The effect of polarisation fluctuations on the optical response function

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Abstract. A method is proposed for the estimation of the optical electron response function in a polar medium without recourse to perturbation theory. It has proved possible to write the temperature Green function of the electron coupled with a short-range potential and interacting (in a dipole approximation) with long-wave polarisation fluctuations proceeding from the functional integral representation. Using the steepest descent method in the high-temperature limit, comparatively simple expressions have been obtained. These are compared with experimental data for impurity ions in polar media and temperature dependences of the edge of the medium absorption band (Urbach rule).

1. Introduction

In the past few years experimental and theoretical studies of optical transitions and conductivity in polar semiconductors and insulators with impurity centres have received considerable attention. Though significant success has been achieved in this field, there are still problems to be solved (Levinson and Rashba 1973, Kagan 1975). For instance, no consistent explanation has yet been given of the characteristics of wide structureless absorption bands, which are interpreted as transitions with a large number of phonons involved. The following characteristic features have been observed which can be classed with the most important general optical properties of condensed media. First, the extinction coefficient decays exponentially with decreasing light frequency near the absorption band edge (the Urbach rule). Second, in the case of strong coupling, an increase in temperature causes a shift to the red side of the absorption maximum. Third, in many systems the following characteristic features of the absorption band shape of impurity centres are displayed: asymmetry (with a drastic fall of the curve on the red side) and a large bandwidth, which cannot be related to the lifetime of excited states.

Attempts have been made to explain these features qualitatively on models with strong coupling with phonons and a specially chosen 'bare' impurity centre spectrum. This spectrum is chosen as an initial one with a rather high degree of arbitrariness.

Nevertheless it has been possible to make some estimates (Levinson and Rashba 1973, Brodsky and Tsarevsky 1980) which show that some characteristic features, for instance, the large widths of absorption bands, cannot be accounted for in such a way. But even without taking account of the results of the estimations made, the generality of the above spectral properties has not been elucidated yet. Finally, the interpretation of the experimental fact that the coefficient in the Urbach rule index tends to a non-zero value at $T \to 0$ (Kagan 1975) presents a fundamental difficulty for the existing theories.

The calculations which are beyond the framework of perturbation theory (with respect to the electron–phonon coupling) are of particular importance for solving the above problems. One of the possible ways of performing such calculations is associated with the use of a long-wave approximation. In such an approximation, it is possible to write analytical expressions for the temperature Green functions, proceeding from their functional integral representation. The dynamic effects of the phonon field fluctuations are taken into account in the Green functions.

In the present paper the programme formulated has been realised for the most simple realistic model of a polar dielectric with the impurity centre described by a short-range potential.

In § 2 an expression for the temperature analogue of the response function has been derived in the form of a functional integral in the phonon field. Such a derivation, corresponding to the case when the integrals in fermion variables are taken first in the expression for the functional integral representation of the Green function, is in many respects analogous to the method applied in quantum electrodynamics for finding infrared asymptotics and differs from that proposed by Feynman (1972), which suggested that an integration in boson variables is to be performed first in the polaron problem and then the non-linear and non-local problem for an electron be solved by the variational method. However, there is a close relation between our approach and that of Redfield and co-workers (Dow and Redfield 1972, Redfield 1963). The main difference between the two approaches is that we solve the truly dynamical electron long-wave polarisation problem in contrast to Redfield, who had introduced an external random polarisation field with an *a priori* given distribution. In § 3 we treat a short-range potential model for an electron.

In conclusion a possible comparison of theory and experiment has been discussed. Appendices present solutions of two independent problems: construction of the Green function for the δ-type potential in the presence of an external field and the problem of taking functional integrals in boson variables.

2. The functional integral representation of the response function

The Lagrangian $\mathscr{L}(t)$ describing the interaction of non-relativistic electrons, corresponding to the function $\psi(x, t)$, with the phonon field $b(q, t)$ and the potential of some centre $U(x)$ is taken in the following specific form:

$$\mathscr{L}(t) = \mathscr{L}_e(t) + \mathscr{L}_b(t) + \mathscr{L}_{int}(t)$$

$$\mathscr{L}_e(t) = \int_v \left[-\frac{i}{2}\left(\frac{\partial \psi^+}{\partial t}\psi - \psi^+\frac{\partial \psi}{\partial t}\right) - \psi^+\left(\frac{\hat{p}^2}{2m} + U(x)\right)\psi \right] dv$$

$$\mathscr{L}_b(t) = \frac{\varepsilon}{8\pi}\sum_q \left(\frac{\partial b^+(q, t)}{\partial t}\frac{\partial b(q, t)}{\partial t} - \omega^2 b^+(q, t)b(q, t)\right) \tag{1}$$

$$\mathscr{L}_{int}(t) = \frac{1}{2m}\int_v \left[\psi^+\left(\frac{2e}{v^{1/2}}\sum_q \frac{iqp}{q}b(q, t)\right.\right.$$

$$\left.\left. -\frac{e^2}{v}\sum_{q,q'}\frac{qq'}{qq'}b^+(q, t)b(q, t)\right)\psi \right] dv$$

$$\hbar = 1 \qquad \hat{p} = -i\partial/\partial x \qquad b^+(q, t) = b(-q, t).$$

