the following expression:

$$\omega=s\omega_n(p_0)-\frac{1}{2}s\omega_n''(p_0)\left[\frac{2\pi^{4/3}\beta\omega_n(p_0)[\hbar\Omega(p_0)]^{1/3}L_{ns}}{3^{2/3}\omega_n''(p_0)[p_y'(p_0)v_y'(p_0)]^{1/3}(n-1/4)^{2/3}}\right]^2\frac{i}{\tau}. \tag{A.1}$$

Bearing in mind the overestimation of the integral (2.19) in Ref. 1, let us also write the formula (A.1) for a spherical Fermi surface in the case when $p_z^F\beta=(B_0/1+B_0)/4\pi$:

$$\omega=s\omega_n(0)+\Omega[B_0L_{ns}/(1+B_0)]^2(\hbar\Omega/\varepsilon_F)^{1/3}\times s(n-1/4)^{-5/3}\pi^{4/3}2^{-13/3}\cdot3^{-2/3}-i/\tau,$$

where $\Omega=|e|B/mc$, m being the electron mass on the spherical Fermi surface.

In order for the frequency shift to exceed the frequency decrement, the second term on the right-hand side of (A.1) should be greater than the third term. This implies that the inequality

$$1/\tau<|s\omega_n''/2|[2\pi^{4/3}\beta3^{-2/3}\omega_n(p_0)[\hbar\Omega(p_0)]^{1/3}L_{ns}/\omega_n''(p_0)\times[p_y'(p_0)v_y'(p_0)]^{1/3}(n-1/4)^{2/3}]^2.$$

should be fulfilled. In the case of bismuth, when it is assumed that $p_z^F\beta=0.1$, the latter inequality implies that, in fields of intensity $B=10$ Oe, $1/\tau<10^9$ sec^{-1}.

[1] V. P. Silin and O. M. Tolkachev, Zh. Eksp. Teor. Fiz. 70, 639 (1976) [Sov. Phys. JETP 43, 331 (1976)].
[2] M. S. Khaĭkin, Zh. Eksp. Teor. Fiz. 39, 212 (1960); Usp. Fiz. Nauk 96, 409 (1968) [Sov. Phys. JETP 12, 152 (1961); Sov. Phys. Usp. 11, 785 (1969)].
[3] T. W. Nee and R. E. Prange, Phys. Lett. 25A, 583 (1967).
[4] É. A. Kaner and N. M. Makarov, Zh. Eksp. Teor. Fiz. 58, 1972 (1970) [Sov. Phys. JETP 31, 1063 (1970)].
[5] T. W. Nee, J. E. Koch, and R. E. Prange, Phys. Rev. 174, 758 (1968).
[6] H. J. Fishbeck and J. Mertsching, Phys. Status Solidi 27, 345 (1968).
[7] A. A. Abrikosov, Vvedenie v teoriyu normal'nykh metallov (Introduction to the Theory of Normal Metals), Nauka, M., 1972 (Eng. Transl. in: Solid State Physics, Suppl. 12, Academic Press, New York, 1972).
[8] V. P. Silin, Fiz. Met. Metallov. 29, 681 (1970) [Phys. Met. Metallogr. 29, No. 4, 7 (1970)].
[9] K. Fuchs, Proc. Camb. Philos. Soc. 34, 100 (1938).
[10] É. A. Kaner, N. M. Makarov, and I. M. Fuks, Zh. Eksp. Teor. Fiz. 55, 931 (1968) [Sov. Phys. JETP 28, 483 (1969)].
[11] J. F. Koch and J. D. Jensen, Phys. Rev. 184, 643 (1969).
[12] V. S. Edel'man, Adv. Phys. 25, 555 (1970).
[13] G. P. Alodzhants, Zh. Eksp. Teor. Fiz. 59, 1429 (1970) [Sov. Phys. JETP 32, 780 (1971)].
[14] V. P. Silin and A. A. Rukhadze, Élektromagnitnye svoĭstva plazmy i plazmopodobnykh sred (Electromagnetic Properties of a Plasma and Plasma-like Media), Atomizdat, 1961.
[15] V. S. Édel'man, Usp. Fiz. Nauk 102, 55 (1970) [Sov. Phys. Usp. 13, 583 (1971)].

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Theory of nonradiative processes in the "non-Condon" approximation

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The exact solution of a model with shifted and distorted terms is obtained by expressing the transition probability in terms of a correlation function and applying the functional differentiation method. The nondiagonal terms are allowed for within the perturbation theory framework. It is shown that the dependence of the matrix element of a transition on the nuclear coordinates gives rise to an additional factor in the correlation function. In some specific cases an analytic expression can be obtained for this factor by solving an appropriate differential equation. The expression for the transition rate constant reduces to quadrature in the case of an arbitrary dependence of the matrix element of the transition on the nuclear coordinates if this matrix element can be represented as a Fourier integral. The validity criterion of the Condon approximation is obtained. The results may be used to describe various multiquantum processes.

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In studies of multiquantum processes—such as radiative and nonradiative transitions in impurity centers in crystals or transitions in polyatomic molecules, neutron scattering by lattice vibrations, vibrational relaxation of impurity molecules, and chemical reactions—it is necessary to isolate two subsystems between which energy is exchanged in the course of a quantum transition. In such processes the matrix element of the first subsystem generally depends on the coordinates of the second subsystem. This dependence may become unimportant for large separations between the terms and then the Condon approximation may be used to describe multiquantum processes. This case has been investigated quite thoroughly.[1-5] However, there are certain optical phenomena which cannot be explained employing the Condon approximation.[6,7] It is also known that, in contrast to optical transitions, the influence of the dependence of the matrix element on the nuclear coordinates is much more important in nonradiative transitions since such transitions occur in the case when the nuclear configuration is far from equilibrium and the dependence of the matrix element near the term quasicrossing point is of resonant nature. Moreover, in the case of a strong electron-vibrational

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interaction the representation of a matrix element of a transition in the $\lambda d/dR$ form is generally invalid for nonradiative processes because it leads to an unphysical oscillatory dependence of the terms on the nuclear coordinates.[8]

The published papers [9-12] on the calculation of the matrix element and probability of a nonradiative transition caused by a change in an equilibrium position of the nuclei in the "non-Condon" approximation are limited to the case when a transition occurs far from the term quasicrossing point. For transitions due to the frequency effect,[13] the frequency change is assumed to be small and the generating function has been calculated by decoupling correlation functions, which is difficult to justify. The calculations carried out have shown that in the range of their validity the deviations from the Condon approximation may increase by 2–3 orders of magnitude the rate of transitions to higher vibrational levels of the final state.

Thus, the results obtained in the theory of nonradiative transitions indicate the need to go beyond the Condon approximation framework. However, rigorous calculations of the rate constants in the most important practical case of high temperatures and large term shifts have not yet been carried out.

