On the Theory of Thermally Weighted Electron-Phonon Transition Probabilities

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We present a refined calculation method for the phonon part (Franck-Condon Overlaps) of the transition probabilities of electron-phonon radiative and non-radiative transitions in crystals. The evaluation of the thermal averaged Franck-Condon integrals is a purely algebraic method and the transition probabilities we use are derived from first principles and completely atomistic. For the electronic transitions we take into account the frequency shift of the lattice and the change of the phonon normal coordinates. Explicit formulae of the phonon parts are derived and it is shown that the common transition probabilities used in literature are special cases of our functional calculation technique.

Introduction

Reviews of the evaluation of Franck-Condon integrals in connection with thermally weighted transition probabilities were given by Meyer [1], Stasiw [2] and Haug [3]. By these authors the non-algebraic approach with non-resonant transition probabilities is described. This approach starts with a Fourier expansion of the energy conserving δ-distribution which results from perturbation theory. Afterwards completeness relations for oscillator functions, so-called Slater sums, are applied. However, this method only works in the continuous part of the spectrum, as was already emphasized by Meyer [1]; that means, it is not allowed to calculate non-radiative transitions between discrete states by this method.

In addition to the direct integration technique mentioned above, several approaches have been developed in order to circumvent such direct integrations. The method of moments was introduced by Lax [4] and developed by various other authors. As in practice only a few moments can be calculated, this is a drastic restriction of the information to be gained, and for generalizations going beyond the static approximation the method seems not very well suited. Last not least the method of moments is not energy conserving. The method of correlation functions is frequently used, but finally the radiative transition probability is a semiclassical expression with respect to the radiation field.

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The most promising approach to calculate radiative and non-radiative transitions is the algebraic procedure which has been initiated by Koide [5] and put forward by Witschel [6] who used a purely algebraic method to calculate Franck-Condon transitions. Heinzel [7] demonstrated that by algebraic methods even thermal averages of phonon transition generating functions can be calculated.

In this paper we follow the method developed by Heinzel and derive an expression for the phonon part of radiative as well as non-radiative transition probabilities with arbitrary electron-phonon coupling. Our model is based on a theory developed by Stumpf and coworkers [8–19]. In this theory in a first step a microblock model is proposed to describe processes at one impurity center. In a second step these microblocks are collected to form a mosaic-block. By means of this theory we investigate resonance transitions and obtain explicit formulae for thermally weighted transition probabilities resp. for a phonon part with multidimensional harmonic oscillators frequency shift of the lattice and change of the phonon normal coordinates which is, as will be shown, even in lowest approximation in good agreement with the transitions studied in literature.

1. Fundamentals

For the derivation of transition probabilities in semiconductors with point defects we use the mosaicblock model introduced by Stumpf [8]. In this model, for a complete description of the crystal or of the mosaicblock, respectively, we have to

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consider the system consisting of crystal, radiation field, heat reservoir, and their mutual interactions. The Hamiltonian of this model is given by

$$H = K + S + W + H^{s} + H^{w} \tag{1.1}$$

with K, S, W as the energy operators of the whole mosaicblock, free radiation field and heat reservoir, and H^{s}, H^{w} as the interaction operators of the mosaicblock with the radiation field and the heat reservoir, resp.

This system is described by the base system

$$|a\rangle = |n\,m\,\nu\,\varrho\rangle = |n\,m\rangle \otimes |\nu\rangle \otimes |\varrho\rangle \tag{1.2}$$

with the representatives of the subsystems

$|nm\rangle$ dynamic electron lattice states of the crystal with electronic quantum number n and lattice quantum number m,

$|\nu\rangle, |\varrho\rangle$ eigenstates of the radiation field, resp. heat bath.

As the states (1.2) do not diagonalize the total energy may divide H into $H_0 + H_1$, with H_1 due to [19]:

$$H_1 = K^{t} + K^{s} + H^{s} + H^{w}. \tag{1.3}$$

The states $|nm\rangle = |\chi_n\rangle|\varphi_m^n\rangle$ are calculated in the adiabatic electron-nucleon coupling scheme. Thus K^{t} represents the non-adiabatic electron-lattice interaction [19, 20] and is given by

$$K^{t}|\chi_n\rangle|\varphi_m^n\rangle = \left[-\sum_{k=1}^{N}\frac{\hbar^2}{2M_k}\Delta_k|\chi_n\rangle\right]|\varphi_m^n\rangle - 2\sum_{k=1}^{N}\frac{\hbar^2}{2M_k}(\nabla_k|\chi_n\rangle)(\nabla_k|\varphi_m^n\rangle) \tag{1.4}$$

with N the number of lattice ions and M_k the mass of the k-th lattice ion.

K^{t} leads to non-radiative electron-multiphonon transitions, while K^{s} contains electron-electron interactions leading to Auger transitions [19, 21] and direct interactions between impurity centers; H^{s} is responsible for radiative transitions, while H^{w} causes energy dissipation of phonons and relaxation to thermal equilibrium.

To describe the behaviour of the whole mosaicblock system we consider the time-dependent occupation probability $P_a(t)$ for the state $|a\rangle$. As the macroscopic observables are the effect of the microscopic transitions and thus are irreversible, the occupation probabilities satisfy the Pauli-Master equation [9]—[11]

$$\dot{P}_b(t) = \sum_a W_{ba}[P_a(t) - P_b(t)] \tag{1.5}$$

with the transition probabilities W_{ba} given in first order perturbation theory and in thermodynamical limit by

$$W_{ba} = \frac{2\pi}{\hbar}|\langle b|H_1|a\rangle|^2\,\delta(E_b - E_a). \tag{1.6}$$

The transition probabilities are additive with respect to the different subsystems [19].

In the dynamical equation (1.5) all degrees of freedom of the different subsystems are contained. As we are only interested in the electronic reactions, all other degrees of freedom must be eliminated. This was done by Stumpf and coworkers [8—10, 12] leading to

$$\dot{P}_n(t) = \sum_{n'}[W^{k}_{nn'}(T) + W^{s}_{nn'}(t,T)]\,P_{n'}(t) - \sum_{n'}[W^{k}_{n'n}(T) + W^{s}_{n'n}(t,T)]\,P_n(t), \tag{1.7}$$

where $P_n(t)$ is the occupation probability of the electronic state $|\chi_n\rangle$ and

$$W^{k}_{nn'}(T) = \sum_{mm'} f_{m'}(T)\frac{2\pi}{\hbar}|\langle n\,m|K^{s} + K^{t}|n'\,m'\rangle|^2\,\delta(E^{n}_{m} - E^{n'}_{m'}), \tag{1.8}$$

$$W^{s}_{nn'}(t,T) = \sum_{\nu\nu' mm'} P_{\nu'}(t)\,f_{m'}(T)\frac{2\pi}{\hbar}|\langle n\,m\,\nu|H^{s}|n'\,m'\,\nu'\rangle|^2\,\delta(E^{n}_{m} + E_{\nu} - E^{n'}_{m'} - E_{\nu'}) \tag{1.9}$$

are total non-radiative resp. radiative transition probabilities.

In ionic crystal semiconductors the impurity center electrons are mainly coupled to the long wave part of the longitudinal optical phonon branch and to single impurity center lattice vibrations. For point defects the impurity center lattice vibrations are always outside of the phonon bands [22]. Therefore, a calculation between discrete states has to be derived, as most of the electronic energy is

transferred into the localized phonon states. Stumpf and coworkers [8, 13—17] evaluated a calculation method of non-radiative transition probabilities by observing the resonance character of the crystal states. As the resonance character is mainly due to the decay of the phonon excitations [15], Stumpf introduced dressed phonon states [10], whereby the resonance behaviour was incorporated in these states. For actual calculations the dressed phonons have to be represented by harmonic phonons [9, 10, 16]; this has been done by Heinzel [17] who used the resolvent representation of the anharmonic system in terms of harmonic states.

