \mathbf{A}\mathbf{z} + \mathbf{b}} = 2\pi\left(\det \mathbf{A}_-\right)^{-1/2} e^{\frac{1}{2}\mathbf{b}^T \mathbf{A}_-^{-1}\mathbf{b}}, \quad \int d\mathbf{z}'\, e^{-\frac{1}{2}\mathbf{z}'^T \mathbf{A}\mathbf{z}'} = 2\pi\left(\det \mathbf{A}_+\right)^{-1/2}. \tag{3.18}$$

One can use the following rule for calculating an inverse matrix,

$$\mathbf{b}^T \mathbf{A}^{-1}\mathbf{b} = \frac{a_{22}b_1^2 - (a_{12} + a_{21})b_1 b_2 + a_{11}b_2^2}{a_{11}a_{22} - a_{12}a_{21}}. \tag{3.19}$$

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[10] known as canonical form

Thus, in case of averaging over Boltzmann's ensemble and two-mode mixing, the characteristic function equals

$$g(t) = 4\left(\frac{\Omega_1\Omega_2\omega_1\omega_2}{S_1S_2s_1s_2}\right)^{1/2} \frac{\sinh\left(\frac{1}{2}\beta\omega_1\right)\sinh\left(\frac{1}{2}\beta\omega_2\right)}{\left(\det \mathbf{A}_- \det \mathbf{A}_+\right)^{1/2}} \times$$
$$\times e^{-\frac{1}{2}\mathbf{b}^T\mathbf{A}_-^{-1}\mathbf{b}} e^{-\Omega_1 y_{01}^2(C_1-1)S_1^{-1}-\Omega_2 y_{02}^2(C_2-1)S_2^{-1}}. \tag{3.20}$$

3.3. Low Temperature Limit

One may consider the special case of Boltzmann's averaging over canonical ensemble, when all the phonons are in the ground state (the case of T=0). The characteristic function (3.2) yields

$$g(t)\big|_{T=0} = \prod_{j=1}^{2} \iint dy_j dy_j' e^{-it\omega_j/2}\psi_0(x_j)\psi_0^*(x_j')\rho(y_j,y_j';\mu\Omega_j) = \prod_{j=1}^{2} g_{0j}, \tag{3.21}$$

where $\psi_0(x)$ is the harmonic oscillator eigenfunction for the ground state, defined in (2.28), and integration is performed over excited-state coordinates (y). Using definitions above,

$$g_{0j} = \pi^{-1}\left(\frac{\Omega_j\omega_j}{2S_j}\right)^{1/2} e^{-it\omega_j/2}\iint dy_j dy_j' e^{-(x_j^2+x_j'^2)\omega_j/2}e^{-\left[(y_j^2+y_j'^2)C_j-2y_jy_j'\right]\Omega_j/2S_j}. \tag{3.22}$$

Unwrapping x's in terms of y's and introducing coordinate transformation

$$z_j = (2)^{-1/2}\left(y_j + y_j'\right), \quad z_j' = (2)^{-1/2}\left(y_j - y_j'\right), \quad j=1,2, \tag{3.23}$$

one has decoupled quadratic form in the exponent of characteristic function, namely

$$g(t)\big|_{T=0} = \pi^{-2}\left(\frac{\Omega_1\Omega_2\omega_1\omega_2}{4S_1S_2}\right)^{1/2} e^{-it(\omega_1+\omega_2)/2}e^{-(\omega_1 x_{01}^2+\omega_2 x_{02}^2)}\int d\mathbf{z}\, e^{-\frac{1}{2}\mathbf{z}^T\mathbf{A}_-\mathbf{z}+\mathbf{b}}\int d\mathbf{z}'\, e^{-\frac{1}{2}\mathbf{z}'^T\mathbf{A}_+\mathbf{z}}, \tag{3.24}$$

where[11]

---

[11] note that matrices defined here are different from those have been used concerning the finite temperatures

$$\mathbf{A}_{\mp} = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}, \quad \text{where} \quad \begin{cases} a_{11} = \omega_1 \cos^2 \varphi + \omega_2 \sin^2 \varphi + \Omega_1 (C_1 \mp 1) S_1^{-1} \\ a_{22} = \omega_1 \sin^2 \varphi + \omega_2 \cos^2 \varphi + \Omega_2 (C_2 \mp 1) S_2^{-1} \\ a_{12} = \omega_2 \sin 2\varphi \\ a_{21} = -\omega_1 \sin 2\varphi \end{cases}, \quad (3.25)$$

$$\mathbf{b} = \begin{pmatrix} b_1 \\ b_2 \end{pmatrix}, \quad \text{where} \quad \begin{cases} b_1 = -\sqrt{2} \left(\omega_1 x_{01} \cos \varphi + \omega_2 x_{02} \sin \varphi \right) \\ b_2 = -\sqrt{2} \left(-\omega_1 x_{01} \sin \varphi + \omega_2 x_{02} \cos \varphi \right) \end{cases}. \quad (3.26)$$

In case of zero temperature and two-mode mixing, the characteristic function equals

$$g(t)\big|_{T=0} = 2 \left(\frac{\Omega_1 \Omega_2 \omega_1 \omega_2}{S_1 S_2 \det \mathbf{A}_- \det \mathbf{A}_+} \right)^{1/2} e^{-\frac{1}{2} \mathbf{b}^T \mathbf{A}_-^{-1} \mathbf{b}} e^{-it(\omega_1 + \omega_2)/2} e^{-(\omega_1 x_{01}^2 + \omega_2 x_{02}^2)}. \quad (3.27)$$

3.4. Numerical Study of Duschinsky Rotation Effects

The effects of mode mixing can be illustrated by direct calculation of the line shape functions defined in (2.40). For the given parameters, characteristic functions have been calculated with subsequent Fourier transform. One can easily see that even in the case of zero temperature the mixing parameter significantly affects the optical spectra. On Figure 3.1 the dependence of the absorption line-shape on the sign an absolute value of mixing parameter is given[12], when frequency shift is relatively small. Further investigation of the detailed structure of the spectra shows that depending on the Duschinsky rotation angle, resulted spectra may contain whether single-, multi-phonon, or even phononless transitions with a given (excited-state) frequency. In other words, the structure of the spectrum is defined by a linear combination of vibrational frequencies of the excited state.

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[12] In present thesis, the X-axis represents dimensionless frequencies; the Y-axis represents spectral intensity (also dimensionless). In some cases of multiple plots in the figure, X-values should be treated as relative frequencies rather than absolute.
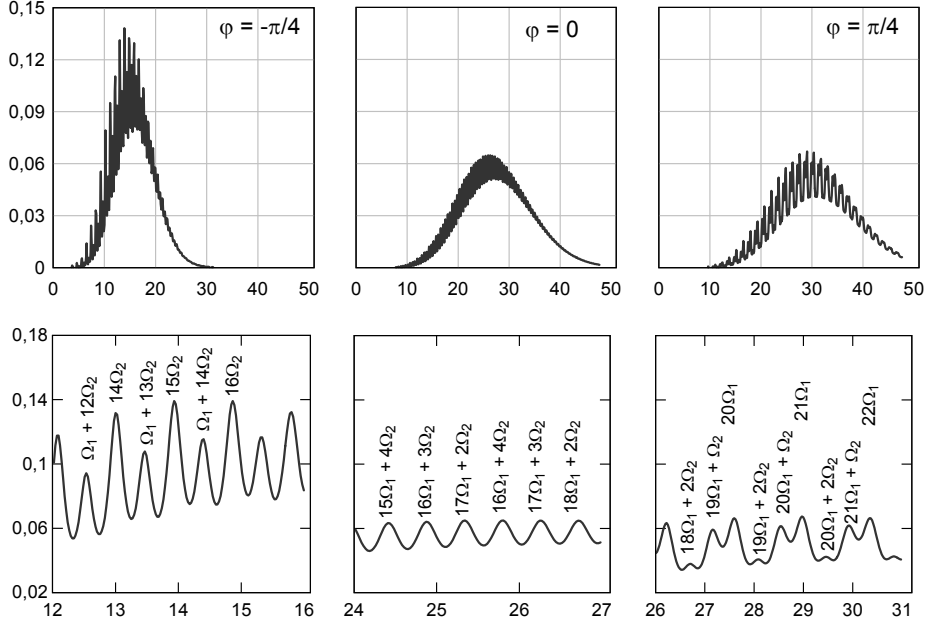
Figure 3.1 Absorption line shape dependence on the value of Duschinsky rotation angle (ω_1=1.0, Ω_1=1.38, ω_2=0.9, Ω_2=0.93, φ=−45º/0/45º, x_0=(5.0,3.0)). Lower set of images illustrates the detailed structure of corresponding curves.

The structure of the line shapes is also affected by the linear translation parameter. If the normal coordinates are not shifted from equilibrium site (the corresponding translation vector has zero length), the corresponding frequency does not manifest in the spectrum.

There is plenty of line shape one can obtain by setting different interaction parameters. In the case when there is no frequency change in the transition, the line-shape is essentially non-Gaussian (see Fig 3.2a) due to the presence of mode mixing.

Rising temperature remarkably affects both spectral lines and spectrum width. The higher the temperature, the more likely become transitions with annihilation of phonons. The number of lines rapidly grows and so does their density. High enough temperature populates anti-Stokes region of spectrum as well. The mode mixing also affects essentially the absorption and fluorescence profiles. A strong mixing remarkably violates the mirror symmetry of these spectra (see Fig 3.2b).

Figure 3.2 Simulated optical spectra: (a) case of pure mode mixing ($\omega_1 = \Omega_1 = 3.0$, $\omega_2 = \Omega_2 = 1.0$, $\varphi = -45°$, $x_0 = (5.0, 2.0)$); (b) symmetry violation by the mode mixing ($\omega_1 = 1.0$, $\Omega_1 = 1.38$, $\omega_2 = 0.9$, $\Omega_2 = 0.93$, $\varphi = 45°$, $x_0 = (5.0, 3.0)$.

