

Application of the Method of Generating Function to Radiative and Non-Radiative Transitions of a Trapped Electron in a Crystal

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Using the method of generating function, we have discussed the shape of the absorption band and the probability for non-radiative transition of a trapped electron in insulating or semiconducting crystal, especially their temperature dependence. We have thereby chosen a model for the vibrational motion of the lattice as general as possible, the normal modes for any two electronic states being different as regards not only their equilibrium positions but also the principal axes and frequencies. For non-radiative transition, we have derived, in comparatively general cases, the high and low temperature behaviors of the probability which correspond to the process through activated states and the tunneling of the lattice co-ordinates, respectively. The result is applied to calculations of the probability for thermal ionization of trapped electrons (or holes) and the capture cross-section of impurities for free electrons (or holes) in non-polar semiconductors. Further, the high temperature expansion of a density matrix is used to discuss the transitions on a most general model in which lattice vibration is no longer of harmonic type. Two problems related to the degeneracy of electronic states are discussed briefly.

§ 1. Introduction

The temperature dependence of an absorption band due to a trapped electron in insulating or semiconducting crystal has been studied by a number of authors. The simplest but most essential explanation of the broadening effect is found in the text-book of Mott and Gurney,¹⁾ where they take a one-dimensional model for the lattice configuration space to discuss the breadth of the F -absorption band. More general discussion has been given by Muto²⁾ on a quantum mechanical basis. Inui and Uemura,³⁾ with one dimensional model, explained the shift of the F -absorption peak by the thermal expansion of the lattice, taking advantage of Ivey's empirical law. Quantum mechanical calculation of adiabatic potentials was first carried out by Williams⁴⁾ for KCl : Tl crystal, with one dimensional model. Huang and Rhys⁵⁾ discussed the shape of the F -absorption band and the thermal ionization probability of the F -electron, taking into account all the longitudinal waves of optical modes of vibration which interact strongly with the electron. Their mathematical technique, though very ingenious in itself, is confined to a single frequency model, and can hardly be generalized to a many-frequency model which involves, for instance, the acoustical modes.

Under these circumstances it is very desirable to have a mathematical tool which enables one to discuss radiative and non-radiative transitions on a general model of lattice vibration. One of the present authors⁶⁾ developed the method of generating function several years ago,

and an example of its application to the thermal ionization of a trapped electron was already reported. Independently Lax⁷⁾ also found essentially the same technique, applied it to the discussion of Franck-Condon principle in optical absorption and also compared the result with that of Huang and Rhys.

In the present paper, we apply the method of generating function to the discussion of radiative and non-radiative transitions of a trapped electron from a unified point of view, the model for the lattice vibrational motion being taken as general as possible; at the same time, we have aimed at obtaining conclusions which are directly applicable to actual crystals and serve in analysing experimental data.

§ 2. Summary of the method of generating function

Though the essential framework of the method of generating function has been given in a previous paper,⁶⁾ we shall summarize it here in such a way as is convenient for the treatment which we present in later sections.

As is well known, an electron trapped at some crystal imperfection, which may be an impurity atom, an interstitial ion, or a vacant lattice site, causes one or more absorption bands in the otherwise transparent region of wave-length. The remarkable temperature dependence of the shape of the absorption band is due to the electron-lattice interaction, which is also responsible for the thermal excitation or ionization of the electron. Denoting the co-ordinates of the electron and the lattice by r and Q , respectively, we can write down the Hamiltonian of the system as

$$H(r, Q) = H_e(r) + H_L(Q) + H_I(r, Q), \quad (2.1)$$

where H_e , H_L and H_I mean the energy of the electron, that of the lattice vibration and the interaction between them, respectively. If the electron is in a discrete bound state of the imperfection, we can utilize the adiabatic approximation: that is, by solving

$$\{H_e(r) + H_I(r, Q)\} \varphi_i(r, Q) = W_i(Q) \varphi_i(r, Q), \quad (2.2)$$

$$\{H_L(Q) + W_i(Q)\} \zeta_{lv}(Q) \equiv H_{[l] \zeta_{lv}} = E_{lv \zeta_{lv}}(Q), \quad (2.3)$$

we can write the wave function of the total system in the form:

$$\Psi_{lv}(r, Q) = \varphi_i(r, Q) \zeta_{lv}(Q), \quad (2.4)$$

where l and v are used to specify the electronic and vibrational states, respectively. Strictly speaking, this wave function does not correspond to a stationary state, because, due to the Q -dependence of the electronic wave function φ_i , the quantity defined by

$$\{H - E_{lv}\} \Psi_{lv} = H' \Psi_{lv} = H_L(\varphi_i \zeta_{lv}) - \varphi_i(H_L \zeta_{lv}) \quad (2.5)$$

does not vanish identically, which fact is nothing but the limitation of the applicability of the adiabatic approximation.

When there comes an incident light of appropriate frequency ν , the electron in the ground state l' can undergo optical transition to some higher electronic state l'' . If there are N_i such impurity electrons per unit volume, the optical absorption constant of the

crystal for this frequency is given by

$$k(\nu) = (8\pi^3 N_i / 3nc) \nu F_M(h\nu), \quad (2.6)$$

$$F_M(h\nu) = F_M(E) = 1/\Delta E \sum_{v'} \sum_{v''}^{E < E_f - E_i < E + \Delta E} |(f|\mathbf{M}|i)|^2 w_i, \quad (2.7)$$

where c and n mean the light velocity in vacuum and index of refraction, $\mathbf{M} = e\mathbf{r}$ denotes the dipole moment operator of the electron, and $i = (l', v')$ and $f = (l'', v'')$ specify corresponding to the initial and final states respectively the electronic and vibrational quantum numbers. w_i means the probability that the system is initially in the v' -th vibrational state. The intensity distribution of the emitted light by the electron can be written in a similar way as the above expression.

The system, however, can undergo transition to another electronic state l'' without external perturbation, owing to the non-stationariness of the state Ψ_{lv} . The probability for this process which one may call non-radiative transition or thermal transition is given by the formula

$$W = 2\pi/\hbar F_{H'}(0), \quad (2.8)$$

$$F_{H'}(E) = 1/\Delta E \sum_{v'} \sum_{v''}^{E < E_f - E_i < E + \Delta E} |(f|H'|i)|^2 w_i, \quad (2.9)$$

the non-adiabatic Hamiltonian H' defined by (2.5) playing the rôle of perturbation in this case.

The central problem common to the above two cases is to carry out the double summation

$$F_T(E) = 1/\Delta E \sum_{v'} \sum_{v''}^{E < E_f - E_i < E + \Delta E} |(f|T|i)|^2 w_i \quad (2.10)$$

for an operator T . For a very special case where all the modes of lattice vibration in both of the electronic states have a common single frequency ω , Huang and Rhys⁵⁾ worked out the above summation with the use of an ingenious technique, which, however, is not applicable for more general cases important in practical problems. It is more convenient to calculate the Laplace transform

$$f_T(\lambda) = \int_{-\infty}^{\infty} F_T(E) \exp(-\lambda E) dE \quad (2.11)$$

instead of $F_T(E)$ itself for the following reason. Denoting the density matrix for the vibrational motion in the l -th electronic state by

$$\rho_l(\lambda) = \exp(-\lambda H_{[l]}) = \sum_v \exp(-\lambda E_{lv}) P[\zeta_{lv}], \quad (2.12)$$

where $P[\zeta_{lv}]$ means the projection operator to the state ζ_{lv} , and using the initial distribution of the system over the various vibrational states:

$$w_i = w_{lv} = \exp(-\beta E_{lv}) / \text{trace } \rho_l(\beta), \quad \beta = 1/kT, \quad (2.13)$$

we can easily see that

$$\begin{aligned}
f_T(\lambda) &= \sum_{v'} \sum_{v''} | \langle f | T | i \rangle |^2 e^{-\beta E_{i'v'}} e^{-\lambda(E_{i''v''} - E_{i'v'})} / \text{trace } \rho_{vv'}(\beta) \\
&= \sum_{v'} \sum_{v''} \langle l'v' | T | l''v'' \rangle e^{-\lambda E_{i''v''}} \langle l'v' | T | l'v' \rangle e^{-(\beta - \lambda) E_{i'v'}} / \text{trace } \rho_{vv'}(\beta) \\
&= \text{trace} \{ T_{vv''} \rho_{v''}(\lambda) T_{v''v'} \rho_{v'}(\beta - \lambda) \} / \text{trace } \rho_{vv'}(\beta),
\end{aligned} \tag{2.14}$$

which no more contains intractable summation as is prescribed in the expression (2.10). The matrix element

$$T_{vv''} = \langle \varphi_{v''}^* (r, Q) | T | \varphi_v (r, Q) \rangle = T_{v''v}^* \tag{2.15}$$

is still an operator as regards the vibrational motion. Once the generating function $f_T(\lambda)$ is calculated, one can easily go back to the original distribution function by utilizing the inverse formula⁸⁾ for the Laplace transformation :

$$F_T(E) = 1/2\pi i \int_{-i\infty}^{+i\infty} f_T(\lambda) \exp(\lambda E) d\lambda, \tag{2.16}$$

where integration should be carried out inside the convergence region of (2.11).

