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Theory of vibronic transitions between states with hard and soft local phonon dynamics

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Abstract

Optical spectra of centers with strongly reduced local elastic springs of excited electronic states are studied. In this case, a resonant mode of a very low frequency appears in the local phonon density of states of the phonon spectrum. Qualitatively this corresponds to the case when optical transitions take place to the vicinity of a flat minimum of the potential energy in the configurational coordinate space, where the density of states of low–frequency phonons is considerably increased. We perform fully quantum–mechanical calculation of the absorbtion spectrum, taking into account all possible degrees of freedom of acoustic phonons. The applied method allows one to take explicitly into account the mixing of all modes in the electronic transition. It is found that then the optical spectra depend essentially on the type of the vibronic interaction. If the low–frequency resonance contributes to both the linear and the quadratic vibronic coupling, then the zero–phonon line (ZPL) will be practically absent in the spectrum; instead there will be a lambda–shaped phonon sideband (PS).

Contents

Chapter 1

Introduction

The problem of vibronic transitions in optical centers in crystals has a long history. Theoretical explanation of the shape of such a spectra was given by Lax [1], Kubo and Toyozawa [2], Rebane [3]. The essence and the behaviour of zero–phonon line (ZPL) is covered in [4]. It appeared that in harmonic approximation only the case of the linear vibronic coupling can be treated exactly. However, the problem of quadratic coupling till now was solved only in some special cases: weak coupling, neglecting of the mode mixing, exact consideration of two–mode mixing only [5].

It should be noted that Kubo and Toyozawa in their famous paper [2] gave an exact solution of the problem. However, the equation proposed by them requires calculating of high order determinants (in case of the quasi–continuous phonon spectrum, determinants of the matrixes are of the order of $N \times N$, where N is Avogadro's number). Efficient methods for calculating of such determinants has not been proposed so far.

In the thesis we present a solution to the problem of the vibronic transition in case of strong quadratic and arbitrary linear vibronic coupling when transitions between states with hard and soft local phonon dynamics occur. In this case the main contribution to the spectrum is given by the low frequency part of the phonon continuum. The main attention is paid to the shape of the phonon sideband of the zero–phonon line. Only the zero temperature case is considered. It is shown that optical spectra in this case essentially differ from the conventional ones. Note also that the thermal behaviour of zero–phonon line in present model was considered in attached publications [6]– [8].

To solve the problem we apply the method of transformation of phonon operators [9]. 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 [10]. In the present work it is shown that the set of N–equations ($N \sim$ Avogadro's number) for the one and two–phonon amplitudes derived in [9] 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 [1], where such an enhancement was actually observed. We have in mind here the so called λ–shaped spectra [11], where one does not see the zero–phonon line at all; instead one observes jump–like appearance of the spectral intensity of type $\Theta(\omega - \omega_0)\mathcal{F}(\omega)$, where ω_0 is the resonant frequency, Θ is the Heaviside step function and $\mathcal{F}(\omega)$ smoothly decreases with ω.

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 essentially reduce the local elastic springs in crystals. For the problem under consideration it is essential 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 through the experimental investigation of the system with different optical transitions between electronic states with soft phonon dynamics.

Besides the instability of optical spectra, the problem of quadratic vibronic interaction is important also 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} (see [12] for details). Therefore a jump of the vacancy can be described as a vibronic transition determined by the soft phonon dynamics.

[1] See also *Section 4.3 Model of single vibration*

Chapter 2

The quadratic interaction problem

In this chapter we introduce some notations which will be used in the current and further chapters. We also deduce a global formula for the spectral intensity distribution with respect to the quadratic interaction. Explicit calculation of this formula is provided in the next chapters.

2.1 Optical spectra

In the adiabatic approximation, different Hamiltonians are used to describe phonons in different electronic states. In the adiabatic and Condon approximation (see e.g. [1], [3]) the optical spectrum corresponding to a transition between different electronic states is determined by the expression

$$I(\omega) = \frac{\omega^{2\mp 1} C}{2\pi} \int\limits_{-\infty}^{\infty} F(t) e^{-i(\omega-\omega_0)t-\gamma_0|t|}\, dt, \tag{2.1}$$

where C is a constant, the "–" sign corresponds to the absorption spectrum and the "+" sign stands for the emission spectrum, γ_0 is the natural line width of the excited level and ω_0 is the frequency of pure electronic transition. The Fourier transform of the spectrum has the form

$$F(t) \equiv \langle \hat{f}_t \rangle = Sp\left[e^{-\frac{H_1}{kT}} \hat{f}_t\right] Sp^{-1}\left[e^{-\frac{H_1}{kT}}\right] = \langle e^{itH_2} e^{-itH_1} \rangle. \tag{2.2}$$

Actually, Fourier transform should be written as $F(t) = \langle M e^{itH_2} M e^{-itH_1} \rangle$, but in the Condon approximation only the constant term in the expansion of the electronic matrix element M is taken into account, that is why $M \approx M_0 = Const$ and M_0 is normalized to unity.

Taking into account the quadratic interaction, the vibrational Hamiltonian of the final (exited) electronic state can be expressed in the form

$$H_2 = H_1 + V, \tag{2.3}$$

$$V = \omega_0 + a_0 q + \frac{1}{2} b q^2, \tag{2.4}$$

where ω_0 is the frequency of a purely electronic transition, a_0, b are vector and tensor

parameters of the electron-phonon interaction, q is the configurational coordinates vector depending on the normal coordinates as follows:

$$q = \sum_j e_{1j}x_j = \sum_k e_{2k}(y_k - y_{0k}) = \sum_k e_{2k}y_k - q_0, \tag{2.5}$$

The vibrational Hamiltonians H_1 and H_2 can also be presented in the form[1]

$$H_1 = \frac{1}{2}\sum_j \Big(-\frac{\partial^2}{\partial x_j^2} + \omega_{1j}^2 x_j^2\Big), \tag{2.6}$$

$$H_2 = \overline{\omega}_0 + \frac{1}{2}\sum_k \Big(-\frac{\partial^2}{\partial y_k^2} + \omega_{2k}^2 y_k^2\Big), \tag{2.7}$$

the expression for $\overline{\omega}_0$ is given below.

The normal coordinates of the initial (j) and the final (k) electronic states are related by the orthogonal transforms

$$x_j = \sum_k c_{jk}(y_k - y_{0k}) = \sum_k c_{jk}y_k - x_{0j}, \tag{2.8}$$

$$y_k = \sum_j c_{jk}(x_k + x_{0j}) = \sum_j c_{jk}x_k + y_{0k}, \tag{2.9}$$

where

$$c_{jk} = \frac{be_{1j}e_{2k}}{\omega_{2k}^2 - \omega_{1j}^2} \tag{2.10}$$

is the Duschinsky rotation matrix given by [13], e_{1j} and e_{2k} are the components of the vector q in the space of normal coordinates, which satisfy the conditions

$$e_{2k} = \sum_j c_{jk}e_{1j}, \qquad \sum_j e_{1j}^2 = \sum_k e_{2k}^2 = 1. \tag{2.11}$$

If we combine (2.10) with (2.11), we get

$$\sum_j c_{jk}e_{1j} = b\sum_j \frac{e_{1j}^2 e_{2k}}{\omega_{2k}^2 - \omega_{1j}^2},$$

hence it follows that

$$\sum_j \frac{e_{1j}^2}{\omega_{2k}^2 - \omega_{1j}^2} = \sum_k \frac{e_{2k}^2}{\omega_{2k}^2 - \omega_{1j}^2} = b^{-1}. \tag{2.12}$$

Constant terms in (2.5) – (2.9) are considered in *Appendix A.1 Displacements of the normal coordinates*. It appears that

$$x_{0j} = \frac{\big(a_0 - bq_0\big)e_{1j}}{\omega_{1j}^2}, \tag{2.13}$$

$$y_{0k} = \frac{a_0 e_{2k}}{\omega_{2k}^2}. \tag{2.14}$$

2.2 Debye's model

In Debye's model of acoustic continuum modes the local density of the phonon states is $\propto \omega^2$ in three–dimensional lattices. Let x_j be a normal coordinate of the crystal. By $\rho_i(\omega)$ denote the local phonon density, which corresponds to a configurational coordinate

[1] We use $\hbar = 1$ units

$q_i = \sum_j e_{ij} x_j$:

$$\rho_i(\omega) \stackrel{\text{def}}{=} \sum_j e_{ij}^2 \delta(\omega - \omega_{ij}), \qquad i = 1, 2. \tag{2.15}$$

Below we are interested in the low–frequency phonons only. This allows us to use the approximation $\rho_i(\omega) \approx A\omega^4$. Here we take into account that configurational coordinates q are the differences of displacements of nearest atoms. This difference in the long–wave (small ω) limit results in the additional ω^2 factor in the equation for ρ_i to usual $\propto \omega^2$ density of states in $3\mathcal{D}$ case. As a result, $\rho_i(\omega) \sim \omega^4$, when $\omega \to 0$.

The normalization condition for this function has the form

$$\Psi_i \int_0^{\omega_D} \rho_i(\omega) d\omega = 1, \qquad i = 1, 2, \tag{2.16}$$

where ω_D is the maximum frequency of phonons in Debye's model, Ψ_i is a normalization factor. Suppose that $\omega_D = 1$, then $\rho_1(\omega) = 5\omega^4$. Indeed,

$$\Psi_1^{-1} = \int_0^1 5\omega^4 \mathrm{d}\omega = \omega^5 \big|_0^1 = 1, \tag{2.17}$$

so ρ_1 appears to be normalized, as it should be.

Let $G(\omega)$ be the dynamical Green's function (in the spectral representation, see [9] for details) defined by

$$G_i(\omega) \stackrel{\text{def}}{=} \int_0^1 \frac{\rho_i(\omega')\, d\omega'}{\omega^2 - \omega'^2 - i\epsilon}, \qquad i = 1, 2, \quad \epsilon = +0. \tag{2.18}$$

There exists a relationship between Green's function and local phonon density:

$$\rho_i(\omega) = \frac{2\omega}{\pi} \operatorname{Im} G_i(\omega), \qquad i = 1, 2. \tag{2.19}$$

An analytical form of ρ_i is found in *Appendix A.2 Green's functions*. It is shown that

$$\rho_1(\omega) = 5\omega^4, \tag{2.20}$$

$$\rho_2(\omega) = \frac{5}{9}\omega^4 \Big(\Big[\alpha + \omega^2 - 0.5\omega^3 \ln\big((1+\omega)/(1-\omega)\big) \Big]^2 + 0.25\pi^2\omega^6 \Big)^{-1}, \tag{2.21}$$

where $\alpha = 1/(5b) + (1/3)$.

However, function $\rho_2(\omega)$ appears to be unnormed. It is still allowed because Debye's model becomes inaccurate in case of large frequencies. However, in case of small ω this model is correct.

Debye's model gives a correct description of optical spectra in the low–frequency range. It works fine in the initial state where by our assumption there is no quasilocal vibrations. In the excited state, however, quasilocal vibrations occur that leads us to use another model in order to describe low–frequency vibrations in the final electronic state. The model must have the phonon density peak in the low–frequency range. In order to obtain the functional dependence for $\rho_2(\omega)$ Dyson's equation were used.

We should also note that the quadratic interaction violates the mirror symmetry of the emission and the absorbtion spectra. In our approach it is caused by difference of Green's functions in initial and final electronic states (see [3], [14] for details).

2.3 Phonon operators

Our computations require using the framework of secondary quantization. According to [15], Hamiltonians acquire the form

$$H_1 = \sum_j \hbar\omega_{1j}\big(a_{1j}^\dagger a_{1j} + 1/2\big), \tag{2.22}$$

$$H_2 = \overline{\omega}_0 + \sum_k \hbar\omega_{2k}\big(a_{2k}^\dagger a_{2k} + 1/2\big). \tag{2.23}$$

Phonon creation and annihilation operators take into account the mixing of the normal coordinates when the electronic transition occurs. Detailed derivation of these operators is given in *Appendix A.3 Secondary quantization*, we just reveal here the final formulae:

$$a_{1j}^\dagger = -\xi_{1j} + \frac{1}{2}\sum_k \frac{c_{jk}}{\sqrt{\omega_{1j}\omega_{2k}}}\Big[(\omega_{1j}+\omega_{2k})a_{2k}^\dagger + (\omega_{1j}-\omega_{2k})a_{2k}\Big], \tag{2.24a}$$

$$a_{2k}^\dagger = \xi_{2k} + \frac{1}{2}\sum_j \frac{c_{jk}}{\sqrt{\omega_{1j}\omega_{2k}}}\Big[(\omega_{1j}+\omega_{2k})a_{1j}^\dagger + (\omega_{2k}-\omega_{1j})a_{1j}\Big], \tag{2.24b}$$

$$a_{1j} = -\xi_{1j} + \frac{1}{2}\sum_k \frac{c_{jk}}{\sqrt{\omega_{1j}\omega_{2k}}}\Big[(\omega_{1j}+\omega_{2k})a_{2k} + (\omega_{1j}-\omega_{2k})a_{2k}^\dagger\Big], \tag{2.24c}$$

$$a_{2k} = \xi_{2k} + \frac{1}{2}\sum_j \frac{c_{jk}}{\sqrt{\omega_{1j}\omega_{2k}}}\Big[(\omega_{1j}+\omega_{2k})a_{1j} + (\omega_{2k}-\omega_{1j})a_{1j}^\dagger\Big], \tag{2.24d}$$

where

$$\xi_{1j} \stackrel{\text{def}}{=} \sqrt{\frac{\omega_{1j}}{2}}x_{0j} = \frac{\big(a_0 - bq_0\big)e_{1j}}{\sqrt{2\omega_{1j}^3}}, \tag{2.25}$$

$$\xi_{2k} \stackrel{\text{def}}{=} \sqrt{\frac{\omega_{2k}}{2}}y_{0k} = \frac{a_0 e_{2k}}{\sqrt{2\omega_{2k}^3}}, \tag{2.26}$$

and

$$\xi_{1j} = \sqrt{\omega_{1j}}\sum_k c_{jk}\frac{\xi_{2k}}{\sqrt{\omega_{2k}}}. \tag{2.27}$$