The framework presented in this section is applicable when standard spectral methods do not give desirable results. However, it is limited to the cases of a small number of vibrational coordinates. There is plenty of models where one has to deal with the whole continuum of modes, like impurity centre of small radii, molecules trapped in liquid helium droplets and many others. To do so, one needs another theory, more suitable for description of such cases. An attempt to extend the framework is provided in the next section.

4.   LOCAL PHONON DYNAMICS: THE METHOD OF FOURIER AMPLITUDES

4.1. Approximation of Soft Dynamics

One can obtain an analytical solution also in the case the vibronic transition takes place between states with different local phonon dynamics and with strong mixing of modes of phonon continuum. Here we have in mind the case (studied in [III]) when phonon dynamics in the final state is changed so strongly that the mean phonon frequencies in this state become much smaller than in the initial state and the main contribution to the spectrum is due to the continuum of the low-frequency pseudo-local vibration which exists in the final state but does not appear in the initial state. The main attention is paid to the shape of the phonon sideband of the zero-phonon line. Only the zero temperature case is considered.

The solution is based on the phonon operator transformation method introduced by Hizhnyakov [50]. This method allows one to obtain exact equation for one and two-phonon Fourier amplitudes of the vibronic transition. Note that these amplitudes determine the entire Fourier transform of the vibronic transition. Previously this method was used for investigation of the effect of mode mixing in the resonant Raman scattering. In the present work it shown that the set of N-equations ($N \sim$ Avogadro's number) for the one and two-phonon amplitudes in the case of the vibronic transition between states with hard and soft phonon dynamics can be reduced to a few closed equations that can be solved explicitly.

One of the reasons for the theoretical investigation of the effect of the soft phonon dynamics in optical spectra is a strong sensitivity of latter in the vicinity of the pure electronic transition on the vibronic interaction with low-frequency phonons. An enhancement of the vibronic interaction results in increase of this part of the optical spectrum. There exist some experimental facts, where such an enhancement was actually observed. We have in mind here the so called λ-shaped spectra, where one does not see the zero-phonon line at all; instead one observes jump-like appearance of the spectral intensity of the type $\theta(\omega - \omega_0)F(\omega)$, where ω_0 is the resonant frequency, θ is the Heaviside step function and $F(\omega)$ smoothly decreases with ω. Such spectra have been observed e.g. in glasses [73] and in droplets of superfluid ^4He with Na_2 and Na_3 complexes attached to the surface of the droplet [86].

Another reason is the importance of this problem for understanding the role of the lattice fluctuations in the phase transitions. Indeed, one of the commonly accepted models of the second order phase transitions supposes the existence of the soft phonon mode(s), the frequency(es) of which gets to zero (or almost to zero) at the phase transition. Thereat the transition often takes place as a series of the mesoscopic phase transitions near defects. Some of these transitions can occur at low temperatures. Applying of already rather moderate hydrostatic

pressure to these crystals allows one to change essentially the transition temperature, sometimes to shift the temperature even to $T \leq 0$. In this case the pressure allows one to substantially reduce the local elastic springs in crystals. For the problem under consideration it is significant that the local softening of the lattice near the optical center may take place first for one of the electronic states of the center, and then also for another state (at higher pressure). This allows one to carry out the experimental investigation of the system with different optical transitions between electronic states with soft phonon dynamics.

Besides the optical spectra, the problem of quadratic vibronic interaction is also important for chemical reactions and diffusion. Thus, for example, a vacancy causes strong local softening of the lattice, as a result a low-frequency quasilocal mode(s) appears. In a simple cubic lattice this mode has E_g symmetry, in *bcc* lattice the symmetry is T_{1g}. Therefore the vacancy jump can be described as a vibronic transition determined by the soft phonon dynamics [39].

4.2. Debye's Model

The Debye theory approximates the frequency distribution by using the low frequency distribution for all frequencies, cutting it off at a value chosen to give the correct total number of frequencies. This model gives a correct description of the phonon spectrum in the low-frequency limit, when the initial state is free of quasi-local vibrations. It is supposed here that due to strong quadratic vibronic coupling leading to the reduction of local elastic springs, in the final (excited) state such vibrations take place, and one should consider another model having the phonon density peak.

In Debye model of acoustic continuum modes the configurational coordinate is of the order of ω, that is a difference in displacements of configurational coordinates. The corresponding density of states $\sim \omega^2$, since it always contains squared coordinate (from correlation function)

Let us denote $\rho_i(\omega)$ the local density of states (LDOS), which corresponds to the configurational coordinate q (index i stands for either initial (1) or final (2) electronic state):

$$\rho_i(\omega) = \sum_j e_{ij}^2 \delta(\omega - \omega_{ij}) \quad i = 1, 2. \tag{4.1}$$

Considering low-frequency part of phonon spectrum, one can introduce the approximation $\rho(\omega) \propto A\omega^4$. Here an additional ω^2-factor arises from the definition of configurational coordinate as the displacement of adjacent atoms. The normalization constant is obtained from the definition of Debye cutoff

frequency, which we normalize to unity. Thus, in the initial state, $\rho_1(\omega) = 5\omega^4$ and normalization yields

$$\int_0^{\omega_D} \rho_1(\omega)d\omega = \int_0^1 5\omega^4 d\omega = 1.$$ (4.2)

We can use integral instead of sum,

$$\sum_j e_{1j}^2 \omega_j^{-1} = \int_0^1 \rho_1(\omega)\omega^{-1}d\omega = 5/4$$ (4.3)

From the well-known relation between the local density of states and Green's function (see Maradudin et al. [88]),

$$\rho(\omega) = 2\omega\pi^{-1}\operatorname{Im}G(\omega),$$ (4.4)

one can calculate the excited-state LDOS using the Green's function method. For the ground state, the dynamical Green's function in the spectral representation yields

$$G_1(\omega) = \int_0^1 \frac{\rho_1(\omega')d\omega'}{\omega^2 - \omega'^2} = -5\left[\frac{1}{3} + \omega^2 - \frac{\omega^3}{2}\ln\frac{1+\omega}{1-\omega} - i\frac{\pi}{2}\omega^3\right].$$ (4.5)

The excited-state Green's function follows from the Dyson equation,

$$G_2(\omega) \equiv G_1(1 - bG_1)^{-1} = b^{-1}\left[-1 + \left(1 - b(\operatorname{Re}G_1 - i\operatorname{Im}G_1)\right)|1 - bG_1|^{-2}\right]$$ (4.6)

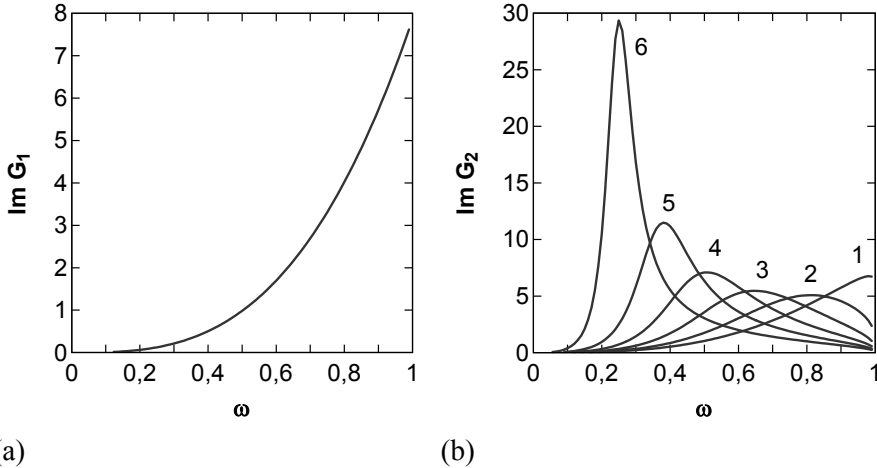(a)   (b)

Figure 4.1. Imaginary part of Green's function. Drawing (a) corresponds to non-perturbed Green's function (for the initial state); drawing (b) stands for the final-state Green's function with the following values of quadratic vibronic interaction parameter: $1 - b = -0.01$, $2 - b = -0.1$, $3 - b = -0.3$, $4 - b = -0.4$, $5 - b = -0.5$

Imaginary parts of Green's functions are presented in Figure 4.1. One can see that in the case of small $b - b_0$, where $b_0 = -0.6$, the low-frequency peak (called pseudo-local mode) appears in the $\mathrm{Im}\, G_2$-distribution. By inserting the imaginary part of (4.5) into (4.6) and (4.4), one gets

$$\rho_2(\omega) = \frac{5}{9}\omega^4\left(\left[\alpha + \omega^2 - \frac{1}{2}\omega^3 \ln\frac{1+\omega}{1-\omega}\right]^2 + \frac{\pi^2\omega^6}{4}\right)^{-1}, \qquad (4.7)$$

where $\alpha = (5b)^{-1} + (1/3)$. This density function (4.7) is not normalized, but still acceptable in Debye's model for the case of small frequencies.

In present approach the difference of Green's functions in initial and final electronic states is the origin of the mirror symmetry violation between the emission and the absorption spectra.