The volume v with one potential centre is introduced into equation (1). The centres are assumed to be widely spaced and the effects of their correlation unimportant. At $\varepsilon = \varepsilon_\infty \varepsilon_0 / (\varepsilon_0 - \varepsilon_\infty)$ the Lagrangian (1) is reduced through phase transformation to the Lagrangian of Fröhlich interaction† taken in a dipole approximation. The required quantity is the electron susceptibility, which is proportional with a universal constant to the quantity $\alpha_{ij}(\Omega)$:

$$\alpha_{ij}(\Omega) = \int_0^\infty dt \int_v d^3x_1 \, d^3x_2 \, e^{i\Omega t} \langle [j_i(x_1, t), j_j(x_2, 0)] \rangle \tag{2}$$

where $j_{ij}(x, t)$ are the operators of current, the square brackets indicate the commutator and the angular brackets denote the quantum and statistical averaging. The dynamical characteristics of the behaviour of electrons in a weak variable long-wave external field are given in terms of α_{ij}. Electron operators of second quantisation have been introduced into (2) for a more uniform description of electrons and phonons. In addition, the procedure used allows direct generalisation for the case where production of electron–hole pairs may take place. The central point in constructing α_{ij} is obtaining the temperature (Matsubara) (Lifshitz and Pitaevsky 1978) two-point Green function $\mathcal{Y}(\tau_1, x_1; \tau_2, x_2)$ which admits the functional integral representation

$$\mathcal{Y}(\tau_1, x_1; \tau_2, x_2) = Z^{-1} \int \delta\psi \delta\psi^+ \delta b \Big\{ \psi(\tau_1, x_1) \psi^*(\tau_2, x_2)$$

$$\times \exp\Big[\int_0^\beta d\tau \Big(\mathcal{L}(\tau) + \mu \int_v \psi(x, \tau) \psi^*(x, \tau) \, d^3x \Big) \Big] \Big\} \tag{3}$$

$$Z = \int \delta\psi \delta\psi^* \delta b \Big\{ \exp\Big[\int_0^\beta d\tau \Big((\mathcal{L}/\tau) + \mu \int_v \psi(x, \tau) \psi^*(x, \tau) \, d^3x \Big) \Big] \Big\} \qquad \beta = 1/T.$$

Here $\delta\psi$, $\delta\psi^*$ and δb, in accordance with standard designations (Vasil'ev 1976), imply integration by non-commutative and commutative quantities $\psi(x, \tau)$, $\psi^*(x, \tau)$ and $b(q, \tau)$, respectively, under the additional condition $b^*(q, \tau) = b(-q, -\tau)$.

Equation (3) corresponds to the transition to the imaginary time $t \to -i\tau$ and a summand, proportional to the electron chemical potential μ, is added to the action.

Let us perform first a functional integration over $\delta\psi$, $\delta\psi^*$ in equation (3). We obtain

$$\mathcal{Y}(\tau_1, x_1; \tau_2, x_2) = \frac{\int \delta b z_e(b) \mathcal{Y}_e(\tau_1, x_1; \tau_2, x_2 | b) \exp(\int_0^\beta \mathcal{L}_b(\tau) \, d\tau)}{\int \delta b z_e(b) \exp(\int_0^\beta \mathcal{L}_b(\tau) \, d\tau)}. \tag{4}$$

The electron Green function $\mathcal{Y}_e(\tau_1, x_1; \tau_2, x_2 | b)$, corresponding to the motion of an electron in the external classical field $b(q, \tau)$, which depends periodically on τ, appears

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† Without a dipole approximation the sum over q entering into $\mathcal{L}_{int}$ would have the form

$$\frac{2e}{v^{1/2}} \sum_q \frac{ipq}{q} \Big[\exp\Big(\frac{iqx}{2m} \Big) b(q, t) + CC \Big]$$

where the sum over q is cut off at inverse interatomic distances. In considering the temperature dependence of the response function we mean division of the sum over q into two intervals $|q| < q_0$ and $|q| > q_0$ and assume that the interaction with short-wave phonons leads only to a change of U and to renormalisation of the coupling constant. The quantity q_0 is supposed less than the inverse radius of the bound state in the potential U. This assumption makes it possible to expand into a series the exponent in $\mathcal{L}_{int}$. It is essential that, owing to the introduction of q_0, the number of parameters in the final result does not increase—all the temperature dependences observed are expressed in terms of the renormalised coupling constant (cf Itzykson and Zuber 1979). Note that the expression for $\mathcal{L}_{int}(t)$ (1) is identical to that used by Redfield.

in equation (4). The function $\mathcal{Y}_e$ obeys the following equation and additional conditions resulting from the determination of the temperature Green function:

$$\left(-\frac{\partial}{\partial \tau_1} - U(x_1) + \mu - \frac{1}{2m} \hat{p}(\tau_1|b)\hat{p}^*(\tau_1|b) \right) \mathcal{Y}_e(\tau_1, x_1; \tau_2, x_2|b)$$

$$= \pi T \delta(\sin(\tau_1 - \tau_2)\pi T)\delta^3(x_1 - x_2)$$

$$-\mathcal{Y}_e(\tau_1 + \beta, x_1; \tau_2, x_2|b)$$

$$= \mathcal{Y}_e(\tau_1, x_1; \tau_2, x_2|b)$$

$$= \mathcal{Y}_e^*(\tau_2, x_2; \tau_1, x_1|b^*)$$

$$\hat{p}(\tau|b) = \hat{p} - \frac{e}{v^{1/2}} \sum_q \frac{iq}{q} b(q, \tau).$$

The factor $z_e(b)$ enters into equation (4) under the integral. It is determined by equation (6) to an accuracy of non-essential normalisation:

$$z_e(b) = \int \delta\psi\delta\psi^* \exp\left[\int_0^\beta d\tau \left(\mathcal{L}_e(\tau) + \mathcal{L}_{int}(\tau) + \mu \int_v d^3x\, \psi^2(x, \tau)\psi(x, \tau) \right) \right]. \tag{6}$$