To derive the resulting expression of $W^{s,k}_{nn'}$ the completeness relation

$$\sum_m |m\rangle\langle m| = \sum_m |m\rangle^h{}^h\langle m| = 1$$

and the good approximation for the initial states $|m'\rangle = |m'\rangle^h$ is used with the harmonic phonon states $|m\rangle^h$ and $|nm\rangle^h = |n\rangle \otimes |m\rangle^h$. Then the following expression for the transition probabilities results

$$W^k_{nn'}(T) = \frac{2\pi}{\hbar} \sum_{mm'} f_{m'}(T) \, |{}^h\langle nm| K^s + K^t |n'm'\rangle^h|^2 \, \delta_\gamma(E^n_m - E^{n'}_{m'}) \tag{1.10}$$

and analogously

$$W^s_{nn'}(t, T) = \frac{2\pi}{\hbar} \sum_{\nu\nu' mm'} P_{\nu'}(t) f_{m'}(T) \, |{}^h\langle nm\nu| H^s |n'm'\nu'\rangle^h|^2 \, \delta_\gamma(E^n_m + E_\nu - E^{n'}_{m'} - E_{\nu'}) \tag{1.11}$$

with the line breadth function

$$\delta_\gamma(x) = \frac{1}{2\pi} \frac{\gamma(T)}{x^2 + \frac{1}{4}\gamma(T)^2} \tag{1.12}$$

and thermal averaged phonon line breadth $\gamma(T)$.

The advantage of this representation is that for explicit evaluation of the transition probabilities we can now use harmonic phonons without having lost the anharmonic coupling which is contained in the line breadth function $\delta_\gamma(x)$. In the following we denote for abbreviation $|nm\rangle^h$ by $|nm\rangle$.

2. Radiative Transition Probabilities

In this section we only take into account the electron-photon interaction while direct photon-phonon interaction is neglected. Then, due to the electron-lattice coupling, electron-photon interactions are accompanied by indirect phonon excitations. For the derivation of the energy operator H^s from relativistic quantum electrodynamics we refer to [19]. Then for H^s follows

$$H^s = \frac{e}{mc} \sum_i \boldsymbol{A}(\boldsymbol{r}_i) \boldsymbol{p}_i \tag{2.1}$$

with electronic momentum $\boldsymbol{p}_i$ and the quantized vector potential $\boldsymbol{A}(\boldsymbol{r}_i)$. The sum i runs over $z = M + s$ (s: impurity center electrons, M: shell electrons). In the approximation (2.1) the coupling of electrons to static external electric fields and spin interactions with magnetic fields are suppressed; further we only took into account absorption and emission of one photon.

The vector potential is given by

$$\boldsymbol{A}(\boldsymbol{r}) = \sum_\varkappa \left(\frac{2\pi c \hbar}{|k| V} \right)^{1/2} \boldsymbol{e}_\varkappa (a_\varkappa e^{i\boldsymbol{k}w} + a^+_\varkappa e^{-i\boldsymbol{k}w}), \tag{2.2}$$

$a^+_\varkappa$, $a_\varkappa$: creation and annihilation operators of the mode $\varkappa$;

$\boldsymbol{k}$: wave vector;

$\boldsymbol{e}_\varkappa$: polarization vector;

V: box in which the radiation field is enclosed;

$\varkappa$: runs over all eigenmodes.

For further evaluation we use dipole approximation with $\omega_{nn'} \approx \omega_\varkappa$ and characterize the states of the radiation field by occupation numbers, and we replace the electronic matrix element by the mean value over all directions of $\boldsymbol{k}$ and over all polarizations perpendicular to $\boldsymbol{k}$. These approximations were made in [17, 19, 20, 23].

This leads from transition probability (1.11) to equations for emission and absorption:

Emission: $$W^s_{nn'} = \sum_\varkappa W_{nn'}(\varkappa)(\bar{\nu}_\varkappa + 1), \tag{2.3}$$

Absorption: $$W^s_{nn'} = \sum_\varkappa W_{nn'}(\varkappa) \bar{\nu}_\varkappa \tag{2.4}$$

with $\bar{\nu}_\varkappa$ as the mean photon number of the mode $\varkappa$ and

$$W_{nn'}(\varkappa) = \frac{(2\pi)^2 \omega_\varkappa}{3V} \sum_{mm'} f_{m'} |\langle n\, m| \sum_i e\, \boldsymbol{r}_i |\, n'\, m'\rangle|^2 \cdot \delta_\gamma(E_m^n + E_\nu - E_{m'}^{n'} - E_{\nu'}) . \tag{2.5}$$

Now we treat the crystal part of the transition probability. A representation of the total electronic wave function by suitable one-particle functions is given by

$$|\chi_n\rangle = {}^{\mathrm{P}}\Sigma(-1)^{\mathrm{P}} z!^{-1/2} \cdot [\psi_{\lambda_1}^n(\boldsymbol{r}_{\mu_1}, \boldsymbol{R}) \dots \psi_{\lambda_z}^n(\boldsymbol{r}_{\mu_z}, \boldsymbol{R})] \tag{2.6}$$

where $\mu_1 \dots \mu_z$ provides the antisymmetrization, while λ denotes a special sequence of the $z = M + s$ one-particle states, n means the dependence of the general electronic state, $\boldsymbol{r}$ the position of the electron, $\boldsymbol{R}$ the position of the nucleon. The crystal matrix element of the transition probability (2.5) can now be evaluated with respect to one particle transitions [19]. In a new notation which we denote by $|\lambda_1 \dots \lambda_\alpha \dots \lambda_z m\rangle$ for the matrix element of the transition (2.5) follows

$$\langle \lambda_1 \dots \lambda_\alpha \dots \lambda_z m| \sum_i e\, \boldsymbol{r}_i |\, \lambda_1 \dots \lambda_\alpha' \dots \lambda_z\, m'\rangle = \int \psi_{\lambda_\alpha}^n(\boldsymbol{r}, \boldsymbol{R}) \times e\, \boldsymbol{r}\, \psi_{\lambda'_\alpha}^{n'}(\boldsymbol{r}, \boldsymbol{R})\, \varphi_m^n(\boldsymbol{R}) \times \varphi_{m'}^{n'}(\boldsymbol{R})\, \mathrm{d}\boldsymbol{r}\, \mathrm{d}\boldsymbol{R} . \tag{2.7}$$

This means that we have obtained a one-particle transition, while all other transitions vanish.

Since every electronic state has its own normal coordinates, the following representation is valid [17, 19] for the one-electron functions

$$\psi_j^n(\boldsymbol{r}, \boldsymbol{R}) = \sum_{\nu=0}^{\infty} \frac{1}{\nu!} \sum_{t_1 \dots t_\nu} f_{t_1 \dots t_\nu}^n(j, \boldsymbol{r})\, q_{t_1}^n \dots q_{t_\nu}^n . \tag{2.8}$$

With (2.8), (2.7) leads to

$$\langle \lambda_1 \dots \lambda_\alpha \dots \lambda_z m| \sum_i e\, \boldsymbol{r}_i |\, \lambda_1 \dots \lambda'_\alpha \dots \lambda_z\, m'\rangle = \sum_{\substack{\nu t_1 \dots t_\nu \\ \mu l_1 \dots l_\mu}} A_{l_1 \dots l_\mu}^{t_1 \dots t_\nu} \binom{nn'}{\lambda_\alpha \lambda_{\alpha'}} \langle \varphi_m^n |\, q_{t_1}^n \dots q_{t_\nu}^n q_{l_1}^{n'} \dots q_{l_\mu}^{n'} |\, \varphi_{m'}^{n'} \rangle \tag{2.9}$$

by defining the quantity

$$A_{l_1 \dots l_\mu}^{t_1 \dots t_\nu} \binom{nn'}{\lambda_\alpha \lambda_{\alpha'}} = \frac{1}{\nu!} \frac{1}{\mu!} \int f_{t_1 \dots t_\nu}^n(\lambda_\alpha, \boldsymbol{r}) \times e\, \boldsymbol{r}\, f_{l_1 \dots l_\mu}^{n'}(\lambda'_\alpha, \boldsymbol{r})\, \mathrm{d}\boldsymbol{r} . \tag{2.10}$$