4.3. Derivation of Phonon Amplitudes

At zero temperature (T=0) all particles occupy the ground state (of lowest energy). One can define the state of lowest energy by $H_1|0\rangle = 0$ and normalize it to $\langle 0|0\rangle = 1$. Then $e^{itH_2}e^{itH_1} = e^{itH_2}$ and characteristic function (2.41) acquires the form

$$g(t) = \langle 0|e^{itH_2}|0\rangle. \qquad (4.8)$$

Taking a derivative of g with respect to time,

$$-ig'(t) = \langle 0|e^{itH_2}V|0\rangle = \omega_0 g + a_0\langle 0|e^{itH_2}q|0\rangle + \tfrac{1}{2}b\langle 0|e^{itH_2}q^2|0\rangle =$$
$$\equiv \omega_0 g + a_0 g_1 + b g_2. \qquad (4.9)$$

Introducing phonon operators, configurational coordinates (2.18) are linear functions in normal coordinates (2.32), that is functions of creation and annihilation operators. Using properties of ladder operators

$$a_j|0\rangle = 0, \quad \langle 0|a_j^\dagger = 0, \quad (a_j + a_j^\dagger)(a_{j'} + a_{j'}^\dagger)|0\rangle = \delta_{jj'} + a_j^\dagger a_{j'}^\dagger, \quad (4.10)$$

one gets

$$g_1 \equiv \langle 0|e^{itH_2}q|0\rangle = \sum_j e_{1j}(2\omega_j)^{-1/2}\langle 0|e^{itH_2}a_j^\dagger|0\rangle, \qquad (4.11)$$

$$g_2 \equiv \tfrac{1}{2}\langle 0|e^{itH_2}q^2|0\rangle = \tfrac{1}{4}\sum_j e_{1j}^2\omega_j^{-1}g + \tfrac{1}{4}\sum_{jj'}e_{1j}e_{1j'}(\omega_j\omega_{j'})^{-1/2}\langle 0|e^{itH_2}a_j^\dagger a_{j'}^\dagger|0\rangle. \ (4.12)$$

In order to calculate terms g_1 and g_2 (we refer them as phonon amplitudes), one can introduce the following time-dependent function

$$\varphi_n(t) \equiv \sum_k e_{2k}^2 \Omega_k^{-n} e^{it\Omega_k}, \quad \varphi_n \equiv \varphi_n(t), \quad \varphi_{n0} \equiv \varphi_n(0), \qquad (4.13)$$

to express the solution of Eq. (4.8) in terms of few integrable functions. To accommodate the mode mixing, we first express phonon amplitudes in the excited-state phonon operators and then isolate the solution by recalling the ground-state phonon operators.

I. *Derivation of g_1.*
Let us first calculate matrix elements containing single-phonon operators. From (4.11), (4.10), (2.31) and (2.20), it follows that

$$\langle 0|e^{itH_2} a_j^\dagger|0\rangle \equiv \langle 0|e^{itH_2}\left(a_j + a_j^\dagger\right)|0\rangle =$$

$$= \langle 0|e^{itH_2}\omega_j^{1/2}\left[-2^{1/2}x_{0j} + \sum_k S_{jk}\Omega_k^{-1/2}(A_k + A_k^\dagger)\right]|0\rangle = \quad (4.14)$$

$$= \sum_k S_{jk}\omega_j^{1/2}\left[-2y_{0k}g + \Omega_k^{-1/2}\langle 0|e^{itH_2}(A_k + A_k^\dagger)|0\rangle\right],$$

Using (2.34) and (2.21)

$$\langle 0|e^{itH_2}(A_k + A_k^\dagger)|0\rangle = \left(e^{it\Omega_k} + 1\right)\langle 0|e^{itH_2}A_k|0\rangle =$$

$$= \left(e^{it\Omega_k} + 1\right)\left(\frac{\Omega_k^{1/2}}{2^{1/2}}y_{0k}g + \sum_{j'}\frac{S_{j'k}(\Omega_k - \omega_{j'})}{2\Omega_k^{1/2}\omega_{j'}^{1/2}}\langle 0|e^{itH_2}a_{j'}^\dagger|0\rangle\right) = \quad (4.15)$$

$$= \left(e^{it\Omega_k} + 1\right)\left(\frac{\Omega_k^{1/2}}{2^{1/2}}y_{0k}g + \frac{be_{2k}}{2\Omega_k^{1/2}}\sum_{j'}\frac{e_{1j'}\omega_{j'}^{-1/2}}{\Omega_k + \omega_{j'}}\langle 0|e^{itH_2}a_{j'}^\dagger|0\rangle\right).$$

Inserting (4.15) into (4.14), expanding $y_{0k} = a_0 e_{2k}\Omega_k^{-2}$, using definition for (4.13) and the soft dynamics approximation $(\Omega_k + \omega_j)^{-1} \approx \omega_j^{-1}$, one gets immediately

$$g_1 \cong \frac{1}{2}\left\{\left[\varphi_2(t) - \varphi_2(0)\right]a_0 g + \left[\varphi_1(t) + \varphi_1(0)\right]b\tilde{g}_1\right\},$$

$$\tilde{g}_1 \equiv \sum_j \omega_j^{-1}e_{1j}(2\omega_j)^{-1/2}\langle 0|e^{itH_2}a_j^\dagger|0\rangle, \qquad (4.16)$$

where $\tilde{g}_1$ resembles g_1 in (4.11) except an additional ω_j factor in deno-
minator. In a case of $\tilde{g}_1$ one has to calculate sums $\sum_j e_{1j}S_{jk}\omega_j^{-1}$ in contrast to
$\sum_j e_{1j}S_{jk} = e_{2k}$ for g_1. This can be accomplished by explicitly calculating
principal value of corresponding integral (see remark below).

<u>Remark</u>: **Calculation of spectral poles.**

An essential part of soft dynamics approximation is calculation of the sums containing ground-state frequencies and resolvent $(\Omega_k^2 - \omega_j^2)^{-1}$. In the case of non-zero parameter of quadratic vibronic interaction, two discrete sets of frequencies appear below Debye cut-off, whilst the excited-state frequencies are set out between the ground-state frequencies. As far as frequencies do not coincide, the sum does not contain any pole unlike the integral. Thus one needs to calculate a principal value of the integral to account all terms in the sum.

Let us denote F(ω) the function of ground-state frequencies. Then

$$\sum_j \frac{F(\omega_j)e_{1j}}{\Omega_k^2 - \omega_j^2} = \beta_k F(\Omega_k) + \wp \int_0^1 \frac{F(\omega)e_{1j}^2}{\Omega_k^2 - \omega^2 - i\varepsilon\pi} d\omega, \qquad (4.17)$$

where $\varepsilon \to 0$ and its sign is determined by the requirement of imaginary part of integral in (4.17) to be negative. The first term is contribution of spectral poles $(\omega_j = \Omega_k)$ and parameter β_k is defined by the condition (2.24), which corresponds to the case of $F(\omega_j) = F(\Omega_k) = F(\omega) = 1$. Thus

$$\sum_j \frac{e_{1j}^2}{\Omega_k^2 - \omega_j^2} = \beta_k + \wp \int_0^1 \frac{e_1^2(\omega)}{\Omega_k^2 - \omega^2} d\omega \equiv b^{-1}, \qquad (4.18)$$

and since the local density of states (in present model) is $\rho_1(\omega) = e_1^2(\omega) = 5\omega^4$, the parameter β_k becomes

$$\beta_k = b^{-1} - \wp \int_0^1 \frac{5\omega^4}{\Omega_k^2 - \omega^2} d\omega = b^{-1} + \frac{5}{2} \wp \int_0^1 \omega^3 \left(\frac{1}{\omega + \Omega_k} + \frac{1}{\omega - \Omega_k} \right) d\omega = \qquad (4.19)$$

$$= b^{-1} + \operatorname{Re} G_1(\Omega_k).$$

{*end of remark*} ☐

From (2.21), (2.22)

$$\sum_j \frac{e_{1j}S_{jk}}{\omega_j} = e_{2k}b \sum_j \frac{e_{1j}^2}{\omega_j \left(\Omega_k^2 - \omega_j^2 \right)}. \qquad (4.20)$$

On the other hand, using (4.17) one gets (in accordance with notation in the previous remark, $F(\omega) = \omega^{-1}$)

$$\sum_j \frac{e_{1j}S_{jk}}{\omega_j} = b^{-1} \left(1 - b\operatorname{Re} G_1(\Omega_k) \right) \frac{e_{2k}}{\Omega_k} + e_{2k}b\wp \int_0^1 \frac{e_1^2(\omega)\omega^{-1}}{\Omega_k^2 - \omega^2} d\omega. \qquad (4.21)$$

Principal value integral yields

$$\wp\int_0^1 \frac{5\omega^3 d\omega}{\Omega_k^2 - \omega^2} = 5\Omega_k^2\wp\int_0^1 \frac{\omega d\omega}{\Omega_k^2 - \omega^2} - 5\int_0^1 \omega d\omega = -\frac{5}{2}\left(1 - \Omega_k^2 \ln\frac{\Omega_k^2}{1 - \Omega_k^2}\right), \quad (4.22)$$

Hence it follows that

$$\sum_j \frac{e_{1j}S_{jk}}{\omega_j} = \frac{5be_{2k}}{\Omega_k}\left(\frac{1}{5b} + \frac{1}{3} + \Omega_k^2 - \frac{\Omega_k^3}{2}\ln\frac{1 + \Omega_k}{1 - \Omega_k}\right) - \frac{5be_{2k}}{2}\left(1 - \Omega_k^2 \ln\frac{\Omega_k^2}{1 - \Omega_k^2}\right). \quad (4.23)$$

Assuming in approximation that excited-state frequencies are negligibly small quantities, one can neglect such frequencies and their powers,

$$\sum_j \frac{e_{1j}S_{jk}}{\omega_j} \approx \frac{5be_{2k}}{\Omega_k}\left(\frac{1}{5b} + \frac{1}{3} - \frac{\Omega_k}{2}\right). \quad (4.24)$$

Near critical point, $b \approx b_0 = -3/5$ and $\sum_j e_{1j}S_{jk}\omega_j^{-1} \approx 3/2\, e_{2k}$. Using this result, one can obtain expression for $\tilde{g}_1$. It follows that

$$\tilde{g}_1 \cong \frac{3}{4}\left\{[\varphi_2 - \varphi_{20}]a_0 g + [\varphi_1 + \varphi_{10}]b\tilde{g}_1\right\}. \quad (4.25)$$

Taking into account both (4.25) and (4.16), the single-phonon amplitude in the case of $b \approx -0.6$ yields

$$g_1 = \frac{\frac{1}{2}a_0(\varphi_2 - \varphi_{20})}{1 + \frac{9}{20}(\varphi_1 + \varphi_{10})}g \equiv K_1 g. \quad (4.26)$$