Instead of the distribution $F_T(E)$ itself, it is often more convenient, especially in case of optical absorption, to calculate the moments of it. If we expand $f_T(\lambda)$ in a power series :

$$f_T(\lambda) = f_T(0) \left\{ 1 + \sum_{n=1}^{\infty} \mu_n (-\lambda)^n / n! \right\}, \tag{2.17}$$

the n -th coefficient μ_n is nothing but the n -th moment of $F_T(E)$:

$$\mu_n = \overline{E^n} = \int_{-\infty}^{+\infty} E^n F_T(E) dE / \int_{-\infty}^{+\infty} F_T(E) dE, \tag{2.18}$$

$$f_T(0) = \int_{-\infty}^{+\infty} F_T(E) dE, \tag{2.19}$$

as is evident from the equation (2.11). If we expand the logarithm of $f_T(\lambda)$ as

$$f_T(\lambda) = f_T(0) \exp \left[\sum_{n=1}^{\infty} A_n (-\lambda)^n / n! \right], \tag{2.20}$$

the coefficients are semi-invariants of $F_T(E)$, which are related to the moments by

$$\begin{aligned}
A_1 &= \mu_1 = E, \\
A_2 &= \mu_2 - \mu_1^2 = \overline{(E - E)^2}, \\
A_3 &= \mu_3 - 3\mu_2\mu_1 + 2\mu_1^3 = \overline{(E - E)^3}.
\end{aligned} \tag{2.21}$$

§ 3. An assemblage of harmonic oscillators as a model for vibrational motion

The Hamiltonian for the lattice vibration (2.3) consists of kinetic part K_L and potential part U_i

$$H_L(Q) + W_\nu(Q) = K_L + U_i, \tag{3.1}$$

Let us choose lattice co-ordinates Q_j ($j=1, 2, \dots, N$) in such a way that K_L takes a unit quadratic form :

$$K_L = 1/2 \cdot \sum_{j=1}^N P_j^2, \quad (3.2)$$

The potential energy U_ν for the ground state can be expanded in a Taylor series around the minimum point $(Q_1', Q_2', \dots, Q_N')$. If we take a quadratic approximation (harmonic oscillator model), we can write

$$U_\nu(Q) = 1/2 \sum_j \sum_k (\mathcal{Q}^{l/2})_{jk} (Q_j - Q_j') (Q_k - Q_k'). \quad (3.3)$$

which can be brought into a diagonal form

$$U_\nu = 1/2 \sum_i \omega_i'^2 (q_i - q_i')^2. \quad (3.3')$$

The direction of principal axes, as well as the characteristic frequencies ω_i' and the minimum point $(Q_1', Q_2', \dots, Q_N')$ are different for each of the electronic states. Consequently we take the form (3.3) rather than (3.3'), or its tensor expression

$$U_\nu = 1/2 (\mathbf{Q} - \mathbf{Q}') \mathcal{Q}^{l/2} (\mathbf{Q} - \mathbf{Q}'), \quad (3.4)$$

where \mathcal{Q}' and \mathbf{Q} are N -dimensional tensor and vector, respectively. The adiabatic potential for an excited electronic state l'' , the minimum of which is higher than that of the ground state l' by ε_0 , can be written as

$$U_{l''} = 1/2 (\mathbf{Q} - \mathbf{Q}'') \mathcal{Q}^{l/2} (\mathbf{Q} - \mathbf{Q}'') + \varepsilon_0. \quad (3.4')$$

Making use of the well-known formula⁹⁾ for the density matrix of a one dimensional harmonic oscillator with unit mass and frequency ω :

$$\begin{aligned} \langle q | \rho(\lambda) | \bar{q} \rangle &= \{2\pi\hbar \sinh(\beta\hbar\omega)/\omega\}^{-1/2} \\ &\times \exp \left[-(\omega/4\hbar) \tanh(\beta\hbar\omega/2) (q + \bar{q})^2 - (\omega/4\hbar) \coth(\beta\hbar\omega/2) (q - \bar{q})^2 \right], \end{aligned} \quad (3.5)$$

we have only to take the product of these expressions for all normal modes $(q_i - q_i')$ of (3.3') in order to obtain the density matrix for the multidimensional harmonic oscillator, which again can conveniently be written in a tensor expression :

$$\begin{aligned} \langle \mathbf{Q} | \rho'(\beta - \lambda) | \bar{\mathbf{Q}} \rangle &= [\det(2\pi\hbar \mathcal{Q}'^{-1} \sinh\{(\beta - \lambda)\hbar \mathcal{Q}'\})]^{-1/2} \\ &\times \exp \left[-1/4 (\mathbf{Q} + \bar{\mathbf{Q}} - 2\mathbf{Q}') \{\hbar^{-1} \mathcal{Q}' \tanh((\beta - \lambda)/2 \cdot \hbar \mathcal{Q}')\} (\mathbf{Q} + \bar{\mathbf{Q}} - 2\mathbf{Q}') \right. \\ &\quad \left. - 1/4 (\mathbf{Q} - \bar{\mathbf{Q}}) \{\hbar^{-1} \mathcal{Q}' \coth((\beta - \lambda)/2 \cdot \hbar \mathcal{Q}')\} (\mathbf{Q} - \bar{\mathbf{Q}}) \right]. \end{aligned} \quad (3.6)$$

The corresponding one for the excited state l'' is obtained by replacing $\beta - \lambda$, \mathcal{Q}' and \mathbf{Q}' with λ , \mathcal{Q}'' and \mathbf{Q}'' , respectively, and by multiplying a factor $\exp(-\lambda\varepsilon_0)$.

The operator $T_{\nu l''}$ for the optical absorption is the dipole moment :

$$T_{\nu l''}(\text{opt.}) = \mathbf{M}(Q) = \int \varphi_{\nu l'}^*(r, Q) \mathbf{e} r \varphi_{\nu l''}(r, Q) dr. \quad (3.7)$$

Let us define the Fourier transform of $M(Q)$ by

$$M(Q) = \int \exp(i\mathbf{K} \cdot \mathbf{Q}) M_{\mathbf{K}} d\mathbf{K}. \quad (3.8)$$

For the thermal transition we have

$$\begin{aligned} T_{\nu\nu'}(\text{therm.}) &= H'_{\nu\nu'} = \int \varphi_{\nu'}^* \sum \{P_j \varphi_{\nu} P_j + 1/2 (P_j^2 \varphi_{\nu})\} dr \\ &= \hbar^{-1} \mathbf{S}(Q) \cdot \mathbf{P} + \mathcal{S}(Q), \end{aligned} \quad (3.9)$$

as is evident from (2.5), (3.1) and (3.2). Neglecting the second term and the Q -dependence of \mathbf{S} , we have

$$H_{\nu\nu'}' = \hbar^{-1} \mathbf{S} \cdot \mathbf{P} = -i\mathbf{S} \cdot \partial / \partial \mathbf{Q} \quad (3.9')$$

which is Hermitian. We have defined the N -dimensional vector \mathbf{S} by

$$S_j = -i\hbar^2 \int \varphi_{\nu'}^* \partial / \partial Q_j \varphi_{\nu} dr. \quad (3.10)$$

Putting (3.6), (3.8) and (3.9') into (2.14) and carrying out $2N$ dimensional integration over the variables \mathbf{Q} and $\bar{\mathbf{Q}}$, we get the generating functions for the optical and thermal transitions :

$$f_M(\lambda) = f_0(\lambda) g_M(\lambda), \quad (3.11)$$

$$f_H(\lambda) = f_0(\lambda) g_H(\lambda), \quad (3.12)$$

where the common factor $f_0(\lambda)$ is defined by

$$f_0(\lambda) = f_{\Delta}(\lambda) f_{\Gamma}(\lambda) \exp(-\lambda \mathcal{E}_0), \quad (3.13)$$

$$f_{\Delta}(\lambda) = \exp[-\Delta \theta_1' (\theta_1' + \theta_1'')^{-1} \theta_1'' \Delta], \quad (3.14)$$

$$f_{\Gamma}(\lambda) = \{\det \Phi\}^{-1/2} = \exp[-1/2 \text{ trace}(\log \Phi)], \quad (3.15)$$

and the other factors are given by

$$\begin{aligned} g_M(\lambda) &= \int d\mathbf{K} d\bar{\mathbf{K}} M_{\bar{\mathbf{K}}}^* M_{\mathbf{K}} \exp[i(\mathbf{K} - \bar{\mathbf{K}}) \cdot \{\Delta_+ - 1/2 (\theta_1' + \theta_1'')^{-1} (\theta_1' - \theta_1'') \Delta\} \\ &\quad - 1/4 (\mathbf{K} - \bar{\mathbf{K}}) (\theta_1' + \theta_1'')^{-1} (\mathbf{K} - \bar{\mathbf{K}}) - 1/4 (\mathbf{K} + \bar{\mathbf{K}}) (\theta_2' + \theta_2'')^{-1} (\mathbf{K} + \bar{\mathbf{K}})] \end{aligned} \quad (3.16)$$

$$\begin{aligned} g_H(\lambda) &= |\mathbf{S} \theta_1' (\theta_1' + \theta_1'')^{-1} \theta_1'' \Delta|^2 + 1/2 \cdot \mathbf{S}^* \{ \theta_2' (\theta_2' + \theta_2'')^{-1} \theta_2'' \\ &\quad - \theta_1' (\theta_1' + \theta_1'')^{-1} \theta_1'' \} \mathbf{S} \end{aligned} \quad (3.17)$$