The present paper reports a calculation of the probability of nonradiative transitions in the "non-Condon" approximation. Allowance is made for the term shifts and for the frequency effect. The results obtained can be used to describe various multiquantum processes. In particular, they give directly the exact solution of the model of multiphonon relaxation of an impurity molecule.[14]

2. MODEL

The total Hamiltonian of the system will be represented in the form

$$H=H_e(r)+H_N(R)+V(r,R), \tag{1}$$

where r and R are, respectively, the coordinates of electrons and nuclei. The adiabatic approximation will be used to separate the variables; then, $\Psi_{\alpha n}(r,R)=\psi_\alpha(r,R)\varphi_{\alpha n}(R)$. The functions ψ_α and $\varphi_{\alpha n}$ are found from

$$[H_e(r)+V(r,R)]\psi_\alpha(r,R)=E_\alpha(R)\psi_\alpha(r,R), \tag{2}$$

$$[H_N(R)+E_\alpha(R)]\varphi_{\alpha n}(R)=E_{\alpha n}\varphi_{\alpha n}(R). \tag{3}$$

If a molecule is in an adiabatic state, nonradiative transitions are due to the operator (see, for example, the paper of Konoplev *et al.*[15])

$$L=H_N(\psi_\alpha\varphi_{\alpha n})-\psi_\alpha(H_N\varphi_{\alpha n}). \tag{4}$$

The dependence $L(R)$ can be found by determining the explicit form of the functions $\psi_\alpha(r,R)$. This can be done exactly in a two-level model[9,16] which is applicable if the levels in question are separated by a wide energy interval from the others.

Let us assume that $R_{\alpha 0}$ are the values of the coordinates minimizing the function $E_\alpha(R)$. We shall use

$$\psi_\alpha(r,R)=[\psi_\alpha^{(0)}(r)+\alpha(R)\psi_\beta^{(0)}(r)][1+\alpha^2(R)]^{-1/2},$$
$$\psi_\beta(r,R)=[\psi_\beta^{(0)}(r)-\alpha(R)\psi_\alpha^{(0)}(r)][1+\alpha^2(R)]^{-1/2}, \tag{5}$$

where $\psi_\alpha^{(0)}(r)$ is the solution of Eq. (2) for $R=R_{\alpha 0}$. Then, we obtain the following equations for the determination of $\alpha(R)$ and of the exact adiabatic potentials $E_\alpha(R)$:

$$\alpha(R)=V_{\beta\alpha}(R)/[E_\alpha(R)-E_\beta^{(1)}(R)], \tag{6}$$

$$E_\alpha(R)=E_\alpha^{(1)}(R)+V_{\beta\alpha}(R)V_{\alpha\beta}(R)/[E_\alpha(R)-E_\beta^{(1)}(R)], \tag{7}$$

where

$$E_\gamma^{(1)}=E_\gamma^{(0)}+V_{\gamma\gamma}(R),\quad V_{\gamma\delta}(R)=\int\psi_\gamma^{(0)}(r)[V(r,R)-V(r,R_{\alpha 0})]\psi_\delta^{(0)}(r)\,dr.$$

Next, we can adopt one of the two very different methods. If we assume[17] that $V_{\gamma\delta}(R)=\Sigma V_{\nu\delta q}R_q$ (the origin of the coordinate system is assumed to be at the point $R=R_{\alpha 0}$), we find that Eq. (7) gives anharmonic potentials used earlier.[10] It follows from Eqs. (5)–(7) that

$$\begin{aligned}&\psi_\alpha(r,R)\approx\psi_\alpha^{(0)}(r),\quad E_\alpha(R)\approx E_\alpha^{(1)}(R)\quad\text{for}\quad R<R^*,\\&\psi_\alpha(r,R)\approx\psi_\beta^{(0)}(r),\quad E_\alpha(R)\approx E_\alpha^{(1)}(R)\quad\text{for}\quad R>R^*,\end{aligned} \tag{8}$$

where R^* is the crossing point of the terms $E_\alpha^{(1)}(R)$ and $E_\beta^{(1)}(R)$. Similar relationships apply also to $\psi_\beta(r,R)$ and $E_\beta(R)$. Kovarskiĭ[9] calculated the transition probability using the wave functions $\psi_{\alpha\beta}(r,R)$ and the terms $E^{(1)}_{\alpha,}(R)$, which correspond to one another—as is seen from Eq. (8)—only if $R<R^*$. Therefore, the model proposed by Kovarskiĭ and Sinyavskiĭ[9,10] is valid only at low temperatures and for small term shifts when a transition occurs under a barrier and not too close to R^*. At high temperatures a transition occurs near the point R^*[18] and transitions between anharmonic terms must be considered in the model of Kovarskiĭ and Sinyavskiĭ.[9,10] Clearly, at present this model can not be solved exactly. Approximate calculations are very cumbersome. In view of this situation it seems desirable to formulate the problem differently. We can follow Gregory and Siebrand[16] in assuming the terms $E_\gamma(R)$ and $E_\gamma^{(1)}(R)$ to be harmonic and we can determine $V_{\alpha\beta}(R)$ and $\alpha(R)$ from Eqs. (6) and (7). This approach is justified for processes with small term shifts. If the shift is sufficiently large, it is desirable to describe the terms $E_\gamma(R)$ as the sums of an harmonic part and a function $\Delta(R,R^*)$ which depends strongly on R near the quasicrossing point, thus reflecting the strong anharmonicity of the problem. Information on $E_\gamma(R)$ makes it possible to determine the dependence $\alpha(R)$ on the nuclear coordinates. It then follows from Eqs. (6) and (7) that

$$V_{\alpha\beta}^2(R)=(E_{\beta\alpha}-\Delta E_\alpha)\Delta E_\alpha, \tag{9}$$

where

$$\begin{aligned}&\Delta E_{\beta\alpha}=\bar{E}_\beta-E_\alpha=E_0+\Sigma A_qR_q+\Sigma B_{qq_1}R_qR_{q_1}+2\Delta(R,R^*),\\&E_0=E_\beta(0)-E_\alpha(0),\quad \Delta E_\alpha=E_\alpha^{(1)}-E_\alpha=\Sigma C_{qq_1}R_qR_{q_1}+\Delta(R,R^*)=-\Delta E_\beta,\\&A=-\omega_\beta^2R_{\beta 0},\quad B\sim(\omega_\beta^2-\omega_\alpha^2),\quad C\sim(\omega_\alpha^0)^2-\omega_\alpha^2,\end{aligned} \tag{10}$$

$R_{\beta 0}$ is the shift of the minimum of the term β relative to $R_{\alpha 0}$, ω_γ is the vibration frequency in a state γ, and $\omega_\alpha - \omega_\alpha^0$ is the change in the frequencies due to the electron-vibrational interaction. It finally follows from Eqs. (9) and (10) that

$$\alpha(R)=\left[\frac{E_\alpha-E_\alpha^{(1)}}{E_\alpha-E_\beta^{(1)}}\right]^{1/2}=\left[\frac{\Sigma C_{qq_1}R_qR_{q_1}+\Delta(R,R^\cdot)}{E_0+\Sigma A_qR_q+\Sigma(B_{qq_1}-C_{qq_1})R_qR_{q_1}-\Delta(R,R^\cdot)}\right]^{1/2}. \tag{11}$$

For $\Delta=0$ this expression is inapplicable[16] in the case of a large shift of the terms when the quasicrossing point lies between their minima. In such problems it is necessary to consider a transition from one minimum of a potential curve to another, including the upper term, where the nonadiabatic scattering may terminate. In this case the rate of the reaction is governed by the probability that the system remains at the lower term.