II. *Derivation of g_2.*
One can obtain the expression for the two-phonon amplitude in the same manner as the single-phonon one. Taking the same steps and using (4.12) and (4.3) , one gets

$$g_2 = \left\{\frac{\left[\varphi_{10} - \frac{9}{40}(\varphi_1^2 - \varphi_{10}^2)\right] + a_0^2(\varphi_2 - \varphi_{20})^2 \frac{1 - \frac{9}{40}(\varphi_1 - \varphi_{10})}{1 + \frac{9}{20}(\varphi_1 + \varphi_{10})}}{16\left[1 + \left(\frac{9}{40}\right)^2(\varphi_1^2 - \varphi_{10}^2)\right]} - \frac{5}{16}\right\}g \equiv K_2 g. \quad (4.27)$$

31

4.4. Calculation of Spectra: Numerical Study

The spectra have been calculated using the following expression

$$G(\omega) = \frac{1}{2\pi} \int\limits_{-\infty}^{\infty} g(t) e^{-i\omega t - \gamma |t|} dt. \qquad (4.28)$$

Characteristic function is found as a solution of differential equation

$$g'(t) = i\left(\omega_0 + K_1 + K_2\right) g(t), \qquad (4.29)$$

where function $D(t)$ yields from (4.9), (4.26)–(4.27). One can chose the zero-point energy to be the origin of our coordinate system by taking $\omega = 0$. Then

$$g(t) = \exp\left\{ i\int\limits_{o}^{t} \left[K_1(\tau) + K_2(\tau)\right] d\tau \right\}, \qquad (4.30)$$

where φ-functions (4.13) are evaluated by integrating over frequencies. Taking into account that $e_2^2(\omega) = \rho_2(\omega)$ and explicit definition (4.7), one gets

$$\varphi_n(t) = \int\limits_{0}^{1} \frac{\rho_2(\omega)}{\omega^n} e^{it\omega} d\omega, \qquad (4.31)$$

We performed numerical calculation of optical transitions spectra to the electronic state characterized by soft dynamics in the final state for the different values of coupling parameters. Two series of the calculations of spectra are presented: the series for fixed value of the linear coupling parameter a but slightly different values of the parameter b of quadratic vibronic coupling, all close to b_0, and the series for fixed value of the parameter b of the quadratic vibronic interaction but different values of the linear interaction parameter a. On Figure 4.2a one can see the dependence of calculated spectral function on vector (linear) parameter of vibronic interaction. Calculated line-shape obtains the specific λ–shaped profile and ZPL disappears with rising of the interaction parameter. Another effect which is clearly demonstrated by presented results is a strong enhancement of the effect of linear coupling with decreasing of the mean frequency of vibrations in the final state. This effect is especially becomes apparent on Figure 4.2b: the total width of the spectrum only slightly changes with α while the mean frequency of phonons (the frequency of the pseudolocal mode) rapidly decreases with α. Besides, the formation of the Gaussian shape is also an evidence of multiphonon transitions: the larger is the mean number of contributing phonons the closer is the shape of the spectrum to the Gaussian. However, one can easily recognize this effect also in Figure 4.2a: for small $|b-b_0|$ (small mean frequency in the final state in our model) one obtains the Gaussian shape of the spectrum already for $a = 0.5$. This means that the

spectrum is determined by multiphonon transitions. In case of small $|b|$ (large α, since $b\sim 1/\alpha$) one gets the spectrum consisting of the intensive zero-phonon line and weak phonon wing, mostly given by the one-phonon transitions.

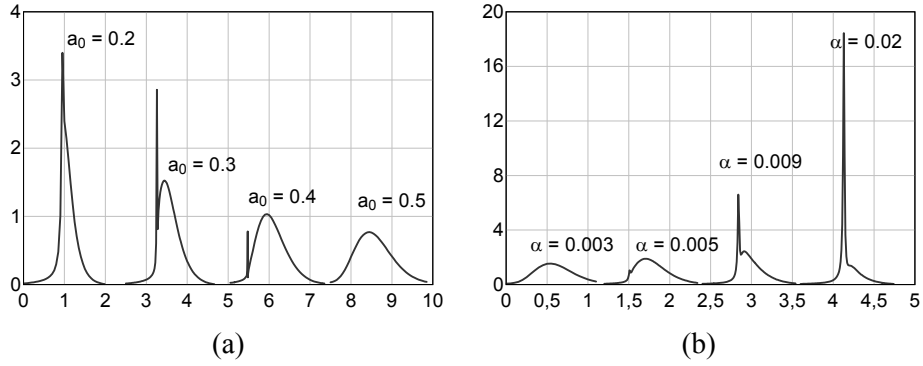

(a)   (b)

Figure 4.2 The dependence of the line shape on the linear (a) and quadratic (b) coupling parameters. The parameter α is defined as $\alpha = (5b)^{-1} + 1/3$.

5. ELECTRON-LATTICE COUPLING: A PATH INTEGRAL APPROACH

The results of quantum-mechanical calculations can always be expressed by the trace of multiple operator products. The elementary procedure for calculating a trace is to calculate a matrix representation for each factor, and then calculate the multiple sums over products of matrix elements. This procedure can be significantly simplified by working out a formal solution of a problem by introducing some useful operator techniques [25].

The starting point of this method is the following Gaussian integral formula

$$e^{A^2} = \pi^{-1/2} \int_{-\infty}^{\infty} e^{-x^2 - 2xA} dx \qquad (5.1)$$

The linearization of the operator A^2 in the exponential is accomplished with the use of a one-dimensional Gaussian average. This procedure was used by Stratonovich and Hubbard in their study of strongly-correlated electronic systems; then A was taken to be a quadratic operator in the number of particles and A^2 contained altogether four creation and destruction operators. In following, we apply this procedure to the case when A is a linear boson operator. Then one can apply the Lax method to reduce the problem to the calculation of the determinants of matrices, the elements of which are given by the pair correlation functions of the contributing configurational coordinates. For the numerical calculation we apply here a modified Debye model.

5.1. Application of Stratonovich-Hubbard Method to Quadratic Vibronic Coupling

Our task is to calculate the Fourier transform of the spectral function (2.41) – the average of the product of two exponential operators[13]. The calculation is still restricted with harmonic and Condon approximations, and the interaction Hamiltonian (2.15) is quadratic in configurational coordinates. Omitting the constant term, the vibronic interaction can be written in diagonal form,

$$V = aq + \tfrac{1}{2} q^T bq = \sum_n \left(a_n q_n + \tfrac{1}{2} b q_n^2 \right), \qquad (5.2)$$

where configurational coordinates q_n are mutually orthogonal. Taking into account that the symmetry of H is not lower than the symmetry of V, every q_n

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[13] In this section we use angular brackets for the quantum-statistical averaging, i.e. $Av[...] \equiv \langle ... \rangle$.

belongs to one of the representations (or to one of the rows of the same representation) of *H*. Below we only consider the coordinates with essential contribution to the quadratic vibronic coupling (other coordinates can be treated separately by perturbation theory). This consideration is justified for the centers of a small radius, where a strong vibronic coupling comes from the symmetrized combinations of relative displacements of the center (with adjacent atoms). In the centers of a high symmetry (usually) only one q_n of a particular symmetry essentially contributes to the particular row of the given representation. Then the contributions of different coordinates are independent of each other and the characteristic function factorizes into the *n*-product of single-coordinate characteristic functions. In the case of more than one q_n the generalization is available, that includes all the contributing coordinates [53].

Since $g(t) = g^*(-t)$, one can consider positive times only, and using the interaction representation (facilitated by Feynman [26]) to "disentangle" excited-state operators contained in the exponential,

$$e^{itH_2} \equiv e^{it(H_1+V)} = T \exp\left[i\int_0^t V(\tau)d\tau \right] e^{itH_1}, \quad \text{where} \quad V(t) = e^{itH_1}Ve^{-itH_1} \quad (5.3)$$

Presenting the integral as the sum of $N \to \infty$ terms, one divides the continuous-time evolution of the system in the final (excited) state into N discrete (infinitesimal) time steps. This gives in the $N \to \infty$ limit

$$e^{it(H_1+V)} \simeq T \exp\left[\sum_{n=1}^{N} itV(t_n)/N \right] e^{itH_1} = \prod_{n=1}^{N} e^{itV(t_n)/N} e^{itH_1}, \quad t_n = \frac{tn}{N}, \quad (5.4)$$

where the time-ordering operator *T* rearranges the operators in the exponential, if necessary, such that the operators stand in such order that time increases from left to right.

First we consider the case when the linear coupling is absent ($a = 0$). Then

$$e^{itV/N} = e^{itbq^2/2N}. \tag{5.5}$$

Following Hubbard [63], one can make use of identity

$$\mathrm{e}^{x^2/2} = \left(2\pi\right)^{-1/2} \int_{-\infty}^{\infty} e^{-u^2/2} e^{xu} du \tag{5.6}$$

to replace the quadratic coupling by the fluctuating linear coupling,

$$\lim_{N\to\infty} \mathrm{e}^{it\left(H+bq^2/2\right)} = \left(\prod_n \int_{-\infty}^{\infty} \frac{du_n}{\sqrt{2\pi}} e^{-u_n^2/2} \right) T \exp\left\{ \sum_n \sqrt{itb/N}\, q(t_n)u_n \right\} e^{itH}. \tag{5.7}$$

The following calculation of $F(t)$ can be done by Lax method. Using the Bloch-DeDominicis theorem [7] of pair correlations, one gets the following equation

$$g_Q(t) = \left(\prod_n \int_{-\infty}^{\infty} du_n (2\pi)^{-1/2} e^{-u_n^2/2} \right) e^{\frac{tb}{2N} u^T Du}. \qquad (5.8)$$

Here[14] $u^T Du = \sum_{n,n'} D_{nn'} u_n u_{n'}$ and $D_{nn'} = i\langle Tq(t_n)q(t_{n'})\rangle$ is the causal pair-correlation function. The integration over all u_n can be easily done,

$$g_Q(t) = \exp\left\{ -\tfrac{1}{2} \ln | I - (tb/N)D(t) | \right\}, \qquad (5.9)$$

where D is a matrix with the elements $D_{nn'} = D(|t_n - t_{n'}|)$ and $|...|$ stands for the determinant of the matrix. The pair-correlation function $D(t)$ is calculated by standard methods.