2.4 Zero temperature case

At zero temperature $(T = 0)$ it is convenient to choose the energy reference frame such that $H_1|0\rangle = 0$. Then $\hat{f}_t = e^{itH_2}e^{-it0} \equiv e^{itH_2}$ and Fourier transform acquires a form

$$F \stackrel{\text{def}}{=} \langle 0|\hat{f}_t|0\rangle = \langle 0|e^{itH_2}|0\rangle. \tag{2.28}$$

In such a case,

$$\begin{aligned} F' &\equiv \frac{dF}{dt} = i\langle 0|e^{itH_2}|0\rangle = i\langle 0|\hat{f}_t V|0\rangle = \\ &= i\Big[\omega_0 F + a_0\langle 0|\hat{f}_t q|0\rangle + \frac{b}{2}\langle 0|\hat{f}_t q^2|0\rangle\Big] = i\Big[\omega_0 F + F_1' + F_2'\Big]. \end{aligned} \tag{2.29}$$

If we represent the configurational coordinate q (see (2.5)) as well as its square q^2 via secondary quantization (see *Section 2.3 Phonon operators*), i.e.

$$q = \sum_j e_{1j}x_j = \sum_j e_{1j}\sqrt{\frac{\hbar}{2\omega_{1j}}}\left(a_{1j} + a_{1j}^\dagger\right),$$

$$q^2 = \frac{1}{2}\sum_{jj'} \frac{e_{1j}e_{1j'}}{\sqrt{\omega_{1j}\omega_{1j'}}}\big(a_{1j} + a_{1j}^\dagger\big)\big(a_{1j'} + a_{1j'}^\dagger\big),$$

then taking into consideration that in our units $\hbar = 1$ and due to the relations

$$\left.\begin{array}{c} a_{1j}|0\rangle = 0 \\ \langle 0|a_{1j}^\dagger = 0 \end{array}\right\} \quad \Rightarrow \big(a_{1j} + a_{1j}^\dagger\big)\big(a_{1j'} + a_{1j'}^\dagger\big)|0\rangle = \delta_{jj'} + a_{1j}^\dagger a_{1j'}^\dagger|0\rangle$$

we obtain

$$\begin{aligned} \langle 0|\hat{f}_t q|0\rangle &= \frac{1}{\sqrt{2}}\sum_j \frac{e_{1j}}{\sqrt{\omega_{1j}}}\langle 0|\hat{f}_t a_{1j}^\dagger|0\rangle, \\ \langle 0|\hat{f}_t q^2|0\rangle &= \frac{1}{2}\sum_{jj'} \frac{e_{1j}e_{1j'}}{\sqrt{\omega_{1j}\omega_{1j'}}}\langle 0|\hat{f}_t a_{1j}^\dagger a_{1j'}^\dagger|0\rangle + \frac{1}{2}\sum_j \frac{e_{1j}^2}{\omega_{1j}}F. \end{aligned}$$

Therefore

$$\boxed{-iF' = \overline{\omega}_0 F + \frac{a_0}{\sqrt{2}}A + \frac{b}{4}P,} \tag{2.30}$$

where

$$A = \sum_j e_{1j}A_j, \tag{2.31}$$

$$P = \sum_{jj'} \frac{e_{1j}e_{1j'}}{\sqrt{\omega_{1j}\omega_{1j'}}}p_{jj'}, \tag{2.32}$$

$$A_j = \frac{1}{\sqrt{\omega_{1j}}}\langle 0|\hat{f}_t a_{1j}^\dagger|0\rangle, \tag{2.33}$$

$$p_{jj'} = \langle 0|\hat{f}_t a_{1j}^\dagger a_{1j'}^\dagger|0\rangle, \tag{2.34}$$

$$\overline{\omega}_0 = \omega_0 + \frac{b}{4}\sum_j \frac{e_{1j}^2}{\omega_{1j}}. \tag{2.35}$$

Note that introduced here terms A_j and $p_{jj'}$ describe also resonant Raman scattering (RRS). Actually, they are the first and the second–order Fourier amplitudes of RRS (see [9] for details).

Chapter 3

Derivation of Fourier amplitudes

In this chapter we perform a fully quantum–mechanical calculation of the optical spectra when the average phonon frequencies in the excited state are much smaller than in the ground state. It will be shown that in this case one can explicitly calculate $A(t)$, $P(t)$ and $F(t)$.

3.1 Equation for the first-order amplitude

In order to calculate Fourier amplitudes $A(t)$, several important steps need to be taken. The following *algorithm* can be implemented:

1. Initially, matrix element A_j depends on secondary quantization operators $a_{1j}^{\dagger}, a_{1j}$. For our purpose these operators have to be substituted with $a_{2k}^{\dagger}, a_{2k}$ using formulae obtained in *Section 2.3 Phonon operators*.
2. Operators $\hat{f}_t a_{2k}^{\dagger}$ should be reordered. An additional exponential factor arise during the transformation.
3. Quantum–mechanical averaging over zero–point state of operators $a_{2k}^{\dagger}\hat{f}_t$ leads to the averaging of $\hat{f}_t a_{2k}$.
4. Again, operators a_{2k} can be expressed through $a_{1j}^{\dagger}, a_{1j}$. Operator $\hat{f}_t$ stays on the LHS.
5. Considering that $a|0\rangle = 0$, the equation recurrent by A_j will be obtained.
6. By introducing new variables and taking into account the approximation of soft dynamics in the initial state, the equation for the first-order amplitude will be derived.

Using previous algorithm (for detailed derivation see *Appendix A.5 Explicit calculation of* $A(t)$), one gets equation

$$A(t) = \frac{\frac{a_0}{\sqrt{2}}\Big(\varphi_2(t) - \varphi_2(0)\Big)}{1 + (9/20)\big(\varphi_1(t) + \varphi_1(0)\big)} F(t), \tag{3.1}$$

where the following functions are introduced

$$\varphi_n(t) = \sum_k \frac{e_{2k}^2}{\omega_{2k}^n} e^{it\omega_{2k}}.$$

3.2 Second-order amplitude

An analytical view of $P(t)$ can be obtained by the same way. The only difference is the complexity of corresponding *algorithm*:

1. Since matrix $P(t)$ is nothing more but the set of QM–averaged $\hat{f}_t a_1^\dagger a_1^\dagger$ operators [1], the first creation operator can be expressed in terms of $a_2^\dagger, a_2$ operators.
2. Applying the commutation rule to the $a_2 a_1^\dagger$ returns the sum of $a_1^\dagger a_2$ and a constant term.
3. Operators $a_2^\dagger \hat{f}_t$ must be reordered.
4. Operators a_2 and $a_2^\dagger$ can be expressed through a_1 and $a_1^\dagger$. Since $\langle 0|a^\dagger = 0$ and $a|0\rangle = 0$, matrix elements of $P(t)$ can be expressed as a linear combination of four QM–averaged quantities: $\hat{f}_t$, $\hat{f}_t a_1^\dagger$, $\hat{f}_t a_1^\dagger a_1^\dagger$, $a_1 \hat{f}_t a_1^\dagger$ (note that creation operator is on the RHS), they corresponds to F, A, P, S (the last one is a supplementary matrix connected with P).
5. We have obtained a system of two linear homogeneous equations for F, A, P, S, whilst only P and S are independent variables. The solution of the system yields $P = P(F)$.

Complete derivation of second-order Fourier amplitude is given in *Appendix A.6 Explicit calculation of* $P(t)$. It follows that

$$P = \frac{K_1 + Q_1 A_1}{T_1} F, \tag{3.2}$$

where

$$A_1 = \frac{(a_0/\sqrt{2})\big(\varphi_2(t) - \varphi_2(0)\big)}{1 + (9/20)\big(\varphi_1(t) + \varphi_1(0)\big)}, \tag{3.3}$$

$$K_1 = (1/4)\big[\varphi_1(0) - (9/40)(\varphi_1^2(t) - \varphi_1^2(0))\big], \tag{3.4}$$

$$Q_1 = \frac{a_0}{2\sqrt{2}}\big(\varphi_2(t) - \varphi_2(0)\big)\big[1 - (9/40)\big(\varphi_1(t) - \varphi_1(0)\big)\big], \tag{3.5}$$

$$T_1 = 1 + (9/40)^2\big(\varphi_1^2(t) - \varphi_1^2(0)\big). \tag{3.6}$$

[1] In this section we skip alphabetical indexes in secondary quantization operators. We just trying to get the hole picture about the method used here. These indexes are only important when all kind of matrix transformations take place.

Chapter 4

Numerical experiments

4.1 Calculation of spectra

According to (2.1), the spectral function can be expressed as

$$F(\omega) = \frac{1}{2\pi} \int\limits_{-\infty}^{\infty} F(t) e^{-i\omega t - \gamma_0 |t|}\, dt, \tag{4.1}$$

If one calculates $F(\omega)$, it will be possible to obtain absorption (emission) spectra as well. Function $F(t)$ can be obtained from (2.30):

$$\frac{dF}{dt} = i \left[\overline{\omega}_0 F(t) + \frac{a_0}{\sqrt{2}} A(t) + \frac{b}{4} P(t) \right] = iD(t)F(t), \tag{4.2}$$

In equation (2.35) integration can be used instead of summing up. Keeping in mind that $\omega_0 = 0$ and $e_1^2(\omega) = \rho_1(\omega) = 5\omega^4$,

$$\overline{\omega}_0 = \frac{b}{4} \int\limits_0^1 \frac{\rho_1(\omega)}{\omega}\, d\omega = \frac{b}{4} \int\limits_0^1 \frac{5\omega^4}{\omega}\, d\omega = \frac{5}{8} b.$$

According to (3.1), (3.2)–(3.6) and also taking into account that $b \approx b_0 = -3/5$, we obtain

$$D(t) = -\frac{3}{8} + \frac{a_0}{\sqrt{2}} A_1 - \frac{3}{20} \frac{K_1 + Q_1 A_1}{T_1}, \tag{4.3}$$

where

$$A_1 = \frac{(a_0/\sqrt{2})\big(\varphi_2(t) - \varphi_2(0)\big)}{1 + (9/20)\big(\varphi_1(t) + \varphi_1(0)\big)}, \tag{4.4}$$

$$K_1 = (1/4)\big[\varphi_1(0) - (9/40)(\varphi_1^2(t) - \varphi_1^2(0))\big], \tag{4.5}$$

$$Q_1 = \frac{a_0}{2\sqrt{2}} \big(\varphi_2(t) - \varphi_2(0)\big)\big[1 - (9/40)\big(\varphi_1(t) - \varphi_1(0)\big)\big], \tag{4.6}$$

$$T_1 = 1 + (9/40)^2 \big(\varphi_1^2(t) - \varphi_1^2(0)\big). \tag{4.7}$$

Variables can be separated in (4.2). From $dF(t)/F = iD(t)dt$ it follows that

$$F(t) = e^{g(t)}, \qquad \text{where} \qquad g(t) = i \int\limits_0^t D(t')\, dt'. \tag{4.8}$$

In (4.3) functions $\varphi_n(t) = \sum_k e_{2k}^2 \omega_{2k}^{-n} e^{it\omega_{2k}}$ should be calculated. Again, integration can

be used instead of summing up. Taking into account that $e_2^2(\omega) = \rho_2(\omega)$, function $\varphi_n(t)$ can be expressed in the form

$$\varphi_n(t) = \int_0^1 \frac{\rho_2(\omega)}{\omega^n} e^{it\omega}\, d\omega, \tag{4.9}$$

where

$$\rho_2(\omega) = \frac{5}{9}\omega^4 \Big(\Big[\alpha + \omega^2 - 0.5\omega^3 \ln\big((1+\omega)/(1-\omega)\big) \Big]^2 + 0.25\pi^2\omega^6 \Big)^{-1}. \tag{4.10}$$

4.2 Computer simulations

For numerical computation of optical spectra we use C++ compiler, program listing is given in *Appendix B*. The explanation for the mathematical routines can be found in [5]. For visualization Origin™7.5 and Maple™9.03 were used.