In the above expressions we have used the following abbreviations :

$$\begin{aligned} \theta_1' &= (1/\hbar) \mathcal{Q}' \tanh \{(\beta - \lambda) \hbar \mathcal{Q}' / 2\}, \quad \theta_1'' = (1/\hbar) \mathcal{Q}'' \tanh (\lambda \hbar \mathcal{Q}'' / 2), \\ \theta_2' &= (1/\hbar) \mathcal{Q}' \coth \{(\beta - \lambda) \hbar \mathcal{Q}' / 2\}, \quad \theta_2'' = (1/\hbar) \mathcal{Q}'' \coth (\lambda \hbar \mathcal{Q}'' / 2), \end{aligned} \quad (3.18)$$

$$\Delta = \mathbf{Q}'' - \mathbf{Q}', \quad \Delta_+ = 1/2 (\mathbf{Q}' + \mathbf{Q}'') \quad (3.19)$$

$$\begin{aligned} \Phi &= \{2 \sinh ((\beta/2) \hbar \mathcal{Q}')\}^{-2} \mathcal{Q}'^{-1} \sinh \{(\beta - \lambda) \hbar \mathcal{Q}'\} \hbar^2 (\theta_1' + \theta_1'') (\theta_2' + \theta_2'') \\ &\quad \times \mathcal{Q}''^{-1} \sinh (\lambda \hbar \mathcal{Q}''). \end{aligned} \quad (3.20)$$

For the above expressions we must note the following: (1) When one takes $M(Q)$ to be constant, $g_M(\lambda)$ reduces to a constant. (2) If the difference of the frequency tensors

$$Q'^2 - Q^2 = \Gamma \quad (3 \cdot 21)$$

is equal to zero, $f_\Gamma(\lambda)$ turns out to be unity. (3) $\Delta = 0$ evidently results in $f_\Delta = 1$. When these conditions are not fulfilled, each of the original distribution functions $G_M(E)$, $F_\Gamma(E)$ and $F_\Delta(E)$ which are obtained from the corresponding generating functions $g_M(\lambda)$, $f_\Gamma(\lambda)$ and $f_\Delta(\lambda)$, has some broadening instead of reducing to a sharp line. These broadenings contribute to that of the optical absorption band in such a manner as is suggested by the convolution theorem⁸⁾. Thus we can consider g_M , f_Γ and f_Δ as the generating functions which correspond to the broadenings due to the Q -dependence of dipole moment, the difference in vibrational frequencies and the difference in equilibrium lattice positions, respectively.

§ 4. Linear approximation of the interaction

As is well known, the Hamiltonian for the electron-lattice system with an imperfection giving a potential $V(\mathbf{r})$ for the electron, in case of ionic crystals, can be written down¹⁰⁾⁵⁾ as

$$\begin{aligned} H = & -\hbar^2/2m^* \cdot \Delta + V(\mathbf{r}) + 1/2 \sum_{\sigma} \sum_{\mu=1,2} (P_{\sigma\mu}^2 + \omega^2 Q_{\sigma\mu}^2) \\ & - \frac{1}{\sqrt{N}} 4\pi e \omega \left[\frac{1}{2\pi v_0} \left(\frac{1}{\kappa_0} - \frac{1}{\kappa} \right) \right]^{1/2} \sum_{\sigma}' 1/\sigma \{ Q_{\sigma,1} \sin(\sigma \cdot \mathbf{r}) + Q_{\sigma,2} \cos(\sigma \cdot \mathbf{r}) \} \end{aligned} \quad (4 \cdot 1)$$

where κ and κ_0 are the static and high frequency dielectric constants, $\omega/2\pi$ the frequency, assumed to be constant, of the optical longitudinal vibrations, σ the wave number vector, v_0 the volume of a unit cell, and N the total number of unit cells. \sum' means that the summation should be carried out over a half of the σ -space, for instance $\sigma_z \geq 0$.

For non-polar crystals the corresponding Hamiltonian is given by

$$\begin{aligned} H = & -\frac{\hbar^2}{2m^*} \Delta + V(\mathbf{r}) + \frac{1}{2} \sum_{\sigma}' \sum_{\mu=1,2} (P_{\sigma\mu}^2 + \omega_{\sigma}^2 Q_{\sigma\mu}^2) \\ & - \frac{1}{\sqrt{N}} \frac{2\sqrt{2}}{3} \frac{C}{\sqrt{M}} \sum_{\sigma}' \sigma \{ Q_{\sigma,1} \sin(\sigma \cdot \mathbf{r}) + Q_{\sigma,2} \cos(\sigma \cdot \mathbf{r}) \}, \end{aligned} \quad (4 \cdot 2)$$

where M is the mass of each atom, and the interaction constant C with dimension of energy can be determined from the mobility data.¹¹⁾¹²⁾ Since the lattice vibrations to be considered here is the longitudinal acoustical modes, ω_{σ} is no longer constant but is related with σ by

$$\omega_{\sigma} = c\sigma, \quad (4 \cdot 3)$$

where c means the longitudinal sound velocity.

The above Hamiltonians are based on somewhat idealized model: in fact the normal

modes of lattice vibrations are more or less distorted near the imperfection and it is even possible that some of them are localized in its neighbourhood, and interact with the trapped electron more strongly than the other modes. Denoting the normal co-ordinate (whether it may be localized or extends over the crystal) by Q_j , when there is no electron, and expanding the interaction $H_I(r, Q)$ to the first order in Q_j 's, we have

$$H_L = 1/2 \sum_j (P_j^2 + \omega_j^2 Q_j^2), \quad (4.4)$$

$$H_I = - \sum_j u_j(r) Q_j^*, \quad (4.5)$$

the zero-th term of H_I being removed into H_0 . This linear approximation of H_I includes (4.1) and (4.2) as special cases.

Let us solve the equation (2.2) with H_I given by (4.5) as perturbation. If we define

$$u_{jll'} = \int \varphi_l^{(0)*} u_j(r) \varphi_{l'}^{(0)} dr \quad (4.6)$$

where $\varphi_l^{(0)}$ is the l -th electronic state of the non-perturbed system with energy $\varepsilon_l^{(0)}$, the wave function for the perturbed system can be written as

$$\varphi_i(r, Q) = \varphi_i^{(0)}(r) + \sum_j \sum_{l'} u_{jll'} \varphi_{l'}^{(0)}(r) Q_j / (\varepsilon_i^{(0)} - \varepsilon_{l'}^{(0)}) \quad (4.7)$$

and the adiabatic potential in (2.3) is given by

$$U_i(Q) = \varepsilon_i^{(0)} + 1/2 \sum_j \omega_j^2 Q_j^2 - \sum_j u_{j, i} Q_j + \sum_j \sum_{l'} (\sum_{l''} u_{jll''} u_{jll''} / (\varepsilon_i^{(0)} - \varepsilon_{l''}^{(0)})) Q_j Q_{j'}. \quad (4.8)$$

If we neglect the last term, we have

$$U_i(Q) = \varepsilon_i + 1/2 \sum_j \omega_j^2 (Q_j - Q_j^0)^2, \quad (4.9)$$

$$\varepsilon_i = \varepsilon_i^{(0)} - \sum_j (u_{j, i}^2 / 2\omega_j^2), \quad (4.10)$$

$$Q_j^0 = u_{j, i} / \omega_j^2, \quad (4.11)$$

the last quantity denoting the displacement of equilibrium lattice position from that position when the electron is not trapped. Taking account of the last term in (4.8) causes the change in frequency tensor. This may give rise to some localized modes of lattice vibration even if one starts from the plane wave approximation as in (4.1).

When we compare two electronic states l' and l'' as regards the equilibrium positions and vibrational frequencies, we have

$$A_j = (u_{jll''} - u_{jll'}) / \omega_j^2, \quad (4.12)$$

$$\text{trace } \Gamma = 2 \sum_j \{ \sum_{l'} |u_{jll'}|^2 / (\varepsilon_{l'}^{(0)} - \varepsilon_l^{(0)}) - \sum_{l'} |u_{jll'}|^2 / (\varepsilon_{l'}^{(0)} - \varepsilon_l^{(0)}) \}. \quad (4.13)$$

* Although the neglect of terms quadratic in Q_j 's is not satisfactory when one discusses the higher order terms in u_j as in § 5, there seems to be no reliable way of estimating the order of magnitude of their coefficients at present.

The transition dipole moment between these states is expanded as

$$M(Q) = M_{\nu'\nu}^{(0)} + \sum_j \sum_{l(\neq \nu', \nu)} \left(\frac{u_{j\nu'l}}{\varepsilon_{\nu'}^{(0)} - \varepsilon_l^{(0)}} M_{\nu'l}^{(0)} + \frac{u_{j\nu'\nu}}{\varepsilon_{\nu'}^{(0)} - \varepsilon_l^{(0)}} M_{\nu'\nu}^{(0)} \right) Q_j, \quad (4 \cdot 14)$$

and for the non-radiative transition we have

$$S_j = -i\hbar^2 u_{j\nu'\nu} / (\varepsilon_{\nu'}^{(0)} - \varepsilon_{\nu'}^{(0)}). \quad (4 \cdot 15)$$

§ 5. The shape of an optical absorption band

We discuss here the shape of an optical absorption band by making use of the generating function $f_M(\lambda)$ obtained in § 3. We begin with the most simple and important case.