The matrix element of the nonadiabaticity operator for the adopted wave functions is

$$L_{\beta\alpha}=\langle\psi_\beta|L(R)|\psi_\alpha\rangle=-\Sigma\omega_q{}^0\left\langle\psi_\beta\left|\frac{\partial}{\partial R_q}\right|\psi_\alpha\right\rangle\frac{\partial}{\partial R_q}$$
$$-\frac{1}{2}\Sigma\omega_q{}^0\left\langle\psi_\beta\left|\frac{\partial^2}{\partial R_q{}^2}\right|\psi_\alpha\right\rangle=\frac{1}{1+\alpha^2}\Sigma\frac{1}{2}\omega_q{}^2[P_q{}^2,\alpha]$$
$$-\Sigma\omega_q{}^0\frac{\alpha}{(1+\alpha^2)^2}\left(\frac{\partial\alpha}{\partial R_q}\right)^2=\frac{1}{2}\Sigma\omega_q{}^0[P_q{}^2,\theta], \tag{12}$$

where P_q is the momentum operator and $\tan\theta=\alpha(R)$.

3. CALCULATION OF THE PROBABILITY OF A NONADIABATIC TRANSITION

The adopted model leads to the Hamiltonian

$$H=\Sigma E_\gamma a_\gamma{}^+a_\gamma+\Sigma\omega_qb_q{}^+b_q+\Sigma A_q{}^\gamma a_\gamma{}^+a_\gamma(b_q+b_q{}^+)$$
$$+\Sigma B_{qq_1}{}^\gamma a_\gamma{}^+a_\gamma(b_q+b_q{}^+)(b_{q_1}+b_{q_1}{}^+)+L,\quad \gamma=\alpha,\ \beta, \tag{13}$$

where the first term describes the positions of the electron levels, the second the vibrations of the nuclei in the initial state, the third is the term shift, and the fourth is the change in the frequencies in the forms of the vibrations in the course of an electronic transition. Here, without loss of generality, we can assume that $A_q^\alpha = B_{qq1}^\alpha = 0$.

In the first approximation of the nonstationary perturbation theory the transition rate constant $k=k(E=0)$ can be obtained from the expression for the spectral function[19,20]

$$k(E)=\frac{1}{\langle n_\alpha\rangle}\operatorname{Re}\int_0^\infty dt e^{-iEt}\langle L_{\beta\alpha}a_\alpha{}^+a_\beta|a_\beta{}^+a_\alpha L_{\alpha\beta}\rangle, \tag{14}$$

where $\langle\ldots\rangle$ denotes averaging over a Gibbs ensemble with the vibrational Hamiltonian of the initial electronic state, and $n_\alpha = a_\alpha^+ a_\alpha$. We shall calculate the correlation functions in Eq. (14) by the method of functional derivatives, introducing the T exponential function[21-23] in the density matrix:

$$\rho=Q^{-1}e^{-\beta H}T\exp\left\{\int_0^\infty dt\,\Sigma[u_q(t)(b_q(t)+b_q{}^+(t))]\right\}, \tag{15}$$

where Q is the normalization factor which depends functionally on classical fields $u_q(t)$. This approach makes it possible to reduce the calculation of the higher correlation functions, containing the nuclear coordinates, to the functional differentiation of $G(t) = \langle a_\alpha^+ a_\beta | a_\beta^+ a_\alpha\rangle$. Calculation of the function $G(t)|_{u=0}$ is also of intrinsic interest because it governs the nonradiative relaxation rate constant in the Condon approximation.[5] The question of the influence of the frequency term on $G(t)|_{u=0}$ has been considered on many occasions[4,24-29] but the exact result has been obtained only recently without assuming the smallness of the diagonal terms B_{qq}.[30]

The functional $G(t)$ satisfies the equation of motion[31]

$$i\frac{d}{dt}G=[-(E_\alpha-E_\beta)+\Sigma A_q\hat{D}_q+\Sigma B_{qq_1}\hat{D}_q\hat{D}_{q_1}]G;$$
$$\hat{D}_q(t)=\langle b_q(t)+b_q{}^+(t)\rangle+\delta/\delta u_q(t). \tag{16}$$

The solution of Eq. (16) will be sought in the form of a functional series

$$G(t,u)=G_0(t)\exp\left\{\sum_{N=0}^\infty\int_0^\infty\mu_{q_1\ldots q_N}(t_1,\ldots,t_N)u_{q_1}(t_1)\ldots u_{q_N}(t_N)dt_1\ldots dt_N\right\}. \tag{17}$$

It has been shown[32] that, for the Hamiltonian investigated here, the series in Eq. (17) terminates at the second term in the zeroth order in respect of the nonadiabaticity parameter. This is due to the fact that the expansion (17) is, in fact, made in terms of the powers of the correlations between the particles in the vibrational subsystem, which is described by the harmonic Hamiltonian but in such a system we can only have pair correlations. Substituting Eq. (17) into Eq. (16) and going to the limit $U_q\to 0$, we obtain

$$i\frac{d}{dt}G(t)=[-(E_\alpha-E_\beta)+\Sigma A_qM_q(t)+\Sigma B_{qq_1}(M_q(t)M_{q_1}(t)+f_{qq_1}(t,t))]G(t),$$
$$G(0)=\langle n_\alpha\rangle,\quad M_q(t)=\mu_q(t)+\langle b_q{}^+(t)+b_q(t)\rangle, \tag{18}$$
$$f_{qq_1}(t,t_1)=\mu_{qq_1}(t,t_1)+\langle[b_q(t)+b_q{}^+(t)][b_{q_1}(t_1)+b_{q_1}{}^+(t_1)]\rangle=\delta M_{q_1}(t_1)/\delta u_q(t).$$

The functions $M_q(t)$ and $f_{qq1}(t,t_1)$ are found from[32]

$$M_q(t)=\langle b_q(t)+b_q{}^+(t)\rangle-i\Sigma A_{q_1}\int_0^t f_{qq_1}(t,t_1)dt_1-2i\Sigma B_{q_1q_2}\int_0^t M_{q_1}(t_1)f_{qq_2}(t,t_1)dt_1, \tag{19}$$

$$f_{qq_1}(t,t_1)=\delta_{qq_1}[N_q\exp\{i\omega_q(t-t_1)\}+(N_q+1)\exp\{-i\omega_q(t-t_1)\}]$$
$$-2i\Sigma B_{q_2q_3}\int_0^{t_1}f_{qq_2}(t,t_2)f_{q_1q_3}(t_1,t_2)dt_2, \tag{20}$$

where $N_q = \langle b_q^+ b_q\rangle - \langle b_q^+\rangle\langle b_q\rangle$.