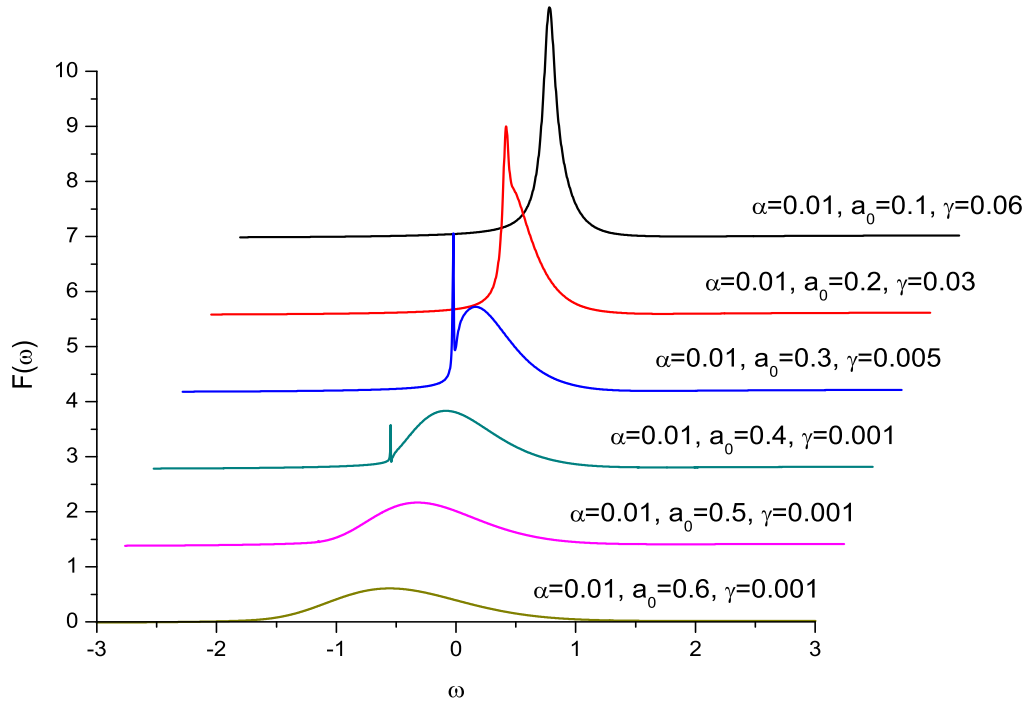

Figure 4.1: The dependence of the spectral function on the coupling parameter a_0.

The spectra observed in [11] match qualitatively the spectra obtained in our theory. Figure 4.1 describes the essential dependence of calculated spectral functions on vector parameter a_0 of electron–phonon interaction [1]. One can see the specific λ–shaped profile when $\sqrt{\alpha} \simeq a_0$. Another convincing result is ZPL disappearance [2] with growing of parameter a_0.

[1] Note that position of the zero–phonon line depends on a_0!

[2] The linewidth for the ZPL had to be enlarged in order to fit all the data plots.

The parameter b is also important (see Figure 4.2). Since $\alpha \sim b^{-1}$, both a_0 and b leads to the enlargement of the phonon sideband while ZPL practically vanishes.

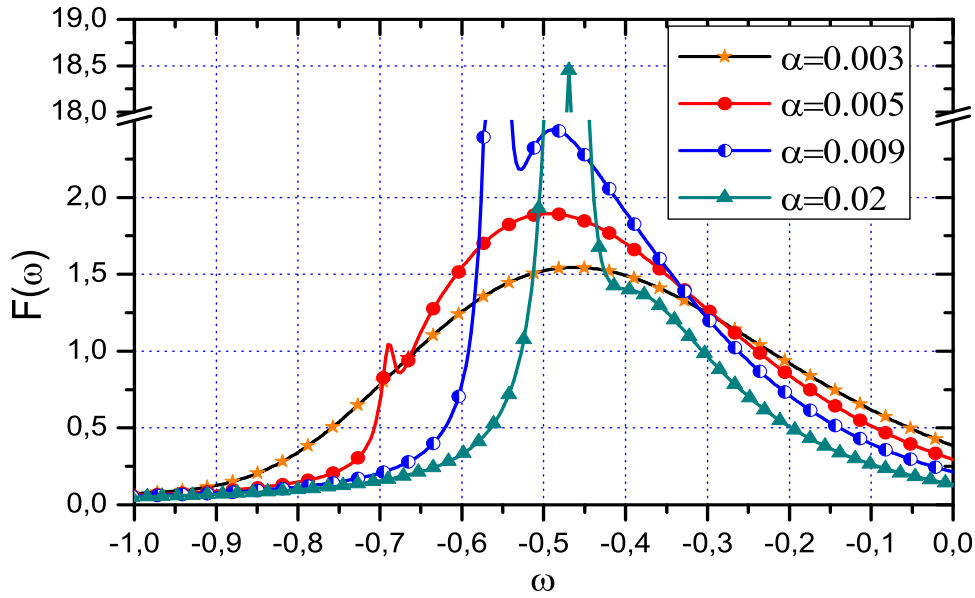

Figure 4.2: The dependence of the spectral function on the coupling parameter b, while a_0 and γ remain unchanged ($a_0 = 0.2$, $\gamma = 0.1$).

4.3 Model of single vibration

To understand qualitatively the effect of the soft dynamics in the excited state, we consider a single vibration model. In this model the potential energies in the initial and the final electronic states equal

$$U_1(q) = \frac{1}{2}\omega_1^2 q^2, \qquad U_2(q) = \omega_0 + a_0 q + \frac{1}{2}\omega_2^2 q^2.$$

In this case the equation for the Fourier transform of the absorption spectrum reads [3]

$$F(t) = \langle 0|e^{itH_2}|0\rangle,$$

where $H_2 = \hat{p}^2/2 + U_2(q)$. If $a_0, \omega_2 \to 0$, then the Fourier transform of the absorption spectrum gets the form:

$$F(t) = e^{it\omega_0}\langle 0|e^{it\hat{p}^2/2}|0\rangle.$$

To calculate this $F(t)$, we use the momentum representation, in which the momentum operator is the c–number. In this representation

$$F(t) = \int_{-\infty}^{\infty} e^{itp^2/2}\rho(p)\,dp,$$

[3] We still use $\hbar = 1$ units...

where

$$\rho(p) = \sqrt{\frac{\hbar\omega_1}{\pi}} e^{-p^2/\omega_1}$$

is the momentum distribution function in the zero-point state. In this case the absorption spectral function is equal

$$J(\omega) = 2\int_0^\infty \rho(p)\delta\left(\Omega - \frac{p^2}{2}\right) dp = \Theta(\omega)\sqrt{\frac{\omega_1}{2\pi\Omega}} e^{-2\Omega/\omega_1},$$

where $\Omega = \omega - \omega_0$. The hole burning spectrum in this case is given by the convolution of two $J(\omega)$–functions:

$$I(\omega) \propto \int_0^\infty J(x)J(|\Omega| - x)\, dx = \frac{1}{2}\omega_1 e^{-2|\Omega|/\omega_1}.$$

The obtained absorption and hole burning spectra are given on Fig. 4.3.

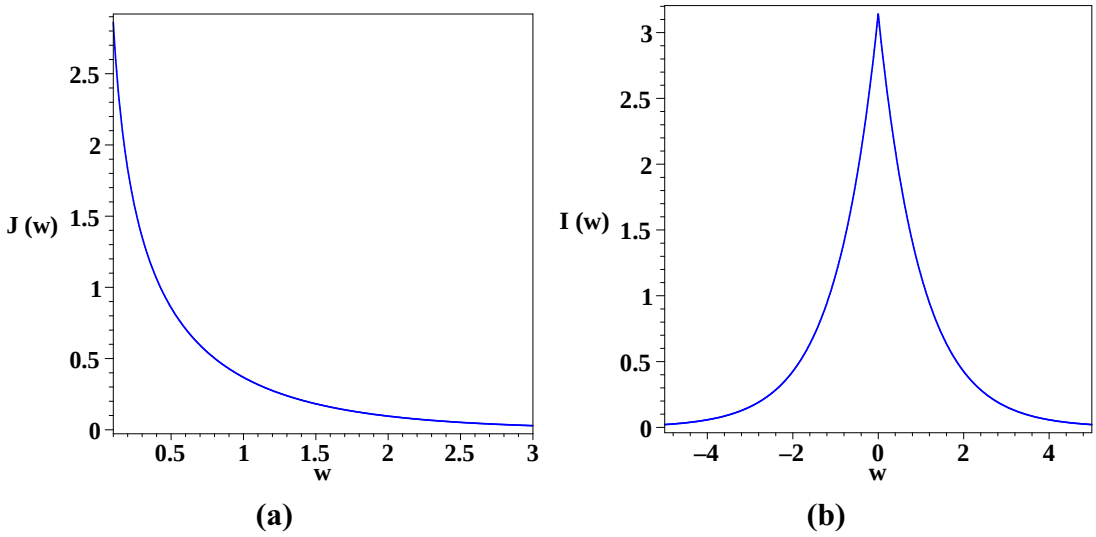

Figure 4.3: The absorption (a) and the hole burning (b) spectra in case of $a_0 = 0$ and $\omega_2 = 0$

One can see that in the case under consideration the long–wave part of the absorption spectrum is strongly enhanced: it has root singularity at $\omega = \omega_0$. Note that this singularity corresponds to the singularity in the density of states of free one–dimensional motion in the excited state. The remain exponential factor stays for the kinetic energy distribution in the zero–point state of the harmonic oscillator in the ground electronic state.

The hole burning spectrum has the sharp tip, where the first derivative of the spectrum has the step–vice singularity. The hole burning spectrum of this type was indeed observed in [11].

Chapter 5

Conclusions

In the thesis the problem of optical spectra calculation in the electronic transitions between states with hard and soft local phonon dynamics has been explicitly solved by the operator transformation method.

Till now, the bottleneck of this problem was taking into account the effect of mode mixing. In the model under consideration the mixing of the normal coordinates plays the significant role. The operator transformation method allows one to obtain a system of few closed equations. By using a hard–soft dynamics approximation, an analytical expression for the Fourier transform of the spectrum has been derived and the rigorous quantum–mechanical solution has been obtained. It has been shown that the phonon sideband amplification takes place in a low–frequency part of spectra, while the zero–phonon line practically disappears.

The simplified single–mode model has been also presented. This model assumes the existence of a single vibrational mode, the frequency of which in the excited state is considerably smaller than in the ground state. The theory presented here gives an explanation of the spectral anomaly observed in some low–temperature organic materials.

The calculation of the spectra was restricted with the zero temperature case only. For further investigation the non–zero temperature case is also of interest, especially for the theory of chemical reactions and quantum diffusion.

Vibroonsiirete teooria jäiga ja pehme lokaalse foonondünaamikaga seisundite korral

Vadim Boltrušhko

Kokkuvõte

Käesolevas väitekirjas on täpselt lahendatud optiliste spektrite arvutusprobleem elektronsiirete jaoks jäiga ja pehme lokaalse foonondünaamikaga seisundite vahel, kasutades operaatorite transformatsiooni meetodit.

Probleemi kitsaskohaks on seni olnud võnkemoodide segunemise mõju arvestamine. Käsitletavas mudelis mängib normaalkoordinaatide segunemine olulist rolli. Operaatorite transformatsiooni meetod taandab probleemi väikese arvu võrrandite suletud süsteemiks. Kasutades jäiga–pehme dünaamika lähendust, on tuletatud analüütiline avaldis optilise spektri Fourier pöörde jaoks ning saadud range kvantmehaaniline lahend. Näidati, et spektri madalsageduslikus osas leiab aset foononriba võimendumine, kusjuures foononvaba joon praktiliselt kaob.

Ühtlasi on esitatud lihtne ainumood-mudel. See mudel eeldab üheainsa võnkemoodi olemasolu, mille sagedus ergastatud olekus on tunduvalt madalam kui põhiolekus. Esitatud teooria selgitab spektraalset anomaaliat, mida on mõõdetud mõningates orgaaniliste ainetes madalatel temperatuuridel.

Spektri arvutustes on piirdutud null–temperatuuriga. Seoses keemiliste reaktsioonide ja kvantdifusiooni teooriaga on edaspidiseks huvipakkuv nullist erinevate temperatuuride käsitlemine.

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Appendix A

Preliminaries

A.1 Displacements of the normal coordinates

According to (2.8)–(2.9),

$$x_{0j} = \sum_k c_{jk} y_{0k}, \qquad y_{0k} = \sum_j c_{jk} x_{0j}. \tag{A.1}$$

Let us find analytical expressions for these terms.