Choosing a normalisation so that $z_e(0) = 1$, we have

$$z_e(b) = \exp(\mathrm{Sp}\ln \hat{\mathcal{Y}}_e^{-1}(b)\hat{\mathcal{Y}}_e(0)). \tag{7}$$

The higher Green functions for $\mathcal{Y}$ can be obtained from expressions of the type (4). For instance, introducing an additional source into the Lagrangian and differentiating the two-point Green function with respect to such a source, one may obtain an expression for the Matsubara analogue (Lifshiftz and Pitaevsky 1979) of the susceptibility:

$$\alpha_{ij}(2\pi isT) = \frac{1}{Zm^2} \int_0^\beta d\tau \exp(i2\pi sT\tau) \int \delta b z_e(b) \exp\left(\int_0^\beta \mathcal{L}_b(\tilde{\tau})\, d\tilde{\tau} \right)$$

$$\times \int_v d^3x_1\, d^3x_2\, \hat{p}_i\mathcal{Y}_e(\tau, x_1; 0, x_2|b)\hat{p}_j\mathcal{Y}_e|0, x_2; \tau, x_1|b) \tag{8}$$

$$Z = \int \delta b z_e(b) \exp\left(\int_0^\beta \mathcal{L}_b(\tilde{\tau})\, d\tilde{\tau} \right).$$

3. Short-range potential

For further consideration it is required that the Green function should be constructed in a field $b(q, \tau)$. The simplest case when this is possible is that of the absence of a potential, $U = 0$. Then it follows from (5) that

$$\mathcal{Y}_e^0(\tau_1, x_1; \tau_2, x_2|b) = \frac{1}{(2\pi)^3} \int d^3p \exp[ip(x_1 - x_2)]\mathcal{Y}_e^0(p; \tau_1, \tau_2|b)$$

$$\mathcal{Y}_e^0(p; \tau_1, \tau_2|b) = i \exp\left[\frac{e}{mv^{1/2}} \sum_q \frac{qp}{q} \int_{\tau_2}^{\tau_1} \tilde{y}(q, \tau)\, d\tau - \frac{e^2}{2mv} \sum_{q,q'} \frac{qq'}{qq'} \right.$$

$$\left. \times \int_{\tau_1}^{\tau_2} \left(y(q, \tau)y(q', \tau) - \frac{1}{\beta} \int_0^\beta y(q, \tilde{\tau})y(q', \tilde{\tau})\, d\tilde{\tau} \right) d\tau \right]$$

$$\times \frac{1}{\beta} \sum_s \left[(2s+1)\mathrm{i}\pi T + \mu - \frac{1}{2m} \right.$$

$$\times \left(p^2 - \frac{2e}{v^{1/2}} \sum_q \frac{\boldsymbol{qp}}{q} \frac{1}{\beta} \int_0^\beta y(\boldsymbol{q}, \tau)\, \mathrm{d}\tau \right.$$

$$\left. \left. + \frac{e^2}{v} \sum_{q,q'} \frac{\boldsymbol{qq'}}{qq'} \frac{1}{\beta} \int_0^\beta y(\boldsymbol{q}, \tau) y(\boldsymbol{q'}, \tau)\, \mathrm{d}\tau \right) \right]^{-1}$$

$$\times \exp[-(2s+1)\mathrm{i}\pi(\tau_1 - \tau_2)/\beta]$$

$$y(\boldsymbol{q}, \tau) = \operatorname{Im} b(\boldsymbol{q}, \tau)$$

$$\tilde{y}(\boldsymbol{q}, \tau) = y(\boldsymbol{q}, \tau) - \frac{1}{\beta} \int_0^\beta y(\boldsymbol{q}, \tilde{\tau})\, \mathrm{d}\tilde{\tau}.$$

One should bear in mind the particular role of secular terms of the interaction with $b(\boldsymbol{q}, \tau)$ in equation (9). The sum over s in (9) is obtained as follows:

$$\frac{1}{\beta} \sum_s \frac{\exp[-(2s+1)\mathrm{i}\pi\tau/\beta]}{(2s+1)\mathrm{i}\pi/\beta - C} = \frac{\mathrm{e}^{-C\tau}}{2\cosh\frac{1}{2}\beta C} \begin{cases} -\mathrm{e}^{\beta C/2} & 0 < \tau < \beta \\ \mathrm{e}^{-\beta C/2} & -\beta < \tau < 0. \end{cases} \tag{10}$$

Further, we consider a more interesting case (from the physical point of view), when $U(x)$ is a short-range potential with one bound state, corresponding to the energy $-\varkappa^2/2m$. The given potential can be approximated by the zero-radius potential. In what follows we assume that the condition

$$1/\beta \ll -\mu \lesssim \varkappa^2/2m \tag{11}$$

is fulfilled. It is in agreement with the realistic physical situation when only a sufficiently deep bound state is populated. It follows from appendix 1 that if the inequality (11) is satisfied, $\mathcal{Y}_e(b)$ and $z_e(b)$ can be expressed in terms of $\mathcal{Y}_e^0(b)$:

$$\mathcal{Y}_e(\tau_1, \boldsymbol{p}_1; \tau_2, \boldsymbol{p}_2 | b) = \mathcal{Y}_e^0(\boldsymbol{p}_1 - \boldsymbol{p}_2; \tau_1, \tau_2 | b)$$