(i) $\Delta \neq 0$, $\Omega' = \Omega''$, $M(Q) = \text{const.}$ This approximation, which takes into account only the difference in equilibrium position, corresponds to the first order perturbation, that is, the energy is approximated to the first order, and the wave function to the zero-th order. Inserting (3·18) we have

$$\begin{aligned} f_M(\lambda) &= M^* M \exp(-\lambda \varepsilon_0) \exp\{-\Delta \theta_1' (\theta_1' + \theta_1'')^{-1} \theta_1'' \Delta\} \\ &= M^* M \exp[-\lambda \varepsilon_0 - 1/2\hbar \cdot \Delta \Omega' \{\sinh(\lambda \hbar \Omega') + \coth(\beta \hbar \Omega'/2) (1 - \cosh \lambda \hbar \Omega')\} \Delta] \end{aligned} \quad (5 \cdot 1)$$

from which we can calculate the semi-invariants:

$$\begin{aligned} A_1 &= \varepsilon_0 + (1/2) \Delta \Omega'^2 \Delta = \bar{E}, \\ A_n &= (\hbar^{n-1}/2) \Delta \Omega'^{n+1} \Delta, \quad (n: \text{odd}, > 1) \\ A_n &= (\hbar^{n-1}/2) \Delta \Omega'^{n+1} \coth(\beta \hbar \Omega'/2) \Delta. \quad (n: \text{even}) \end{aligned} \quad (5 \cdot 2)$$

For the special case where there is only one frequency ω ($\Omega' = \omega I$), we can calculate explicitly the inverse transform (2·16) of the generating function (5·1), leading to Huang's formula⁵⁾ as was already shown by Lax.⁷⁾ Even when the frequencies distribute over a certain range, as is the case for acoustical modes, we can expect qualitatively a similar temperature dependence of the absorption curve to the above mentioned simplest case. We see, for instance, that the peak of the absorption band ($\equiv E = A_1$) does not shift with temperature, and the dispersion ($\{\overline{E - \bar{E}}^2\}^{1/2} = A_2^{1/2}$) or breadth of the band is proportional to \sqrt{T} at high temperatures, retaining the shape of the band which tends to a Gaussian form with increasing temperature. The last statement can be proved as follows. Transforming the energy measure E through

$$(E - \bar{E}) / \sqrt{A_2} = E',$$

we have a distribution function of $F_M(E) = F_{M'}(E')$ with E' as a variable, the average E' being zero and the dispersion $\overline{(E' - \bar{E}')^2} = 1$. Since the semi-invariants in the new system are given by

$$A_n' = A_n A_2^{-n/2}, \quad (n > 1)$$

they all tend to zero with increasing temperature, leaving $A_2' = 1$ alone, which means that $F_M'(E')$ tends to a Gaussian distribution.

(ii) $\Delta \neq 0$, $\Omega' \neq \Omega''$, $M = \text{const.}$ In this case, we expand the expressions in the exponents of (3.14) and (3.15) into power series in λ , using (3.18) and (3.19). Each of f_Δ and f_Γ contributes to the semi-invariants additively; the results up to the third moment are as follows.

$$\begin{aligned} \overline{E} &= A_1 = \varepsilon_0 + 1/2 \cdot \Delta \Omega'^2 \Delta + \hbar/4 \text{ trace } \{ \Omega'^{-1} \coth(\beta \hbar \Omega'/2) \Gamma \}, \\ \overline{(E - \overline{E})^2} &= A_2 = \hbar/2 \cdot \Delta \Omega'^2 \Omega'^{-1} \coth(\beta \hbar \Omega'/2) \Omega'^2 \Delta \\ &\quad + \hbar^2/8 \text{ trace } [\{ \Omega'^{-1} \coth(\beta \hbar \Omega'/2) \Gamma \}^2], \\ \overline{(E - \overline{E})^3} &= A_3 = \hbar^2/2 \cdot \Delta \Omega'^2 \{ 1 + 3/2 \cdot \Omega'^{-1} \coth(\beta \hbar \Omega'/2) \Gamma \Omega'^{-1} \coth(\beta \hbar \Omega'/2) \} \\ &\quad \Omega'^2 \Delta + \hbar^3/4 \text{ trace } \{ \Omega'^{-1} \coth(\beta \hbar \Omega'/2) \Gamma \}^2 + \hbar^3/8 \text{ trace } [\{ \Omega'^{-1} \\ &\quad \coth(\beta \hbar \Omega'/2) \Gamma \}^3]. \end{aligned} \quad (5.3)$$

(iii) $\Delta \neq 0$, $\Omega' = \Omega''$, $M \neq \text{const.}$ To take into account the Q -dependence of the transition dipole moment, we expand it at the equilibrium position Q' of the initial electronic state :

$$M(Q) = M(Q') + (Q - Q') \cdot (\partial M / \partial Q)_{Q'} = M + (Q - Q') \cdot M'. \quad (5.4)$$

According to (3.8), this is equivalent to

$$M_x \exp(iK \cdot Q') = M \delta(K) + i \delta'(K) M'. \quad (5.4')$$

Inserting (5.4') and (3.18) in (3.16), we have

$$\begin{aligned} g_M(\lambda) &= M^* M + (1/2) \hbar M'^* \Omega'^{-1} \coth(\beta \hbar \Omega'/2) M' \\ &\quad - (1/2) \lambda \hbar [- (M^* M' + M M'^*) \Omega' \coth(\beta \hbar \Omega'/2) \Delta + \hbar M' M'^*] \\ &\quad + (1/4) \lambda^2 \hbar^2 [- (M^* M' + M M'^*) \Omega'^2 \Delta + |M' \Omega' \coth(\beta \hbar \Omega'/2) \Delta|^2 \\ &\quad + \hbar M'^* \Omega' \coth(\beta \hbar \Omega'/2) M'] + \dots \end{aligned} \quad (5.5)$$

The expression for $f_0(\lambda)$ is the same as in case (ii).

(iv) Order estimation of the moments. According to the linear approximation discussed in § 4, the order of magnitude of the electron-lattice interaction in bound electronic states is characterized by the matrix elements $u_{j\mu}$. We denote it symbolically

$$u_{j\mu} = 0(u). \quad (5.6)$$

In a similar way we write

$$\Omega = 0(\omega), \quad (5.7)$$

where ω is an appropriate average of the frequencies of the normal modes which interact effectively with the trapped electron. According to (4.12) and (4.13) we have

$$\Delta = 0(u/\omega^2), \quad (5.8)$$

$$\Gamma = 0(u^2/\varepsilon_0). \quad (5.9)$$

Let us introduce a dimensionless quantity γ , which characterizes the interaction strength, by the definition

$$\gamma = \Delta Q^2 \Delta / \varepsilon_0 = 0(u^2/\varepsilon_0 \omega^2). \quad (5.10)$$

In the first approximation discussed in (i) of this section, the peak and the breadth of the absorption band at high temperatures are given by

$$\varepsilon_0 + \Delta Q^2 \Delta / 2 \text{ and } \sqrt{(\Delta Q^2 \Delta) kT},$$

respectively, and therefore, the two quantities ε_0 and $\Delta Q^2 \Delta$ can be estimated from the observed adsorption curve if available.* The values of γ thus determined from the F -bands in alkali-halides range from 0.6 to 1. γ can also be estimated theoretically if an appropriate Hamiltonian and electron wave functions are used. In non-polar crystals such as silicon and germanium, an electron (or a hole) can be trapped in the neighborhood of an impurity atom with a shielded potential $-e^2/\kappa_0 r$. If we take the Hamiltonian (4.2) and consider the $1s \rightarrow 2p$ transition, γ can be estimated by the formula

$$\gamma = \frac{2}{27\pi} \frac{60299}{62208} \frac{1}{\kappa_0} \frac{C^2}{\varepsilon_H M c^2} \frac{v_0}{a_H^3} \left(\frac{m^*}{m} \right)^2 \quad (\varepsilon_H = 13.6 \text{ ev.}, a_H = 0.53 \text{ \AA})$$

Inserting the values of κ_0 , C , $M c^2$, v_0 and m^* , we have γ ranging from 0.2 to 0.4 for these substances, the values for holes being larger than those for electrons.

If the value of γ is known, we can estimate the order of magnitude of each term in the moment expressions. Let us discuss the results (5.3) obtained in case (ii) of this section. In the first equation for the absorption peak, the second term amounts to $\varepsilon_0 \{\gamma/2 \pm 0(\gamma^2)\}$, by (5.9) and (3.21). (Here and in the following discussions we use \pm to show that we cannot tell about the sign of the quantity considered.) This term corresponds to the fact that the adiabatic energy difference in the equilibrium lattice configuration of the ground state is larger than ε_0 by $\Delta Q^2 \Delta / 2$ because of the difference Δ in the equilibrium positions for the two states. The third term causes the peak shift with temperature; at high temperatures it amounts to $\pm 0(\gamma) kT$.**

In the second equation of (5.3), the first and second terms are $\{\gamma \pm 0(\gamma^2)\} \varepsilon_0 kT$ and $\pm 0(\gamma^2) (kT)^2$, respectively. The ratio of the latter to the former, $0(\gamma) kT/\varepsilon_0$, is at most

* Physically $\frac{1}{2} \Delta Q^2 \Delta / 2$ is the polarization or redistribution energy which means the amount of energy liberated into lattice vibration when the electron excitation occurs at the equilibrium configuration of the ground state. Thus γ is twice the ratio of the polarization energy to ε_0 (see Fig. 1), and the breadth of the absorption band is given by

$$\sqrt{\gamma \varepsilon_0 kT} = \{\gamma/(1+\gamma/2)\}^{1/2} \sqrt{\hbar \nu kT}$$

which is to be compared with the estimation due to Mott and Gurney.¹⁾

** The terms $\pm 0(\gamma) kT$ for the peak shift and Δ_3 for the asymmetry have effects on the shape of the absorption band with the same order of magnitude as the factor ν in the absorption formula (2.6) has. Note that our discussion applies, strictly speaking, to $k(\nu)/\nu$, not to $k(\nu)$, itself.

of the order of $1/10$ for highest temperatures in ionic crystals where γ is large. Thus \sqrt{T} -law of the breadth of the absorption band is expected to be fairly good.

The asymmetry of the absorption curve is characterized by the third expression of (5.3) in which the magnitudes of the four terms are

$$+0 \{ \gamma \varepsilon_0 (\hbar\omega)^2 \}, \quad \pm 0 \{ \gamma^2 \varepsilon_0 (kT)^2 \}, \quad +0 \{ \gamma^2 (\hbar\omega)^2 kT \}, \quad \pm \{ \gamma^3 (kT)^3 \},$$

respectively. At high temperatures the second term is expected to be dominant, and the normalized (see (i) of this section) asymmetry is estimated to be

$$A_3/A_2^{3/2} = \pm 0 \{ (\gamma kT / \varepsilon_0) \}^{1/2}$$

which may in some cases be appreciable. This asymmetry is of course due to the difference in the frequency tensor \mathcal{Q} ; $\mathcal{Q}' = \mathcal{Q}''$ leads to a symmetric Gaussian distribution at high temperatures as was shown in (i).