Because of Hamiltonian can be expressed as the sum of kinetical and potential energy, Eq. (2.3) can be re-written in the following manner:

$$H_2 = H_1 + V = T + U_1 + V \equiv T + U_2,$$

where

$$\begin{aligned} U_1 &= \frac{1}{2}\sum_j \omega_{1j}^2 x_j^2, \\ U_2 &= \frac{1}{2}\sum_k \omega_{2k}^2 y_k^2 = \frac{1}{2}\sum_j \omega_{1j}^2 x_j^2 + \omega_0 + a_0 q + \frac{1}{2} b q^2. \end{aligned}$$

In order to get rid of q–linear term in potential U_2, one should introduce a new variable $\overline{x}_j = x_j + x_{0j}$. By choosing the right value of constant x_{0j} linear terms will be eliminated. With $\overline{x}_j$ the normal coordinate of the initial state acquires a form $x_j = \overline{x}_j - x_{0j}$. Then

$$\begin{aligned} U_2 &= \frac{1}{2}\sum_j \omega_{1j}^2 \left(\overline{x}_j - x_{0j}\right)^2 + a_0 \sum_j e_{1j}\left(\overline{x}_j - x_{0j}\right) + \\ &\quad + \frac{1}{2} b \sum_{jj'} e_{1j} e_{1j'} \left(\overline{x}_j - x_{0j}\right)\left(\overline{x}_j - x_{0j}\right) + \omega_0 = \\ &= \frac{1}{2}\sum_j \omega_{1j}^2 \overline{x}_j^2 - \sum_j \omega_{1j}^2 \overline{x}_j x_{0j} + a_0 \sum_j e_{1j}\overline{x}_j + \\ &\quad + \frac{1}{2} b \sum_{jj'} e_{1j} e_{1j'} \overline{x}_j \overline{x}_{j'} - b \sum_{jj'} e_{1j} e_{1j'} \overline{x}_j x_{0j'} + C_1, \end{aligned}$$

where

$$C_1 = \omega_0 + \frac{1}{2}\sum_j \omega_{1j}^2 x_{0j}^2 - a_0 \sum_j e_{1j} x_{0j} + \frac{1}{2} b \sum_{jj'} e_{1j} e_{1j'} x_{0j} x_{0j'} = Const.$$

Let's equate linear terms to zero:

$$\sum_j \Big[-\omega_{1j}^2 x_{0j} + a_0 e_{1j} - b e_{1j} \underbrace{\sum_{j'} e_{1j'} x_{0j'}}_{q_0}\Big]\overline{x}_j = 0.$$

It's obviously that the expression in parenthesis should be equal to zero also. Therefore

$$\boxed{x_{0j} = \frac{\big(a_0 - bq_0\big)e_{1j}}{\omega_{1j}^2}.} \tag{A.2}$$

We can modify potential V (2.4) by defining a new vector

$$\begin{aligned} \overline{q} = q + q_0 \;\; &= \;\; \sum_k e_{2k} y_k - q_0 + q_0 = \sum_k e_{2k} y_k, \\ &\Rightarrow q = \overline{q} - q_0. \end{aligned}$$

Now

$$V = a_0(\overline{q} - q_0) + \frac{1}{2} b(\overline{q} - q_0)^2 + \omega_0 = (a_0 - bq_0)\overline{q} + \frac{1}{2} b\overline{q}^2 + C_2,$$

where

$$C_2 = \omega_0 - a_0 q_0 + \frac{1}{2} b q_0^2 = Const.$$

In that case

$$U_1 = U_2 - V = \frac{1}{2}\sum_k \omega_{2k}^2 y_k^2 - (a_0 - bq_0)\sum_k e_{2k} y_k - \frac{1}{2} b \sum_{kk'} e_{2k} e_{2k'} y_k y_{k'} - C_2.$$

And like before, to get rid of the linear terms we introduce a new variable $\overline{y}_k = y_k + y_{0k}$. In the new coordinates

$$\begin{aligned} U_1 \;\; = \;\; &\frac{1}{2}\sum_k \omega_{2k}^2 \overline{y}_k^2 + \sum_k \omega_{2k}^2 \overline{y}_k y_{0k} - (a_0 - bq_0)\sum_k e_{2k}\overline{y}_k - \\ &-\frac{1}{2} b \sum_{kk'} e_{2k} e_{2k'} \overline{y}_k \overline{y}_{k'} - b\sum_{kk'} e_{2k} e_{2k'} \overline{y}_k y_{0k'} + C_3, \end{aligned}$$

where

$$\begin{aligned} C_3 \;\; = \;\; &-C_2 + \frac{1}{2}\sum_k \omega_{2k}^2 y_{0k}^2 - (a_0 - bq_0)\sum_k e_{2k} y_{0k} - \\ &-\frac{1}{2} b \sum_{kk'} e_{2k} e_{2k'} y_{0k} y_{0k'} = Const. \end{aligned}$$

Equating all linear terms to zero

$$\sum_k \Big[\omega_{2k}^2 y_{0k} - (a_0 - bq_0)e_{2k} - b e_{2k} \underbrace{\sum_{k'} e_{2k'} y_{0k'}}_{q_0}\Big]\overline{y}_k = 0.$$

Finally

$$\boxed{y_{0k} = \frac{a_0 e_{2k}}{\omega_{2k}^2}.} \tag{A.3}$$

A.2 Green's functions

According to (2.19),

$$\rho_{1,2}(\omega) = \frac{2\omega}{\pi} \operatorname{Im} G_{1,2}(\omega), \tag{A.4}$$

where

$$G_{1,2}(\omega) = \int\limits_0^1 \frac{\rho_{1,2}(\omega')\,d\omega'}{\omega^2 - \omega'^2}. \tag{A.5}$$

Let us introduce short notation $G_{1,2}(\omega) \equiv G_{1,2}$. In the ground state

$$\begin{aligned} G_1 &= \int\limits_0^1 \frac{\rho_1(\omega')\,d\omega'}{\omega^2 - \omega'^2} = \int\limits_0^1 \frac{5\omega'^4\,d\omega'}{\omega^2 - \omega'^2} = -\frac{5}{2}\int\limits_0^1 \left[\frac{1}{(\omega' - \omega)} - \frac{1}{(\omega' - \omega)}\right]\omega'^3\,d\omega' = \\ &= -5\left[\frac{1}{3} + \omega^2 - \frac{\omega^3}{2}\ln\frac{1+\omega}{1-\omega} - i\frac{\pi}{2}\omega^3\right]. \end{aligned}$$

According to the Dyson's equation,

$$G_2 = G_1 + G_1 b G_2, \tag{A.6}$$

the dynamical Green's function of the excited state can be written as follows:

$$\begin{aligned} G_2 &\equiv \frac{G_1}{1 - bG_1} = \frac{1}{b}\frac{G_1}{1/b - G_1} = -\frac{1}{b}\frac{G_1}{G_1 - 1/b} = -\frac{1}{b}\frac{(G_1 - 1/b) + 1/b}{G_1 - 1/b} = \\ &= \frac{1}{b}\left[-1 + \frac{1}{1 - bG_1}\right] = \frac{1}{b}\left[-1 + \frac{1}{1 - b(\operatorname{Re} G_1 + i \operatorname{Im} G_1)}\right] = \\ &= \frac{1}{b}\left[-1 + \frac{1 - b\operatorname{Re} G_1 + ib\operatorname{Im} G_1}{(1 - b\operatorname{Re} G_1)^2 + (b\operatorname{Im} G_1)^2}\right] = \frac{1}{b}\left[-1 + \frac{1 - b(\operatorname{Re} G_1 - i\operatorname{Im} G_1)}{|1 - bG_1|^2}\right]. \end{aligned}$$

Denominator equals

$$\begin{aligned} 1 - bG_1 &= 1 + 5b\left[\frac{1}{3} + \omega^2 - \frac{\omega^3}{2}\ln\frac{1+\omega}{1-\omega} - i\frac{\pi}{2}\omega^3\right] = \\ &= 5b\left[\alpha + \omega^2 - \frac{\omega^3}{2}\ln\frac{1+\omega}{1-\omega} - i\frac{\pi}{2}\omega^3\right], \end{aligned}$$

where

$$\alpha \stackrel{\text{def}}{=} \frac{1}{5b} + \frac{1}{3}.$$

Since the local phonon densities only depends on imaginary parts of Green's functions,

$$\begin{aligned} \operatorname{Im} G_1 &= \frac{5}{2}\pi\omega^3, \\ \operatorname{Im} G_2 &= \frac{\operatorname{Im} G_1}{|1 - bG_1|^2} = \frac{\frac{5}{2}\pi\omega^3}{25b^2\left(\alpha + \omega^2 - \frac{\omega^3}{2}\ln\frac{1+\omega}{1-\omega}\right)^2 + 25b^2\frac{\pi^2}{4}\omega^6} = \\ &= \frac{\frac{1}{10}\pi b^{-2}\omega^3}{\left(\alpha + \omega^2 - \frac{\omega^3}{2}\ln\frac{1+\omega}{1-\omega}\right)^2 + \frac{\pi^2}{4}\omega^6}. \end{aligned}$$

In this case

$$\begin{aligned} \rho_1(\omega) &= \frac{2\omega}{\pi}\frac{5}{2}\pi\omega^3 = 5\omega^4, \\ \rho_2(\omega) &= \frac{5}{9}\omega^4\Big(\Big[\alpha + \omega^2 - 0.5\omega^3\ln\big((1+\omega)/(1-\omega)\big)\Big]^2 + 0.25\pi^2\omega^6\Big)^{-1}. \end{aligned}$$

A.3 Secondary quantization

In case of harmonic oscillations with frequency ω, creation and annihilation operators were introduced (see e.g. [15] for details):

$$\begin{aligned}\hat{a}^\dagger &= \frac{1}{\sqrt{2}}\left(\sqrt{\frac{m\omega}{\hbar}}\hat{X} - \frac{i}{\sqrt{m\omega\hbar}}\hat{P}\right),\\ \hat{a} &= \frac{1}{\sqrt{2}}\left(\sqrt{\frac{m\omega}{\hbar}}\hat{X} + \frac{i}{\sqrt{m\omega\hbar}}\hat{P}\right),\end{aligned}$$

it is also known that the following correlation takes place:

$$\hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a} = 1.$$

Ignoring operator's "hats" and getting rid of masses by introducing the reduced displacements $x = \sqrt{m}Q$, and also considering

$$P = -i\hbar\frac{d}{dX} = -i\hbar\sqrt{m}\frac{d}{dx} = \sqrt{m}p,$$

where p is a reduced momentum, we obtain

$$a^\dagger = \frac{1}{\sqrt{2\omega\hbar}}(\omega x - ip), \tag{A.7}$$

$$a = \frac{1}{\sqrt{2\omega\hbar}}(\omega x + ip). \tag{A.8}$$

Adding/subtracting (A.7) and (A.8),

$$x = \sqrt{\frac{\hbar}{2\omega}}\left(a + a^\dagger\right), \tag{A.9}$$

$$\frac{d}{dx} = \sqrt{\frac{\omega}{2\hbar}}\left(a - a^\dagger\right). \tag{A.10}$$

In case of large amount of oscillating atoms, the reduced displacements transform into the normal coordinates and provide oneself with lower indexes, full derivatives become partial. Assume that $\hbar = 1$. According to (A.9), (A.10), and also (2.8)– (2.10), the following values of the ground (x) and exited (y) state coordinates can be obtained:

$$x_j = \frac{1}{\sqrt{2\omega_{1j}}}\left(a_{1j} + a_{1j}^\dagger\right) = -x_{0j} + \sum_k c_{jk}\frac{1}{\sqrt{2\omega_{2k}}}\left(a_{2k} + a_{2k}^\dagger\right), \tag{A.11}$$

$$y_k = \frac{1}{\sqrt{2\omega_{2k}}}\left(a_{2k} + a_{2k}^\dagger\right) = y_{0k} + \sum_j c_{jk}\frac{1}{\sqrt{2\omega_{1j}}}\left(a_{1j} + a_{1j}^\dagger\right), \tag{A.12}$$

correspondingly

$$\frac{\partial}{\partial x_j} = \sqrt{\frac{\omega_{1j}}{2}}\left(a_{1j} - a_{1j}^\dagger\right) = \sum_k c_{jk}\sqrt{\frac{\omega_{2k}}{2}}\left(a_{2k} - a_{2k}^\dagger\right), \tag{A.13}$$

$$\frac{\partial}{\partial y_k} = \sqrt{\frac{\omega_{2k}}{2}}\left(a_{2k} - a_{2k}^\dagger\right) = \sum_j c_{jk}\sqrt{\frac{\omega_{1j}}{2}}\left(a_{1j} - a_{1j}^\dagger\right). \tag{A.14}$$

Let us add/subtract (A.11) and (A.13), (A.12) and (A.14). It follows that

$$\begin{aligned}a_{1j}^\dagger &= -\sqrt{\frac{\omega_{1j}}{2}}x_{0j} + \frac{1}{2}\sum_k \frac{c_{jk}}{\sqrt{\omega_{1j}\omega_{2k}}}\left[(\omega_{1j} + \omega_{2k})a_{2k}^\dagger + (\omega_{1j} - \omega_{2k})a_{2k}\right],\\ a_{2k}^\dagger &= \sqrt{\frac{\omega_{2k}}{2}}y_{0k} + \frac{1}{2}\sum_j \frac{c_{jk}}{\sqrt{\omega_{1j}\omega_{2k}}}\left[(\omega_{1j} + \omega_{2k})a_{1j}^\dagger + (\omega_{2k} - \omega_{1j})a_{1j}\right],\end{aligned}$$

$$a_{1j} = -\sqrt{\frac{\omega_{1j}}{2}}x_{0j} + \frac{1}{2}\sum_k \frac{c_{jk}}{\sqrt{\omega_{1j}\omega_{2k}}}\left[(\omega_{1j}+\omega_{2k})a_{2k} + (\omega_{1j}-\omega_{2k})a_{2k}^\dagger\right],$$

$$a_{2k} = \sqrt{\frac{\omega_{2k}}{2}}y_{0k} + \frac{1}{2}\sum_j \frac{c_{jk}}{\sqrt{\omega_{1j}\omega_{2k}}}\left[(\omega_{1j}+\omega_{2k})a_{1j} + (\omega_{2k}-\omega_{1j})a_{1j}^\dagger\right].$$

We use the following symbolics (with reference to (2.13) and (2.14)):

$$\xi_{1j} \stackrel{\text{def}}{=} \sqrt{\frac{\omega_{1j}}{2}}x_{0j} = \frac{\big(a_0 - bq_0\big)e_{1j}}{\sqrt{2\omega_{1j}^3}},$$

$$\xi_{2k} \stackrel{\text{def}}{=} \sqrt{\frac{\omega_{2k}}{2}}y_{0k} = \frac{a_0 e_{2k}}{\sqrt{2\omega_{2k}^3}}.$$

These two quantities satisfy a condition:

$$\xi_{1j} \equiv \sqrt{\frac{\omega_{1j}}{2}}x_{0j} = \sqrt{\frac{\omega_{1j}}{2}}\sum_k c_{jk}y_{0k} = \sqrt{\omega_{1j}}\sum_k c_{jk}\frac{\xi_{2k}}{\sqrt{\omega_{2k}}}.$$