$$+ \frac{1}{(2\pi)^3} \int_0^\beta \mathrm{d}\tau'\, \mathrm{d}\tau''\, \mathcal{Y}_e^0(\boldsymbol{p}_1; \tau_1, \tau' | b)\, T(\tau', \tau'' | b)\, \mathcal{Y}_e^0(\boldsymbol{p}_2; \tau'', \tau_2 | b)$$

$$T(\tau', \tau'' | b) = -\frac{2\pi\mathrm{i}\varkappa}{m} \theta(\tau'' - \tau') \exp\left[\left(\mu + \frac{\varkappa^2}{2m} \right)(\tau' - \tau'') \right.$$

$$+ \frac{e^2}{mv} \sum_{q,q'} \frac{\boldsymbol{qq'}}{qq'} \left(\frac{1}{\beta} \int_0^\beta y(\boldsymbol{q}, \tau)\, \mathrm{d}\tau \int_{\tau'}^{\tau''} y(\boldsymbol{q'}, \tilde{\tau})\, \mathrm{d}\tilde{\tau} \right.$$

$$\left. \left. - \int_{\tau'}^{\tau''} y(\boldsymbol{q}, \tau) y(\boldsymbol{q'}, \tau)\, \mathrm{d}\tau \right) \right] \tag{12}$$

$$z_e(b) = \exp\left[\frac{e^2}{2mv} \sum_{q,q'} \frac{\boldsymbol{qq'}}{qq'} \left(\int_0^\beta y(\boldsymbol{q}, \tau) y(\boldsymbol{q'}, \tau)\, \mathrm{d}\tau \right. \right.$$

$$\left. \left. - \frac{1}{\beta} \int_0^\beta y(\boldsymbol{q}, \tau) y(\boldsymbol{q'}, \tilde{\tau})\, \mathrm{d}\tau\, \mathrm{d}\tilde{\tau} \right) \right].$$

Equation (12) is written out using (7), (A1.1), (A1.8) and taking account of (10) and (11). Substitution of (12) into (8) yields

$$\alpha_{ij} = \alpha_{ij}^{\mathrm{I}}(2\pi\mathrm{i}sT) + \alpha_{ij}^{\mathrm{II}}(2\pi\mathrm{i}sT) + \alpha_{ij}^{\mathrm{III}}(2\pi\mathrm{i}sT)$$

$$\alpha_{ij}^{\mathrm{I}}(2\pi\mathrm{i}sT) = \frac{1}{Z(2\pi)^3 v} \int_0^\beta \mathrm{d}\tau \exp(2\pi\mathrm{i}sT\tau) \int \delta b \exp\left(\int_0^\beta \mathcal{L}_b(\tilde{\tau})\, \mathrm{d}\tilde{\tau} \right)$$

$$\times z_e(b) \int d^3 p \mathcal{Y}_e^0(\tau, 0; \boldsymbol{p}|b) \mathcal{Y}_e^0(0, \tau; \boldsymbol{p}|b) \boldsymbol{p}_i \boldsymbol{p}_j$$

$$\alpha_{ij}^{11}(2\pi i s T) = \frac{1}{Z(2\pi)^3 v} \int_0^\beta d\tau \exp(2\pi i s T \tau) \int \delta b \exp\left(\int_0^\beta \mathcal{L}_b(\tilde{\tau}) d\tilde{\tau}\right) \tag{13}$$

$$\times z_e(b) \int d^3 p \, \boldsymbol{p}_i \boldsymbol{p}_j \int_0^\beta d\tau_1 \, d\tau_2 [\mathcal{Y}_e^0(\boldsymbol{p}; 0, \tau_1|b)$$

$$\times T(\tau_1, \tau_2|b) \mathcal{Y}_e^0(\boldsymbol{p}; \tau_2, \tau|b) \mathcal{Y}_e^0(\boldsymbol{p}; \tau, 0|b) + \mathcal{Y}_e^0(\boldsymbol{p}; 0, \tau|b)$$

$$\times \mathcal{Y}_e^0(\boldsymbol{p}; \tau, \tau_1|b) T(\tau_1, \tau_2|b) \mathcal{Y}_e^0(\boldsymbol{p}; \tau_2, 0|b)]$$

$$\alpha_{ij}^{111} = \frac{1}{Z(2\pi)^3 v} \int_0^\beta d\tau \exp(i2\pi s T \tau) \int \delta b \exp\left(\int_0^\beta \mathcal{L}_b(\tilde{\tau}) d\tilde{\tau}\right) z_e(b) \int d^3 p \, d^3 p' \, \boldsymbol{p}_i \boldsymbol{p}_j'$$

$$\times \int_0^\beta d\tau_1 \, d\tau_1' \, d\tau_2 \, d\tau_2' \mathcal{Y}_e^0(\boldsymbol{p}; 0, \tau_1|b) T(\tau_1, \tau_2|b)$$

$$\times \mathcal{Y}_e^0(\boldsymbol{p}'; \tau_2, \tau|b) \mathcal{Y}_e^0(\boldsymbol{p}'; \tau, \tau_1'|b) T(\tau_1', \tau_2'|b) \mathcal{Y}_e^0(\boldsymbol{p}; \tau_2', 0|b).$$