Thus, the problem is reduced to the calculation of the determinant of the symmetric matrix, which has equal diagonal elements and, as a maximum, N–1 distinct non-diagonal elements. This task is much simpler than the problem of calculation of the corresponding matrix of $2N$ x $2N$ – order and its determinant in the case of Kubo and Toyozawa approach. In our case, the correlation matrix $D(t)$ has only N distinct elements determined by the pair-correlation function at the given time difference.

One possible way to calculate the determinant is to diagonalize the quadratic form by means of the unitary transformation $u_n = \sum_k S_{kn} s_k$:

$$\sum_{n,n'} D_{nn'} u_n u_{n'} = \sum_k D_k s_k^2, \qquad (5.10)$$

where D_k are the elements of the diagonal matrix $S^{-1}DS$. Then the characteristic function yields

$$g_Q(t) = \exp\left\{ -\tfrac{1}{2} \sum_k \ln\left[1 - (tb/N)D_k \right] \right\}. \qquad (5.11)$$

In this connection, one should note that the problem of the diagonalization of the matrix D is equivalent to the problem of the calculation of the monoatomic chain spectrum with the long-range interaction.

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[14] one should distinguish similar notations for matrix transposition and operator ordering

In case of both linear and quadratic vibronic coupling $(a \neq 0, b \neq 0)$,

$$e^{it(H+V)}e^{-itH} = \prod_{n=1}^{N} e^{it(a/N)q(t_n)}e^{itbq^2(t_n)/2N},$$ (5.12)

and using the above technique, one gets

$$g(t) = g_L(t)g_Q(t),$$ (5.13)

where g_Q is determined by (5.9) and g_L is the contribution of the linear coupling term,

$$g_L = \exp\left\{\frac{ia^2t^2}{2N^2}\sum_{nn'}\left((I - tbD/N)^{-1}D\right)_{nn'}\right\}.$$ (5.14)

The inverse matrix $(I - tbD/N)^{-1}$ describes the renormalization of the linear interaction by the quadratic interaction.

If the quadratic coupling is absent $(b = 0)$, then

$$g(t) = \exp\left\{\frac{ia^2t^2}{2N^2}\sum_{nn'}D_{nn'}\right\} = -\tfrac{1}{2}a^2\iint_0^t d\tau d\tau' \langle Tq(\tau)q(\tau')\rangle,$$ (5.15)

that is the Lax equation for the logarithm of the Fourier transform of the spectrum.

This method has been verified for compliance with an analytical solution in the case of two mixed modes [53], it is also applicable in the case of arbitrary number of the configurational coordinates of the same symmetry. The non-Condon terms were taken into consideration in latest publications.

5.2. Numerical: Modified Debye Model

We applied this method for calculating the optical spectra for the case when the system is closed to the dynamical instability in the final electronic state(s) that results in significant softening of local acoustic phonons. One can use the (modified) Debye model, where the cut-off is replaced by the exponential dumping in the initial-state phonon DOS,

$$\tilde{\rho}_1(\omega) = \tfrac{1}{3}\omega^3 e^{-\omega}\theta(\omega),$$ (5.16)

where $\theta(\omega)$ is the Heaviside step-function, and phonon frequencies are in dimensionless units. This model is used because of the simple form of correlation function, which at zero temperature is given by

$$D(t) = i\langle q(t)q(0)\rangle = i(t+i)^{-4}.$$ (5.17)

At the same time, this model gives a correct description of the low-frequency acoustic phonons giving the main contribution to the spectrum under given conditions.

The characteristic function and its Fourier transform have been calculated in the case when the final state is close to dynamical instability. The calculation for sufficiently large number of time-steps enables one to obtain high-accuracy line shapes (see Figure 5.1). Since an abrupt cut-off of the characteristic function at large times results in the appearance of noise, the small damping factor was introduced to get rid of it. The values of vibronic interaction parameters have been chosen so that most of the features of soft dynamics would become visible.
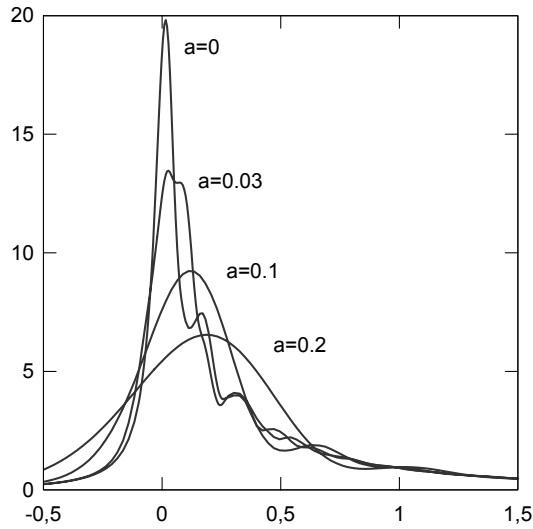

Figure 5.1. Optical spectra in the case of the Debye model with a strong quadratic coupling. The parameter of the quadratic coupling $b = -1.496$ corresponds to the soft dynamics in the excited electronic state; the parameter of the linear vibronic coupling (a) varies from 0.03 to 0.2. The damping exponential factor with $\gamma = 0.05$ is used. The determinant and the inverse matrix calculated in 1024 time points with $t_{MAX} = 160$.

The quadratic vibronic coupling parameter chosen here ($b = -1.496$) is close to the critical value ($b_{cr} = -1.5$) of the dynamical instability: for $b < b_{cr}$ the phonon LDOS of the final state contains imaginary frequencies distinctive for the dynamical instability in the final state. Purely quadratic vibronic coupling ($a = 0$) results in the long-wave pseudo-local mode appearance in the spectrum (the maxima of $a = 0$ curve). The line shape itself resembles an asymmetric lambda letter, and for $a \neq 0$ it has the Airy oscillations characteristic of a slow motion of a quantum particle after the transition.

6. RESULTS AND DISCUSSION

In the present study, a theory of electronic transition with taking into account the quadratic vibronic interaction in multimode systems is developed. The most common approach is a method of generating function, facilitated by Kubo and Toyozawa. However, it has serious flaws; namely, it requires dealing with $2N$ x $2N$ (this number arises from the contribution of N Avogadro modes) distinct complex matrices used to describe the characteristic function (Fourier transform of the spectral function). Since there is no efficient algorithm for calculating of such matrices, used methods vary from author to author. The researchers were forced to consider the simplest cases of a weak coupling (accompanied by simplified treatment of mode mixing effects) or to use the approximate method of cumulant expansion.

If the coupling is not weak, then one can use the method of cumulants in calculation of the asymptotical behavior of characteristic function at large times; in this case one can sum up the contribution of all the cumulants [80]. This asymptotics describes the width and spectral position of ZPL. In attached publications one finds the consideration of ZPL in the optical spectra of impurity centers in the case when the optical transition takes place between non-degenerate and two-fold degenerate electronic E-states. In such systems the optical transition takes place to the vicinity of a flat minimum (or a flat potential barrier) in the space of configurational coordinates, where the density of states of low-frequency phonons is strongly enhanced. It was found that a strong Jahn-Teller effect in the excited state of a trigonal center leads to the T^3– type dependence of the homogenous width of ZPL instead of usual T^7– dependence. The theoretical calculations of the position and width of a zero-phonon line (ZPL) are in agreement with experimental data.

In this study the author re-examined some popular methods, providing whether improvements or new approaches to the problem. First, the case of two-mode mixing has been revisited. A slightly modified version of the density-matrix method was developed, which takes into account both the rotation and distortion of potential energy surfaces due to the electronic transition. Numerical study showed an impact of the mode mixing on the calculated optical line shapes. In particular, mode mixing resulted in:

1. non-monotonous distribution of the intensities of the spectral lines;
2. strong dependence not only on the absolute value but also on the sign of the mixing parameter (the Duschinsky rotation angle);
3. various internal structures of the line shapes due to phononless, single- and multi-phonon transitions.

Second, a further development of method of Fourier-amplitudes was made. Corresponding framework was initially developed in 1986 by Hizhnyakov who used it considering resonant Raman scattering. This method is based on the

exact equations for the phonon-assisted transitions. In multimode systems with quadratic coupling there are N^2 of such equations, and method allows one to downscale this number to four in the case of soft final-state dynamics. Derived equations determine the first derivative of the Fourier transform of the spectral function. Calculations of the spectra for different coupling parameters were performed. The quadratic coupling parameters were chosen to correspond to the vicinity of the dynamical instability of the center in the final electronic state. The main results of the analysis are as follows:

1. at sufficiently small linear coupling the spectrum resembles the lambda letter;
2. softening of the phonon dynamics in the final state results in strong enhancement of vibronic coupling with low-frequency phonons;
3. coupling with pseudo-local mode (PLM) of low-frequency and re-markable linear coupling produces Gaussian line shape;
4. at non-zero linear coupling and small frequency of contributing PLM, the width of the spectrum is mostly determined by the value of the linear coupling parameter and slightly depends on the actual frequency of PLM.

Third, a rather new path-integral based method was applied considering the optical centers with essentially reduced force constants in the final state. It was initially proposed in 2006 by Hizhnyakov and Tehver. Benefits of this method are that it provides a recipe for calculating optical spectra with the arbitrary (linear and quadratic) coupling for the case of a few contributing configurational coordinates. The latter assumption is usually a rule for the impurity centers of small radius. The disadvantage of the method is that it relies on lengthy computations that can be significantly accelerated by using distributed computing. The method utilizes the time-ordering expansion, the Hubbard-Stratonovich transformation and the Bloch-DeDominicis theorem for pair-correlations. Applying this method, it was found that

1. calculated spectral shapes reveal a superstructure;
2. peaks of it are disconnected with the frequency of PLM;
3. origin of this new superstructure is the Airy oscillations.

This-type oscillations have been observed in the hot luminescence of self-trapped excitons in *Xe* crystals and, probably, in the superfluid ^4He droplets, where they may result from the free-like motion of excited-state atom trapped on the surface of the droplet. Previously, Airy oscillations have been studied theoretically in the simple molecular systems having a few vibrational degrees of freedom.