Thus, in new variables, the creation and annihilation operators acquire the form

$$a_{1j}^\dagger = -\xi_{1j} + \frac{1}{2}\sum_k \frac{c_{jk}}{\sqrt{\omega_{1j}\omega_{2k}}}\left[(\omega_{1j}+\omega_{2k})a_{2k}^\dagger + (\omega_{1j}-\omega_{2k})a_{2k}\right],$$

$$a_{2k}^\dagger = \xi_{2k} + \frac{1}{2}\sum_j \frac{c_{jk}}{\sqrt{\omega_{1j}\omega_{2k}}}\left[(\omega_{1j}+\omega_{2k})a_{1j}^\dagger + (\omega_{2k}-\omega_{1j})a_{1j}\right],$$

$$a_{1j} = -\xi_{1j} + \frac{1}{2}\sum_k \frac{c_{jk}}{\sqrt{\omega_{1j}\omega_{2k}}}\left[(\omega_{1j}+\omega_{2k})a_{2k} + (\omega_{1j}-\omega_{2k})a_{2k}^\dagger\right],$$

$$a_{2k} = \xi_{2k} + \frac{1}{2}\sum_j \frac{c_{jk}}{\sqrt{\omega_{1j}\omega_{2k}}}\left[(\omega_{1j}+\omega_{2k})a_{1j} + (\omega_{2k}-\omega_{1j})a_{1j}^\dagger\right].$$

A.4 Contribution of the "poles"

In calculations we need to find sums containing functions of ground state frequencies and resolvent $(\omega_{2k}^2 - \omega_{1j}^2)^{-1}$:

$$\sum_{j=1}^{N} \frac{F(\omega_{1j})e_{1j}}{\omega_{2k}^2 - \omega_{1j}^2},$$

where number of elements in sum is on the order of Avogadro's number ($N \sim 10^{23}$). If the parameter of quadratic interaction b is different from zero, then in range of frequencies from zero to ω_{max} two discrete frequency sets spring up, whilst frequencies of excited state are set out between frequencies of ground state:

$$\omega_{1j} = \omega_{2k} + \frac{\xi}{N},$$

here $N \to \infty$ is the number of degrees of freedom. The sum contains two important parts, one of them is the contribution of terms with frequencies ω_{1j}, which differs from frequencies ω_{2k} on finite number, the other one describes the contribution of terms which differs on infinitely small number. So long as the frequencies do not coincide, the sum do not contain any pole, whilst integral does. Principle value integral takes into account all terms of sum, in which frequencies ω_{1j} and ω_{2k} are finitely spaced.

The value of sum can be calculated, if instead of integrating over all frequencies we

will take a principle value integral:

$$\sum_j \frac{F(\omega_{1j})e_{1j}}{\omega_{2k}^2-\omega_{1j}^2} = \beta_k F(\omega_{2k}) + \int\!\!\!\!\!\!-_0^1 \frac{F(\omega)e_1^2(\omega)}{\omega_{2k}^2-\omega^2-i\varepsilon\pi}d\omega, \tag{A.15}$$

where $\varepsilon \to 0$. The ε sign is chosen so that imaginary part of integral is smaller than zero.

The first item in formulae (A.15) is nothing more than contribution of spectral "poles" ($\omega_{1j}=\omega_{2k}$). Parameter β_k can be determined from a condition (2.12):

$$\sum_j \frac{e_{1j}^2}{\omega_{2k}^2-\omega_{1j}^2} = b^{-1}.$$

As we can see, the last formula presents the particular case of the sum we are looking for, with initial values $F(\omega_{1j})=F(\omega_{2k})=F(\omega)=1$. So,

$$\sum_j \frac{e_{1j}^2}{\omega_{2k}^2-\omega_{1j}^2} = \beta_k + \underbrace{\int\!\!\!\!\!\!-_0^1 \frac{e_1^2(\omega)d\omega}{\omega_{2k}^2-\omega^2}}_{J} \equiv b^{-1}.$$

Since $\rho(\omega_{1j})=e_1^2(\omega)=5\omega^4$,

$$\begin{aligned} J &= \int\!\!\!\!\!\!-_0^1 \frac{5\omega^4 d\omega}{\omega_{2k}^2-\omega^2} = -\frac{5}{2}\int\!\!\!\!\!\!-_0^1 \omega^3\Big(\frac{1}{\omega+\omega_{2k}}+\frac{1}{\omega-\omega_{2k}}\Big)d\omega = \\ &= -\frac{5}{2}\left(\frac{2}{3}+2\omega_{2k}^2-\omega_{2k}^3\ln\frac{1+\omega_{2k}}{1-\omega_{2k}}\right) = \operatorname{Re}G_1(\omega_{2k}). \end{aligned}$$

Thus,

$$\beta_k = \frac{1}{b}\big(1-b\operatorname{Re}G_1(\omega_{2k})\big).$$

Let us calculate the sum find the following sum $\sum_j \frac{e_{1j}}{\omega_{1j}}c_{jk}$. According to (2.10) and (2.11),

$$\sum_j \frac{e_{1j}}{\omega_{1j}}c_{jk} = e_{2k}b\sum_j \frac{e_{1j}^2}{\omega_{1j}(\omega_{2k}^2-\omega_{1j}^2)}. \tag{A.16}$$

On the other hands,

$$\sum_j \frac{e_{1j}}{\omega_{1j}}c_{jk} = \frac{1}{b}\left(1-b\operatorname{Re}G_1(\omega_{2k})\right)\frac{e_{2k}}{\omega_{2k}} + (e_{2k}b)\underbrace{\int\!\!\!\!\!\!-_0^1 \frac{e_1^2(\omega)d\omega}{\omega(\omega_{2k}^2-\omega^2)}}_{J_1}.$$

Let us calculate an integral J_1:

$$\begin{aligned} J_1 &= \int\!\!\!\!\!\!-_0^1 \frac{5\omega^3 d\omega}{\omega_{2k}^2-\omega^2} = 5\omega_{2k}^2\int\!\!\!\!\!\!-_0^1 \frac{\omega d\omega}{\omega_{2k}^2-\omega^2} - 5\int_0^1 \omega d\omega = \\ &= -\frac{5}{2}\Big(1+\omega_{2k}^2\int\!\!\!\!\!\!-_0^1 \frac{dx}{x-\omega_{2k}^2}\Big) = -\frac{5}{2}\left(1-\omega_{2k}^2\ln\frac{\omega_{2k}^2}{1-\omega_{2k}^2}\right). \end{aligned}$$

Substituting this integral into sum we have to compute, we obtain

$$\sum_j \frac{e_{1j}}{\omega_{1j}}c_{jk} = \left(\frac{1}{b}+\frac{5}{3}+5\omega_{2k}^2-\frac{5}{2}\omega_{2k}^3\ln\frac{1+\omega_{2k}}{1-\omega_{2k}}\right)\frac{e_{2k}}{\omega_{2k}} -$$

$$-\frac{5}{2}b\left(1-\omega_{2k}^2\ln\frac{\omega_{2k}^2}{1-\omega_{2k}^2}\right)e_{2k}.$$

If $b\approx b_0=-3/5$, then

$$\begin{aligned}\sum_j\frac{e_{1j}}{\omega_{1j}}c_{jk} &= \left(5\omega_{2k}^2-\frac{5}{2}\omega_{2k}^3\ln\frac{1+\omega_{2k}}{1-\omega_{2k}}\right)\frac{e_{2k}}{\omega_{2k}}- \\ &+\frac{3}{2}\left(1-\omega_{2k}^2\ln\frac{\omega_{2k}^2}{1-\omega_{2k}^2}\right)e_{2k}.\end{aligned}$$

According to our assumption frequencies ω_{2k} are set to be small enough, so we can neglect corresponding frequencies and their powers,

$$\boxed{\sum_j\frac{e_{1j}}{\omega_{1j}}c_{jk}\approx\frac{3}{2}e_{2k}.} \tag{A.17}$$

Again, the same result can be obtained by taking $\omega_{2k}\ll\omega_{1j}$ in Eq. (A.16):

$$\sum_j\frac{e_{1j}}{\omega_{1j}}c_{jk}=e_{2k}b\sum_j\frac{e_{1j}^2}{\omega_{1j}(\omega_{2k}^2-\omega_{1j}^2)}\approx-e_{2k}b\sum_j\frac{e_{1j}^2}{\omega_{1j}^3}$$

If $b\approx b_0=-3/5$, then (A.17) takes place.

A.5 Explicit calculation of $A(t)$

The Fourier amplitude $A(t)$ can be calculated explicitly using method proposed in [9]. According to (2.30), q–linear term can be written as

$$-iF_1'=\frac{a_0}{\sqrt{2}}\sum_j e_{1j}A_j. \tag{A.18}$$

Let us derive equations for A_j. We should note that:

$$\underline{\hat{f}_t a_{2k}^\dagger}=\left\{e^{itH_2}a_{2k}^\dagger e^{-itH_2}\right\}e^{itH_2}=\underline{a_{2k}^\dagger e^{it\omega_{2k}}\hat{f}_t}, \tag{A.19}$$

$$\begin{aligned}\underline{\langle 0|a_{2k}^\dagger\hat{f}_t|0\rangle} &= \langle 0|a_{2k}^\dagger\hat{f}_t\Big(\sum_m|m\rangle\langle m|\Big)|0\rangle= \\ &= \sum_m\langle 0|a_{2k}^\dagger|m\rangle e^{itE_m}\langle m|0\rangle= \\ &= \sum_m\langle 0|m\rangle e^{itE_m}\langle m|a_2k|0\rangle= \\ &= \sum_m\langle 0|e^{itH_2}|m\rangle\langle m|a_2k|0\rangle= \\ &= \langle 0|e^{itH_2}\Big(\sum_m|m\rangle\langle m|\Big)a_{2k}|0\rangle= \\ &= \langle 0|e^{itH_2}a_{2k}|0\rangle=\underline{\langle 0|\hat{f}_t a_{2k}|0\rangle},\end{aligned} \tag{A.20}$$

$$a_{1j}^\dagger+a_{1j}=-2\xi_{1j}+\sum_k c_{jk}\sqrt{\frac{\omega_{1j}}{\omega_{2k}}}\left(a_{2k}^\dagger+a_{2k}\right). \tag{A.21}$$

For the (A.19)–(A.21) the following relations were used:

$$\sum_m|m\rangle\langle m|=1,$$

$$H_2|m\rangle=E_m|m\rangle\quad\Rightarrow\quad e^{itH_2}|m\rangle=e^{itE_m}|m\rangle,$$

$$\langle 0|m\rangle=\langle m|0\rangle\quad\Rightarrow\quad\langle 0|a_{2k}^\dagger|m\rangle=\langle m|a_{2k}|0\rangle.$$

As appears from (A.19) and (A.20),

$$\langle 0|\hat{f}_t(a_{2k}^{\dagger}+a_{2k})|0\rangle = e^{it\omega_{2k}}\langle 0|a_{2k}^{\dagger}\hat{f}_t|0\rangle + \langle 0|\hat{f}_t a_{2k}|0\rangle = \\ = e^{it\omega_{2k}}\langle 0|\hat{f}_t a_{2k}|0\rangle + \langle 0|\hat{f}_t a_{2k}|0\rangle. \tag{A.22}$$

By substituting (A.21) into (2.33) and according to (A.22)

$$\begin{aligned} A_j &= \frac{1}{\sqrt{\omega_{1j}}}\langle 0|\hat{f}_t\Big(-2\xi_{1j}+\sum_k c_{jk}\sqrt{\frac{\omega_{1j}}{\omega_{2k}}}(a_{2k}^{\dagger}+a_{2k})\Big)|0\rangle = \\ &= \frac{-2\xi_{1j}}{\sqrt{\omega_{1j}}}\langle 0|\hat{f}_t|0\rangle + \sum_k \frac{c_{jk}}{\sqrt{\omega_{2k}}}\langle 0|\hat{f}_t(a_{2k}^{\dagger}+a_{2k})|0\rangle = \\ &= \frac{-2\xi_{1j}}{\sqrt{\omega_{1j}}}F + \sum_k \frac{c_{jk}}{\sqrt{\omega_{2k}}}\left(e^{it\omega_{2k}}+1\right)\langle 0|\hat{f}_t a_{2k}|0\rangle. \end{aligned} \tag{A.23}$$

The annihilation operator a_{2k} that takes into account the mode mixing is given by (2.24d). Considering also that $a|0\rangle = 0$,

$$\begin{aligned} \langle 0|\hat{f}_t a_{2k}|0\rangle &= \langle 0|\hat{f}_t\Bigg\{\xi_{2k}+\frac{1}{2}\sum_{j'}\frac{c_{j'k}}{\sqrt{\omega_{1j'}\omega_{2k}}}\times \\ &\quad \times\Big[(\omega_{1j'}+\omega_{2k})a_{1j'}+(\omega_{2k}-\omega_{1j'})a_{1j'}^{\dagger}\Big]\Bigg\}|0\rangle = \\ &= \xi_{2k}F+\frac{1}{2}\sum_{j'}\frac{c_{j'k}}{\sqrt{\omega_{2k}}}(\omega_{2k}-\omega_{1j'})A_{j'}, \end{aligned} \tag{A.24}$$

the formula (A.23) can be re-written as follows:

$$\begin{aligned} A_j &= \Big[-2\frac{\xi_{1j}}{\sqrt{\omega_{1j}}}+\sum_k\frac{c_{jk}\xi_{2k}}{\sqrt{\omega_{2k}}}\left(e^{it\omega_{2k}}+1\right)\Big]F + \\ &\quad +\frac{1}{2}\sum_{kj'}\frac{c_{jk}c_{j'k}}{\omega_{2k}}(\omega_{2k}-\omega_{1j'})(e^{it\omega_{2k}}+1)A_{j'}. \end{aligned} \tag{A.25}$$