In the same way we can discuss the effect of the Q -dependence of $M(Q)$ on the absorption band. Making use of (4.14) we have

$$\mathbf{M}' = 0 (\mathbf{M}u / \varepsilon_0), \quad (5.11)$$

from which the contribution of $g_M(\lambda)$, (5.5), to the peak shift is estimated to be

$$(\mathbf{M}^* \mathbf{M}' + \mathbf{M} \mathbf{M}'^* / \mathbf{M}^* \mathbf{M}) \cdot \Delta kT = \pm 0 (\gamma) kT.$$

This is of the same order of magnitude as the contribution from the difference of frequencies. For the second and third moments the effect of $g_M(\lambda)$ is essentially the same as that of $f_T(\lambda)$ discussed above.*

In case of the F -bands in alkali-halides it seems more plausible to relate the temperature shift of the peak with thermal expansion of lattice or asymmetry of the vibrational potential³⁾ because the observed shift is several times of kT which is too large to be related with the difference of frequencies or non-constancy of the transition dipole moment.

(v) Forbidden transitions. There is an interesting case where the Q -dependence of $M(Q)$ is of primary importance. When an impurity atom, in a crystal with high symmetry, occupies a symmetrical site, the surrounding lattice will displace from its normal position in the symmetrical manner. Thus some of the transitions of the atom which are forbidden in free state would still remain forbidden after introduced in the crystal, were it not for the lattice vibration. Actually, the transitions are possible even at absolute zero of temperature, owing to the zero-point vibration.

In this case we can set $M(Q') = M = 0$ at the equilibrium lattice configuration Q' in the ground state, while M' is expected to be of the same order of magnitude as in an allowed transition, that is, its order of magnitude is given by (5.11) with M for an allowed one. Making use of (5.5) we can derive the following properties of the absorption band.

* The higher order terms neglected in the expansion (5.4) of course have some influence upon these moments, but the qualitative conclusions presented here are not altered.

(a) The total intensity of the absorption band is determined by

$$(\hbar/2) \mathbf{M}'^* \Omega'^{-1} \coth (\beta \hbar \Omega'/2) \mathbf{M}'$$

instead of $\mathbf{M}^* \mathbf{M}$. Thus it is proportional to T at high temperatures, and tends to a certain value at $T=0^\circ K$. The order of magnitude, compared with an allowed transition, is

$$0(\gamma kT/\varepsilon_0) \text{ or } 0(\gamma \hbar \omega/\varepsilon_0)$$

at high or low temperatures, respectively; numerically it is 10^{-2} or less.

(b) The Q -dependence of $\mathbf{M}(Q)$ does not contribute to the peak shift primarily.

(c) It contributes, however, to the square of dispersion through the expression

$$\hbar |\mathbf{M}' \Omega' \coth (\beta \hbar \Omega'/2) \Delta|^2 / \mathbf{M}' \Omega'^{-1} \coth (\beta \hbar \Omega'/2) \mathbf{M}',$$

which is $0(\gamma \varepsilon_0 kT)$ at high temperatures, being of the same order of magnitude as the most important term of dispersion in (5.7). We can conclude, on the basis of (i) and (ii), that both the peak intensity and the breadth increases as \sqrt{T} at high temperatures.

A typical example for this case is the weak absorption band observed in NaCl : Cu cited by Seitz.¹³⁾ It is interpreted to correspond to the transition $d^{10} \rightarrow d^9s$ of Cu. The intensity and temperature dependence of the absorption band are in qualitative agreement with the above results. The observed oscillator strength is of the order of 0.001. This may be associated with a small value of γ , which would be naturally expected since the transition takes place inside the cuprous ion.

§ 6. Non-radiative transition

(i) General features. As was already discussed, the non-radiative transition from one electronic state l' to another l'' can be calculated through the generating function (3.12). For simplicity, we confine ourselves to the special but most important case of $\Delta \neq 0$ and $\Omega' = \Omega''$ throughout this section. Then, the expression (3.17) can easily be calculated, leading to

$$\begin{aligned} g_H(\lambda) &= |\mathbf{S} \Omega' \{ \coth (\beta \hbar \Omega'/2) (1 - \cosh \lambda \hbar \Omega') + \sinh \lambda \hbar \Omega' \} \Delta / 2 \hbar|^2 \\ &\quad + \mathbf{S}^* \Omega' \{ \coth (\beta \hbar \Omega'/2) \cosh \lambda \hbar \Omega' - \sinh \lambda \hbar \Omega' \} \mathbf{S} / 2 \hbar \\ &= |\sum_j (\omega_j S_j A_j / 2 \hbar) \{ (2n_j + 1) - n_j \exp(\lambda \hbar \omega_j) - (n_j + 1) \exp(-\lambda \hbar \omega_j) \}|^2 \\ &\quad + \sum_j (\omega_j |S_j|^2 / 2 \hbar) \{ n_j \exp(\lambda \hbar \omega_j) + (n_j + 1) \exp(-\lambda \hbar \omega_j) \}, \end{aligned} \quad (6.1)$$

where

$$n_j = 1 / \{ \exp(\beta \hbar \omega_j) - 1 \}$$

is the average number of phonons for the j -th mode of vibration. The inverse transform $G_H(E)$ of (6.1) is nothing but the summation of δ -functions such as $\delta(E)$, $\delta(E \pm \hbar \omega_j)$, and $\delta(E \pm \hbar \omega_j \pm \hbar \omega_{j'})$; that is, the function $G_H(E)$ is different from zero within $2\hbar\omega$ on both sides of $E=0$. Thus $g_H(\lambda)$ causes at most two phonon processes: the many phonon

process is made possible only through $f_0(\lambda)$. By the convolution theorem⁽⁸⁾ we can write

$$W = \frac{2\pi}{\hbar} \frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} f_0(\lambda) g_{H'}(\lambda) d\lambda = \frac{2\pi}{\hbar} \int_{-\infty}^{+\infty} F_0(E) G_{H'}(-E) dE. \quad (6.2)$$

Making use of the property of $G_{H'}(E)$ stated above, we see that the value of $F_0(E)$ near $E=0$, that is, the optical absorption intensity at zero frequency, is important in determining the non-radiative transition. If we neglect the variation of $F_0(E)$ in the range $0(\hbar\omega)$ near $E=0$, we have

$$W = \frac{2\pi}{\hbar} F_0(0) \int_{-\infty}^{+\infty} G_{H'}(E) dE = \frac{2\pi}{\hbar} F_0(0) g_{H'}(0). \quad (6.2')$$

At high temperatures where the higher order semi-invariants Λ_n of $f_0(\lambda)$ are not important in comparison with Λ_2 as was discussed in (i) of § 5, $F_0(E)$ is approximately of Gaussian form :

$$F_0(E) = (2\pi\Lambda_2)^{-1/2} \exp [-(E-\Lambda_1)^2/2\Lambda_2]. \quad (6.3)$$

Inserting the high temperature approximations for $g_{H'}(0)$, Λ_1 and Λ_2 into (6.3) and (6.2'), one can derive the formula

$$W = (2\pi)^{1/2} \hbar^{-3} \gamma^{-1/2} S^* S (kT/\varepsilon_0)^{1/2} \exp(-\varepsilon^*/kT), \quad (6.4)$$

where the activation energy

$$\varepsilon^* = (\varepsilon_0 + \Delta \Omega'^2 \Delta/2)^2 / (2\Delta \Omega'^2 \Delta) = \varepsilon_0 \{1 + (\gamma/2)\}^2 / (2\gamma) \geq \varepsilon_0 \quad (6.5)$$

corresponds to the point of minimum energy along the intersection of the two adiabatic energy surfaces represented by (3.4), as one can prove by a simple tensor algebra.

For very low temperatures where $\beta\omega \gg 1$, we can use the expansion

$$\coth(\beta\hbar\Omega'/2) \doteq 1 + 2 \exp(-\beta\hbar\Omega').$$

After substituting $\lambda = \beta + x$ into (5.1), we have

$$\begin{aligned} f_0(\lambda) = & \exp(-\beta\varepsilon_0) \exp[-x\varepsilon_0 - \Delta \Omega' \{1 - \exp(x\hbar\Omega')\} \Delta/2\hbar] \\ & \times \exp[-\Delta \Omega' \exp(-\beta\hbar\Omega') \{2 - \exp(-x\hbar\Omega') - \exp(-x\hbar\Omega' - \beta\hbar\Omega')\} \Delta/2\hbar]. \end{aligned}$$

When the integration on the complex plane of x is carried out along such a line that $|\operatorname{Re}(x)| \ll \beta$, we can equate the third factor to unity because of the relation $\beta\hbar\omega \gg 1$. Putting $F_0(0)$, which is thus obtained from $f_0(\lambda)$, and the low temperature approximation for $g_{H'}(0)$, into (6.2'), we get

$$\begin{aligned} W = & \pi \hbar^{-2} (S^* \Omega' S) \exp(-\beta\varepsilon_0) \\ & \times (2\pi i)^{-1} \int_{-i\infty}^{+i\infty} \exp[-x\varepsilon_0 - \Delta \Omega' \{1 - \exp(x\hbar\Omega')\} \Delta/2\hbar] dx. \end{aligned} \quad (6.6)$$