The information in Eqs. (19) and (20) is sufficient for a complete description of the behavior of a system in the Condon and non-Condon calculation schemes, so that we shall consider in greater detail the solutions of these equations.

For impurity centers without local vibrations there is no frequency change as a result of an electronic transition and the solution of Eqs. (19) and (20) is self-evident. In the case of impurity centers with local vibrations and also for polyatomic molecules the frequency effect may be considerable and in some cases it may be the main cause of a nonradiative transition.[13]

Equations (19) and (20) have an exact solution for the diagonal frequency effect. The final result can be written in the form

$$f_q(t,t)=\frac{\Omega_q-\omega_q}{2B_q}-\frac{i}{2B_q}\frac{d}{dt}\ln(x_q^2-y_q^2), \tag{21}$$

$$M_q(t)=-\frac{2A_q\omega_q}{\Omega_q(\Omega_q+\omega_q)}\frac{[N_q+1+N_q\exp(i\omega_qt)][\exp(-i\Omega_qt)-1]}{x_q-y_q}, \tag{22}$$

where

$$\Omega_q=[\omega_q^2+4\omega_qB_q]^{1/2},\quad x_q=N_q+1-N_q\exp[i(\omega_q-\Omega_q)t],$$
$$y_q=\frac{\Omega_q-\omega_q}{\Omega_q+\omega_q}[(N_q+1)\exp(-i\Omega_qt)-N_q\exp(i\omega_qt)].$$

Substituting these solutions in Eq. (18), we obtain an expression for $G(t)|_{u=0}$, which is identical with that obtained by Osad'ko.[30]

The general case when the matrix B is nondiagonal cannot be solved exactly but it can be investigated by approximate methods or numerically. If we analyze Eq. (20) by the perturbation theory, we note that its solution can be represented in the form

$$f_{qq_1}(t,t_1)=\exp(i\omega_qt)\varphi_{qq_1}(t_1)+\exp(-i\omega_qt)\chi_{qq_1}(t_1). \tag{23}$$

Substituting Eq. (23) into Eq. (20), we obtain a system of integral equations for φ and χ, which is readily solved by the iteration method. We shall now give the results obtained in the approximation of short times, which are applicable at high temperatures and for a sufficiently strong dispersion of the vibrations:

$$\varphi_{qq_1}(t)=\delta_{qq_1}N_q-it[\delta_{qq_1}\omega_qN_q+2B_{qq_1}N_q(2N_{q_1}+1)]+\ldots, \tag{24}$$

$$\chi_{qq_1}(t)=\delta_{qq_1}(N_q+1)+it[\delta_{qq_1}\omega_q(N_q+1)-2B_{qq_1}(N_q+1)(2N_{q_1}+1)]+\ldots, \tag{25}$$

$$M_q(t)=-itA_q(2N_q+1)+(it)^23(2N_q+1)\Sigma B_{qq_1}A_{q_1}(2N_{q_1}+1)+\ldots. \tag{26}$$

Clear results are also obtained in the case of intermediate temperatures for a model of one local vibration ω_1 interacting with a set of soft vibrations ω_q. If we assume that $\omega_1\gg\omega_q$ $(q\neq 1)$, $N_1\ll 1$, the only nonzero quantities are $B_{1q}=B_{q1}$ and A_1; applying then the perturbation theory to B_{1q} we obtain a series which contains secular terms that result in divergences. These divergences are removed by frequency renormalization. It should be noted that in analogous cases the frequency renormalization has either not been carried out[33] or carried out incorrectly[34] so that the resultant temperature dependence of the vibrational spectrum has no physical basis. The frequency renormalization can be made unambiguous by an additional requirement that the renormalized frequencies are independent of temperature. To within second order in B_{1q}, the renormalized frequencies are given by

$$\Omega_q=\omega_q+8\Sigma\frac{B_{qq_1}\omega_{q_1}}{\omega_q^2-\omega_{q_1}^2}. \tag{27}$$

Finally, we obtain the following expressions for φ and χ:

$$\varphi_{qq_1}^{(0)}=\delta_{qq_1}\{N_q\exp(-i\Omega_qt)+N_q^2[\exp(-i(\Omega_q-\omega_q)t)-1)\}, \tag{28}$$

$$\chi_{qq_1}^{(0)}=\delta_{qq_1}\{(N_q+1)\exp(i\Omega_qt)-(N_q+1)^2[\exp(i(\Omega_q-\omega_q)t)-1]\}, \tag{29}$$

$$\varphi_{qq_1}^{(1)}=2B_{qq_1}\left\{\frac{N_qN_{q_1}}{\omega_q+\omega_{q_1}}[\exp(-i\omega_qt)-\exp(i\omega_{q_1}t)]\right.$$
$$\left.+\frac{N_q(N_{q_1}+1)}{\omega_q-\omega_{q_1}}[\exp(-i\omega_qt)-\exp(-i\omega_{q_1}t)]\right\}, \tag{30}$$

$$\chi_{qq_1}^{(1)}=-2B_{qq_1}\left\{\frac{(N_q+1)(N_{q_1}+1)}{\omega_q+\omega_{q_1}}[\exp(i\omega_qt)-\exp(-i\omega_{q_1}t)]\right.$$
$$\left.+\frac{(N_q+1)N_{q_1}}{\omega_q-\omega_{q_1}}+[\exp(i\omega_qt)-\exp(i\omega_{q_1}t)]\right\}. \tag{31}$$