It was shown in Appendix 2.3, that ξ_{1j} can be expressed through ξ_{2k} according to (2.27). Because of orthogonality of c_{jk},

$$\begin{aligned} \boldsymbol{A_j} &= \sum_k\frac{c_{jk}\xi_{2k}}{\sqrt{\omega_{2k}}}\left(e^{it\omega_{2k}}-1\right)F + \\ &\quad +\frac{1}{2}\sum_{kj'}c_{jk}c_{j'k}\left[\Big(1-\frac{\omega_{1j'}}{\omega_{2k}}\Big)e^{it\omega_{2k}}+1-\frac{\omega_{1j'}}{\omega_{2k}}\right]\boldsymbol{A_{j'}} = \\ &= \sum_k\frac{c_{jk}\xi_{2k}}{\sqrt{\omega_{2k}}}\left(e^{it\omega_{2k}}-1\right)F+\frac{1}{2}\boldsymbol{A_j} + \\ &\quad +\frac{1}{2}\sum_{kj'}c_{jk}c_{j'k}\left[\Big(1-\frac{\omega_{1j'}}{\omega_{2k}}\Big)e^{it\omega_{2k}}-\frac{\omega_{1j'}}{\omega_{2k}}\right]\boldsymbol{A_{j'}}. \end{aligned} \tag{A.26}$$

By introducing

$$\beta_j \stackrel{\text{def}}{=} 2\sum_k\frac{c_{jk}\xi_{2k}}{\sqrt{\omega_{2k}}}\left(e^{it\omega_{2k}}-1\right), \tag{A.27}$$

$$R_{jj'} \stackrel{\text{def}}{=} \sum_k c_{jk}c_{j'k}\left[\Big(1-\frac{\omega_{1j'}}{\omega_{2k}}\Big)e^{it\omega_{2k}}-\frac{\omega_{1j'}}{\omega_{2k}}\right], \tag{A.28}$$

we obtain for the normalized first-order RRS Fourier amplitude

$$A_j = \beta_j F + \sum_{j'} R_{jj'}A_{j'}. \tag{A.29}$$

Derived equation can be written in a different way. Let us substitute $c_{j'k}$ (2.10) into $R_{jj'}$ (A.28) taking into account the orthogonality condition $\sum_k c_{jk}c_{j'k} = \delta_{jj'}$:

$$\begin{aligned} R_{jj'} &= \sum_k c_{jk}c_{j'k}\left[\Big(1-\frac{\omega_{1j'}}{\omega_{2k}}\Big)(e^{it\omega_{2k}}+1)-1\right] = \\ &= -\delta_{jj'} + \sum_k c_{jk}c_{j'k}\Big(1-\frac{\omega_{1j'}}{\omega_{2k}}\Big)(e^{it\omega_{2k}}+1) = \\ &= -\delta_{jj'} + b\sum_k \frac{c_{jk}e_{1j'}e_{2k}}{\omega_{2k}(\omega_{2k}+\omega_{1j'})}(e^{it\omega_{2k}}+1). \end{aligned} \tag{A.30}$$

As a result,

$$A_j = \tilde{\beta}_j F + \sum_{j'} \tilde{R}_{jj'}A_{j'}, \tag{A.31}$$

where

$$\tilde{R}_{jj'} \stackrel{\text{def}}{=} \frac{b}{2}\sum_k \frac{c_{jk}e_{1j'}e_{2k}}{\omega_{2k}(\omega_{2k}+\omega_{1j'})}(e^{it\omega_{2k}}+1), \tag{A.32}$$

$$\tilde{\beta}_j \stackrel{\text{def}}{=} \frac{\beta_j}{2} = \sum_k \frac{c_{jk}\xi_{2k}}{\sqrt{\omega_{2k}}}\left(e^{it\omega_{2k}}-1\right). \tag{A.33}$$

Let us define a new variable

$$\tilde{\beta} \stackrel{\text{def}}{=} \sum_j e_{1j}\tilde{\beta}_j. \tag{A.34}$$

According to (2.31), (2.11), the complete first-order Fourier amplitude A acquires a form:

$$\boxed{A = \tilde{\beta}F + \sum_{jj'} e_{1j}\tilde{R}_{jj'}A_{j'}.} \tag{A.35}$$

According to (A.33), (A.34) and (2.11),

$$\begin{aligned} \tilde{\beta} &= \sum_j e_{1j}\tilde{\beta}_j = \sum_j e_{1j}\sum_k \frac{c_{jk}\xi_{2k}}{\sqrt{\omega_{2k}}}\left(e^{it\omega_{2k}}-1\right) = \\ &= \sum_k \frac{e_{2k}\xi_{2k}}{\sqrt{\omega_{2k}}}\left(e^{it\omega_{2k}}-1\right). \end{aligned} \tag{A.36}$$

Let us define the following function:

$$\varphi_n(t) \stackrel{\text{def}}{=} \sum_k \frac{e_{2k}^2}{\omega_{2k}^n}e^{it\omega_{2k}}. \tag{A.37}$$

With respect to the (2.26),

$$\tilde{\beta} = \frac{a_0}{\sqrt{2}}\sum_k \frac{e_{2k}^2}{\omega_{2k}^2}\left(e^{it\omega_{2k}}-1\right) = \frac{a_0}{\sqrt{2}}\big(\varphi_2(t)-\varphi_2(0)\big). \tag{A.38}$$

It follows from (A.32) that

$$\begin{aligned} \sum_{jj'} e_{1j}\tilde{R}_{jj'}A_{j'} &= \sum_{jj'} e_{1j}\Big(\frac{b}{2}\sum_k \frac{c_{jk}e_{1j'}e_{2k}}{\omega_{2k}(\omega_{2k}+\omega_{1j'})}(e^{it\omega_{2k}}+1)\Big)A_{j'} = \\ &= \frac{b}{2}\sum_k \frac{e_{2k}^2}{\omega_{2k}}\left(e^{it\omega_{2k}}+1\right)\sum_{j'}\frac{e_{1j'}A_{j'}}{(\omega_{2k}+\omega_{1j'})}. \end{aligned} \tag{A.39}$$

Here the case of soft dynamics in the final state is considered. This case is described by the relation $\overline{\omega}_{2k} \ll \overline{\omega}_{1j}$, where $\overline{\omega}_{2k}, \overline{\omega}_{1j}$ are mean values of corresponding frequencies.

In this case the following approximation is used:

$$\frac{1}{(\omega_{2k}+\omega_{1j'})} \approx \frac{1}{\omega_{1j'}}. \tag{A.40}$$

This is the key approximation of this study! Introducing new variable

$$\tilde{A} \stackrel{\text{def}}{=} \sum_{j'} \frac{e_{1j'}}{\omega_{1j'}} A_{j'},$$

we get

$$\sum_{jj'} e_{1j} \tilde{R}_{jj'} A_{j'} \approx \frac{b}{2}\big(\varphi_1(t)+\varphi_1(0)\big)\tilde{A}. \tag{A.41}$$

Hence it follows that

$$\boldsymbol{A} = \frac{a_0}{\sqrt{2}}\big(\varphi_2(t)-\varphi_2(0)\big)\boldsymbol{F} + \frac{b}{2}\big(\varphi_1(t)+\varphi_1(0)\big)\tilde{\boldsymbol{A}}. \tag{A.42}$$

Next step will be finding equation for $\tilde{A}$. According to $\tilde{A}$ definition and also (A.31)–(A.33),

$$\begin{aligned}
\tilde{A} &\equiv \sum_j \frac{e_{1j}}{\omega_{1j}} \boldsymbol{A_j} = \sum_j \frac{e_{1j}}{\omega_{1j}} \big(\tilde{\beta}_j F + \sum_{j'} \tilde{\boldsymbol{R}}_{\boldsymbol{jj'}} A_{j'}\big) = \\
&= \sum_j \frac{e_{1j}}{2\omega_{1j}} \big(\beta_j F + b \sum_{j'k} \frac{c_{jk} e_{1j'} e_{2k}}{\omega_{2k}(\omega_{2k}+\omega_{1j'})} (e^{it\omega_{2k}}+1) A_{j'}\big).
\end{aligned}$$

Using approximation (A.40),

$$\begin{aligned}
\tilde{A} &\approx \sum_j \frac{e_{1j}}{2\omega_{1j}} \big(\beta_j F + b \sum_k \frac{e_{2k}}{\omega_{2k}} (e^{it\omega_{2k}}+1) c_{jk} \sum_{j'} \frac{e_{1j'}}{\omega_{1j'}} A_{j'}\big) = \\
&= \frac{1}{2} F \sum_j \frac{e_{1j}}{\omega_{1j}} \beta_j + \frac{b}{2} \tilde{A} \sum_k \frac{e_{2k}}{\omega_{2k}} (e^{it\omega_{2k}}+1) \sum_j \frac{e_{1j} c_{jk}}{\omega_{1j}}.
\end{aligned}$$

In derived equation we first meet the sum $\sum_j \frac{e_{1j}c_{jk}}{\omega_{1j}}$. It is shown in *Appendix A.4 Contribution of the "poles"* that this sum equals $\frac{3}{2}e_{2k}$. Keeping in mind definitions (A.37), (A.27), we obtain

$$\tilde{A} \approx \frac{3}{4} b\big(\varphi_1(t)+\varphi_1(0)\big)\tilde{A} + \frac{1}{2} F \sum_j \frac{e_{1j}c_{jk}}{\omega_{1j}} \cdot 2 \sum_k \frac{\xi_{2k}}{\sqrt{\omega_{2k}}} (e^{it\omega_{2k}}-1).$$

Taking into account (2.11) and (A.34),

$$\begin{aligned}
\tilde{A} &\approx \frac{3}{4} b\big(\varphi_1(t)+\varphi_1(0)\big)\tilde{A} + \frac{3}{2} F \sum_{jk} \frac{c_{jk} e_{1j} \xi_{2k}}{\sqrt{\omega_{2k}}} (e^{it\omega_{2k}}-1) = \\
&= \frac{3}{2}\tilde{\beta} F + \frac{3}{4} b\big(\varphi_1(t)+\varphi_1(0)\big)\tilde{A},
\end{aligned}$$

hence it follows that

$$\tilde{A} = \frac{\frac{3}{2}\tilde{\beta}F}{1-\frac{3}{4}b\big(\varphi_1(t)+\varphi_1(0)\big)}.$$

Substituting $\tilde{A}$ into (A.42), we obtain

$$A = \tilde{\beta}F + \frac{\frac{3}{2}\tilde{\beta}F \cdot \frac{b}{2}\big(\varphi_1(t)+\varphi_1(0)\big)}{1-\frac{3}{4}b\big(\varphi_1(t)+\varphi_1(0)\big)} = \frac{\tilde{\beta}F}{1-\frac{3}{4}b\big(\varphi_1(t)+\varphi_1(0)\big)}.$$

Finally, when $b \approx b_0 = -3/5$,

$$\boxed{A = \frac{\frac{a_0}{\sqrt{2}}\Big(\varphi_2(t)-\varphi_2(0)\Big)}{1+(9/20)\big(\varphi_1(t)+\varphi_1(0)\big)} F.} \tag{A.43}$$

A.6 Explicit calculation of $P(t)$

q–Quadratic term in (2.30) can be written as

$$-iF_2' = \frac{b}{4}\sum_{jj'}\frac{e_{1j}e_{1j'}}{\sqrt{\omega_{1j}\omega_{1j'}}}p_{jj'}. \tag{A.44}$$

Let us substitute $a_{1j}^\dagger$ (2.24a) into $p_{jj'}$ (2.34):

$$\begin{aligned} p_{jj'} &= -\xi_{1j}\langle 0|\hat{f}_t a_{1j'}^\dagger|0\rangle + \\ &+\frac{1}{2}\sum_k \frac{c_{jk}}{\sqrt{\omega_{1j}\omega_{2k}}}\langle 0|\hat{f}_t\Big[(\omega_{1j}+\omega_{2k})a_{2k}^\dagger + (\omega_{1j}-\omega_{2k})a_{2k}\Big]a_{1j'}^\dagger|0\rangle. \end{aligned} \tag{A.45}$$

We need to find the multiplicity $a_{2k}a_{1j'}^\dagger$. It follows directly from the commutation rule that $a_{2k}a_{1j'}^\dagger = a_{1j'}^\dagger a_{2k} + \left[a_{2k}, a_{1j'}^\dagger\right]$. Thus our problem is to find the commutator of a_{2k} and $a_{1j'}^\dagger$. As it was shown in (2.24a),

$$\begin{aligned} a_{1j'}^\dagger &= -\xi_{1j'} + \frac{1}{2}\sum_{k'}\frac{c_{j'k'}}{\sqrt{\omega_{1j'}\omega_{2k'}}}\times \\ &\times\left[(\omega_{1j'}+\omega_{2k'})a_{2k'}^\dagger + (\omega_{1j'}-\omega_{2k'})a_{2k'}\right]. \end{aligned}$$

The creation and annihilation operators obey the following commutation rules:

$$\begin{aligned} \left[a_{2k}, a_{2k'}^\dagger\right] &= \delta_{kk'}, \\ \left[a_{2k}, a_{2k'}\right] &= 0. \end{aligned}$$