The results of this study open new possibilities for calculations of processes in solids with essential contribution of phonon-assisted transitions.

SUMMARY IN ESTONIAN

Tugeva mittelineaarse vibrooninteraktsiooniga tahkiste elektronsiirete teooria

Käesolevas töös on arendatud elektronsiirete teooriat paljumoodiliste süsteemide jaoks, arvestades ruutvibrooninteraktsiooni. Enamkasutatud lähenemisviisiks on siin genereetitava funktsiooni meetod, mida töötasid välja Toyozawa ja Kubo. Paraku on selle oluliseks puuduseks asjaolu, et siin tuleb käsitleda $2N$ x $2N$ komplektseid maatrikseid (see arv on seotud N Avogadro võnkemoodide arvuga, mis osalevad protsessis), et kirjeldada karakteristlikku funktsiooni (spektraalfunktsiooni Fourier pööret). Kuna puudub efektiivne algoritm selliste maatriksite arvutamiseks, siis kasutatud meetodid varieeruvad koos autoritega. Uurijad olid sunnitud piirduma lihtsaimate, nõrga interaktsiooni juhtudega (millega kaasnes võnkemoodide segunemise efektide lihtsustatud käsitlus) või siis kasutama kumulatiivse reaksarenduse lähendusmeetodit.

Kui vibrooninteraktsioon on nõrk, on võimalik kasutada kumulantide meetodit arvutamaks karakteristliku funktsiooni asümptootilist käitumist suurtel aegadel. See asümptootika kirjeldab foononvaba joone laiust ja spektraalset asukohta. Lisatud publikatsioonides on toodud foononvaba joone käsitlus lisanditsentrite optilistes spektrites juhul, kui optilised siirded leiavad aset kõdumata ja kahekordselt kõdunud elektroonse E-seisundi vahel. Sellistes süsteemides toimuvad optilised üleminekud konfiguraatsioonkoordinaatide ruumis lameda miinimumi (või lameda potentsiaalbarjääri) lähedal, kus madalsageduslike foononite tihedus on tugevalt suurenenud. Leiti, et trigonaalsete tsentrite korral tugev Jahn-Telleri efekt ergastatud seisundis viib foononvaba joone homogeense laiuse T^3– sõltuvusele tavalise T^7– sõltuvuse asemel. Foononvaba joone asukoha ja laiuse arvutused on kooskõlas katseandmetega.

Käesolevas dissertatsioonis on autor taaskasutanud enimtuntud meetodeid, viies sisse täiendusi või siis kasutades uusi lähenemisviise probleemile. Eelkõige on taaskäsitletud kahe moodi segunemisjuhtu. Selleks on arendatud veidi modifitseeritud tihedusmaatriksi meetodit, arvestades elektroniirdel nii potentsiaalenergia pindade rotatsiooni kui ka häiritust. Numbriline arvutus näitas moodide segunemise toimet joonte jaotusele optilistes spektrites. Sealhulgas, moodide segunemine tekitab

1. joonte intensiivsuste ebaühtluse jaotuse;
2. spektrite sõltuvuse oluliselt nii segunemisparameetri absoluutväärtusest kui selle märgist;
3. spektri tugeva komplitseerumise temperatuuri tõustes.

Teiseks, on edasi arendatud Fourier-amplituutide meetodit. Vastav skeem oli välja arendatud Hiznjakovi poolt (1986), kes kasutas seda resonantse Ramani

hajumise puhul. Meetod põhineb foononitega kaasatud siirete täpsetel võrranditel. Ruutinteraktsiooniga paljumoodilistes süsteemides on selliseid võrrandeid N^2 tükki, kuid meetod võimaldab seda arvu vähendada neljani juhul, kui on tegu pehme dünaamikaga lõppseisundis. Tuletatud võrrandid määravad spektraalfunktsiooni Fourier pöörde esimese tuletise. Viidi läbi spektri arvutusi interaktsiooni parameetrite erinevate väärtuste korral. Ruutinteraktsiooni parameetrid valiti optilise tsentri lõppseisundi dünaamilise ebastabiilsuse läheduses. Saadud tulemuste analüüs andis järgmist:

1. piisavalt nõrga lineaarinteraktsiooni korral meenutab spekter oma kujult lambda-tähte;
2. foonondünaamika pehmenemine lõppseisundis kutsub esile vibroon-interaktsiooni tugevnemise madalsageduslike foononitega;
3. madalsageduslik pseudolokaalne mood, mis tekib tugeva ruutinteraktsiooni tõttu, ja märgatav lineaarne interaktsioon annavad joonele Gaussi kõvera kuju;
4. viimasel juhul on spektri laius määratud lineaarse interaktsiooni parameetriga, sõltudes nõrgalt pseudolokaalse moodi aktuaalsest sagedusest.

Kolmandaks, rakendati uut, rajaintegraalidel põhinevat meetodit käsitlemaks optilisi tsentreid kahanenud elastsuskonstantidega lõppseisundis. Meetod oli algselt pakutud Hiznjakovi ja Tehveri poolt 2006. aastal. See võimaldab arvutada optilisi spektreid meelevaldse (lineaarse ja ruut) vastastikmõju korral juhul, kui panustavate konfiguratsioonkoordinaatide arv on väike. Viimane eeldus on tavareegel väikese raadiusega lisanditsentrite korral. Meetodi puuduseks on, et see eeldab suuremahulisi arvutusi, mida saab aga märkimisväärselt kiirendada paralleelarvutust kasutades. Teooria kasutab ajas korrastatud reaksarendust, Hubbard-Stratonovichi teisendust ning Bloch-DeDominicise teoreemi paariskorrelaatorite jaoks. Tulemuseks saadi:

1. arvutatud joonekujud ilmutavad superstruktuuri;
2. viimase maksimumid ei ole seotud pseudolokaalse moodi sagedusega;
3. uue superstruktuuri teke on seotud Airy ostsillatsioonidega.

Selliseid ostsillatsioone on vaadeldud autolokaliseeritud eksitonide kuumas luminestsentsis *Xe* kristallis ja – tõenäoliselt – ülivoolava ^4He tilkades, kus nad võivad olla esile kutsutud tilga pinnal lõksustatud ergastatud aatomi peaaegu vabast liikumisest. Varem on Airy ostsillatsioone teoreetiliselt uuritud lihtsate molekulaarsüsteemide korral, millel on väike arv vabadusastmeid.
Käesoleva uurimistöö tulemused avavad uusi võimalusi arvutuste läbiviimiseks tahkistes toimuvate protsesside jaoks, millest võtavad osa foononid.

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REFERENCES

1. Abdalla M., *Quantum treatment of the time-dependent coupled oscillators*, J. Phys. A Math. Gen. **29**, 1997–2012 (1996)
2. Arfken G. and Weber H., *Mathematical Methods for Physicists. 6th Edition* (Elsevier Academic Press, 2005)
3. Barker A.S., Sievers A.J., *Optical Studies of the Vibrational Properties of Disordered Solids*, Rev. Mod. Phys. **47** (Suppl. 2), S1–S179 (1975)
4. Bell R.J., *The Dynamics of Disordered Lattices*, Rep. Prog. Phys. **35**, 1315–1409 (1972)
5. Bell R.J., *Vibrational Properties of Amorphous Solids*. In Methods in Computational Physics vol. 15 (Academic Press, 1976)
6. Bellac M., *Quantum and Statistical Field Theory* (Clarendon Press, Oxford, 1991)
7. Bloch C., De Dominicis C., *Un développement du potentiel de gibbs d'un système quantique composé d'un grand nombre de particules (I, II)*, Nucl. Phys. **7**, 459 (1956); **10**, 181 (1959)
8. Bogolubov N., *Polaron Theory: Model Problems* (CRC Press, 2000)
9. Boltrushko V., Holmar S. , Tehver I., Hizhnyakov V., *Vibronic Transitions in the Vicinity of the Dynamical Instability of the Final State*, J. Mol. Struct. **838**, 164–169 (2007)
10. Born M. and Huang K., *Dynamical Theory of Crystal Lattices* (Oxford, London, 1954)
11. Bron W.E., *Bound-Electron-Lattice Coupling and Vibronic Spectra*, Phys. Rev. **140**, 2005–2014 (1965)
12. Brüesch P., *Phonons: Theory and Experiments I. Lattice Dynamics and Models of Interatomic Forces* (Springer, 1982)
13. Callaway J., *Quantum theory of the Solid State* (Academic Press, New York, 1974)
14. Cheng Z., *Unified Quantum Field Theory of Light Absorption by Defect Centers*, Phys. Rev. (b) **60**, 15747–15765 (1999)
15. Croitoru M., Grecu D., *Effect of Atomic Force Constant Changes on the Localized Vibrational Modes – A Perturbation Approach*, Phys. Stat. Sol. **42**, 137–146 (1970)
16. Davies G., *Vibronic Spectra in Diamond*, J. Phys. C: Solid State Phys. **7**, 3797–3809 (1974).
17. Dean P., *Atomic Vibrations in Solids*, J. Inst. Math. **3**, 98–165 (1967)
18. Dehestani M., Islampour R., *Effects of Distortion-Rotation of Potential Energy Surfaces on Absorption and Resonance Raman Cross Sections of trans-Stilbene Molecule*, Int J. Quant. Chem. **103**, 119–126 (2005)
19. Dexter D., *Shapes of Absorption and Emission Lines of Impurities in Solids*, Phys. Rev. **96**, 615–616 (1954)
20. Duschinsky F., *The Importance of the Electron Spectrum in Multi Atomic Molecules. Concerning the Franck-Condon Principle*, Acta Physicochym. U.R.S.S. **7**, 551 (1937)
21. Economou E., *Green's Functions in Quantum Physics. 3rd Edition* (Springer, 2006)
22. Elliott R., Dawber P., *Theory of Optical Absorption by Vibrations of Defects in Silicon*, Proc. Phys. Soc. **81**, 453–460 (1963)