The last terms in the braces in Eqs. (30) and (31) are secular if $\omega_q=\omega_{q1}(q\neq q)$. In this case they have to be included in the frequency renormalization both in Eqs. (28) and (29) but excluded from Eqs. (30) and (31). The expression for M_q is found from Eq. (19):

$$M_q^{(0)}=\frac{A_q}{\omega_q}[\exp(-i\Omega_qt)-1]\delta_{1q}, \tag{32}$$

$$M_q^{(1)}=2B_{1q}A_1\left[\frac{N_q}{\omega_1-\omega_q}\left(\frac{\exp(i(\Omega_1-\omega_q)t)-\exp(i\omega_qt)}{\omega_1}-\right.\right.$$
$$\left.-\frac{1-\exp(i\omega_qt)}{\omega_q}\right)+\frac{N_q+1}{\omega_1+\omega_q}\left(\frac{\exp(i(\Omega_1+\omega_q)t)-\exp(-i\omega_qt)}{\omega_1}\right.$$
$$\left.+\frac{1-\exp(-i\omega_qt)}{\omega_q}\right)+\frac{N_q}{\omega_1}\left(\frac{\exp(i\omega_qt)-1}{\omega_q}+\frac{\exp(i\Omega_1t)-\exp(i\omega_qt)}{\omega_1+\omega_q}\right.$$
$$\left.\left.+\frac{N_q+1}{\omega_1}\left(\frac{1-\exp(-i\omega_qt)}{\omega_q}+\frac{\exp(-i\Omega_1t)-\exp(-i\omega_qt)}{\omega_1-\omega_q}\right)\right)\right]. \tag{33}$$

In spite of the fact that the anharmonicity is important in local vibrations, the results obtained describe correctly the influence of the frequency effect also in the above case, because for transitions due to the frequency effect the cubic anharmonicity—which usually dominates the rate constant[31]—appears only in the second order because of the symmetry of the problem and it can be considered separately.

4. ALLOWANCE FOR "NON-CONDON" CORRECTIONS

We shall assume that the operator generating a transition can be expanded as a Harzberg–Teller series in terms of the nuclear displacements:

$$L_{\beta\alpha}(R)=\Sigma L_{\beta\alpha}^{(n)}R^n,\quad L_{\beta\alpha}^{(n)}=\frac{1}{n!}\frac{d^nL_{\beta\alpha}(R)}{dR^n}\Bigg|_{R=0}, \tag{34}$$

where R is a set of dimensionless normal coordinates and $R_q=b_q+b_q^+$. The expression for the rate constant is then of the form

$$k_{\alpha\beta}=\frac{1}{\langle n_\alpha\rangle}\operatorname{Re}\sum_{n=0}^{\infty}\sum_{m=0}^{\infty}L_{\beta\alpha}^{(n)}L_{\alpha\beta}^{(m)}\int_0^\infty G_{nm}(t)\,dt, \tag{35}$$

where

$$G_{nm}(t)=\langle(b+b^+)^na_\alpha^+a_\beta|a_\beta^+a_\alpha(b+b^+)^m\rangle. \tag{36}$$

The indices of the boson operators are omitted for the sake of simplicity. They can be easily restored in the final result.

We shall introduce a new function g_{nm} in accordance with the expression

$$g_{nm}(t)G(t)=G_{nm}(t), \tag{37}$$

which has the following form in the harmonic approximation

$$g_{nm}(t)=\left[M(t)+\frac{\delta}{\delta u(t)}\right]^n\left[S(t)+\frac{\delta}{\delta u(0)}\right]^m\langle I\rangle, \tag{38}$$

where $S(t)G(t) = \langle a_\alpha^+ a_\beta | a_\beta^+ a_\alpha (b+b^+) \rangle$ and I is a unit operator. Using the general properties of the correlation functions, we can show that $S(t) = M(t)$ in the limit $U_q(t) \to 0$. The equality (38) follows from the definitions of the functions $M(t)$ and $S(t)$ and from their property[32]

$$\frac{\delta}{\delta u_{q_1}(t_1)} \frac{\delta}{\delta u_{q_2}(t_2)} M_q(t) \equiv 0.$$

Representation of $g_{nm}(t)$ in the form (38) makes it possible to obtain the recurrence formula for this function:

$$\begin{aligned} g_{nm}(t) = M(t)\,[M(t)\,g_{n-1,\,m-1} + (n-1) f(0,t)\,g_{n-2,\,m-1} \\ + (m-1) f(t,t)\,g_{n-1,\,m-2} + \delta_{m0} g_{n-1,\,0}] + (n-1) f(t,t)\,[M(t)\,g_{n-2,\,m-1} \\ + (n-2) f(0,t)\,g_{n-3,\,m-1} + (m-1) f(t,t)\,g_{n-2,\,m-2} + \delta_{m0} g_{n-2,\,0}] \\ + m f(0,t)\,g_{n-1,\,m-1} + \delta_{n0}[M(t)\,g_{0,\,m-1} + (m-1) f(t,t)\,g_{0,\,m-2} + \delta_{m0}], \end{aligned} \tag{39}$$

where M and f are, respectively, the functions $M_q(t)$ and $f_{qq1}(t, t_1)$ defined in Sec. 3.

In spite of its cumbersome form, Eq. (39) has a simple structure and for some values of $L_{\beta\alpha}(R)$ it allows exact summation of the whole series (35). In the simplest case of an exponential dependence of the matrix element of a transition on R, when $L_{\beta\alpha}(R) \propto e^{\xi R}$, we have to calculate the sum

$$W = \Sigma g_{nm} \frac{\xi_1{}^n}{n!} \frac{\xi_2{}^m}{m!}. \tag{40}$$

Using Eq. (39), we obtain the following differential equation for W:

$$\begin{aligned} \frac{\partial^2 W}{\partial \xi_1 \partial \xi_2} - f(0,t)\,\xi_2 \frac{\partial W}{\partial \xi_2} = (M^2(t) + M(t) f(0,t)\,\xi_1 \\ + M(t) f(t,t)\,(\xi_1 + \xi_2) + f(0,t) f(t,t)\,\xi_1{}^2 + f^2(t.t)\,\xi_1 \xi_2)\,W, \end{aligned} \tag{41}$$

subject to the boundary conditions

$$W(\xi_2 = 0) = \exp\{M\xi_1 + {}^1\!/_2 f(t,t)\,\xi_1{}^2\}, \quad W(\xi_1 = 0) = \exp\{M\xi_2 + {}^1\!/_2 f(t,t)\,\xi_2{}^2\}. \tag{42}$$

Equation (41) has an exponential solution of the bilinear form of the variables ξ_1 and ξ_2. Having determined the coefficients, we obtain

$$W = \exp\{M(t)\,(\xi_1 + \xi_2) + {}^1\!/_2 f(t,t)\,(\xi_1{}^2 + \xi_2{}^2) + f(0,t)\,\xi_1 \xi_2\}. \tag{43}$$