Introducing generating functions for the polynomials [17] by

$$\hat{A} \binom{nn'}{\lambda\lambda'} = \sum_{\substack{\nu t_1 \dots t_\nu \\ \mu l_1 \dots l_\mu}} A_{l_1 \dots l_\mu}^{t_1 \dots t_\nu} \binom{nn'}{\lambda_\alpha \lambda_{\alpha'}} \left(\frac{\partial}{\partial \varrho_{t_1}} \dots \frac{\partial}{\partial \varrho_{t_\nu}}\right) \left(\frac{\partial}{\partial \varrho'_{l_1}} \dots \frac{\partial}{\partial \varrho'_{l_\mu}}\right) . \tag{2.11}$$

The matrix element (2.9) gives (2.12)

$$\langle \lambda_1 \dots \lambda_\alpha \dots \lambda_z m| \sum_i e\, \boldsymbol{r}_i |\, \lambda_1 \dots \lambda'_\alpha \dots \lambda_z m'\rangle = \hat{A} \binom{nn'}{\lambda\lambda'} \langle \varphi_m^n |\, \exp\{\sum_t q_t^n\, \varrho_t\} \exp\{\sum_l q_l^{n'}\, \varrho_l'\} |\, \varphi_{m'}^{n'} \rangle_{\varrho = \varrho' = 0} .$$

The matrix element contains different sets of normal coordinates $\{q_t^n\}$, $\{q_l^{n'}\}$. As these states are linearly dependent, the integral over the normal coordinates can be evaluated. The transformation to normal coordinates is given by

$$(\boldsymbol{R}_k - \boldsymbol{R}_k^{n'}) = \sum_l M_k^{-1/2} (A^{n'})_{kl}\, q_l^{n'} \tag{2.13}$$

with $\boldsymbol{R}_k$ as the actual position of the k-th lattice ion and $\boldsymbol{R}_k^{n'}$ as equilibrium position. From (2.13) follows

$$q_l^{n'} = \sum_{k,j} (A^{n'})_{lk}^{-1} (A^n)_{kj}\, q_j^n + a_l^{nn'} \tag{2.14}$$

with the zero-point shifts of the oscillators

$$a_l^{nn'} = \sum_k M_k^{1/2} (A^{n'})_{lk}^{-1} (\boldsymbol{R}_k^n - \boldsymbol{R}_k^{n'}) . \tag{2.15}$$

Since the lattice only endures a small frequency shift by an electronic transition, its holds approximately $\sum_k (A^{n'})_{lk}^{-1} (A^n)_{kj} \approx \delta_{lj}$. Thus for (2.14) we have a translation

$$q_l^{n'} = q^n + a_l^{nn'} . \tag{2.16}$$

Introducing the new variables $\xi_t = \varrho_t + \varrho_t'$ and ϱ_t with (2.16) for the matrix element follows

$$\langle \lambda_1 \dots \lambda_\alpha \dots \lambda_z m| \sum_i e\, \boldsymbol{r}_i |\, \lambda_1 \dots \lambda_\alpha' \dots \lambda_z m'\rangle = \hat{A} \binom{nn'}{\lambda\lambda'} \exp\left\{\sum_t a_t^{nn'} (\xi_t - \varrho_t)\right\} \langle \varphi_m^n |\, \exp\left\{\sum_t q_t^n\, \xi_t\right\} |\, \varphi_{m'}^{n'} \rangle_{\varrho = \xi = 0} \tag{2.17}$$

and $W_{nn'}(\varkappa)$ resp. the formulas for emission and absorption give

$$W_{nn'}(\varkappa) = \frac{4\pi^2\omega_\varkappa}{3V} |\hat{A}(^{nn'}_{\lambda\lambda'})|^2 \exp\left\{\sum_t a_t^{nn'}(\xi_t - \varrho_t + \bar{\xi}_t - \bar{\varrho}_t)\right\} \Pi(\beta, \Omega) \tag{2.18}$$

with the phonon part of the transition probability

$$\Pi(\beta, \Omega) = \sum_{mm'} f_{m'}(T) |\langle \varphi_m^n | \exp\left\{\sum_t q_t^n \xi_t\right\} | \varphi_{m'}^{n'}\rangle|^2 \cdot \delta_\gamma(E_m^n - E_{m'}^{n'} - \Omega)_{\varrho=\xi=0} \tag{2.19}$$

where for brevity we put $E_{\nu'} - E_\nu = \Omega$, and the variables $\bar{\xi}$, $\bar{\varrho}$ result from the square of the matrix elements.

3. Non-Radiative Transition Probabilities

The main idea for resonance transitions is a continuous background spectrum to which the discrete states are coupled. It is sufficient to consider the anharmonic coupling of the local modes to the non-local ones [10, 13, 18, 19]. The non-radiative transition probability is given by (1.10). Since here we consider only bimolecular processes it is possible to neglect K^s [19]. The matrix element, resp. the transition probability of (1.10) may then be divided into

$$W_{nn'}^k = W_{nn'}^{k0} + W_{nn'}^{k1} \tag{3.1}$$

$W_{nn'}^{k_1}$ belongs to $K^s + K_1^t$ and describes reactions of higher order, whereas $W_{nn'}^{k_0}$ belongs to K_0^t and describes only bimolecular reactions. As the different reactions are connected with transitions between different state configurations, the division (3.1) is possible. In the following we treat only $W_{nn'}^{k_0}$.

Then the non-radiative transition probability for bimolecular processes is given by [19]

$$W_{nn'}^k(T) = \frac{2\pi}{\hbar} \sum_{mm'} f_{m'}(T) |\langle n\, m | K_0^t | n'\, m'\rangle|^2 \delta_\gamma(E_m^n - E_{m'}^{n'}) . \tag{3.2}$$

Assuming a state description due to (2.6) and (2.8) the matrix element of (3.2) can be evaluated analogously to the crystal part of the radiative transition probability in the preceding section. After transforming to normal coordinates and specifying to one-particle transitions, for the nonradiative transition probability follows [17, 19, 24]

$$\begin{aligned} W_{nn'}^k(T) = \frac{2\pi}{\hbar} \sum_{mm'} f_{m'}(T) |\hat{N}(^{nn'}_{\lambda\lambda'})|^2 |\langle \varphi_m^n | \exp\left\{\sum_l q_l^n \varrho_l\right\} \\ \cdot \exp\left\{\sum_l q_l^{n'} \varrho_l'\right\} \exp\left\{i \sum_l p_l \delta_l\right\} | \varphi_{m'}^{n'}\rangle|^2 \delta_\gamma(E_m^n - E_{m'}^{n'}) \end{aligned} \tag{3.3}$$

by using the definitions

$$\begin{aligned} \hat{N}(^{nn'}_{\lambda\lambda'}) = \sum_{\substack{\nu t_1 \dots t_\nu \\ \mu l_1 \dots l_\mu l}} N_{l_1 \dots l_\mu l}^{t_1 \dots t_\nu} \left(\frac{\partial}{\partial \varrho_{t_1}} \cdots \frac{\partial}{\partial \varrho_{t_\nu}}\right)\left(\frac{\partial}{\partial \varrho_{l_1}'} \cdots \frac{\partial}{\partial \varrho_{l_\mu}'}\right) \frac{\partial}{\partial \delta_l} \\ + \sum_{\substack{\nu t_1 \dots t_\nu \\ \mu l_1 \dots l_\mu ll}} N_{l_1 \dots l_\mu ll}^{t_1 \dots t_\nu} \left(\frac{\partial}{\partial \varrho_{t_1}} \cdots \frac{\partial}{\partial \varrho_{t_\nu}}\right)\left(\frac{\partial}{\partial \varrho_{l_1}'} \cdots \frac{\partial}{\partial \varrho_{l_\mu}'}\right), \end{aligned} \tag{3.4}$$

$$N_{l_1 \dots l_\mu l}^{t_1 \dots t_\nu}(^{nn'}_{\lambda_\alpha \lambda_{\alpha'}}) = \frac{1}{\nu!} \frac{1}{\mu!} (-\hbar) \int f_{t_1 \dots t_\nu}^n(\lambda_\alpha, \boldsymbol{r}) \times f_{l_1 \dots l_\mu l}^{n'}(\lambda_{\alpha'}', \boldsymbol{r})\, \mathrm{d}\boldsymbol{r} , \tag{3.5}$$

$$N_{l_1 \dots l_\mu ll}^{t_1 \dots t_\nu}(^{nn'}_{\lambda_\alpha \lambda_{\alpha'}}) = \frac{1}{\nu!} \frac{1}{\mu!} \left(-\frac{\hbar^2}{2}\right) \int f_{t_1 \dots t_\nu}^n(\lambda_\alpha, \boldsymbol{r}) \times f_{l_1 \dots l_\mu ll}^{n'}(\lambda_\alpha' \boldsymbol{r})\, \mathrm{d}\boldsymbol{r} , \tag{3.6}$$

with $i p_l = \hbar \dfrac{\partial}{\partial q_l^{n'}} = \hbar \dfrac{\partial}{\partial q_l^n}$.