It is interesting to examine the physical sense of the components α_{ij}. The quantity α_{ij}^1 corresponds to transitions from the continuous spectrum and is proportional, as can be easily verified, to the population of states of this spectrum, i.e. it involves an exponentially small factor $e^{\mu/T}$. The component α_{ij}^{11} corresponds to optical transitions from the discrete spectrum to the continuous one. The quantity α_{ij}^{11} can be evaluated in independent optical experiments by measuring photoconduction. Finally, α_{ij}^{111}, containing the T matrix twofold, describes the indirect interaction of light and phonons. In the first non-vanishing order of perturbation theory, this term corresponds to the virtual transition of a localised electron upon light absorption to a continuous spectrum with subsequent return of the electron to the initial level and emission of the appropriate number of phonons. When there is no interaction with phonons, α_{ij}^{111} becomes zero. At $\Omega - \varkappa^2/2m > 0$ and a finite temperature, the contribution of the term $\alpha_{ij}^{111}(\Omega)$ to absorption turns out to be less than that of $\alpha_{ij}^{11}(\Omega)$ due to the small value of the corresponding accessible finite phase volume. However, at $\Omega - \varkappa^2/2m \ll 0$ and $T \to 0$ it is $\alpha_{ij}^{111}(\Omega)$ that appears greatest. It is important that this component produces a non-zero contribution to the light absorption at $T \to 0$.

We present a detailed calculation of the quantity $\chi = \alpha_{ij}^{11}/\text{Sp}\, \mathcal{Y}_{|\tau_1 \approx \tau_2}$ which is proportional to the extinction coefficient. Using (9)–(12) and performing some transformations this can be given, with an accuracy of the order of $e^{\mu/T}$, in the form

$$\chi(2\pi i s T) = \frac{1}{Z_0} \int \delta y(\boldsymbol{q}, \tau) \exp\left[-\int_0^\beta \frac{\varepsilon}{4\pi} \sum_q y(\boldsymbol{q}, \tilde{\tau}) \right.$$

$$\times \left(-\frac{\partial^2}{\partial \tilde{\tau}^2} + \omega^2 \right) y(\boldsymbol{q}, \tilde{\tau}) d\tilde{\tau} \left] \int d^3 p \, p_i^2 \int_0^\beta d\tau \, d\tau_1 \, d\tau_2 \right.$$

$$\times \theta(\tau_1 - \tau_2) [\theta(\tau - \tau_1) + \theta(\tau_2 - \tau)] \exp\left(i2\pi s T \tau - \frac{\varkappa^2 + p^2}{2m} \right.$$

$$\times (\beta + \tau_2 - \tau_1) \left) \exp\left(-\frac{e^2}{2mv} \sum_{q,q'} \frac{\boldsymbol{q} \boldsymbol{q}'}{qq'} \int_{\tau_1}^{\tau_2 + \beta} \tilde{y}(\boldsymbol{q}, \tilde{\tau}) \tilde{y}(\boldsymbol{q}', \tilde{\tau}) d\tilde{\tau} \right.$$

$$+ \frac{e}{mv^{1/2}} \sum_q \frac{\boldsymbol{q} \boldsymbol{p}}{q} \int_{\tau_2}^{\tau_1} \tilde{y}(\boldsymbol{q}, \tilde{\tau}) d\tilde{\tau} \right)$$

$$= \frac{1}{3Z_0} \int d^3p \int_0^\beta d\tau \int_{-\tau/2}^{\tau/2} d\tau_1 \, d\tau_2 \exp\left(-\frac{\varkappa^2 + p^2}{2m} \tau + i2\pi sT(\tau_1 + \tau_2) \right)$$

$$\times \int \delta y(\boldsymbol{q}, \tau) \left(\boldsymbol{p} + \frac{e}{v^{1/2}} \sum_{\boldsymbol{q}} \frac{\boldsymbol{q}}{q} \frac{1}{\tau} \int_{-\tau/2}^{\tau/2} y_1(\boldsymbol{q}, \tilde\tau) \, d\tilde\tau \right)^2$$

$$\times \exp\left\{ -\int_{-\beta/2}^{\beta/2} d\tilde\tau \left[\sum_{\boldsymbol{q}} y(\boldsymbol{q}, \tilde\tau) \frac{\varepsilon}{4\pi} \left(-\frac{\partial^2}{\partial\tilde\tau^2} + \omega^2 \right) y(\boldsymbol{q}, \tilde\tau) \right. \right.$$

$$+ \sum_{\boldsymbol{q}, \boldsymbol{q}'} y_1(\boldsymbol{q}, \tilde\tau) \frac{e^2}{2mv} \frac{\boldsymbol{q}\boldsymbol{q}'}{qq'} \theta(\tfrac{1}{2}\tau - |\tilde\tau|) \Big(y_1(\boldsymbol{q}', \tilde\tau)$$

$$\left. \left. - \frac{1}{\tau} \int_{-\tau/2}^{\tau/2} y_1(\boldsymbol{q}', \tau') \, d\tau' \right) \right] \right\} \tag{14}$$

$$Z_0 = \int \delta y(q, \tau) \exp\left\{ -\int_{-\beta/2}^{\beta/2} d\tilde\tau \left[\sum_{\boldsymbol{q}} y(\boldsymbol{q}, \tilde\tau) \frac{\varepsilon}{4\pi} \left(-\frac{\partial^2}{\partial\tilde\tau^2} + \omega^2 \right) y(\boldsymbol{q}, \tilde\tau) \right] \right\}$$

$$y_1(\boldsymbol{q}, \tau) = \tfrac{1}{2}[y(\boldsymbol{q}, \tau) + y(\boldsymbol{q}, -\tau)].$$