At low temperatures, therefore, the activation energy is ε_0 itself, in contrast with $\varepsilon^* (> \varepsilon_0)$ at high temperatures. In order to get a deeper insight into the mechanism, let us consider

the shape of the absorption band at absolute zero of temperature, which is obtained by equating \coth in (5.1) to unity and transforming it:

$$F_0(E) = (2\pi i)^{-1} \int_{-\infty}^{+\infty} \exp[-\lambda(\varepsilon_0 - E) - \Delta \Omega' \{1 - \exp(-\lambda \hbar \Omega')\} \Delta / 2\hbar] d\lambda.$$

If we replace λ by $-x$, the intensity at $E = 2\varepsilon_0$ is given by the same integral as in (6.6). Being at absolute zero of temperature, the system is initially in the lowest vibrational state belonging to the ground electronic state, and the optical absorption of energy $2\varepsilon_0$ corresponds to the transition to the vibrational state $A'' B''$ of the excited state as is shown in

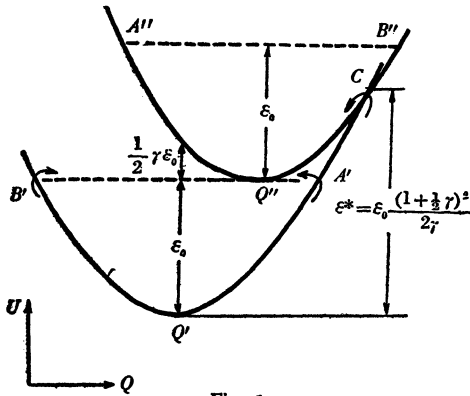


Fig. 1

(6.6). At high temperatures the excitation to higher vibrational states occurs frequently, and the system prefers the classical path through C to the tunneling course $A'Q''$ or $B'Q''$ which is rather difficult. This feature of a non-radiative transition, which seems to be valid quite generally, was first pointed out by one of the authors⁶⁾ for a special case. In § 7, we shall give a proof of the high temperature feature for the most general adiabatic potential.

(ii) Case of a single frequency. Assuming $\Omega' = \Omega'' = \omega I$, we can easily derive the formula which was already derived by Huang and Rhys⁵⁾

$$\begin{aligned} W = & (2\pi/\hbar) \hbar^{-3} \omega |B|^2 \left[\{(n+1/2)^2 + n(n+1)/2\} R_p - n(n+1/2) R_{p+1} \right. \\ & \left. - (n+1)(n+1/2) R_{p-1} + n^2 R_{p+2}/4 + (n+1)^2 R_{p-2}/4 \right] \\ & + (2\pi/\hbar) \hbar^{-2} C^2 / 2 [n R_{p+1} + (n+1) R_{p-1}], \end{aligned}$$

where

$$R_p = \exp[-(2n+1)D] (n+1)^{p/2} n^{-p/2} I_p(2D\sqrt{n(n+1)}),$$

$$p = -\varepsilon_0/\hbar\omega, \quad n = 1/\{\exp(\beta\hbar\omega) - 1\},$$

$$B = \mathbf{S} \cdot \mathbf{\Delta}, \quad C^2 = \mathbf{S}^* \cdot \mathbf{S}, \quad D = \omega \mathbf{\Delta} \cdot \mathbf{\Delta} / 2\hbar,$$

and I_p is the Bessel's I -function of the order p . Making use of the relations¹⁴⁾

$$I_{-p} = I_p,$$

Fig. 1. $F_0(2\varepsilon_0)$ is nothing but the square of the overlap integral of wave functions for these two vibrational states. Because of $\Omega' = \Omega''$, this quantity is the same for the vibrational states $A'B'$ of the ground state and the lowest vibrational state of the excited state. Thus, we see that non-radiative transition at low temperatures takes place mainly by tunneling of the lattice through the points A' or B' to Q'' . The probability that the vibrational energy is excited to $A'B'$ is proportional to the factor $\exp(-\beta\varepsilon_0)$ which appears in

$$I_p(z) \sim (z/2)^p / p!, \quad (p > 0, z \ll p)$$

$$I_p(z) \sim (2\pi z)^{-1/2} \exp(z - p^2/2z), \quad (p^2 \gg 1, z \gg |p|)$$

we have, at low temperatures ($\beta \hbar \omega \gg 1$),

$$R_p \sim \exp(-\beta \varepsilon_0) \exp(-D) D^{|p|} / |p|! \quad (p < 0, \varepsilon_0 > 0; \text{excitation}),$$

$$R_p \sim \exp(-D) D^p / p! \quad (p > 0, \varepsilon_0 < 0; \text{de-excitation}),$$

and at high temperatures ($n \sim 1/\beta \hbar \omega \gg 1, n \gg p/D$),

$$R_p \sim (4\pi D n)^{-1/2} \exp[-\beta(p-D)^2 \hbar \omega / (4D)].$$

It is easy to show that the activation energy

$$\hbar \omega (p-D)^2 / (4D)$$

is equal to ε^* or $\varepsilon^* - \varepsilon_0$ in Fig. 1 according as $p < 0$ or $p > 0$. Thus the low and high temperature features have again been established for this special case.

In case of ionic crystals, where the Hamiltonian is given by (4.1), the high temperature formula for the probability of the excitation ($l' \rightarrow l''$) becomes

$$W = \sqrt{2\pi} \gamma' \gamma^{-1/2} (\hbar \omega^2 / \varepsilon_0) (kT / \varepsilon_0)^{1/2} \exp(-\beta \varepsilon^*),$$

while at low temperatures we have

$$W = \sqrt{\pi/8} (\hbar \omega / \varepsilon_0)^{1/2} \{ \gamma/2 \exp(1 - \gamma/2) \}^{\varepsilon_0 / \hbar \omega} [(2/\gamma - 1)^2 \gamma'^{1/2} + 4/\gamma^2 \cdot (\gamma\gamma' - \gamma'^2) \hbar \omega / \varepsilon^0] \\ \times \omega \exp(-\beta \varepsilon_0).$$

The interaction constant γ is given by

$$\gamma = 1 / (4\pi \varepsilon_0) \cdot (1/\kappa_0 - 1/\kappa) \int (E_{\nu} - E_{\nu'})^2 d\mathbf{r},$$

and the other constants γ' and γ'' are defined by the corresponding expressions where the integrand is replaced by $E_{\nu\nu'}^2$ or $E_{\nu\nu'} \cdot (E_{\nu} - E_{\nu'})$. E_{ν} , $E_{\nu'}$ and $E_{\nu\nu'}$ are the electric fields due to the charge distributions $-e\varphi_{\nu}^2$, $-e\varphi_{\nu'}^2$ and $-e\varphi_{\nu} \varphi_{\nu'}$, respectively. In the latter formula the factor $\{ \}^{\varepsilon_0 / \hbar \omega}$ is very sensitive to the value of γ since $\varepsilon_0 \gg \hbar \omega$ for the usual cases. The expression in the bracket is always smaller than unity, the equality corresponding to $\gamma=2$ which means that Q'' coincides with A' in Fig. 1. Thus the transition probability at low temperatures depends sensitively on the distance $Q''A'$ through which the lattice co-ordinate must tunnel.

(iii) The probability of thermal ionization and retrapping of electrons and holes in non-polar crystals. In silicon and germanium, the electrons and holes are occasionally trapped at impurities. Owing to the large dielectric constant κ_0 , the wave function of the trapped electron or the hole is spread over many atoms and it is a fairly good approximation to take the trapping potential in a Coulomb form¹⁵⁾

$$V(r) = -ze^2 / \kappa_0 r,$$

where z is the difference between the valence number of the impurity atom and that of Si or Ge. The $1s$ wave function can be written

$$\begin{aligned}\psi_0 &= (\alpha^3/\pi)^{1/2} \exp(-\alpha r), \quad \alpha = (z/\kappa_0) (m^*/m) (1/a_H), \\ -\varepsilon_0 &= -(z/\kappa_0)^2 (m^*/m) \varepsilon_H.\end{aligned}\quad (6.7)$$

For the final state we take an ionized state with wave number k :

$$\psi_k = V^{-1/2} \exp(i\mathbf{k} \cdot \mathbf{r}), \quad \varepsilon_k = \hbar^2 k^2 / 2m^*.$$

In the latter state the displacement of the equilibrium lattice position is infinitesimal, and we have,

$$\begin{aligned}\gamma_k &= \Delta Q^{1/2} \Delta / (\varepsilon_0 + \varepsilon_k) = (18\pi)^{-1} (z/\kappa_0) C^2 / (\varepsilon_H M c^2) \cdot (m^*/m)^2 \cdot (v_0/a_H^3) \\ &\quad \times \alpha^2 / (\alpha^2 + k^2).\end{aligned}\quad (6.8)$$

To calculate the probability for thermal ionization of the electron or the hole, we have only to carry out the summation of the probabilities for $(0 \rightarrow k)$ processes over all k . We have calculated the probability only for high temperature region by applying (6.4), with the following result

$$\begin{aligned}W_i &= 2\sqrt{2} (m^* c^2 / \hbar) \gamma^2 (kT/\varepsilon_0)^2 \exp(-\varepsilon^*/kT) \\ &= \nu_0 (kT/\varepsilon_0)^2 \exp(-\varepsilon^*/kT),\end{aligned}\quad (6.9)$$

where ε^* is given by (6.5) and (6.8), γ being the value of γ_k for $k=0$.