The solution obtained gives the correlation function explicitly

$$\begin{aligned} \langle \exp\{i\xi\Sigma\tau_{1q}(b_q + b_q{}^+)\}\,a_\alpha{}^+ a_\beta | a_\beta{}^+ a_\alpha \exp\{-i\xi\Sigma\tau_{2q}(b_q + b_q{}^+)\}\rangle \\ = \exp\{i\xi\Sigma M_q(t)\,(\tau_{1q} - \tau_{2q}) - {}^1\!/_2 \xi^2 \Sigma [f_{qq_1}(t,t)\,(\tau_{1q}\tau_{1q_1} + \tau_{2q}\tau_{2q_1}) \\ - 2 f_{qq_1}(0,t)\,\tau_{1q}\tau_{2q_1}]\}\,G(t) = g(t, \tau_1, \tau_2)\,G(t). \end{aligned} \tag{44}$$

The recurrence formula (39) allows us to obtain the differential equation for $g(t, \tau_1, \tau_2)$ and an arbitrary dependence of $L_{\beta\alpha}$ on R but even Eq. (44) gives the general solution of the problem by quadrature if we use the expansion of the matrix element of the transition as a Fourier integral:

$$L_{\beta\alpha}(R) = \int_{-\infty}^{\infty} L_{\beta\alpha}(\tau)\,e^{i\xi\tau R}\,d\tau; \tag{45}$$

then,

$$k_{\alpha\beta} = \frac{1}{\langle n_\alpha \rangle} \operatorname{Re} \int_{-\infty}^{\infty} d\tau_1 \int_{-\infty}^{\infty} d\tau_2 \int_0^{\infty} dt\,L_{\beta\alpha}(\tau_1)\,L_{\alpha\beta}(\tau_2)\,g(t, \tau_1, \tau_2)\,G(t). \tag{46}$$

Although Eq. (46) is derived on the assumption that the function $L_{\beta\alpha}(R)$ is regular in R, it has a more general validity. It is sufficient that $L_{\beta\alpha}(R)$ can be represented as a Fourier integral.

Substituting in Eq. (46) the actual values of $G(t)$, $M_q(t)$, and $f_{qq1}(t, t_1)$ from the preceding section, we can investigate the influence of the "non-Condon" correction in certain special cases.

5. VALIDITY CRITERION ON THE CONDON APPROXIMATION

In practice, the matrix element of a transition is usually calculated employing the Herzberg–Teller expansion (34) and, therefore, it is necessary to find the conditions of convergence of the corresponding series (35).

To estimate the parameter governing the convergence of the series (35) in a clear form, we shall use the limit of zero temperatures separately in the two cases when a transition is due to the term shift and frequency changes.

Let us assume that $\Omega_q = \omega_q$; then, the principal contribution of the n-th order term to the rate constant is

$$2L_{\beta\alpha}^{(0)} L_{\beta\alpha}^{(n)} \int_0^{\infty} G(t)\,M^n(t)\,dt \tag{47}$$

or

$$(L_{\beta\alpha}^{(n)})^2 \int_0^{\infty} G(t)\,M^{2n}(t)\,dt, \tag{48}$$

depending on the relationship between the parameters of the system. Applying the steepest-descent (saddle-point) method, we obtain

$$k_{\alpha\beta}^{(n)} \approx 2L_{\beta\alpha}^{(0)} L_{\beta\alpha}^{(n)} \gamma^n \left(\frac{p-n}{\gamma^2 e}\right)^{n-p}$$

or

$$k_{\alpha\beta}^{(n)} \approx (L_{\beta\alpha}^{(n)})^2 \gamma^{2n} \left(\frac{p-2n}{\gamma^2 e}\right)^{2n-p},$$

where

$$p = \frac{1}{\omega}\left(E_\alpha - E_\beta + \Sigma \frac{A_q{}^2}{\omega_q}\right), \quad \gamma^2 = \left(\frac{A_q{}^2}{\omega_q{}^2}\right)_{\text{eff}}.$$

Hence, it follows that the series (35) converges beginning from the first terms if

$$\varepsilon = \left(\frac{p-n}{\gamma e}\right) \frac{L_{\beta\alpha}^{(n)}}{L_{\beta\alpha}^{(n-1)}} \ll 1, \quad p - n > 1, \tag{49}$$

or

$$\varepsilon_1 = \left(\frac{p-2n}{\gamma e}\right)^2 \left(\frac{L_{\beta\alpha}^{(n)}}{L_{\beta\alpha}^{(n-1)}}\right)^2 \ll 1. \tag{50}$$

The inequalities (49) and (50) represent the criterion of validity of the Condon approximation. If we assume[35] that $L_{\beta\alpha}^{(n)} | L_{\beta\alpha}^{(n-1)} \approx 0.1$, $p = 10$, $\gamma = 0.1$, we find that for small values of n we have $\epsilon = 3$ and $\epsilon_1 \approx 24$, i.e., in this case the terms of the series (35) increase with n. For the same parameters but with $\gamma = 2$, we have $\epsilon = 0.2$ and

$\epsilon_1 = 0.05$. This estimate corresponds to the benzene molecule. It follows from the expressions (49) and(50) that if these inequalities are not satisfied for small values of n, we have to include approximately $n_1 = p-\gamma^2$ terms. However, for $n>n$, the convergence of the series (35) becomes better than the convergence to zero of the sequence $\{L_{\beta\alpha}^{(n)}\}$.

Let us assume that $A_q = 0$; then,

$$\frac{k_{\alpha\beta}^{(2)}}{k_{\alpha\beta}^{(0)}} \approx \frac{L_{\beta\alpha}^{(2)}}{L_{\beta\alpha}^{(0)}} \frac{4p\omega^2}{|\Omega^2-\omega^2|} + \left(\frac{L_{\beta\alpha}}{L_{\beta\alpha}^{(0)}}\right)^2 \left|\frac{\Omega+\omega}{\Omega-\omega}\right|, \tag{51}$$

$$\frac{k_{\alpha\beta}}{k_{\alpha\beta}^{(0)}} \approx 3\frac{L_{\beta\alpha}^{(4)}}{L_{\beta\alpha}^{(0)}}\left(\frac{4p\omega^2}{\Omega^2-\omega^2}\right)^2. \tag{52}$$

Using estimates of the Scharf parameters[35] $|\Omega-\omega| \approx 0.1\omega$, $p=10$, $L_{\beta\omega}^{(n)}/L_{\beta\alpha}^{(n-1)} \approx 0.1$, we obtain

$$k_{\alpha\beta}^{(2)}/k_{\alpha\beta}^{(0)} \approx 2, \quad k_{\alpha\beta}^{(4)}/k_{\alpha\beta}^{(0)} \approx 12.$$

However, beginning from $n \approx p$ the series again converges satisfactorily. It follows from the above formulas that the series (35) converges poorly for small values of the Franck–Condon factors (large values of p and small values of A and $\Omega-\omega$). The physical meaning of the results obtained is quite simple. It is well known that on increase of p the rate constants decrease faster than exponentially. Then, $k_{\alpha\beta}^{(n)}$ has an additional, compared with $k_{\alpha\beta}^{(0)}$, factor $e^{-in\omega t}$, which reduces p by n. If n is small, an increase in n causes the rate constant to rise rapidly because of the factor $e^{-in\omega t}$ and such an increase may be greater than the reduction in the preexponential factor of the $L_{\beta\alpha}^{(n)}\gamma^n$ type. The Franck–Condon factor increases more and more slowly on increase of n and for $n>p-\gamma^2$ it even begins to decrease so that the convergence of the series (35) is determined in the worst case by the convergence of the sequence $\{L_{\beta\alpha}^{(n)}\}$. If many modes participate in a given transition, then the energy p_q carried by the q-th mode may be small for every mode and the Condon approximation becomes valid.