23. Elliott R., *Theory and Properties of Randomly Disordered Crystals*, Rev. Mod. Phys. **46**, 465–543 (1974)
24. Elliott R., *Theory of Correlations and Scattering of Lattice Vibrations by Defects*, Proc. Phys. Soc. **83**, 189–197 (1964)
25. Fano U., *Description of States in Quantum Mechanics by Density Matrix and Operator Techniques*, Rev. Mod. Phys. **29**, 74 (1957)
26. Feynman R., *An Operator Calculus Having Applications in Quantum Electrodynamics*, Phys. Rev. **84**, 108 (1951)
27. Feynman R., Hibbs A., *Quantum Mechanics and Path Integrals* (McGraw-Hill, New York, 1965)
28. Feynman R., *Statistical Mechanics: A Set of Lectures. 7th Edition (1982)* (Benjamin/Cummings, 1972)
29. Flügge S., *Practical Quantum Mechanics* (Springer, 1999)
30. Fonger W., Struck C., *Condon Moments for the Configurational-Coordinate Model*, J. Chem. Phys. **60**, 1994–2002 (1973)
31. Fox M., *Optical Properties of Solids* (Oxford University Press, 2001)
32. Greiner W. and J. Reinhardt, *Field Quantization* (Springer, 1996)
33. Greiner W. et al., *Thermodynamics and Statistical Mechanics* (Springer, 1997)
34. Greiner W., *Quantum Mechanics. An Introduction. 4th Edition* (Springer, 2001)
35. Greiner W., *Quantum Mechanics. Special Chapters* (Springer, 1998)
36. Grosso G and Parravicini G., *Solid State Physics* (Academic Press, 2005)
37. Haken H., *Quantum Field Theory of Solids* (North-Holland, Amsterdam, 1976)
38. Henderson B., Imbusch G., *Optical Spectroscopy of Inorganic Solids* (Clarendon Press, Oxford, 2006)
39. Hizhnyakov V., Benedek G., *Quantum Diffusion: Effect of Defect-Localized Phonon Dynamics*, Eur. Phys. J. (b) **43**, 431–438 (2005)
40. Hizhnyakov V., Benedek G., Tehver I., Boltrushko V., *Optical Spectra of Systems with Nearly Unstable Excited States: Modulated Lambda-Shaped Spectra*, J. Noncryst. Solids **352**, 2558–2561 (2006)
41. Hizhnyakov V., Boltrushko V., *Anomalous Optical Spectra of Centers with Soft Phonon Dynamics in Excited State*, In: Proc. SPIE – Optical Materials and Applications **5946**, 192–201 (2005)
42. Hizhnyakov V., Boltrushko V., Kaasik H, Sildos I., *Strong Jahn-Teller Effect in the Excited State: Anomalous Temperature Dependence of the Zero-Phonon Line*, J. Chem. Phys. **119**, 6290–6295 (2003)
43. Hizhnyakov V., Boltrushko V., Kaasik H., Shelkan A., *Multiphonon Processes in Impurity Centres: Nonperturbative Theory*, Phys. Stat. Sol. (a) **202**, 228–234 (2005)
44. Hizhnyakov V., Boltrushko V., Kaasik H., Sildos I., *Jahn-Teller Effect in the Excited State: Anomalous Temperature Dependence of the Zero-Phonon Line*, Adv. Quant. Chem. **44**, 135–149 (2003)
45. Hizhnyakov V., Boltrushko V., Kaasik H., Sildos I., *Phase Relaxation in the Vicinity of the Dynamic Instability: Anomalous Temperature Dependence of Zero-Phonon Line*, J. Lumin. **107**, 351–358 (2004)
46. Hizhnyakov V., Boltrushko V., Tehver I., *Optical Transitions in the Centres with Soft Dynamics in the Final State*, J. Phys.: Conf. Ser. **21**, 161–166 (2005)
47. Hizhnyakov V., Boltrushko V., Tehver I., *Soft Dynamics of the Excited State: Lambda-Shaped Optical Spectra*, J. Lumin. **127**, 13–18 (2007)

48. Hizhnyakov V., Holmar S., Tehver I., *Theory of Optical Spectra of Impurity Centres in Crystals: General Consideration of Quadratic Vibronic Coupling*, J. Lumin. **127**, 7–12 (2007)

49. Hizhnyakov V., Plekhanov V., Shepelev V., Zavt G., *Hot Luminescence of Self-Trapped Excitons in Alkali Halide Crystals*, Phys. Stat. Sol. (b) **108**, 531–540 (1981)

50. Hizhnyakov V., *Quadratic Vibronic Interaction. The Operator Transformation Method*, J. Phys. C: Solid State Phys., **20**, 6073–6087 (1987)

51. Hizhnyakov V., Seranski K., Schurath U., *Homogeneous Lineshapes and Shifts of the $b^1\Sigma^+ \leftarrow X^3\Sigma^-$ Transition in Matrix-Isolated NH: Comparison with Quadratic Coupling Theory*, Chem. Phys. **162**, 249–256 (1992)

52. Hizhnyakov V., Tehver I., *On the Theory of Hot Luminescence and Resonant Raman Effect of Impurity Centres*, Phys. Stat. Sol. (b) **39**, 67–78 (1970) (+ Appendix in Phys. Stat. Sol. (b) **82**, K89–K93 (1977))

53. Hizhnyakov V., Tehver I., *Optical Transition in an Impurity Centre of a Crystal: Mixing of Phonons*, Chem. Phys. Lett. **422**, 299–302 (2006)

54. Hizhnyakov V., Tehver I., *Theory of Resonant Secondary Radiation due to Impurity Centres in Crystals*, Phys. Stat. Sol. (b) **21**, 755–768 (1967)

55. Hizhnyakov V., *Vibrational Relaxation in the Excited Electronic State*, Phys. Stat. Sol. (b) **114**, 721–730 (1982)

56. Hjalmarson H. et al., *Extraction of Phonon Density of States from Optical Spectra*, Phys. Rev. (b) **32**, 4300–4303 (1985)

57. Hsu D. and Skinner J.L., *Nonperturbative Theory of Temperature-Dependent Optical Dephasing in Crystals. Pseudolocal Phonons*, J. Chem. Phys. **83**, 2097 (1985)

58. Hsu D. and Skinner J.L., *On the Thermal Broadening of Zero-Phonon Impurity Lines in Absorption and Fluorescence Spectra*, J. Chem. Phys. **81**, 1604 (1984)

59. Huang K. and Rhys A., *Theory of Light Absorption and Non-Radiative Transitions in F-centres*, Proc. Roy. Soc. **A204**, 406 (1950)

60. Huang K. *Quantum Field Theory. From Operators to Path Integrals* (Wiley, 1998)

61. Huang K., *Lattice Relaxation and Multiphonon Transitions*, Contemp. Phys. **22**, 599–612 (1981)

62. Huang K., *Statistical Mechanics* (Wiley, 1987)

63. Hubbard J., *Calculation of Partition Functions*, Phys. Rev. Lett. **3**, 77 (1959)

64. Ianconescu R., Pollak E., *Photoinduced Cooling of Polyatomic Molecules in an Electronically Excited State in the Presence of Dushinskii Rotations*, J. Phys. Chem. (a) **108**, 7778–7784 (2004)

65. Islampour R., Dehestani M., Lin S.H., *A New Expression for Multidimensional Franck–Condon Integrals*, J. Mol. Spectrosc. **194**, 179–184 (1999)

66. Jeffrey A. and Dai H., *Handbook of Mathematical Formulas and Integrals, 4th Edition* (Elseiver-Academic Pres, 2008)

67. Jones W. and March N., *Theoretical Solid State Physics* (Courier Dover Publications, 1973)

68. Kaxiras E., *Atomic and Electronic Structure of Solids* (Cambridge University Press, 2003)

69. Keil T., *Shapes of Impurity Absorption Bands in Solids*, Phys. Rev. **140**, 602–617 (1965)

70. Kelley C., *Absorption and Emission Spectra of Impurities in Solids*, Phys. Rev. (b) **6**, 4112–4118 (1972)
71. Kelley C., *Moments of Semiclassical and Classical Absorption and Emission Band Shapes of Impurities in Solids*, Phys. Rev. (b) **20**, 5084–5089 (1979)
72. Kelley C., *Symmetry of Vibrationally Assisted Electronic Absorption and Emission Band Shapes of Impurities in Solids*, Phys. Rev. (b) **8**, 1806–1810 (1973)
73. Kikas J., Suisalu A., Zazubovich V., Vois P., *Anomalous Impurity Spectra in Low-Temperature Glasses*, J. Chem. Phys. **104**(12), 4434–4440 (1996)
74. KimY. and Noz M., *Phase Space Picture of Quantum Mechanics* (Word Scientific, Singapore, 1991)
75. Krivoglaz M.A., *Theory of the Phononless Line Broadening in the Mossbauer or Optical Spectrum*, Sov. Phys. Solid State **6**, 1340–1347 (1964)
76. Kubo R., Toda M., Hashitsume N., *Statistical Physics II – Nonequilibrium Statistical Mechanics* (Springer, 1985)
77. Kubo R., Toyozawa Y., *Application of the Method of Generating Function to Radiative Transitions of Trapped Electron in a Crystal*, Prog. Theor. Phys. **13**, 160 (1955)
78. Lax M., Burstein E., *Broadening of Impurity Levels in Silicon*, Phys. Rev. **100**, 592–602 (1955)
79. Lax M., *The Franck-Condon Principle and Its Applications to Crystals,* J. Chem. Phys. **20**, 1752 (1952)
80. Levenson G., *Influence of Quadratic Interactions on Impurity Absorption Bands in Solids*, Phys. Stat. Sol. (b) **48**, 739 (1971)
81. Levi A., *Applied Quantum Mechanics* (Cambridge University Press, 2006)
82. Lifshitz I., *The Energy Spectrum of Disordered Systems*, Adv. Phys. **13**, 483–536 (1964)
83. Lubchenko A.F., *Effect of Anharmonicity on the Optical Activity of Impurity Centres in Solids*, Phys. Stat. Sol. **13**, 37–44 (1966)
84. Mahan G., *Many-Particle Physics. 3rd Edition* (Springer, 2001)
85. Mair S., Wilkins S., *Anharmonic Debye-Waller Factors Using Quantum Statistics*, J. Phys. C: Solid State Phys. **9**, 1145–1158 (1976)
86. Makarov G.N., *Spectroscopy of Single Molecules and Clusters Inside Helium Nanodroplets. Microscopic Manifestation of ^{4}He Superfluidity*, Sov. Phys. Usp. **47**(3), 217–247 (2004)
87. Maradudin A., Fein A., *Scattering of Neutrons by an Anharmonic Crystal*, Phys. Rev. **128**, 2589–2608 (1962)
88. Maradudin A., Montroll E., Weiss G., *Theory of Lattice Dynamics in the Harmonic Approximation* (Academic Press, New York, 1963)
89. Maradudin A.A., *Some Effects of Point Defects on the Vibrations of Crystal Lattices*, Rep. Prog. Phys. **28**, 331–380 (1965)
90. Masujima M., *Path Integral Quantization and Stochastic Quantization* (Springer, 2000)
91. McCumber D., *Theory of Vibrational Structure in Optical Spectra of Impurities in Solids. II. Multiplets*, J. Math. Phys. **5**, 508 (1964)
92. McMahon D., *Quantum Mechanics Demystified* (McGraw-Hill,2006)
93. Montroll E., Potts R., *Effect of Defects on Lattice Vibrations*, Phys. Rev. **100**, 525–543 (1955)
94. Mostoller M., Ganguly B., Wood R., *Phonon Structure of Impurity-Related Optical Spectra in Insulators*, Phys. Rev. (b) **4**, 2015–2029 (1971)