In the last expression of (14) the following transformations in the integrand were performed in succession: $\tau \to \tau - \tau_1$, $\delta y(\tau) \to \delta y(\tau + \tau_1)$ and the following substitution of variables was made: $\tau_1 + \tau_2 \to \tau$, $\tau_1 - \tau_2 \to \tau_1$, $\tau \to \tau_2$. Further consideration of (14) is rather simple within the framework of perturbation theory for the case of weak coupling. Here we obtain

$$\chi(2\pi i s T) = \frac{\pi}{2} \frac{(2m)^{5/2}}{(2\pi i s T)^2} \int_0^\beta d\tau \frac{\exp(-\varkappa^2/2m)\tau}{\tau^{5/2}} \sin^2 \pi s T\tau$$

$$\times \left(1 + \frac{e^2}{2mvZ_0} \sum_{\boldsymbol{q}, \boldsymbol{q}'} \frac{\boldsymbol{q}\boldsymbol{q}'}{qq'} \int \delta y(\boldsymbol{q}, \tau) \left(\frac{20}{3} \frac{1}{\tau} \right. \right.$$

$$\times \int_0^{\tau/2} d\tau' \, d\tau'' \, y_1(\boldsymbol{q}, \tau') y_1(\boldsymbol{q}', \tau'') - 2 \int_0^{\tau/2} d\tau' \, y_1(\boldsymbol{q}, \tau') y_2(\boldsymbol{q}', \tau') \Big)$$

$$\times \exp\left\{ -\int_{-\beta/2}^{\beta/2} d\tilde\tau \left[\sum_{\boldsymbol{q}} y(\boldsymbol{q}, \tilde\tau) \frac{\varepsilon}{4\pi} \left(-\frac{\partial^2}{\partial\tilde\tau^2} + \omega^2 \right) y(\boldsymbol{q}, \tilde\tau) \right] \right\} \bigg)$$

$$= \frac{1}{3} \frac{(2\pi)^{3/2}(2m)^{5/2}}{(2\pi i s T)^2} \int_0^\beta d\tau \frac{\exp(-\varkappa^2/2m \pm 2\pi i s T)\tau}{\tau^{1/2}}$$

$$\times \left(1 - \frac{e^2}{2m} \frac{(4\pi)^2 q_0^3}{3\varepsilon\omega \sinh \omega/2T} \left[\tfrac{8}{3}(2\pi i s T - \varkappa^2/2m)^3 F_1(\tau) \right. \right.$$

$$+ 8(2\pi i s T - \varkappa^2/2m)^2 F_1'(\tau) + 8(2\pi i s T - \varkappa^2/2m) F_1''(\tau)$$

$$+ 8F_1'''(\tau) + (2\pi i s T - \varkappa^2/2m)^2 F_2(\tau) - 2(2\pi i s T - \varkappa^2/2m)$$

$$\times F_2'(\tau) + F_2(\tau)] \bigg) \tag{15}$$

where q_0 is the cutoff radius of the sums over q in the momentum space, and

$$F_1(\tau) = \int_0^{\tau/2} K_0(\tau', \tau'') \, d\tau' \, d\tau''$$

$$F_2(\tau) = \int_0^{\tau/2} K_0(\tau', \tau') \, d\tau'$$

$$K_0(\tau', \tau'') = \cosh \omega(\tfrac{1}{2}\beta - |\tau' - \tau''|) + \cosh \omega(\tfrac{1}{2}\beta - |\tau' + \tau''|).$$

The case of strong coupling is most interesting. Using the results of appendix 2, one may analytically evaluate the integral over $\delta y(q, \tau)$ in (14):

$$\chi(2\pi i s T) = \frac{(2\pi)^{3/2}(2m)^{5/2}}{3(2\pi i s T)^2} \int_0^\beta d\tau \frac{\exp(-\varkappa^2/2m)\tau}{\tau^{5/2}} \sin^2 \pi s T\tau \left(\left| \frac{D_0(\omega)}{D(\tilde{\omega}, \omega, \tau)} \right| \right)^{3/2}$$

$$\times \left(1 + \frac{\tilde{\omega}^2 - \omega^2}{\tau} \frac{\int_0^{\tau/2} K_1(\tau', \tau'') \, d\tau' \, d\tau''}{1 - [(\tilde{\omega}^2 - \omega^2)/\tau]2\int_0^{\tau/2} K_1(\tau', \tau'') \, d\tau' \, d\tau''} \right)$$

$$K_1(\tau', \tau'') = \frac{\varphi_1(\tau')\varphi_2(\tau'')\theta(\tau'' - \tau') + \varphi_2(\tau')\varphi_1(\tau'')\theta(\tau' - \tau'')}{\varphi_2'(0)} \tag{16}$$

$$\varphi_1(\tilde{\tau}) = \cosh \tilde{\omega}\tilde{\tau}$$

$$\varphi_2(\tilde{\tau}) = \cosh \omega\tfrac{1}{2}(\tau - \beta) \cosh \tilde{\omega}[\tfrac{1}{2}(\tau - \tilde{\tau})] + (\omega/\tilde{\omega}) \sinh \omega\tfrac{1}{2}(\tau - \beta) \sinh \tilde{\omega}(\tilde{\tau} - \tfrac{1}{2}\tau)$$

$$\tilde{\omega}^2 = \omega^2 + \frac{4\pi e^2 q_0^3}{3\varepsilon m} = \omega^2 + \frac{e^2 v_q}{\varepsilon m}.$$

v_q stands for the volume in the momentum space. This volume enters into the renormalised coupling constant $\tilde{\omega}^2 - \omega^2 = e^2 v_q / \varepsilon m$, the only parameter defining the interaction with a phonon field. The expressions for the ratio of the determinants $D_0(\omega)$ and $D(\omega, \tilde{\omega}, \tau)$, are given in appendix 2.