The different sets of normal coordinates are connected by (2.16) and together with the new formal parameters $\xi_t = \varrho_t + \varrho_t'$, ϱ_t, δ_t the expression (3.3) finally gives

$$W^{\mathrm{k}}_{nn'}(T) = \frac{2\pi}{\hbar} |\hat{N}(^{nn'}_{\lambda\lambda'})|^2 \exp\left\{\sum_t a_t^{nn'}(\xi_t - \varrho_t + \bar{\xi}_t - \bar{\varrho}_t)\right\} \Pi(\beta) \tag{3.7}$$

with the phonon part

$$\Pi(\beta) = \sum_{mm'} f_{m'}(T) |\langle \varphi_n^m | \exp\left\{\sum_t q_t^n \xi_t\right\} \exp\left\{i \sum_t p_t \delta_t\right\} | \varphi_m^{n'}\rangle|^2 \delta_\gamma(E_m^n - E_{m'}^{n'})_{\varrho=\xi=\delta=0}. \tag{3.8}$$

The phonon parts of radiative transitions (2.19) and nonradiative transitions (3.8) only differ in the additional variables $\{p_t\}$. But these variables can also be introduced in (2.19), as the effect of these variables only depends on differentiation. If no differential operator occurs for $\delta_t = 0$, the corresponding operator is unity. Thus the phonon parts of both transition probabilities can be written

$$\Pi(\beta, \Omega) \sum_{mm'} f_{m'}(T) |\langle \varphi_m^n | \exp\left\{\sum_t q_t^n \xi_t\right\} \exp\left\{i \sum_t p_t \delta_t\right\} | \varphi_{m'}^{n'}\rangle|^2 \delta_\gamma(E_m^n - E_{m'}^{n'} - \Omega)_{\varrho=\xi=\delta=0}, \tag{3.9}$$

where for nonradiative transitions we put $\Omega = 0$, and in order to calculate the absolute square we introduced by definition the new formal parameters $\bar{\xi}_t$, $\bar{\delta}_t$ for complex conjugation.

4. Evaluation of the Phonon Part $\Pi(\beta, \Omega)$

The phonon part contains generalized Franck-Condon integrals with scalar products of oscillator functions with respect to different frequencies and base systems and polynomials in the normal coordinates. For further evaluation we first have to define the thermal equilibrium state of the lattice.

$$f_{m'}(T) = Z^{-1} \exp\{-\beta E_{m'}^{n'}\}. \tag{4.1}$$

Due to (1.10) ff. we can use harmonic phonons without having lost the anharmonic coupling; thus the product ansatz is valid

$$|\varphi_m^n\rangle = \prod_{\nu=1}^{N3} |\varphi_{m_\nu}^n(q_\nu^n)\rangle. \tag{4.2}$$

The phonon-part now describes a set of one oscillator functions coupled by the δ_γ-function. For the δ_γ-function the following integral representation is possible

$$\delta_\gamma(x) = \int_{-\infty}^{\infty} \exp\{i\tau x - \gamma|\tau|\} \mathrm{d}\tau. \tag{4.3}$$

For the further treatment we express the energies by oscillator energies

$$E_m^n = \sum_t (m_t + \tfrac{1}{2}) \hbar \omega_t^n + U_n(\boldsymbol{R}^n) \tag{4.4}$$

$U_n(\boldsymbol{R}^n)$: static electronic energy,

m_t: occupation numbers of phonon modes,

ω_t^n: phonon frequencies of the mode t and electronic state n.

Additionally, for small line breadths we can replace $E_{m'}^{n'}$ by $E_m^n - \Omega$ in the exponent. Then the products can be calculated and due to [7, 17] the phonon part (3.9) leads to

$$\Pi(\beta, \Omega) = \int_{-\infty}^{\infty} \mathrm{d}\tau \exp\{i\tau(\Delta U_{nn'} - \Omega) - \gamma|\tau|\} \Pi^{nn'}(T) \tag{4.5}$$

with

$$\Pi^{nn'}(T) = \prod_{t=1}^{3N} Z_t^{-1} \exp\left\{\frac{i\tau\hbar}{2}(\omega_t^n - \omega_t^{n'})\right\} \sum_{m_t m_t'} \exp\{-\beta\hbar\omega_t^n m_t\} \cdot \exp\{i\tau\hbar(m_t\omega_t^n - m_t'\omega_t^{n'})\} |\langle \varphi_{m_t}^n | \exp\{q_t^n \xi_t\} \exp\{i p_t \delta_t\} | \varphi_{m_t'}^{n'}\rangle|^2 \tag{4.6}$$

and

$$\Delta U_{nn'} = U_n(\boldsymbol{R}^n) - U_{n'}(\boldsymbol{R}^{n'}), \quad Z_t = (1 - \exp\{-\beta\hbar\omega_t^n\})^{-1}. \tag{4.7), (4.8}$$

Here and in the following we will not always explicitly note that the parameters are to be set equal zero after differentiation. Now we can replace m_t' by the occupation number operator $\hat{m}_t'$ and the expression $\exp\{-i\tau\hbar m_t'\omega_t^{n'}\}$ can be shifted into the brackets.

Since $\sum_{m'_t} |\varphi^{n'}_{m'_t}\rangle\langle\varphi^{n'}_{m'_t}|$ is the unity operator, the expression (4.6) gives

$$\Pi^{nn'}(T) = \prod_t (1 - \exp[-\beta\hbar\omega_t^n]) \exp\left\{\frac{i\tau\hbar}{2}(\omega^n{}_t - \omega_t^{n'})\right\} \sum_{m_t} \exp\{-\beta\hbar\omega_t^n m_t + i\tau\hbar\omega_t^n m_t\}$$
$$\cdot \langle\varphi^n_{m_t}| e^{q_t{}^n \xi_t} e^{ip_t\delta_t} \exp\{-i\tau\hbar\hat{m}'_t\omega_t^{n'}\} e^{-ip_t\bar{\delta}_t} e^{q_t{}^n\bar{\xi}_t} |\varphi^n_{m_t}\rangle . \tag{4.9}$$

Generally, with an electronic transition the phonon coordinates change and the frequencies suffer a shift. We now look for the transformations by which the phonon states $|\varphi^{n'}_{m_t}\rangle$ are transformed if the electronic state changes. From Koide [5] results

$$F(\hat{m}'_t) = U_t V_t F(\hat{m}_t) V_t^{-1} U_t^{-1} \tag{4.10}$$

with

$$U_t = \exp\left\{\frac{i}{\hbar} p_t a_t^{nn'}\right\}, \tag{4.11}$$

$$V_t = \exp\{-A_t(a_t)^2\} \exp\{B_t(a_t^+)^2\} \tag{4.12}$$

and

$$A_t = \frac{\omega_t^n - \omega_t^{n'}}{2(\omega_t^n + \omega_t^{n'})}, \quad B_t = \frac{\omega_t^{n^2} - \omega_t^{n'^2}}{8\omega_t^n\omega_t^{n'}}, \tag{4.13}$$

where a_t and a_t^+ are destruction resp. creation operators and

$$q_t^n = \left(\frac{\hbar}{2\omega_t^n}\right)^{1/2}(a_t^+ + a_t), \quad p_t = i\left(\frac{\hbar\omega_t^n}{2}\right)^{1/2}(a^+{}_t - a_t) \tag{4.14}$$