In the two limiting cases we have to allow for $\sim p$ terms if the Franck–Condon factors are small. Hence, it follows that if both A_q and B_{qq1} differ from zero, we can use the Condon approximation if the series (35) converges in at least one case because the presence of the second mechanism increases the Franck–Condon factor for typical parameters of the problem. It follows from this discussion that the conclusions reached by Scharf[35] on the divergence of the series (35) are incorrect.

At finite temperatures the behavior of the series (35) is quite different. In fact, $M^n(t)$ occurring in Eq. (47) contains a time-independent term $\gamma^n n!\,[N(N+1)]^{n/2}/(n/2)!$ and the parameter governing the convergence of this branch of the series is

$$\varepsilon_n = \frac{L_{\beta\alpha}^{(n)}}{L_{\beta\alpha}^{(n-1)}}\gamma[2enN(N+1)]^{1/2}.$$

Hence, it follows that at sufficiently high temperatures and for large nuclear displacements when $\epsilon_n \gtrsim 1$, the Herzberg–Teller expansion is inapplicable because the corresponding series (35) diverges and the rate constant has to be calculated using Eq. (46).

In spite of the fact that the actual form of $L_{\beta\alpha}(R)$ affects greatly the rate constant, an investigation of the "non-Condon" effects can be carried out in general form because the time-dependent part of the integrand in Eq. (46) is independent of $L_{\beta\alpha}(R)$. In this case we shall consider the integral

$$\int_0^\infty dt\,\exp\{-\Sigma 2M_q(t)\alpha_q + \Sigma[f_{qq_1}(t,t)+f_{qq_1}(0,t)]\alpha_q\alpha_{q_1}\}G(t), \tag{53}$$

where $A_\alpha = -i\tau_{1q}i\tau_{2q}$. In the absence of the frequency effect the influence of the "non-Condon" correction reduces to an asymmetric change in the parameter of the electron–vibrational interaction, which gives

$$\begin{aligned} g(t,\alpha)G(t) = \langle n_\alpha\rangle \exp\Big\{ & i\left(E_\alpha - E_\beta + \Sigma\frac{A_q^2}{\omega_q}\right)t \\ & + \Sigma\left(\frac{A_q}{\omega_q} - \alpha_q\right)^2 N_q[\exp(i\omega_q t) - 1] \\ & + \left(\frac{A_q}{\omega_q} + \alpha_q\right)^2 (N_q+1)[\exp(-i\omega_q t) - 1] + 2\Sigma\alpha_q^2(2N_q+1)\Big\}. \end{aligned} \tag{54}$$

According to Eq. (54), the transition rate constant may vary by several orders of magnitude for large values of α_q if γ is small. For large γ, the influence of α_q decreases. Moreover, as the temperature rises, the integrated probability of the transition becomes greater.

In the presence of only the diagonal frequency terms the expression for gG at zero temperature becomes

$$\begin{aligned} g(t,\alpha)G(t) = \langle n_\alpha\rangle & \left[\prod_q \frac{4\Omega_q\omega_q}{(\Omega_q+\omega_q)^2[1-\Delta_q^2\exp(-2i\Omega_q t)]}\right]^{1/2} \\ & \times\exp\Big\{\Sigma\frac{2A_q^2\omega_q^2}{\Omega_q^3(\Omega_q+\omega_q)}\left(1+\frac{\Omega_q^2\alpha_q}{A_q\omega_q}\right)\left(\frac{\exp(-i\Omega_q t)-1}{1-\Delta_q\exp(-i\Omega_q t)}\right) \\ & + \Sigma\alpha_q^2\exp(-i\omega_q t) + \Sigma\frac{2\alpha_q^2\omega_q}{\Omega_q+\omega_q}\left(\frac{1-\Delta_q\exp(-2i\Omega_q t)}{1-\Delta_q^2\exp(-2i\Omega_q t)}\right) \\ & + i\left(E_\alpha - E_\beta + \Sigma\frac{A_q^2\omega_q}{\Omega_q^2}\right)t - \frac{i}{2}\Sigma(\Omega_q-\omega_q)t\Big\}, \quad \Delta_q = \frac{\Omega_q-\omega_q}{\Omega_q+\omega_q}. \end{aligned} \tag{55}$$

Hence, it follows that the behavior of the rate constant at low temperatures changes qualitatively if allowance is made for the "non-Condon" corrections. When this is done, the spectral function includes the frequency of the initial state whose intensity depends weakly on temperature. In the Condon approximation such frequencies appear only at finite temperatures and their intensity depends strongly on temperature. The appearance of a new frequency in the "non-Condon" approximation is due to the fact that vibrations of the initial state occur in $L_{\beta\alpha}(R)$. In those cases when the spectral function has a pronounced vibrational structure, the appearance of additional frequencies is particularly important because they reduce strongly the dips between neighboring resonances. It is then necessary to allow for the "non-Condon" effect also at low temperatures.

We shall now consider the case of high temperatures and short times. A calculation of the zeroth moment of the integrand of Eq. (53) shows that it differs from zero and is equal to $\exp\{2\Sigma\alpha_q^2(2N_q+1)\}$. The first moment is given by the expression

$$\left\{i\left[E_\alpha-E_\beta+\Sigma\frac{A_q{}^2\omega_q}{\Omega^2}+\Sigma B_{qq}(2N_q+1)+2\Sigma\alpha_q A_q(2N_q+1)\right.\right.$$
$$\left.\left.-\Sigma\alpha_q{}^2\omega_q(2N_q+3)+2\Sigma\alpha_q B_{qq_1}\alpha_{q_1}(2N_{q_1}+1)\right]\right\}\exp\{2\Sigma\alpha_q{}^2(2N_q+1)\},$$

i.e., the changes are slight. The second moment changes by an amount

$$\{\Sigma\alpha_q B_{qq_1}(2N_q+1)[6A_{q_1}(2N_q+1)+4\omega_q N_q]-\Sigma\alpha_q{}^2\omega_q{}^2(2N_q-{}^1/_2)$$
$$+\Sigma 4\alpha_q B_{qq_2}B_{q_2q_1}\alpha_{q_1}(2N_{q_2}+1)(2N_{q_1}+1)\}\exp\{2\Sigma\alpha_q{}^2(2N_q+1)\}$$

and decreases in the case of the large frequency effect, i.e., the dependence of the rate constant on the electronic transition energy becomes stronger. On the other hand, in the case of the small frequency effect, the "non-Condon" corrections increase somewhat the second moment.