The commutator of an operator and a constant is a zero. As a result in $a_{1j'}^\dagger$ there's only one non-zero member of the sum with $k = k'$, accordingly

$$a_{2k}a_{1j'}^\dagger = a_{1j'}^\dagger a_{2k} + \frac{1}{2}\frac{c_{j'k}}{\sqrt{\omega_{1j'}\omega_{2k}}}(\omega_{1j'}+\omega_{2k}). \tag{A.46}$$

Now we can swap operators $a_{2k}^\dagger$ and $\hat{f}_t$ in (A.45). Taking into account (A.19) and (A.46),

$$\begin{aligned} p_{jj'} &= \frac{1}{4\sqrt{\omega_{1j}\omega_{1j'}}}\sum_k \frac{c_{jk}c_{j'k}}{\omega_{2k}}(\omega_{1j}-\omega_{2k})(\omega_{1j'}+\omega_{2k})F + (-\xi_{1j})\langle 0|\hat{f}_t a_{1j'}^\dagger|0\rangle + \\ &+\frac{1}{2}\sum_k \frac{c_{jk}(\omega_{1j}+\omega_{2k})}{\sqrt{\omega_{1j}\omega_{2k}}}e^{it\omega_{2k}}\langle 0|a_{2k}^\dagger \hat{f}_t a_{1j'}^\dagger|0\rangle + \\ &+\frac{1}{2}\sum_k \frac{c_{jk}(\omega_{1j}-\omega_{2k})}{\sqrt{\omega_{1j}\omega_{2k}}}\langle 0|\hat{f}_t a_{1j'}^\dagger a_{2k}|0\rangle. \end{aligned} \tag{A.47}$$

In the last formula operators $a_{2k}^\dagger$ and a_{2k} can be expressed through $a_{1j}^\dagger$ and a_{1j} according to (2.24d) and (2.24b). We should also note that $\langle 0|a_{1j}^\dagger = 0$ and $a_{1j}|0\rangle = 0$. Substitution into (A.47) gives us

$$\begin{aligned} p_{jj'} &= \frac{1}{4\sqrt{\omega_{1j}\omega_{1j'}}}\sum_k \frac{c_{jk}c_{j'k}}{\omega_{2k}}(\omega_{1j}-\omega_{2k})(\omega_{1j'}+\omega_{2k})F + (-\xi_{1j})\langle 0|\hat{f}_t a_{1j'}^\dagger|0\rangle + \\ &+\frac{1}{2}\sum_k \frac{c_{jk}\xi_{2k}}{\sqrt{\omega_{1j}\omega_{2k}}}\Big[e^{it\omega_{2k}}(\omega_{1j}+\omega_{2k}) + (\omega_{1j}-\omega_{2k})\Big]\langle 0|\hat{f}_t a_{1j'}^\dagger|0\rangle + \\ &+\frac{1}{4}\sum_{j''k}\frac{c_{jk}c_{j''k}}{\omega_{2k}\sqrt{\omega_{1j}\omega_{1j''}}}e^{it\omega_{2k}}(\omega_{1j}+\omega_{2k})(\omega_{2k}-\omega_{1j''})\langle 0|a_{1j''}\hat{f}_t a_{1j'}^\dagger|0\rangle + \end{aligned}$$

$$+\frac{1}{4}\sum_{j''k}\frac{c_{jk}c_{j''k}}{\omega_{2k}\sqrt{\omega_{1j}\omega_{1j''}}}(\omega_{1j}-\omega_{2k})(\omega_{2k}-\omega_{1j''})\langle 0|\hat{f}_t a^\dagger_{1j'}a^\dagger_{1j''}|0\rangle. \tag{A.48}$$

It was shown above that

$$\begin{aligned}\langle 0|\hat{f}_t a^\dagger_{1j'}|0\rangle &= \sqrt{\omega_{1j'}}A_{j'},\\ \langle 0|\hat{f}_t a^\dagger_{1j'}a^\dagger_{1j''}|0\rangle &= p_{j'j''}.\end{aligned}$$

But (A.48) also contains $\langle 0|a_{1j''}\hat{f}_t a^\dagger_{1j'}|0\rangle$, so we can define an additional term

$$s_{jj'} \stackrel{\text{def}}{=} \langle 0|a_{1j}\hat{f}_t a^\dagger_{1j'}|0\rangle, \tag{A.49}$$

and by analogy with (2.32)

$$S \stackrel{\text{def}}{=} \sum_{jj'}\frac{e_{1j}e_{1j'}}{\sqrt{\omega_{1j}\omega_{1j'}}}s_{jj'}. \tag{A.50}$$

To increase the readability of the text and to avoid confusion, it is useful to designate factors staying before quantization operators in (A.48). Since all the factors contain $(\omega_{1j}\pm\omega_{2k})$ it is eligible to write down $(\omega_{1j}\pm\omega_{2k})=\omega_{1j}(1\pm\omega_{2k}/\omega_{1j})$ and neglect term ω_{2k}/ω_{1j} (remember that $\omega_{2k}\ll\omega_{1j}$). In this case the following equation for $p_{jj'}$ is obtained:

$$p_{jj'} = \varepsilon_{jj'}F + d_j\sqrt{\omega_{1j}}A_{j'} + \sum_{j''}\big(g_{jj''}p_{j'j''} + h_{jj''}s_{j''j'}\big), \tag{A.51}$$

where

$$\varepsilon_{jj'} \cong \frac{1}{4}\sqrt{\omega_{1j}\omega_{1j'}}\sum_k\frac{c_{jk}c_{j'k}}{\omega_{2k}}\big(1+\frac{\omega_{2k}}{\omega_{1j'}}\big), \tag{A.52}$$

$$d_j \cong \frac{1}{2}\sqrt{\omega_{1j}}\sum_k\frac{c_{jk}\xi_{2k}}{\sqrt{\omega_{2k}}}\big(e^{it\omega_{2k}}-1\big), \tag{A.53}$$

$$g_{jj''} \cong \frac{1}{4}\sqrt{\omega_{1j}}\sum_k\frac{c_{jk}c_{j''k}}{\sqrt{\omega_{1j''}}}\big(1-\frac{\omega_{1j''}}{\omega_{2k}}\big), \tag{A.54}$$

$$h_{jj''} \cong \frac{1}{4}\sqrt{\omega_{1j}}\sum_k\frac{c_{jk}c_{j''k}}{\sqrt{\omega_{1j''}}}\big(1-\frac{\omega_{1j''}}{\omega_{2k}}\big)e^{it\omega_{2k}}. \tag{A.55}$$

It should be noted that in (A.53) condition (2.27) were taken into account.

The same steps can be repeated for $s_{jj'}$. Substituting (2.24c) for a_{1j} in (A.49), we get

$$\begin{aligned}s_{jj'} \equiv\ & \langle 0|a_{1j}\hat{f}_t a^\dagger_{1j'}|0\rangle = -\xi_{1j}\langle 0|\hat{f}_t a^\dagger_{1j'}|0\rangle +\\ &+\frac{1}{2}\sum_k\frac{c_{jk}}{\sqrt{\omega_{1j}\omega_{2k}}}\langle 0|\Big[(\omega_{1j}-\omega_{2k})a^\dagger_{2k}+(\omega_{1j}+\omega_{2k})a_{2k}\Big]\hat{f}_t a^\dagger_{1j'}|0\rangle.\end{aligned} \tag{A.56}$$

Operators a_{2k} and $\hat{f}_t$ can be interchanged according to the rule $a_{2k}\hat{f}_t = \hat{f}_t a_{2k}e^{it\omega_{2k}}$. Taking into account (A.46) and substituting a_{2k}, $a^\dagger_{2k}$ with (2.24d), (2.24b), we obtain

$$\begin{aligned}s_{jj'} =\ & \left(-\xi_{1j}+\frac{1}{2}\sum_k\frac{c_{jk}\xi_{2k}}{\sqrt{\omega_{1j}\omega_{2k}}}\Big[e^{it\omega_{2k}}(\omega_{1j}+\omega_{2k})+(\omega_{1j}-\omega_{2k})\Big]\right)\langle 0|\hat{f}_t a^\dagger_{1j'}|0\rangle +\\ &+\frac{1}{4}\sum_k\frac{c_{jk}c_{j'k}(\omega_{1j}+\omega_{2k})}{\omega_{2k}\sqrt{\omega_{1j}\omega_{1j'}}}(\omega_{1j'}+\omega_{2k})e^{it\omega_{2k}}F +\\ &+\frac{1}{4}\sum_{j''k}\frac{c_{jk}c_{j''k}(\omega_{2k}-\omega_{1j''})}{\omega_{2k}\sqrt{\omega_{1j}\omega_{1j''}}}(\omega_{1j}-\omega_{2k})s_{j''j'} +\end{aligned}$$

$$+\frac{1}{4}\sum_{j''k}\frac{c_{jk}c_{j''k}(\omega_{2k}-\omega_{1j''})}{\omega_{2k}\sqrt{\omega_{1j}\omega_{1j''}}}(\omega_{1j}+\omega_{2k})e^{it\omega_{2k}}p_{j'j''}. \tag{A.57}$$

Neglecting term ω_{2k}/ω_{1j} in $(\omega_{1j}\pm\omega_{2k})=\omega_{1j}(1\pm\omega_{2k}/\omega_{1j})$ and taking into account (2.27) gives us

$$s_{jj'}=\tilde{\varepsilon}_{jj'}F+d_j\sqrt{\omega_{1j}}A_{j'}+\sum_{j''}\big(g_{jj''}s_{j''j'}+h_{jj''}p_{j'j''}\big), \tag{A.58}$$

where

$$\tilde{\varepsilon}_{jj'}\cong\frac{1}{4}\sqrt{\omega_{1j}\omega_{1j'}}\sum_k\frac{c_{jk}c_{j'k}}{\omega_{2k}}\big(1+\frac{\omega_{2k}}{\omega_{1j'}}\big)e^{it\omega_{2k}}. \tag{A.59}$$

Variables with double indexes can be rolled up using the following rule:

$$p_{j''}=\sum_{j'}\frac{e_{1j'}}{\sqrt{\omega_{1j'}}}p_{j'j''}\qquad,\qquad s_{j''}=\sum_{j'}\frac{e_{1j'}}{\sqrt{\omega_{1j'}}}s_{j''j'}. \tag{A.60}$$

We can also designate

$$\varepsilon=\sum_{jj'}\frac{e_{1j}e_{1j'}}{\sqrt{\omega_{1j}\omega_{1j'}}}\varepsilon_{jj'}\quad,\quad\tilde{\varepsilon}=\sum_{jj'}\frac{e_{1j}e_{1j'}}{\sqrt{\omega_{1j}\omega_{1j'}}}\tilde{\varepsilon}_{jj'}\quad,\quad d=\sum_j\frac{e_{1j}}{\sqrt{\omega_{1j}}}d_j. \tag{A.61}$$

Now, according to (2.32) and (2.31),

$$P=\sum_{i=1}^4P_i=\sum_j\frac{e_{1j}}{\sqrt{\omega_{1j}}}p_j=\varepsilon F+dA+\sum_{jj''}\frac{e_{1j}}{\sqrt{\omega_{1j}}}(g_{jj''}p_{j''}+h_{jj''}s_{j''}), \tag{A.62}$$

and correspondingly

$$S=\sum_{i=1}^4S_i=\sum_j\frac{e_{1j}}{\sqrt{\omega_{1j}}}s_j=\tilde{\varepsilon}F+dA+\sum_{jj''}\frac{e_{1j}}{\sqrt{\omega_{1j}}}(g_{jj''}s_{j''}+h_{jj''}p_{j''}), \tag{A.63}$$

Let us take apart a previous expression. Here is the first term:

$$P_1\equiv\varepsilon F=\frac{1}{4}\sum_k\frac{1}{\omega_{2k}}\sum_j e_{1j}c_{jk}\sum_{j'}\big(e_{1j'}c_{j'k}+\omega_{2k}\frac{e_{1j'}c_{j'k}}{\omega_{1j'}}\big)F.$$

From (2.11), (A.37), (A.17), it follows that

$$P_1\approx\frac{1}{4}\varphi_1(0)F. \tag{A.64}$$

For the second term

$$P_2\equiv dA=\frac{1}{2}\sum_k\sum_j e_{1j}c_{jk}\frac{\xi_{2k}}{\sqrt{\omega_{2k}}}\big(e^{it\omega_{2k}}-1\big)A.$$

Using (2.11), (2.26), (A.37), we get

$$P_2\approx\frac{a_0}{2\sqrt{2}}\Big[\varphi_2(t)-\varphi_2(0)\Big]A. \tag{A.65}$$

Derivation of the third term is more complicated.

$$P_3\equiv\sum_{jj''}\frac{e_{1j}}{\sqrt{\omega_{1j}}}g_{jj''}p_{j''}=\frac{1}{4}\sum_{j''k}\sum_j e_{1j}c_{jk}\frac{c_{j''k}}{\sqrt{\omega_{1j''}}}\big(1-\frac{\omega_{1j''}}{\omega_{2k}}\big)p_{j''}.$$