95. Müller-Kirsten H., *Introduction to Quantum Mechanics: Schrödinger Equation and Path Integral* (Word Scientific, 2006)

96. Negele J., Orland H., *Quantum Many-Particle Systems* (Westview Press, 1998)

97. O'Rourke R.C., *Absorption of Light by Trapped Electrons*, Phys. Rev. **91**, 265 (1953)

98. Osad'ko I., *Determination of Electron-Phonon Coupling from Structured Optical Spectra of Impurity Centers*, Sov. Phys. Usp. **22**(5), 311–329 (1979)

99. Osad'ko I., *Selective Spectroscopy of Single Molecules* (Springer, 2003)

100. Osad'ko I., *Zero-Phonon Lines and Phonon Wings in Impurity Absorption and Fluorescence Spectra*, Sov. Phys. Solid State **17**, 2098–2102 (1975)

101. Pantelides S., *The Electronic Structure of Impurities and Other Point Defects in Semiconductors*, Rev. Mod. Phys. **50**, 797–858 (1978)

102. Parry W.E., Turner R.E., *Green Functions in Statistical Mechanics*, Rep. Prog. Phys. **27**, 23–52 (1964)

103. Peluso A., Santoro F., del Re G., *Vibronic Coupling in Electronic Transitions with Significant Duschinsky Effect*, J. Quant. Chem. **63**, 233–244 (1997)

104. Perlin Yu. and Tsukerblat B., *Effects of Electron-Vibrational Interaction in Optical Spectra of Impurity Paramagnetic Ions* (Shtiintsa, Kishinev, 1974)

105. Perlin Yu., *Modern Methods in the Theory of Many-Phonon Processes*, Sov. Phys. Usp. **6**(4), 542–565 (1964)

106. Pike E.R., *A New Identity in the Green's Function Approach to the Many-Body Problem*, Proc. Phys. Soc. **84**, 83–37(1964)

107. Poole C., *The Physics Handbook. Fundamentals and Key Equations* (Wiley, 2006)

108. Rebane K., *Impurity Spectra of Solids* (Plenum Press, New York, 1970)

109. Riley K., Hobson M., Bence S., *Mathematical Methods for Physics and Engineering. 3rd Edition* (Cambridge University Press, 2006)

110. Ritter J., Markman J., *Theory of Electron-Phonon Interaction*, Phys. Rev. **185**, 1201–1213 (1969)

111. Ritter J., *Optical Spectra Line-Shape Representations and Broad Bands in Solids*, J. Chem. Phys. 53, 3461–3468 (1970)

112. Rosenstock H., Klick C., *Vibrational Modes Near Impurities*, Phys. Rev. **119**, 1198–1203 (1960)

113. Rössler U., *Solid State Theory: An Introduction* (Springer, 2004)

114. Sachs I., Sen S., Sexton J., *Elements of Statistical Mechanics. With an Introduction to Quantum Filed Theory and Numerical Simulation* (Cambridge University Press, 2006)

115. Schober H.R., Laird B., *Localized Low-Frequency Vibrational Modes in Glasses*, Phys. Rev. (b) **44**, 6746–6754 (1991)

116. Shpol'skii E., *New Data on the Nature of the Quasilinear Spectra of Organic Compounds*, Sov. Phys. Usp. **6**(3), 411–427 (1963)

117. Shpol'skii E., *Problems of the Origin and Structure of the Quasilinear Spectra of Organic Compounds at Low Temperatures*, Sov. Phys. Usp. **5**(3), 522–531 (1962)

118. Sild O., Haller K. (Eds.), *Zero-Phonon Lines and Spectral Hole Burning in Spectroscopy and Photochemistry* (Plenum Press, New York, 1970)

119. Stoneham A., *Theory of Defects in Solids* (Oxford University Press, 2001)

120. Stoneham A.M., *Non-Radiative Transitions in Semiconductors*, Rep. Prog. Phys. **44**, 1251–1295 (1981)

121. Stratonovich R.L., *On a Method of Calculating Quantum Distribution Functions*, Sov. Phys. Dokl. **2**, 416 (1957)

122. Styer D. et al., *Nine Formulations of Quantum Mechanics*, Am. J. Phys. **70**(3), 288–297 (2002)
123. Tang C., *Fundamentals of Quantum Mechanics For Solid State Electronics and Optics* (Cambridge University Press, 2005)
124. Tang J., Lee M.T., Lin S.H., *Effects of the Duschinsky Mode-Mixing Mechanism on Temperature Dependence of Electron Transfer Processes*, J. Chem. Phys. **119**, 7188–7196 (2003)
125. Tehver I., Kaasik H., Hizhnyakov V., *Transform Method in Resonance Raman Scattering: Effect of Mode Mixing*, J. Raman Spectrosc. **33**, 639–645 (2002)
126. Tewary V.K., *Green-Function Method for Lattice Statics*, Adv. Phys. **22**, 757–810 (1973)
127. Tonks D., Dick B., *Quadratic-Coupling Phonon-Assisted Defect Tunneling Theory Applied to RbCl: Ag^+ off-center system*, Phys. Rev. (b) **19**,1149–1160 (1979)
128. Tonks D., Dick B., *Small-Polaron Theory of Phonon-Assisted Defect Tunneling with Quadratic Defect-Lattice Coupling*, Phys. Rev. (b) **19**,1136–1148 (1979)
129. Toyozawa Y., *Optical Processes in Solids* (Cambridge University Press, 2003)
130. Vallet J.C. et al., *Vibronic Mode Couplings in Adsorbed Molecules Analyzed by Doubly Resonant Sum-Frequency Generation*. Phys. Rev. (a) **53**, 4508–4518 (1996)
131. Van Hove L., *Correlations in Space and Time and Born Approximation Scattering in Systems of Interacting Particles*, Phys. Rev. **95**, 249–262 (1954)
132. Yan Y.J., Mukamel S., *Eigenstate-free, Green Function, Calculation of Molecular Absorption and Fluorescence Line Shapes*, J. Chem. Phys. **85**, 5908–5923 (1986)
133. Ziman J., *Principles of the Theory of Solids* (Cambridge University Press, 1972)
134. Zubarev D.N., *Double-Time Green Functions in Statistical Physics*, Sov. Phys. Usp. **3**, 320–345 (1960)

PUBLICATIONS

Hizhnyakov V., Boltrushko V., Kaasik H., Sildos I.,
*Jahn-Teller effect in the excited state: anomalous temperature dependence
of the zero-phonon line*, Adv. Quant. Chem. **44**, 135–149 (2003).

II

Hizhnyakov V., Boltrushko V., Kaasik H., Sildos I.,
*Phase relaxation in the vicinity of the dynamic instability:
anomalous temperature dependence of zero-phonon line*,
J. Lumin. **107**, 351–358 (2004).

III

Hizhnyakov V., Boltrushko V., *Anomalous optical spectra of centers with soft phonon dynamics in excited state*, In: Proc. SPIE – Optical Materials and Applications, **5946**, 192–201 (2005).

IV

Hizhnyakov V., Boltrushko V., Tehver I., *Optical transitions in the centres with soft dynamics in the final state*, J. Phys.: Conf. Ser. **21**, 161–166 (2005).

V

Hizhnyakov V., Benedek G., Tehver I., Boltrushko V.,
Optical spectra of systems with nearly unstable excited states:
modulated lambda-shaped spectra,
J. Noncryst. Solids **352**, 2558–2561 (2006).

VI

Boltrushko V., Holmar S., Tehver I., Hizhnyakov V.,
*Vibronic transitions in the vicinity of the dynamical instability
of the final state*, J. Mol. Struct. **838**, 164–169 (2007).

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Institution and position held: Institute of Physics, University of Tartu: engineer
                                        since 2005 up to now;
                                        University of Tartu, Doctoral School of Material
                                        Study and Technology (MMTDK): extraordinary
                                        researcher (2005–2007).

Education: University of Tartu, Faculty of Physics and
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                                        M.Sc., 2004.

Scientific work: solid state theory, vibronic interaction, numerical
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                         2005 kuni siiani;
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                         Tehnoloogia Doktorikool (MMTDK): erakorraline
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Teadustegevus: tahkisteooria, vibroonsed võnkumised,
                         numbrilised arvutused

Publikatsioonid: 9 artiklit

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