In thermal equilibrium the ionization process is in balance with the reverse process in

Table 1. Calculated values of the probability W_i for the thermal ionization of trapped electrons (holes) and the cross section σ_i of impurities for thermally trapping free electrons (holes) in Si and Ge, with use of the formulae (6.9) and (6.10).

	silicon		germanium	
density	2.33		5.35	
c (cm/sec) ¹²⁾	0.93×10^6		0.54×10^6	
κ_0	12.5		18.5	
	electron	hole	electron	hole
ε_0 (ev. observed)	0.05	0.08	0.01	0.01
m^*/m	0.58	0.93	0.25	0.25
C (ev.)	19.3	18.6	14.0	19.8
γ	0.15	0.36	0.13	0.26
ν_0 (10^{10} /sec)	3	30	1	4
σ_0 (10^{-16} cm ²)	0.9	2.0	6	23
ε^* (ev)	0.18	0.13	0.04	0.02
$\varepsilon^* - \varepsilon_0$ (ev)	0.13	0.05	0.03	0.01
	T=500°K		T=300°K	
W_i (sec ⁻¹)	3×10^8	4×10^9	1×10^{10}	3×10^{10}
σ_i (cm ²)	5×10^{-18}	6×10^{-17}	2×10^{-16}	1×10^{-15}

which the electrons or holes become trapped at impurities without radiation. Thus, the cross section for the latter process is calculated as

$$\sigma_t = 2\sqrt{2} \pi^2 (\hbar c / \varepsilon_0)^2 \gamma^2 \exp[-(\varepsilon^* - \varepsilon_0)/kT] = \sigma_0 \exp[-(\varepsilon^* - \varepsilon_0)/kT] \quad (6.10)$$

Since $\varepsilon^* - \varepsilon_0 > 0$, the cross section for thermal trapping increases with temperature. As ν_0/ε_0^2 and σ_0 is proportional to z^{-2} , and ε^* and $\varepsilon^* - \varepsilon_0$ increase with z , both of the thermal processes are more effective for shallow traps.

At present there are still left ambiguities about the values of m^* and C although a number of accurate measurements have been carried out on the cyclotron resonances and the mobilities of electrons and holes in semiconductors. For the sake of consistency, we have determined m^* from (6.7), using measured values of κ_0 and ε_0 . Correspondingly the usual C values must be multiplied by $(m/m^*)^{5/4}$ because the mobility is proportional to $C^2 m^{*5/2}$. We have listed in Table 1 the values of the parameters for electrons and holes in Si and Ge. The high temperature approximations (6.9) and (6.10) which we have used, give correct order of magnitude down to the temperatures shown in the examples in the table, in each case. For lower temperatures the more exact calculation gives values larger than (6.9) and (6.10).

§ 7. High temperature approximation

If we confine ourselves to high temperature region, we can discuss radiative and non-radiative transitions for a general form of the adiabatic potential. Normalizing the lattice co-ordinates in such a way that the kinetic energy is written in the form (3.2), we can write down the high temperature approximation of the density matrix for an arbitrary adiabatic potential $U(\mathbf{Q})$ as follows:

$$\langle \mathbf{Q} | \rho(\beta) | \bar{\mathbf{Q}} \rangle = \{2\pi\beta\hbar^2\}^{-N/2} \exp[-(\mathbf{Q} - \bar{\mathbf{Q}})^2 / (2\hbar\beta^2) - \beta U\{(\mathbf{Q} + \bar{\mathbf{Q}})/2\}] \quad (7.1)$$

One can derive this formula by carrying out the integration

$$\rho(\beta) = (2\pi)^{-N} \exp[-(\beta\hbar^2/2)\mathbf{K}^2 - \beta U\{(\mathbf{Q} + \bar{\mathbf{Q}})/2\}] \exp[-i\mathbf{K} \cdot (\mathbf{Q} - \bar{\mathbf{Q}})] d\mathbf{K}$$

which is valid when the temperature is so high that the variation of U within the average de Broglie wave length $\hbar\beta^{1/2}$ of atomic motion (note that masses are normalized to unity) is negligible compared with thermal energy $1/\beta$, that is,

$$(\hbar\beta^{1/2} \partial/\partial Q)^n U \ll 1/\beta. \quad (7.2)$$

Inserting $U'(\mathbf{Q})$ and $U''(\mathbf{Q})$ in (7.1) for the two electronic states l' and l'' , respectively, and then carrying out calculations of the traces in (2.14) with new co-ordinates

$$(\mathbf{Q} + \bar{\mathbf{Q}})/2 = \mathbf{x}, \quad \mathbf{Q} - \bar{\mathbf{Q}} = \mathbf{y}, \quad (7.3)$$

we get the generating function for the optical absorption in the form

$$f_M(\lambda) = \mathbf{M}^* \mathbf{M} \{ \exp[-\beta U'(\mathbf{x}) - \lambda \{U''(\mathbf{x}) - U'(\mathbf{x})\}] d\mathbf{x} \\ \div \int \exp[-\beta U'(\mathbf{x})] d\mathbf{x}, \quad (7.4)$$

under the assumption that $M(\mathbf{Q}) = \text{const.} = M$. The inverse formula (2.16) gives at once the absorption intensity curve :

$$F_M(E) = M^* M \int \exp \{ -\beta U'(\mathbf{x}) \} \delta \{ E - U''(\mathbf{x}) + U'(\mathbf{x}) \} d\mathbf{x} \\ \div \int \exp \{ -\beta U'(\mathbf{x}) \} d\mathbf{x}. \quad (7.5)$$

This is nothing but the mathematical expression of the Franck-Condon principle in its crudest form.

The generating function for non-radiative transition turns out to be

$$f_{H'}(\lambda) = (\beta \hbar^2)^{-1} \mathbf{S}^* \mathbf{S} \int \exp [-\beta U'(\mathbf{x}) - \lambda \{ U''(\mathbf{x}) - U'(\mathbf{x}) \}] d\mathbf{x} \\ \div \int \exp \{ -\beta U'(\mathbf{x}) \} d\mathbf{x}, \quad (7.6)$$

from which one can easily derive the probability :

$$W = 2\pi (\beta \hbar^3)^{-1} \mathbf{S}^* \cdot \mathbf{S} \int \exp \{ -\beta U'(\mathbf{x}) \} \delta \{ U''(\mathbf{x}) - U'(\mathbf{x}) \} d\mathbf{x} \\ \div \int \exp \{ -\beta U'(\mathbf{x}) \} d\mathbf{x}. \quad (7.7)$$

This formula provides the most comprehensive proof of the fact that at high temperatures the non-radiative transition takes place through the activated states where the two adiabatic potential surfaces intersect one another ($U'(\mathbf{x}) = U''(\mathbf{x})$). One can easily verify the formula (6.4) by inserting the harmonic potentials (3.4) in (7.7).

In order to bring (7.7) into comparison with the conventional formula for a rate process, it is convenient to introduce a new set of orthogonal curvilinear co-ordinates (x, \mathbf{X}') instead of the original set (\mathbf{x}) in such a way that $x=0$ represents the $(N-1)$ -dimensional surface of activated states: $U'(\mathbf{x}) = U''(\mathbf{x})$, the other $(N-1)$ co-ordinates being denoted by \mathbf{X}' . Carrying out the integration of the numerator in (7.7) over x , and then multiplying both the numerator and the denominator by a quantity suggested by the following, we have

$$\int \exp \{ -\beta U'(\mathbf{x}) \} \delta \{ U''(\mathbf{x}) - U'(\mathbf{x}) \} d\mathbf{x} / \int \exp \{ -\beta U'(\mathbf{x}) \} d\mathbf{x} \\ = \exp(-\beta F^*) (2\pi kT/\hbar^2)^{1/2} [1/|\text{grad}(U'' - U')|]_{Av. (U''=U')}]$$

where F^* , defined by

$$\exp(-\beta F^*) = \hbar^{-(N-1)} \int \dots \int \exp [-\beta \{ \mathbf{P}'^2/2 + U'(0, \mathbf{X}') \}] d\mathbf{X}' d\mathbf{P}' \\ \div \hbar^{-N} \int \dots \int \exp [-\beta \{ \mathbf{P}^2/2 + U'(\mathbf{x}) \}] d\mathbf{x} d\mathbf{P}, \quad (7.8)$$

is to be interpreted as the free energy for the activation. By comparing W with the formula for a rate process¹⁶⁾

$$W = \kappa (kT/\hbar) \exp(-\beta F^*), \quad (7.9)$$

we see that the transmission coefficient κ is given by

$$\kappa = 4\pi^2 \hbar^{-2} \mathbf{S}^* \cdot \mathbf{S} (2\pi kT/\hbar^2)^{1/2} [1/|\text{grad}(U'' - U')|]_{Av. (U''=U')} \quad (7.10)$$

§ 8. Miscellaneous problems related with degeneracy of electronic states

The foregoing discussions, which were based on the adiabatic approximation, have to be modified when the energies of the two electronic states degenerate or come close to each other. In this section we take up two typical problems related with radiative and non-radiative transitions.

(i) Resonance effect in non-radiative transition. As we have shown in §§ 6 and 7, the non-radiative transition at high temperatures proceeds mainly through the activated states where the two adiabatic potentials intersect each other. One may well ask the applicability of the adiabatic approximation for such a case. Actually, however, the two energy surfaces are expected generally to repulse each other before they intersect, owing to the resonance interaction (see Fig. 2). If we assume this repulsion effect mainly responsible for the non-radiative transition, the following formulation would be appropriate.