Substituting (2.10) for $c_{j''k}$ and taking into account (2.11), (A.37), we obtain

$$P_3=\frac{1}{4}\sum_{j''k}\frac{be_{1j''}e_{2k}^2}{\sqrt{\omega_{1j''}}\omega_{2k}(\omega_{2k}+\omega_{1j''})}p_{j''}\approx\frac{b}{4}\varphi_1(0)\tilde{P},$$

where

$$\tilde{P}=\sum_{j''}\frac{e_{1j''}}{\sqrt{\omega_{1j''}}\omega_{1j''}}p_{j''}$$

and approximation $(\omega_{2k}+\omega_{1j''})^{-1}\approx\omega_{1j''}$ were used. Expression for $\tilde{P}$ has so much in common with the expression for P (A.62). In fact, since all the terms (A.52) – (A.55)

contain the same factor $c_{jk}\sqrt{\omega_{1j}}$, the following simplification can be accomplished using (A.17):

$$\tilde{P} = \sum_j \frac{e_{1j}}{\sqrt{\omega_{1j}}\omega_{1j}} \cdot \sum_k c_{jk}\sqrt{\omega_{1j}}(\ldots) = \sum_k \sum_j \frac{e_{1j}c_{jk}}{\omega_{1j}}(\ldots) \approx \frac{3}{2}\sum_k e_{2k}(\ldots).$$

For P there is no need to use the approximation. According to (2.11),

$$P = \sum_j \frac{e_{1j}}{\sqrt{\omega_{1j}}} \cdot \sum_k c_{jk}\sqrt{\omega_{1j}}(\ldots) = \sum_k \sum_j e_{1j}c_{jk}(\ldots) = \sum_k e_{2k}(\ldots).$$

Therefore, $\tilde{P} \approx \frac{3}{2}P$, hence it follows that

$$P_3 \approx \frac{3}{8}b\varphi_1(0)P. \tag{A.66}$$

Substituting again (2.10) for $c_{j''k}$ and taking into account (2.11), (A.37), the fourth term can be expressed as

$$P_4 \equiv \sum_{jj''} \frac{e_{1j}}{\sqrt{\omega_{1j}}} h_{jj''}s_{j''} \approx \frac{1}{4}b\varphi_1(t)\tilde{S},$$

where

$$\tilde{S} = \sum_{j''} \frac{e_{1j''}}{\sqrt{\omega_{1j''}}\omega_{1j''}} s_{j''}.$$

At the moment,

$$\boldsymbol{P} = \frac{1}{4}\varphi_1(0)\boldsymbol{F} + \frac{a_0}{2\sqrt{2}}\big[\varphi_2(t) - \varphi_2(0)\big]\boldsymbol{A} + \frac{3}{8}b\varphi_1(0)\boldsymbol{P} + \frac{1}{4}b\varphi_1(t)\tilde{\boldsymbol{S}}. \tag{A.67}$$

Function $\tilde{S}$ looks similar to $\tilde{P}$. Consecutively applying the same steps to S (A.63), we obtain $\tilde{S} \approx \frac{3}{2}S$ and

$$\tilde{S} = \frac{3}{8}\varphi_1(t)F + \frac{3a_0}{4\sqrt{2}}\big[\varphi_2(t) - \varphi_2(0)\big]A + \frac{3}{8}b\varphi_1(0)\tilde{S} + \frac{9}{16}b\varphi_1(t)P. \tag{A.68}$$

Equations (A.67) and (A.68) form the system of linear equations in two variables (P, $\tilde{S}$). If we represent P as $P = KF + QA + TP$, then the solution for P is

$$P = \frac{KF + QA}{1 - T}, \tag{A.69}$$

where

$$K = \frac{1}{4}\left[\varphi_1(0) + \frac{(3/8)b\varphi_1^2(t)}{1 - (3/8)b\varphi_1(0)}\right], \tag{A.70}$$

$$Q = \frac{a_0}{2\sqrt{2}}\big(\varphi_2(t) - \varphi_2(0)\big)\left[1 + \frac{(3/8)b\varphi_1(t)}{1 - (3/8)b\varphi_1(0)}\right], \tag{A.71}$$

$$T = \frac{3}{8}b\left[\varphi_1(0) + \frac{(3/8)b\varphi_1^2(t)}{1 - (3/8)b\varphi_1(0)}\right]. \tag{A.72}$$

We can eliminate factor $(1 - (3/8)b\varphi_1(0))$ from both nominator and denominator. Also taking into account that $b \approx b_0 = -3/5$, we obtain

$$P = \frac{K_1 + Q_1A_1}{T_1}F, \tag{A.73}$$

where

$$A_1 = \frac{(a_0/\sqrt{2})\big(\varphi_2(t) - \varphi_2(0)\big)}{1 + (9/20)\big(\varphi_1(t) + \varphi_1(0)\big)}, \tag{A.74}$$

$$K_1 = (1/4)\big[\varphi_1(0) - (9/40)(\varphi_1^2(t) - \varphi_1^2(0))\big], \tag{A.75}$$

$$Q_1 = \frac{a_0}{2\sqrt{2}}\big(\varphi_2(t) - \varphi_2(0)\big)\big[1 - (9/40)\big(\varphi_1(t) - \varphi_1(0)\big)\big], \tag{A.76}$$

$$T_1 = 1 + (9/40)^2\big(\varphi_1^2(t) - \varphi_1^2(0)\big). \tag{A.77}$$

Appendix B

Additional materials

B.1 spektr.cpp

```
#include <complex.h>
#include <iostream.h>
#include <stdio.h>

#define PI      3.141592653589793
#define N       2048            // Number of points (time domain)
#define M       512             // Number of points in Simpson's int.
#define T       2048            // Period
#define epsilon  N/2             // Shift of origin
#define SWAP(a,b) tempr=(a);(a)=(b);(b)=tempr

typedef complex<double> cplx;
double sqr(double a){ return pow(a,2); }

struct buffer {
   double x;
   cplx y;
};
struct ibuffer {
   double x;
   double y;
};

struct buffer  Input[N];
struct buffer  Output[N];
struct ibuffer idata[2*M+1];
double data1[2*N];
cplx   D[N/2];
cplx   d1[N/2];
```

```
//Simpson's numerical integration
double simpson()
{
    double result;

    result = (idata[0].y - idata[2*M].y) / 2.0;
    for(int i=2; i<=2*M; i+=2){
      result = result + idata[i].y + 2.0*idata[i-1].y;}
    result = result * (idata[2*M].x - idata[0].x) / (3.0*M);
    return result;
}


int PrepareInputArray(){

   const double alpha  = 0.01,
                a0     = 0.6,
                gamma  = 0.001,
                lima   = 0.00000000000001,
                limb   = 0.99999999999999,
                dt     = T/(N-1.0);
   double       w;


   //Calculating of fi_1(0)
   for (int p=0; p<=2*M; p++){
     idata[p].x = p*(limb-lima)/(2.0*M);
     w          = idata[p].x;
     idata[p].y = (5.0/9.0)*pow(w,3) / ( sqr(alpha+sqr(w)-
                  0.5*pow(w,3)*log((1.0+w)/(1.0-w)) )+
                  0.25*sqr(PI)*pow(w,6) ) ; }
   double fi10 = simpson();

   //Calculating of fi_2(0)
   for (int p=0; p<=2*M; p++){
     idata[p].x = p*(limb-lima)/(2.0*M);
     w          = idata[p].x;
     idata[p].y = (5.0/9.0)*sqr(w) / ( pow((alpha+sqr(w)-
                  0.5*pow(w,3)*log((1.0+w)/(1.0-w))),2)+
                  0.25*sqr(PI)*pow(w,6) ) ; }
   double fi20 = simpson();

   //1:-------------------------------------------------------------
   for (int k=0; k<N/2; k++){
     double t = -0.5*T + k*T/(N-1.0) + 0.5*T*N/(N-1.0);
```

```
  //Calculating of fi_1(t)
  for (int p=0; p<=2*M; p++){
    idata[p].x = p*(limb-lima)/(2.0*M);
    w          = idata[p].x;
    idata[p].y = (5.0/9.0)*pow(w,3)*cos(w*t)/( pow((alpha+sqr(w)-
                 0.5*pow(w,3)*log((1.0+w)/(1.0-w))),2)+
                 0.25*sqr(PI)*pow(w,6) ) ; }
  double fi1re = simpson();
  for (int p=0; p<=2*M; p++){
    idata[p].x = p*(limb-lima)/(2.0*M);
    w          = idata[p].x;
    idata[p].y = (5.0/9.0)*pow(w,3)*sin(w*t)/( pow((alpha+sqr(w)-
                 0.5*pow(w,3)*log((1.0+w)/(1.0-w))),2)+
                 0.25*sqr(PI)*pow(w,6) ) ; }
  double fi1im = simpson();
  cplx fi1t(fi1re,fi1im);
  //Calculating of fi_2(t)
  for (int p=0; p<=2*M; p++){
    idata[p].x = p*(limb-lima)/(2.0*M);
    w          = idata[p].x;
    idata[p].y = (5.0/9.0)*sqr(w)*cos(w*t)/( pow((alpha+sqr(w)-
                 0.5*pow(w,3)*log((1.0+w)/(1.0-w))),2)+
                 0.25*sqr(PI)*pow(w,6) ) ; }
  double fi2re = simpson();
  for (int p=0; p<=2*M; p++){
    idata[p].x = p*(limb-lima)/(2.0*M);
    w          = idata[p].x;
    idata[p].y = (5.0/9.0)*sqr(w)*sin(w*t)/( pow((alpha+sqr(w)-
                 0.5*pow(w,3)*log((1.0+w)/(1.0-w))),2)+
                 0.25*sqr(PI)*pow(w,6) ) ; }
  double fi2im = simpson();
  cplx fi2t(fi2re,fi2im);

  cplx a1 = a0/sqrt(2.0)*(fi2t-fi20)/(1.0+0.45*(-fi10));
  cplx k1 = 0.25*(fi10-pow(fi10,2));
  cplx q1 = a0/(2.0*pow(2.0,0.5))*(fi2t-fi20)*(1.0-0.225*(-fi10));
  cplx t1 = 1.0+pow(0.225,2)*(-pow(fi10,2));
  D[k]    = -3.0/8.0+a0*a1/sqrt(2.0)-0.15*(k1+q1*a1)/t1;
}

//2:-------------------------------------------------------------

d1[0] = 0.5*D[0]*(-0.5*T + 0.5*T*N/(N-1.0));
for (int k=1; k<N/2; k++){
  d1[k] = d1[k-1] + 0.5 * (D[k]+D[k-1]) * dt;
}
```

```
    //3:-------------------------------------------------------------
    for (int k=0; k<N/2; k++){
      double t = -0.5*T + k*T/(N-1.0) + 0.5*T*N/(N-1.0);
      double cb = imag(d1[k]);
      double ca = real(d1[k]);
      cplx c(-cb,ca);
      cplx g = exp(c);
      cplx f  = exp(-gamma*abs(t)) * g;
      cplx f1  = exp(-gamma*abs(t)) * conj(g);
      Input[k+N/2].x = t;
      Input[k+N/2].y = f;
      Input[N/2-k].x = -t;
      Input[N/2-k].y = f1;
    }

    return 0;
}

//Fast Fourier Transform
void fft(double data[], unsigned long nn)
{
        unsigned long n,mmax,m,j,istep,i;
        double wtemp,wr,wpr,wpi,wi,theta;
        double tempr,tempi;

        n=nn << 1;
        j=1;
        for (i=1;i<n;i+=2) {
                if (j > i) {
                        SWAP(data[j],data[i]);
                        SWAP(data[j+1],data[i+1]);
                }
                m=n >> 1;
                while (m >= 2 && j > m) {
                        j -= m;
                        m >>= 1;
                }
                j += m;
        }
        mmax=2;
        while (n > mmax) {
                istep=mmax << 1;
                theta=-(6.28318530717959/mmax);
                wtemp=sin(0.5*theta);
                wpr = -2.0*wtemp*wtemp;
```

```
                wpi=sin(theta);
                wr=1.0;
                wi=0.0;
                for (m=1;m<mmax;m+=2) {
                        for (i=m;i<=n;i+=istep) {
                                j=i+mmax;
                                tempr=wr*data[j]-wi*data[j+1];
                                tempi=wr*data[j+1]+wi*data[j];
                                data[j]=data[i]-tempr;
                                data[j+1]=data[i+1]-tempi;
                                data[i] += tempr;
                                data[i+1] += tempi;
                        }
                        wr=(wtemp=wr)*wpr-wi*wpi+wr;
                        wi=wi*wpr+wtemp*wpi+wi;
                }
                mmax=istep;
        }
}


int Transform(){

   int k=0;
   for(int i=0; i<2*N; i+=2){
     cplx e1(0.0,2.0*PI*epsilon*k/N);
     cplx a1 = Input[k].y*exp(e1);
     data1[i]   = real(a1);
     data1[i+1] = imag(a1);
     k++;
   }

   fft(data1-1,N);

   int m=0;
   for(int i=0; i<2*N; i+=2){
     cplx a1(data1[i],data1[i+1]);
     cplx e1(0.0 , PI*(m-epsilon)*(N-1.0) / N );
     Output[m].y = T/(2.0*PI*(N-1.0)) * exp(e1)*a1;
     Output[m].x = 2.0*PI*(m-epsilon)*(N-1.0) / (T*N);
     m++;
   }

   return 0;
}
```

```
int main (){
    PrepareInputArray();
    Transform();

    FILE *f1;

    f1 = fopen("output.dat","w");
    if (f1 != NULL){
      for(int k=0; k<N; k++)
       fprintf (f1,"%e    %e\n",Output[k].x, real(Output[k].y));
      fclose(f1);
      fclose(f1);
    }
    else puts ("ERROR!");

  return 0;
}
```