Let us now perform the analytical continuation $2\pi s T i \to \Omega$. Under an additional requirement for limitation on the growth along the real axis this continuation is unambiguous, according to the Carlson theorem. A scheme of such a continuation can be illustrated, for instance, for the first term on the right-hand side of equation (16):

$$\int_0^\beta \frac{\exp[-(\varkappa^2/2m)\tau]}{\tau^{5/2}} \left(\left| \frac{D_0(\omega)}{D(\tilde{\omega}, \omega, \tau)} \right| \right)^{3/2} \frac{\sin^2 \pi s T\tau}{(2\pi s T)^2} \, d\tau$$

$$= -\frac{1}{4\Omega^2} \left(\int_0^{i\infty} - \int_\beta^{\beta + i\infty} \right) d\tau \left[\frac{\exp(-\varkappa^2/2m)\tau}{\tau^{5/2}} \left(\left| \frac{D_0(\omega)}{D(\tilde{\omega}, \omega, \tau)} \right| \right)^{3/2} \right.$$

$$\times [1 + 2\pi s T i\tau - \exp(2\pi s T i\tau)] \right] + \frac{1}{4\Omega^2} \left(\int_{-\infty}^0 - \int_{\beta - i\infty}^\beta \right) d\tau$$

$$\times \left[\frac{\exp(-\varkappa^2/2m)\tau}{\tau^{5/2}} \left(\left| \frac{D_0(\omega)}{D(\tilde{\omega}, \omega, \tau)} \right| \right)^{3/2} [1 - 2\pi s T i\tau - \exp(-2\pi s T i\tau)] \right]$$

$$\Rightarrow \frac{i^{-1/2}}{4\Omega^2} \int_0^\infty d\tau \left[\frac{\exp(-i\varkappa^2/2m)\tau}{\tau^{5/2}} \left(\left| \frac{D_0(\omega)}{D(\tilde\omega, \omega, i\tau)} \right| \right)^{3/2} \right.$$

$$\left. \times [1 + i\Omega\tau - \exp(i\Omega\tau)] \right] + (\Omega \to -\Omega).$$

Applying this scheme to equation (15) we obtain the optical response function within the framework of perturbation theory:

$$\operatorname{Im} \chi(\Omega) = \tfrac{1}{6}\pi^2 (2m)^{5/2} \frac{e^2}{\Omega^2} \left\{ \Omega_f^{3/2}\theta(\Omega_f) + \frac{e^2}{2m} \frac{4\pi v_q}{3\varepsilon\omega^2} \right.$$

$$\times \left[\tfrac{4}{3}(\coth \tfrac{1}{2}\omega\beta) \frac{\Omega_f^{5/2}}{\omega}\theta(\Omega_f) + \frac{\exp(-\tfrac{1}{2}\omega\beta)}{\sinh \tfrac{1}{2}\omega\beta} \left((\Omega_f + \omega)^{3/2} \right. \right.$$

$$\left. + \frac{2}{3\omega}(\Omega_f + \omega)^{5/2} \right) \theta(\Omega_f + \omega) + \frac{\exp(\tfrac{1}{2}\omega\beta)}{\sinh \tfrac{1}{2}\omega\beta} \left((\Omega_f - \omega)^{3/2} \right. \tag{17}$$

$$\left. \left. \left. + \frac{2}{3\omega}(\Omega_f - \omega)^{5/2} \right) \theta(\Omega_f - \omega) \right] \right\}$$

$$\Omega_f = \Omega - \Omega_0 \qquad \Omega_0 = \varkappa^2/2m.$$

Each summand in (17) can be interpreted in terms of optical excitation with absorption and emission of phonons.

After continuing equation (16) to a real t the problem of determining the absorption coefficient for the most interesting case of strong coupling is reduced to calculating the quadratures

$$\operatorname{Im} \chi(\Omega) = \frac{1}{3} \frac{\pi^{3/2}}{\sqrt{2}} (2m)^{5/2} \frac{e^2}{\Omega^2} \operatorname{Re} i^{-1/2} \int_0^\infty dt \frac{\exp(i\Omega_f t + \tfrac{3}{2}i\phi(t))}{t^{1/2}}$$

$$\times [\Omega_f^2(1 + \phi_1(t)) + 2\Omega_f[\phi'(t)(1 + \phi_1(t))$$

$$+ \phi_1'(t)] + \phi''(t)(1 + \phi_1(t)) + 2\phi'(t)\phi_1'(t) - \phi_1''(t)] \tag{18}$$

where

$$\phi(t) = -(\tilde\omega^2 - \omega^2) \int_0^t \left(K(\tfrac{1}{2}i\tau, \tfrac{1}{2}i\tau) + \frac{4}{\tau^2} \int_0^{\tau/2} K(i\tau', i\tau'') \, d\tau' \, d\tau'' \right.$$

$$\left. - \frac{4}{\tau} \int_0^{\tau/2} K(\tfrac{1}{2}i\tau, i\tau') \, d\tau' \right) d\tau$$

$$\phi_1(t) = \tfrac{2}{3}i \frac{\tilde\omega^2 - \omega^2}{t} 4 \int_0^{t/2} K(i\tau', i\tau'') \, d\tau' \, d\tau''$$

$$K(\tau', \tau'') = K_1(\tau', \tau'') + \frac{\tilde\omega^2 - \omega^2}{\tau}$$

$$\times \frac{(2\int_0^{\tau/2} K_1(\tau', \tilde\tau') K_1(\tau'', \tilde\tau'') \, d\tilde\tau' \, d\tilde\tau'')}{[1 - (\tilde\omega^2 - \omega^2/\tau)2\int_0^{\tau/2} K_1(\tilde\tau', \tilde\tau'') \, d\tilde\tau' \, d\tilde\tau'']^{-1}}.$$