is valid. With these relations and the definitions

$$\Theta_t = \left(\frac{\hbar}{2\omega_t^n}\right)^{1/2}\xi_t, \quad \Delta_t = \left(\frac{\hbar\omega_t^n}{2}\right)^{1/2}\delta_t, \tag{4.15}$$

and similar expressions $\bar{\Theta}_t$, $\bar{\Delta}_t$ resulting from the formal parameters $\bar{\xi}_t$, $\bar{\delta}_t$ for complex conjugation, it is possible to write (4.9) in the form [17]

$$\Pi^{nn'}(T) = \prod_t (1 - \exp\{-\beta\hbar\omega_t^n\}) \sum_{m_t} \exp\{-\beta\hbar\omega_t^n m_t\} \tilde{\Pi}^{nn'}(m_t) \tag{4.16}$$

with $k_t^n = \tau\hbar\omega_t^n$

$$\tilde{\Pi}^{nn'}(m_t) = \exp\left\{\frac{i}{2}(k_t^n - k_t^{n'}) + ik_t^n m_t\right\} \langle\varphi^n_{m_t}| \exp\{\Theta_t(a_t^+ + a_t)\}$$
$$\cdot \exp\{-\Delta_t(a_t^+ - a_t)\} \cdot U_t V_t \exp\{-ik_t^{n'}\hat{m}_t\} V_t^{-1} U_t^{-1}$$
$$\cdot \exp\{\bar{\Delta}_t(a_t^+ - a_t)\} \exp\{\bar{\Theta}_t(a_t^+ + a_t)\} |\varphi^n_{m_t}\rangle . \tag{4.17}$$

As the factors (4.17) have the same functional form for all t we suppress this index as long as we only treat the single factors. The expectation value (4.17) can be calculated by normalordering which can be achieved by the repeated application of generalized Hausdorff formulae [7]. By use of the unitary transformation (4.11), (4.14) we obtain

$$U = e^{-\frac{1}{2}\alpha^2} e^{-\alpha a^+} e^{\alpha a} \tag{4.18}$$

with

$$\alpha = \left(\frac{\omega^n}{2\hbar}\right)^{1/2} a^{nn'} \tag{4.19}$$

and therefore (4.17) can be written

$$\tilde{\Pi}^{nn'}(m) = \exp\{\tfrac{1}{2}(d_3 + \bar{d}_3) + ik^n m + \tfrac{1}{2}i(k^n - k^{n'})\}$$
$$\cdot \langle\varphi^n_m| e^{d_1 a^+} e^{d_2 a} V \exp\{-ik^{n'}\hat{m}\} V^{-1} e^{\bar{d}_2 a^+} e^{\bar{d}_1 a} |\varphi^n_m\rangle \tag{4.20}$$

with

$$d_1 = \Theta - \Delta - \alpha, \quad d_2 = \Theta + \Delta + \alpha,$$
$$d_3 = \Theta^2 - (\Delta + \alpha)^2 - 2\Theta(\Delta + \alpha), \tag{4.21}$$

and similar expressions for $\bar{d}_1$, $\bar{d}_2$, $\bar{d}_3$ which arise from (4.21) by replacing Δ and Θ by $\bar{\Delta}$ and $\bar{\Theta}$. For further evaluation due to (4.12) the normal-ordering of exponentials with squared operators is needed. This can be done by means of generating functions from which result some important gener-

alized Hausdorff formulae [7]. Application of this technique to (4.20) gives the following expression in which we have commuted the operator $\exp\{-ik^{n'}\hat{m}\}$ to the states:

$$\widetilde{\Pi}^{nn'}(m) = \exp\left\{-A\left(\frac{\partial}{\partial\alpha_1}\right)^2\right\}\exp\left\{\bar{B}\left(\frac{\partial}{\partial\alpha_2}\right)^2\right\}\exp\left\{A\left(\frac{\partial}{\partial\alpha_3}\right)^2\right\}$$
$$\cdot\langle\varphi_m^n|\, e^{r_1 a^+} e^{r_2 a}\,|\varphi_m^n\rangle \exp\left\{r_3 + im(k^n - k^{n'}) + \frac{i}{2}(k^n - k^{n'})\right\} \tag{4.22}$$

with the definitions

$$\bar{B} = B(e^{ik^{n'}} - e^{-ik^{n'}}), \tag{4.23}$$

$$\begin{aligned} r_1 &= d_1 \exp\{\tfrac{1}{2} i k^{n'}\} + \bar{d}_2 \exp\{-\tfrac{1}{2} i k^{n'}\} + \alpha_2, \\ r_2 &= (d_2 + \alpha_1)\exp\{-\tfrac{1}{2} i k^{n'}\} + (\bar{d}_1 + \alpha_3)\exp\{\tfrac{1}{2} i k^{n'}\}, \\ r_3 &= (d_2\alpha_2 + \alpha_1\alpha_2)\exp\{-\tfrac{1}{2} i k^{n'}\} + (d_2\bar{d}_2 + \bar{d}_2\alpha_1)\exp\{-i k^{n'}\} + \bar{d}_2\alpha_3 + \tfrac{1}{2}(d_3 + \bar{d}_3). \end{aligned} \tag{4.24}$$

We now consider for simplicity the expression (cf. (4.16) and (4.22))

$$\Pi_t^{nn'} := (1 - \exp\{-\beta\hbar\omega_t^n\})$$
$$\cdot \exp\left\{-A\left(\frac{\partial}{\partial\alpha_1}\right)^2\right\}\exp\left\{\bar{B}\left(\frac{\partial}{\partial\alpha_2}\right)^2\right\}\exp\left\{A\left(\frac{\partial}{\partial\alpha_3}\right)^2\right\}\exp\{r_3 + \tfrac{1}{2} i(k^n - k^{n'})\}\, M(\varkappa). \tag{4.25}$$

As the phonon states are given by

$$|\varphi_m^n\rangle = (m!)^{-1/2}(a^+)^m|0\rangle \tag{4.26}$$

together with the related Hausdorff formula [7] for $M(\varkappa)$ follows

$$M(\varkappa) = \sum_m \frac{\varkappa^m}{m!}\langle 0|(r_1 + a)^m(r_2 + a^+)^m|0\rangle \tag{4.27}$$

with

$$\varkappa = \exp\{-\beta\hbar\omega^n + i(k^n - k^{n'})\}. \tag{4.28}$$

By means of generating function technique it is possible to obtain for (4.27) a normalordering with respect to a^+, a [7, 24]. With the restriction $|\varkappa| < 1$ (4.27) lead to

$$M(\varkappa) = \exp\left\{\varkappa\left(\frac{\partial}{\partial j_1}\right)\left(\frac{\partial}{\partial j_2}\right)\right\}\exp\{j_1 r_1\}\exp\{j_2 r_2\}\exp\{j_1 j_2\} = (1 - \varkappa)^{-1}\exp\left\{r_1 r_2 \frac{\varkappa}{1 - \varkappa}\right\}. \tag{4.29}$$

Inserting (4.29) into (4.25) we finally have to calculate $(\alpha_i, \partial/\partial\alpha_i)$. First we have to give the explicit dependency of the exponentials of the α_i $(i = 1, 2, 3)$. With (4.24) follows

$$\exp\left\{r_1 r_2 \frac{\varkappa}{1 - \varkappa} + r_3\right\} = \exp\{L_1\alpha_1\alpha_2 + L_3\alpha_2\alpha_3 + M_1\alpha_1 + M_2\alpha_2 + M_3\alpha_3 + N\} \tag{4.30}$$

with the definitions of L_i, M_i, N given in Appendix.