Denoting the electron wave functions for the two states by φ_1 and φ_2 , in which neither the Q -dependence nor the resonance effect is taken into account, we can write the adiabatic potentials as

$$\int \varphi_i (H - K_L) \varphi_i dr = H_{ii} \quad (i=1, 2)$$

in the first approximation. We introduce a new set of lattice co-ordinates (x, \mathbf{X}') in the same way as in § 7, that is, $x=0$ at the intersection $H_{11}(\mathbf{Q}) = H_{22}(\mathbf{Q})$. The resonance effect can be taken into account by solving the secular equation

$$\begin{vmatrix} H_{11} - U & H_{12} \\ H_{21} & H_{22} - U \end{vmatrix} = 0. \quad (8.1)$$

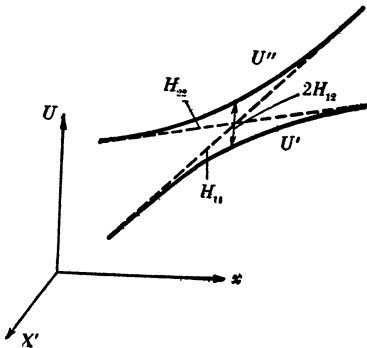


Fig. 2.

In the neighborhood of $x=0$ for a fixed \mathbf{X}' , we can set H_{12} equal to a constant while the difference of H_{11} and H_{22} is proportional to x (see Fig. 2). By a suitable choice of the unit of x one can write

$$\Delta H = H_{11}(x, \mathbf{X}') - H_{22}(x, \mathbf{X}') = 2|H_{12}(\mathbf{X}')|x. \quad (8.2)$$

The difference of the two solutions of (8.1) is given by

$$\Delta U = U'' - U' = 2|H_{12}|(1+x^2)^{1/2}, \quad (8.3)$$

with wave functions

$$\begin{aligned} \varphi' &= 2^{-1/2} [\{1 - x(1+x^2)^{-1/2}\}^{1/2} \varphi_1 - \{1 + x(1+x^2)^{-1/2}\}^{1/2} \varphi_2] \\ \varphi'' &= 2^{-1/2} [\{1 + x(1+x^2)^{-1/2}\}^{1/2} \varphi_1 + \{1 - x(1+x^2)^{-1/2}\}^{1/2} \varphi_2] \end{aligned} \quad (8.4)$$

As assumed above, we take account of the Q -dependence of the wave functions only through these coefficients of linear combinations, and consequently we have

$$S(Q) = -i\hbar^2 (\partial x / \partial Q) \int \varphi'^* (\partial / \partial x) \varphi' dr = i\hbar^2 2^{-1} (1+x^2)^{-1} (\partial x / \partial Q), \quad (8.5)$$

which is no longer constant*. In calculating the high temperature formula for $f_H(\lambda)$ in the same way as in § 7, using (x, X') and (y, Y') defined by (7.3), we make use of the approximation

$$\begin{aligned} \hbar^{-2} S(x + (y/2)) \cdot S^*(x - (y/2)) &= 4^{-1} \{1 + (x + (y/2))^2\}^{-1} \{1 + (x - (y/2))^2\}^{-1} |\partial x / \partial Q|^2 \\ &= 4^{-1} (1+x^2)^{-2} \exp[-y^2/(1+x^2)] |\partial x / \partial Q|^2 \end{aligned} \quad (8.6)$$

and then integrate with respect to y and Y' . The result is:

$$\begin{aligned} f_H(\lambda) &= 1/4 \cdot \int \int (\hbar^2/M_x \beta) (1+x^2)^{-2} \{1 + (\hbar^2/M_x \beta) 2\lambda(\beta-\lambda) (1+x^2)^{-2}\}^{-3/2} \\ &\quad \times \exp[-\beta U'(X) - \lambda \Delta U(X)] dx dX' \div \int \exp[-\beta U'(X)] dX, \end{aligned} \quad (8.7)$$

where we have introduced the mass

$$M_{x'}(X') = 1/|\partial x / \partial Q|_{x=0}^2 = 4|H_{12}|^2/|\text{grad } \Delta H|_{x=0}^2 \quad (8.8)$$

as a result of normalization of x through (8.2).

If we assume

$$|H_{12}|\beta \gtrsim 1, \quad (8.9)$$

we have

$$(\hbar^2 \beta / M_x)^{1/2} = \beta (\hbar^2 \beta^{1/2} |\text{grad } \Delta H|) / (2|H_{12}|\beta) \ll 1, \quad (8.10)$$

and consequently the expression $\{ \}^{-3/2}$ in (8.7) can be approximated by

$$\{1 - (\lambda/\lambda_0)^2\}^{-3/2},$$

where the absolute value λ_0 of the two branch points is given by

$$\lambda_0 = (M_x \beta / 2 \hbar^2)^{1/2} (1+x^2). \quad (8.11)$$

Because of (8.11), (8.9), (8.10) and (8.3), the inequality

$$\lambda_0 \Delta U \gg 1$$

is valid for all values of x , and we can carry out the integration

$$\begin{aligned} (2\pi i)^{-1} \int_{-\infty}^{+\infty} \{1 - (\lambda/\lambda_0)^2\}^{-3/2} \exp(-\lambda \Delta U) d\lambda \\ \sim 6^{-1} \pi^{-1/2} \lambda_0 (\lambda_0 \Delta U)^{1/2} \exp(-\lambda_0 \Delta U) \end{aligned}$$

with the method of the steepest descent.

In integrating over x , too, one can take advantage of (8.9) and (8.10), and finally one gets the result

$$\begin{aligned} W &= (\pi/6)^{3/2} (2\pi M_x \beta)^{-1/2} \int \exp\{- (2M_x \beta / \hbar^2)^{1/2} |H_{12}|\} \exp\{-\beta U'(0, X)\} dX' \\ &\quad \div \int \exp[-\beta U'(x, X')] dx dX', \end{aligned} \quad (8.12)$$

* Correspondingly we should also take account of S in (3.9), but this contributes only a small term at high temperatures.

which again is written in an alternative form

$$W = (\pi/6)^{3/2} [\exp \{ - (2M_{\text{ad}}\beta/\hbar^2)^{1/2} |H_{12}| \}]_{Av. (x=0)} \times (kT/h) \exp(-\beta F^*), \quad (8 \cdot 13)$$

where F^* is defined by (7.7). Owing to (8.9) and (8.10) the transmission coefficient is much smaller than unity, and the factor $\beta^{1/2}$ is expected to cause a temperature dependence which is considerably different from the usual exponential law.

(ii) On the breadth of the absorption band when the electronic states are degenerate. When the absorbing center is of high symmetry, it is possible that two or more of excited states are degenerate in the equilibrium lattice configuration of the ground state. For example the F -center in alkali-halide, which is of cubic symmetry, has the single ground state (A_{1g}) and triply degenerate excited states (F_{1u}) in the equilibrium lattice configuration of the former. As the lattice vibrates around this point, the degeneracy is removed, and one may well expect that this splitting is responsible for a part of the absorption breadth. Let us discuss this effect by treating the lattice motion classically, for the sake of simplicity.

Assuming the harmonic model and linear approximation as in (4.4) and (4.5), we take the equilibrium lattice position in the ground state as the origin of each co-ordinate Q_i , we have

$$\bar{Q}_j = 0, \quad \omega_j^2 \bar{Q}_j^2 / 2 = kT/2. \quad (8 \cdot 14)$$

Denoting the energies and wave functions of the ground state, and a set of degenerate excited states of $H_e(r)$ by ε_0, φ_0 and ε_i, φ_i ($i=1, 2, \dots, g$), we define the matrix elements

$$\int \varphi_i^*(r) H_l(r, Q) \varphi_k(r) dr = H'_{ik}(Q) \quad (i, k=0, 1, 2, \dots, g) \quad (8 \cdot 15)$$

which are linear in Q_j 's. Because of the above assumption we have $H'_{00}(Q) = 0$. For the excited states we have to solve the secular equation

$$\det |H'_{ik} - \varepsilon' \delta_{ik}| = 0. \quad (i, k=1, 2, \dots, g) \quad (8 \cdot 16)$$

The eigenvalues of $H_e + H_l$, therefore, can be written as

$$E_0 = \varepsilon_0 + \varepsilon'_0, \quad E_l = \varepsilon_l + \varepsilon'_l \quad (l=1, 2, \dots, g) \quad (8 \cdot 17)$$

where ε'_l is the l -th root of (8.16). Assuming that the oscillator strength of the transition from the ground state to any of the excited states is equal to one another, as is the case for the F -absorption, we can calculate the second moment of the absorption band:

$$\begin{aligned} \overline{(\hbar\nu - \hbar\bar{\nu})^2} &= g^{-1} \sum_i \{ \overline{(E_i - E_0) - \hbar\bar{\nu}} \}^2 = g^{-1} \sum_i \overline{\varepsilon_i'^2} \\ &= g^{-1} \sum_i \overline{H_{ii}'^2} + g^{-1} \sum_{i \neq j} \overline{H_{ij}'^2}, \end{aligned} \quad (8 \cdot 18)$$

where we have used (8.14) and (8.16). The first term corresponds to the absorption breadth due to the difference in equilibrium positions already discussed in § 5, whereas the second term represents the effect of splitting of degenerate states due to the lattice vibration. Both terms are proportional to T as is evident from (8.14). In case of the F -center, the Hamiltonian (4.1) gives the result

$$\overline{(\hbar\nu - \hbar\nu)^2} = (1/4\pi) (1/\kappa_0 - 1/\kappa) kT \{ (\mathbf{E}_x - \mathbf{E}_s)^2 + 2\mathbf{E}_{xy}^2 \} dr,$$

where \mathbf{E}_s , \mathbf{E}_x and \mathbf{E}_{xy} denote the electric fields due to the charge distributions: $-e\psi_s^2$, $-e\psi_{px}^2$ and $-e\psi_{px}\psi_{py}$, respectively. The second integral, i.e., the effect of the degeneracy is estimated to be about 1/10 of the first integral. It is possible, however, that the degeneracy of the excited states plays an important rôle in some other cases.

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