At intermediate temperatures the argument of the exponential function has a term proportional to the first power of B_{1q}, which is absent in the Condon approximation, and the quantity gG is described, to within the principal term of the first order in B_{1q}, by

$$g(t,\alpha)G(t)=\langle n_\alpha\rangle\exp\left\{i\left(E_\alpha-E_\beta+\frac{A_1{}^2}{\omega_1}\right)t+\left(\frac{A_1}{\omega_1}-\alpha_1\right)^2(e^{-i\Omega_1 t}-1)\right.$$
$$+\Sigma\left(\alpha_q-4\frac{B_{1q}A_1}{\omega_q\omega_1}\right)^2 N_q[\exp(i\omega_q t)-1]$$
$$\left.+\Sigma\left(\alpha_q+4\frac{B_{1q}A_1}{\omega_q\omega_1}\right)^2(N_q+1)[\exp(-i\omega_q t)-1]+2\Sigma\alpha_q{}^2(2N_q+1)\right\}. \quad (56)$$

In this case the broadening of the vibrational resonances is greater than in the Condon approximation and the rate constant may increase considerably. The last term in the exponential function (56) results in a temperature dependence of the integrated value of the spectral function.

[1] K. Huang and A. Rhys, Proc. R. Soc. London Ser. A **204**, 406 (1950).
[2] M. A. Krivoglaz, Zh. Eksp. Teor. Fiz. **25**, 191 (1953).
[3] A. S. Davydov, Zh. Eksp. Teor. Fiz. **24**, 397 (1953).
[4] R. Kubo and Y. Toyozawa, Prog. Theor. Phys. **13**, 160 (1955).
[5] Yu. E. Perlin, Usp. Fiz. Nauk **80**, 553 (1963) [Sov. Phys. Usp. **6**, 542 (1964)].
[6] W. B. Fowler and D. L. Dexter, Phys. Rev. **128**, 2154 (1962).
[7] N. N. Kristofel' and G. S. Zavt, Fiz. Tverd. Tela (Leningrad) **5**, 1279 (1963) [Sov. Phys. Solid State **5**, 932 (1963)].
[8] M. Z. Zgierski and A. P. Penner, Chem. Phys. Lett. **45**, 41 (1977).
[9] V. A. Kovarskiĭ, Fiz. Tverd. Tela (Leningrad) **4**, 1636 (1962) [Sov. Phys. Solid State **4**, 1200 (1963)].
[10] V. A. Kovarskiĭ and É. P. Sinyavskiĭ, Fiz. Tverd. Tela (Leningrad) **4**, 3202 (1962) [Sov. Phys. Solid State **4**, 2345 (1963).
[11] A. Nitzan and J. Jortner, J. Chem. Phys. **56**, 3360 (1972).
[12] Y. Fujimura, H. Kôno, and T. Nakajima, J. Chem. Phys. **66**, 199 (1977).
[13] É. P. Sinyavskiĭ, Fiz. Tverd. Tela (Leningrad) **13**, 1995 (1971) [Sov. Phys. Solid State **13**, 1673 (1972)].
[14] V. Yakhot, Phys. Status Solidi B **76**, 451 (1976).
[15] G. G. Konoplev, A. A. Ovchinnikov, and V. G. Plotnikov, Zh. Eksp. Teor. Fiz. **66**, 1956 (1974) [Sov. Phys. JETP **39**, 962 (1974)].
[16] A. R. Gregory and W. Siebrand, Chem. Phys. Lett. **33**, 447 (1975).
[17] S. I. Pekar, Issledovaniya po élektronnoĭ teorri kristallov, Gostekhizdat, M., 1951 (Research in Electron Theory of Metals, USAEC Translation AEC-tr-5575, 1963); M. A. Krivoglaz and S. I. Pekar, Tr. Inst. Fiz. Akad. Nauk Ukr. SSR No. 4 (1953).
[18] L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika, Fizmatgiz, M., 1963 (Quantum Mechanics: Non-Relativistic Theory, 2nd ed., Pergamon Press, Oxford, 1965).
[19] R. Kubo, J. Phys. Soc. Jpn. **12**, 570 (1957).
[20] T. Yamamoto, J. Chem. Phys. **33**, 281 (1960).
[21] J. Schwinger, Proc. Nat. Acad. Sci. U.S.A. **37**, 452, 455 (1951).
[22] E. S. Fradkin, Dokl. Akad. Nauk SSSR **125**, 66 (1959) [Sov. Phys. Dokl. **4**, 327 (1959)].
[23] N. N. Bogolyubov and D. V. Shirkov, Vvedenie v teoriyu kvantovannykh poleĭ, Nauka, M., 1973 (Translation of earlier edition: Introduction to the Theory of Quantized Fields, Interscience, New York, 1959).
[24] M. A. Krivoglaz, Fiz. Tverd. Tela (Leningrad) **6**, 1707 (1964) [Sov. Phys. Solid State **6**, 1340 (1964)].
[25] A. V. Lukashin and M. D. Frank-Kamenetskiĭ, Dokl. Akad. Nauk SSSR **188**, 391 (1969).
[26] A. V. Lukashin, Opt. Spektrosk. **32**, 661 (1972) [Opt. Spectrosc. (USSR) **32**, 351 (1972)].
[27] J. R. Christie and D. P. Craig, Mol. Phys. **23**, 345, 353 (1972).
[28] A. Nitzan and J. Jortner, J. Chem. Phys. **56**, 2079 (1972).
[29] S. H. Lin, J. Chem. Phys. 58, 5760 (1973).
[30] I. S. Osad'ko, Zh. Eksp. Teor. Fiz. **72**, 1575 (1977) [Sov. Phys. JETP **45**, 827 (1977)].
[31] A. I. Ivanov and O. A. Ponomarev, Opt. Spektrosk. **41**, 744 (1976) [Opt. Spectrosc. (USSR) **41**, 441 (1976)].
[32] A. I. Ivanov and O. A. Ponomarev, Teor. Mat. Fiz. **30**, 382 (1977).
[33] V. A. Kovarskiĭ and E. V. Vitiu, Izv. Akad. Nauk SSSR Ser. Fiz. **31**, 2003 (1967).
[34] D. E. McCumber and M. D. Sturge, J. Appl. Phys. **34**, 1682 (1963).
[35] B. Scharf, Chem. Phys. **7**, 478 (1975).

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