Now it is possible to treat α_1 and α_3 by use of related Hausdorff formulae [7], for example

$$\exp\left\{-A\left(\frac{\partial}{\partial\alpha_1}\right)^2\right\}\exp\{(L_1\alpha_2 + M_1)\alpha_1\} = \exp\{-A L_1^2\alpha_2^2\}\exp\{-2A M_1 L_1\alpha_2\}\exp\{-A M_1^2\}. \tag{4.31}$$

Finally calculation of α_2 gives [7, 24] for the restriction $|4\bar{B}C| < 1$

$$\exp\left\{\bar{B}\left(\frac{\partial}{\partial\alpha_2}\right)^2\right\}\exp\{C\alpha_2^2\}\exp\{D\alpha_2\} = \exp\left\{\bar{B}D^2\sum_{\nu=0}^{\infty}(4\bar{B}C)^\nu\right\}\sum_{n=0}^{\infty}(\bar{B}C)^n\frac{(2n)!}{n!\,n!} \tag{4.32}$$

with the definitions of C, D given in Appendix, and thus the expression (4.16) with (4.25) leads to

$$\Pi^{nn'}(T) = \prod_t (1 - \exp\{-\beta\hbar\omega_t^n\})(1 - \varkappa_t)^{-1}\exp\{\tfrac{1}{2} i(k_t^n - k_t^{n'}) + N_t - A_t M_{1t}^2 + A_t M_{3t}^2\}$$
$$\cdot\exp\{\bar{B}_t D_t^2\sum_\nu(4\bar{B}_t C_t)^\nu\}\sum_n\frac{(2n)!}{n!\,n!}(\bar{B}_t C_t)^n \tag{4.33}$$

whereby we introduced again the index t.

5. Approximations

The restriction $|4\bar{B}_t C_t| < 1$ used in (4.32) means a restriction of the frequencies ω_t^n, $\omega_t^{n'}$ according to (4.23), (4.13) and (A.1). An estimate of this expression [24] leads to

$$|4\bar{B}_t C_t| \leqq 8|A_t B_t| \frac{|\varkappa_t|^2 + 1}{(1 - |\varkappa_t|)^2} \tag{5.1}$$

where $\varkappa_t$ due to (4.28) depends on the mode frequencies. For $T = 0$, the fraction in (5.1) takes the value 1, while for $T = 300^0$ and optical mode frequencies of the magnitude $\omega = 10^{13}\ \mathrm{sec}^{-1}$ this expression approximately takes the value 2.5. Hence we conclude that also $|A_t| \ll 1$ and $|B_t| \ll 1$ has to hold. This has the effect that only small differences between ω_t^n and $\omega_t^{n'}$ are admitted, for instance for optical modes of the magnitude of 30%. Thus it is reasonable to approximate $\varkappa_t$ by $\exp\{-\beta\hbar\omega_t^n\}$ and the power series of $\bar{B}_t C_t$ in (4.33) by their lowest terms with $\nu = n = 0$. Then (4.33) leads to

$$\Pi^{nn'}(T) = \prod_t \exp\{\tfrac{1}{2} i (k_t^n - k_t^{n'})\} \exp\{N_t\} \exp\{A_t(-M_{1t}^2 + M_{3t}^2)\} \exp\{\bar{B}_t D_t^2\}. \tag{5.2}$$

Further in the exponentials of (5.2) we take into account only the linear terms in A_t and $\bar{B}_t$. Then for (5.2) follows

$$\Pi^{nn'}(T) = \prod_t \exp\{\tfrac{1}{2} i (k_t^n - k_t^{n'})\} e^{N_t} e^{P_t} \tag{5.3}$$

with

$$P_t = \frac{\exp\{-i k_t^{n'}\}}{(1 - \exp\{-\beta\hbar\omega_t^n\})^2} \exp\{i k_t^{n'}\} - \exp\{-i k_t^{n'}\}$$
$$[A_t(d_{1t}\exp\{-\beta\hbar\omega_t^n\}\exp\{i k_t^{n'}\} + \bar{d}_{2t})^2 + B_t(\bar{d}_{1t}\exp\{-\beta\hbar\omega_t^n\}\exp\{i k_t^{n'}\} + d_{2t})^2]. \tag{5.4}$$

By substitution of (5.3) into (4.5) we obtain the whole phonon part

$$\Pi(\beta, \Omega) = \int \mathrm{d}\tau \exp\{i\tau(\Delta U_{nn'} - \Omega + \tfrac{1}{2}\hbar \sum_t (\omega_t^n - \omega_t^{n'}))\} - \exp\{-\gamma|\tau|\} \prod_t e^{N_t} e^{P_t}. \tag{5.5}$$

The exponentials in (5.5) can be recasted into

$$e^{N_t} = \sum_{\mu_t = -\infty}^{\infty} \sigma_t(\mu_t, \beta) \exp\{-i\tau\mu_t\hbar\omega_t^{n'}\} \tag{5.6}$$

with

$$\sigma_t(\mu_t, \beta) = \exp\left\{\frac{\exp\{-\beta\hbar\omega_t^n\}}{1 - \exp\{-\beta\hbar\omega_n^t\}}(d_1 d_{2t} + \bar{d}_{1t}\bar{d}_{2t}) + \tfrac{1}{2}(d_{3t} + \bar{d}_{3t})\right\} \sum_m \frac{a_t^{m+\mu_t}}{(m+\mu_t)!} \frac{b_t^m}{m!} \tag{5.7}$$

and

$$a_t = \frac{1}{1 - \exp\{-\beta\hbar\omega_t^n\}} d_{2t}\bar{d}_{2t}, \quad b_t = \frac{\exp\{-\beta\hbar\omega_t^n\}}{1 - \exp\{-\beta\hbar\omega_t^n\}} d_{1t}\bar{d}_{1t}, \tag{5.8}$$

and

$$e^{P_t} = e^{f_{0t}} \sum_{n_1, n_2, n_3, n_4 = 0}^{\infty} \frac{(f_{1t})^{n_1}}{n_1!} \frac{(-f_{1t})^{n_2}}{n_2!} \frac{(f_{2t})^{n_3}}{n_3!} \frac{(f_{3t})^{n_4}}{n_4!}$$
$$\cdot \exp\{i\tau\hbar\omega_t^{n'}(n_1 - n_2 + 2n_3 - 2n_4)\} =: e^{f_{0t}} \sum_{\nu_t = 0}^{\infty} g_{\nu_t} \exp\{i\tau\nu_t\hbar\omega_t^{n'}\} \tag{5.9}$$

with $\nu = n_1 - n_2 + 2n_3 - 2n_4$ and the coefficients

$$f_{0t} = \frac{1}{(1 - \exp\{-\beta\hbar\omega_t^n\})^2}[A_t(\bar{d}_{2t}^2 - \exp\{-2\beta\hbar\omega_t^n\} d_{1t}^2) + B_t(d_{2t}^2 - \exp\{-2\beta\hbar\omega_t^n\}\bar{d}_{1t}^2)],$$

$$f_{1t} = \frac{2\exp\{-\beta\hbar\omega_t^n\}}{(1 - \exp\{-\beta\hbar\omega_t^n\})^2}[A_t d_{1t}\bar{d}_{2t} + B_t\bar{d}_{1t}d_{2t}],$$

$$f_{2t} = \frac{\exp\{-2\beta\hbar\omega_t^n\}}{(1-\exp\{-\beta\hbar\omega_t^n\})^2}[A_t d_{1t}^2 + B_t \bar{d}_{1t}^2],$$

$$f_{3t} = -\frac{1}{(1-\exp\{-\beta\hbar\omega_t^n\})^2}[A_t \bar{d}_{2t}^2 + B_t d_{2t}^2]. \tag{5.10}$$

If one substitutes these expressions in (5.5) and integrates over τ, then it holds

$$\Pi(\beta,\Omega) = \exp\{\sum_t f_{0t}\} \sum_{\substack{\mu_1\ldots\mu_N \\ \nu_1\ldots\nu_N}} \prod_t \sigma_t(\mu_t,\beta) g_{\nu_1}\ldots g_{\nu_N} \delta_\gamma(\Delta E_{nn'} - \Omega - \hbar\sum_{t=1}^{N}(\mu_t\omega_t^{n'} - \nu_t\omega_t^{n'})) \tag{5.11}$$

with the definition

$$\Delta E_{nn'} = \Delta U_{nn'} + \frac{\hbar}{2}\sum_t(\omega_t^n - \omega_t^{n'}). \tag{5.12}$$

$\Pi(\beta,\Omega)$ is a function of the quantities $d_{it}, \bar{d}_{it}$ $(i = 1, 2, 3)$ which themselves depend on the parameters $\varrho_t, \varrho_t', \delta_t, \bar{\varrho}_t, \bar{\varrho}_t', \bar{\delta}_t$.

To gain a better understanding of the meaning of these formulae we make some drastic assumptions

1. Complete degeneracy of the lattice vibrations $\omega_t^n = \omega^n = \omega_t^{n'}$ for all t. Then we have $A_t = B_t = 0$ and due to (5.10) $f_t = 0$ for $(i = 0, 1, 2, 3)$. Thus the phonon part can be written as follows

$$\Pi(\beta,\Omega) = \sum_\mu \sigma(\mu,\beta)\,\delta_\gamma(\Delta U_{nn'} - \Omega - \mu\hbar\omega^n) \tag{5.13}$$

with

$$\sigma(\mu,\beta) = \exp\left\{\frac{\exp\{-\beta\hbar\omega^n\}}{1-\exp\{-\beta\hbar\omega^n\}}\left(\sum_t d_{1t}d_{2t} + \sum_t \bar{d}_{1t}\bar{d}_{2t}\right) + \tfrac{1}{2}\sum_t(d_{3t} + \bar{d}_{3t})\right\}\sum_m \frac{a^{m+\mu}}{(m+\mu)!}\frac{b^m}{m!} \tag{5.14}$$

and

$$a = \frac{1}{1-\exp\{-\beta\hbar\omega^n\}}\sum_t d_{2t}\bar{d}_{2t}, \quad b = \frac{\exp\{-\beta\hbar\omega^n\}}{1-\exp\{-\beta\hbar\omega^n\}}\sum_t \bar{d}_{1t}\bar{d}_{1t} \tag{5.15}$$

2. Static electron lattice coupling. Then all parameters $\varrho_t, \varrho_t' \ldots$ can be put zero and we have

$$d_{1t} = \bar{d}_{1t} = -d_{2t} = -\bar{d}_{2t} = -\alpha_t, \quad d_{3t} = \bar{d}_{3t} = -\alpha_t^2. \tag{5.16}$$

An analysis shows, that the phonon part can be represented by a single function $\sigma^0(\mu,\beta)$, so that $\Pi(\beta,\Omega)$ now takes the form

$$\Pi^0(\beta,\Omega) = \sum_\mu \sigma^0(\mu,\beta)\,\delta_\gamma(\Delta U_{nn'} - \Omega - \mu\hbar\omega^n) \tag{5.17}$$

with

$$\sigma^0(\mu,\beta) = \exp\left\{-\frac{2\exp\{-\beta\hbar\omega^n\}}{1-\exp\{-\beta\hbar\omega^n\}}\alpha^2 - \alpha^2\right\}\sum_m \frac{a^{m+\mu}}{(m+\mu)!}\frac{b^m}{m!} \tag{5.18}$$

and

$$a = \frac{1}{1-\exp\{-\beta\hbar\omega^n\}}\alpha^2, \quad b = \frac{\exp\{-\beta\hbar\omega^n\}}{1-\exp\{-\beta\hbar\omega^n\}}\alpha^2, \tag{5.19}$$

and the shift of the equilibrium positions

$$\alpha^2 = \sum_t \alpha_t^2 \tag{5.20}$$

It is of interest to compare these results with literature. In the Franck-Condon approximation the transition probabilities studied in literature are defined by the golden rule expression [2, 25].

$$W_{nn'} = \frac{2\pi}{\hbar}\sum_{mm'} f_{m'}\,|\langle\varphi_m^n\chi_n|\,\hat{H}^s\,|\,\chi_{n'}\varphi_{m'}^{n'}\rangle|^2\,\delta(E_m^n - E_{m'}^{n'} - \hbar\omega) \tag{5.21}$$

with the Hamiltonian

$$\hat{H}^{s} = \frac{e}{mc} \boldsymbol{A}_0 e^{ikw}(-i\hbar\nabla). \tag{5.22}$$

It is possible to separate (5.21) into an electronic and a phonon part. For the electronic part one uses dipole approximation, eliminates the polarization vector ($\boldsymbol{A}_0 = n A_0$) and replaces the electronic momentum by the position operator equally done as in the preceeding sections. Thus from (5.21) follows

$$W_{nn'} = \frac{(2\pi)^2 \omega_\varkappa}{3V} |\langle \chi_n | e\boldsymbol{r} | \chi_{n'} \rangle|^2 \sum_{mm'} f_{m'} |\langle \varphi_m^n | \varphi_{m'}^{n'} \rangle|^2 \delta(E_m^n - E_{m'}^{n'} - \hbar\omega). \tag{5.23}$$

A similar expression can be obtained by (2.5) or by (2.18) if only the lowest order of $\hat{A}\binom{nn'}{\lambda\lambda'}$ is taken into account

$$W_{nn'}(\varkappa) = \frac{(2\pi)^2 \omega_\varkappa}{3V} |\langle \chi_n | \sum_i e\boldsymbol{r}_i | \chi_{n'} \rangle|^2 \sum_{mm'} f_{m'} |\langle \varphi_m^n | \varphi_{m'}^{n'} \rangle|^2 \delta_\gamma(E_m^n - E_{m'}^{n'} - \Omega). \tag{5.24}$$

Obviously (5.23), (5.24) are different in the factors δ resp. δ_γ. Hence if we treat these two terms we will not expect to get identical, but only similar results. As in this approximation the electron part degenerates to a simple factor, only the phonon parts are of interest. For thermal equilibrium of the lattice the phonon part of (5.24) in our calculation is given by (5.17).

Concerning the phonon part of (5.23) we follow the treatment of O'Rourke [25] and calculations by Stasiw [2] and Haug [3]. The crystal energies E_m^n are given by $U_n^n + \sum_t \hbar\omega_t^n (m_t + \frac{1}{2})$ and therefore for the δ-distribution the following representation is valid

$$\delta(E_m^n - E_{m'}^{n'} - \hbar\omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \exp\{i\tau(\omega_e - \omega)\} \prod_t \exp\{i\tau[\omega_t^n(m_t + \tfrac{1}{2}) - \omega_t^{n'}(m_t' + \tfrac{1}{2})]\} \mathrm{d}\tau \tag{5.25}$$

with $\omega_e = (U_n^n - U_{n'}^{n'})\hbar^{-1}$. Thus the phonon part of (5.23) reads

$$\sum_{mm'} f_{m'} |\langle \varphi_m^n | \varphi_{m'}^{n'} \rangle|^2 \delta(E_m^n - E_{m'}^{n'} - \hbar\omega) = \frac{1}{2\pi\hbar} \int \exp\{i\tau(\omega_e - \omega)\} \prod_t \Theta_t(\tau)\, \mathrm{d}\tau \tag{5.26}$$

with $\Theta_t = \sum_{m_t m_t'} \vartheta_t$ and

$$\vartheta_t = f_{m_t'} |\langle \varphi_{m_t}^n | \varphi_{m_t'}^{n'} \rangle|^2 \exp\{i\tau[\omega_t^n(m_t + \tfrac{1}{2}) - \omega_t^{n'}(m_t' + \tfrac{1}{2})]\}. \tag{5.27}$$

The equilibrium distributions $\{f_{m_t}\}$ can be expressed by

$$f_{m_t} = \exp\{-\beta\hbar\omega_t^n m_t\}(1 - \exp\{-\beta\hbar\omega_t^n\}) = 2\sinh(\tfrac{1}{2}\beta\hbar\omega_t^n) \exp\{-\beta\hbar\omega_t^n(m_t + \tfrac{1}{2})\}. \tag{5.28}$$

Substituting this expression into (5.27) we obtain

$$\Theta_t(\tau) = 2\sinh(\tfrac{1}{2}\beta\hbar\omega_t^{n'}) \sum_{m_t m_t'} |\langle \varphi_{m_t}^n | \varphi_{m_t'}^{n'} \rangle|^2 \exp\{i\tau\omega_t^n(m_t + \tfrac{1}{2}) - (i\tau + \beta\hbar)\omega_t^{n'}(m_t' + \tfrac{1}{2})\}. \tag{5.29}$$

To evaluate (5.29) we explicitly formulate the scalar products of the oscillator functions in coordinate space employing their representation by Hermite polynomials. This gives by interchanging summation and integration [2, 3]

$$\begin{aligned}\Theta_t(\tau) = {} & 2\sinh(\tfrac{1}{2}\beta\hbar\omega_t^{n'}) \int\int \mathrm{d}q_t^n\, \mathrm{d}\overline{q_t^n}\, (\omega_t^n\, \omega_t^{n'})^{1/2} M\hbar^{-1} \\ & \cdot \sum_{m_t'} \frac{\exp\{-\zeta_t(m_t' + \tfrac{1}{2})\}}{2^{m_t'} m_t'!\, \pi^{1/2}} \mathscr{H}_{m_t'}(\alpha_t^{n'} q_t^{n'}) \mathscr{H}_{m_t'}(\alpha_t^{n'} \overline{q_t^{n'}}) \exp\{-\tfrac{1}{2}\alpha_t^{n'^2}(q_t^{n'^2} + \overline{q_t^{n'^2}})\} \\ & \cdot \sum_{m_t} \frac{\exp\{-\xi_t(m_t + \tfrac{1}{2})\}}{2^{m_t} m_t!\, \pi^{1/2}} \mathscr{H}_{m_t}(\alpha_t^n q_t^n) \mathscr{H}_{m_t}(\alpha_t^n \overline{q_t^n}) \exp\{-\tfrac{1}{2}\alpha_t^{n^2}(q_t^{n^2} + \overline{q_t^{n^2}})\}. \end{aligned} \tag{5.30}$$

With $\xi_t = -i\omega_t^n \tau$ and $\zeta_t = i\omega_t^{n'}\tau + \beta\hbar\omega_t^{n'}$, the sums over m and m' can be evaluated by means of Mehler's formula cf. [2, 3]. For the subsequent integration $q_t^n = q_t^{n'} - a_t$ has to be used. Finally from (5.30) the formula

$$\Theta_t(\tau) = \eta_t(\tau) \exp\left\{-a_t^2 \frac{M}{\hbar}\left[(\omega_t^{n'})^{-1} \coth\frac{\zeta_t}{2} + (\omega_t^n)^{-1}\coth\frac{\xi_t}{2}\right]^{-1}\right\} \tag{5.31}$$

results with

$$\eta_t = 2\sinh(\tfrac{1}{2}\beta\hbar\omega_t^{n'})\left[\frac{\sinh\zeta_t \sinh\xi_t}{\omega_t^{n'}\omega_t^n}\left(\omega_t^{n'}\operatorname{tgh}\frac{\zeta_t}{2} + \omega_t^n \operatorname{tgh}\frac{\xi_t}{2}\right)\left(\omega_t^{n'}\coth\frac{\zeta_t}{2} + \omega_t^n\coth\frac{\xi_t}{2}\right)\right]^{-1/2}. \tag{5.32}$$

For comparison with (5.17) we neglect the dependence of the frequencies from the electronic state $\omega_t^n = \omega_t^{n'} = \omega^n$ for all t and n, n'. Then (5.32) takes the value $\eta_t = 1$ and the product of the $\Theta_t(\tau)$ in (5.26) becomes

$$\prod_t \Theta_t(\tau) = \exp\left\{\frac{\omega^n M}{\hbar}\sum_t -a_t^2\left(\coth\frac{\zeta_t}{2} + \coth\frac{\xi_t}{2}\right)^{-1}\right\}. \tag{5.33}$$

On the other hand under these suppositions the expression (5.17) can be written

$$\Pi^\circ(\beta, \Omega) = \int \exp\{i\tau(\Delta U_{nn'} - \Omega)\}\exp\{-\gamma|\tau|\}\sum_\mu \sigma^0(\mu,\beta)\exp\{-i\tau\mu\hbar\omega^n\}\,\mathrm{d}\tau \tag{5.34}$$

if the δ_γ function is represented by a Fourier integral. For vanishing γ the phonon parts on the right-hand side of (5.23), (5.24) are equal. From this follows with (5.34) and (5.26) that the correspondence

$$\sum_\mu \sigma^0(\mu,\beta)\exp\{-i\tau\mu\hbar\omega^n\} \leftrightarrow \prod_t \Theta_t(\tau) \tag{5.35}$$

must hold. We do not formulate this relation, as an equation a priori, as the left-hand side results from a quite different formalism than the right-hand side and the equality has to be demonstrated a posteriori. Using the definition of σ^0 (μ, β) (5.18) we may represent the left-hand side of (5.35) by an exponential expression

$$\sum_\mu \sigma^0(\mu,\beta)\exp\{-i\tau\mu\hbar\omega^n\} \tag{5.36}$$
$$= \exp\left\{\frac{\omega^n}{2\hbar}\sum_t a_t^{nn'^2}\left[-\frac{2\exp\{-\beta\hbar\omega^n\}}{1-\exp\{-\beta\hbar\omega^n\}} + \frac{\exp\{-\beta\hbar\omega^n\}\exp\{i\tau\hbar\omega^n\}}{1-\exp\{-\beta\hbar\omega^n\}} + \frac{\exp\{-i\tau\hbar\omega^n\}}{1-\exp\{-\beta\hbar\omega^n\}} - 1\right]\right\}.$$

If the hyperbolic functions in (5.33) are also expressed by exponentials one gets

$$\prod_t \Theta_t(\tau) \tag{5.37}$$
$$= \exp\left\{\frac{\omega^n M}{2\hbar}\sum_t a_t^2\left[-\frac{2\exp\{-\beta\hbar\omega^n\}}{1-\exp\{-\beta\hbar\omega^n\}} + \frac{\exp\{-\beta\hbar\omega^n\}\exp\{-i\tau\omega^n\}}{1-\exp\{-\beta\hbar\omega^n\}} + \frac{\exp\{i\tau\omega^n\}}{1-\exp\{-\beta\hbar\omega^n\}} - 1\right]\right\}.$$

Both expressions are equal except for the opposite sign of τ and the factor M. The opposite sign results from a different formulation of energy conservation. This is only a convention which can easily be corrected. The factor M results from a different formulation of normalization which can also easily be corrected. So we have demonstrated that the lowest approximation of the formalism of generating functionals leads to the same result as the conventional evaluation of the static phonon part.

Appendix A

Definitions of L_1, L_3, M_1, M_2, M_3, N, C, D.

$$L_{1t} = (1-\varkappa_t)^{-1} X_t^{-1/2},$$

$$L_{3t} = \varkappa_t(1-\varkappa_t)^{-1} X_t^{1/2},$$

$$M_{1t} = \varkappa_t(1-\varkappa_t)^{-1} d_{1t} + (1-\varkappa_t)^{-1}\bar{d}_{2t} X_t^{-1},$$

$$M_{2t} = \varkappa_t(1-\varkappa_t)^{-1}\bar{d}_{1t} X_t^{1/2} + (1-\varkappa_t)^{-1} d_{2t} X_t^{-1/2},$$

$$M_{3t} = \varkappa_t(1-\varkappa_t)^{-1} d_{1t} X_t + (1-\varkappa_t)^{-1} \bar{d}_{2t},$$

$$N_t = \varkappa_t(1-\varkappa_t)^{-1}[d_{1t} d_{2t} + d_{1t} \bar{d}_{1t} X_t + \bar{d}_{1t} \bar{d}_{2t}] + (1-\varkappa_t)^{-1} \cdot d_{2t} \bar{d}_{2t} X_t^{-1} + \tfrac{1}{2}(d_{3t} + \bar{d}_{3t}),$$

$$C_t = A_t(1-\varkappa_t)^{-2}(\varkappa_t^2 X_t - X_t^{-1}) = -A_t L_{1t}^2 + A_t L_{3t}^2,$$

$$D_t = 2A_t(1-\varkappa_t)^{-2}(\varkappa_t X_t - X_t^{-1}) \cdot (\varkappa_t d_{1t} X_t^{1/2} + \bar{d}_{2t} X_t^{-1/2}) + (1-\varkappa_t)^{-1}(\varkappa_t \bar{d}_{1t} X_t^{1/2} + d_{2t} X_t^{-1/2} = -2A_t M_{1t} L_{1t} + 2A_t L_{3t} + M_{2t}.$$

$$X_t = \exp\{i\tau\hbar\omega_t n'\}$$

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