The integral in (18) will be taken by the method of steepest descent, after passing to the integration variable $u = t^{1/2}$. This method can be considered applicable if at least one of the conditions corresponding to strong coupling and/or high temperatures or to the frequency range away from the threshold is fulfilled:

$$|\Omega_f| = |\Omega - \varkappa^2/2m| \gg \tilde{\omega}^2$$

$$(\tilde{\omega}^2 - \omega^2) \coth \tfrac{1}{2}\omega\beta \gg \omega^2. \tag{19}$$

The saddle point lies in the origin and it turns out to be necessary to retain terms of the order of u^6 in the expansion since a term proportional to u^4 enters with a small coefficient, and under conditions (19) it may be omitted, whereas a term proportional to u^2 at $\Omega_f > 0$ does not lead to the temperature dependence of the spectrum. As a result we obtain

$$\operatorname{Im}\chi(\Omega) = \frac{\pi^{3/2}(2m)^{5/2}e^2}{3\Omega^2} \operatorname{Re}\left(i^{-1/2} \int_0^\infty (-\Omega_f^2 + 2i\Omega_b^3 u^2\right.$$

$$\left. + \Omega_f\Omega_b^3 u^4) \exp(i\Omega_f u^2 + i\Omega_b^3 u^6) \, du \right) \tag{20}$$

$$\Omega_b = \left(T\frac{\tilde{\omega}^2}{6\omega^2}(\tilde{\omega}^2 - \omega^2) \right)^{1/3}.$$

In writing equation (20), we considered for simplicity the phonon frequency ω far less than $\tilde{\omega}$ and T, and expanded the trigonometric functions in a series in ω. The integral (20) is performed by the formula

$$\operatorname{Re} i^{-1/2} \int_0^\infty \exp[i(xu^2 + y^3 u^6] \, du$$

$$= \begin{cases} \dfrac{1}{6}\dfrac{|x|}{\sqrt{3}\pi y^{3/2}}\left[K_{1/3}\left(\left(\dfrac{|x|}{3y}\right)^{3/2}\right)\right]^2 & x < 0, y > 0 \\[4mm] \dfrac{\pi^{3/2}x}{4(3y)^{3/2}} H_{1/3}^{(1)}\left(\left(\dfrac{x}{3y}\right)^{3/2}\right)H_{1/3}^{2}\left(\left(\dfrac{x}{3y}\right)^{3/2}\right) & x > 0, y > 0 \end{cases} \tag{21}$$

which is checked by differentiating with respect to x. It is essential that the products of the cylindrical functions $K_{1/3}$, $H_{1/3}^{(1,2)}$ are smoothly varying functions of their arguments, and this allows consideration of different limiting relations of the parameters. Away from the threshold at $|\Omega_f^3| \gg \Omega_b^3$ we obtain

$$\operatorname{Im}\chi \sim \frac{\Omega_f^{3/2}}{\Omega^2} \begin{cases} 1 + \dfrac{15}{8}\dfrac{\Omega_b^3}{\Omega_f^3} + O\left(\left(\dfrac{\Omega_b}{\Omega_f}\right)^6\right) & \Omega_f > 0 \\[4mm] \exp\left(-\dfrac{|\Omega_f|^{3/2}}{2^{8/3}3^{1/3}(\Omega_b)^{3/2}} \right) & \Omega_f < 0. \end{cases} \tag{22}$$

At $\Omega_f \sim 0$ we have

$$\operatorname{Im}\chi \sim \frac{1}{\Omega^2}\left((\Omega_b)^{1/2}\Omega_f + \frac{3^{4/3}}{4}\Omega_b^{3/2} \right). \tag{23}$$

4. Conclusion

The calculations performed admit direct generalisation to describing optical transitions on centres with more than one discrete level and interactions with different-type phonons. Without using these generalisations, the results obtained at the end of the previous section can be applied to describing the optical transitions in systems with negative impurity ions possessing only one discrete level in polar media. The curves for optical absorption of solvated electrons and negative ions in polar media are asymmetrical, the asymmetry growing with temperature (see Brodsky and Tsarevsky 1980). On moving to the red side of the absorption maximum, the drop changes from the threshold '$\Omega_f^{3/2}$ low' to a linear low and then turns to an exponential damping when $\Omega_f < 0$, $|\Omega_f| > \Omega_b$. All these characteristic properties at reasonable values of parameters are described quantitatively by (22).
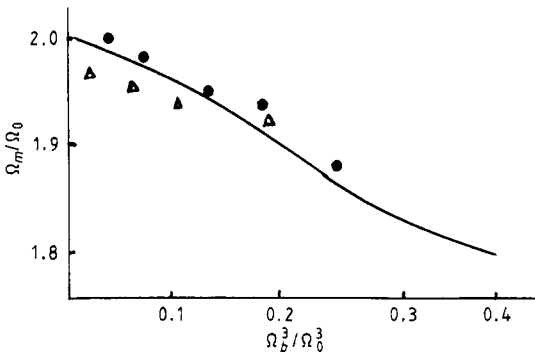

Figure 1. Peaks of absorption of solvated electrons in methanol ($\bullet$) and water ($\triangle$) against $\hbar\Omega_b$.
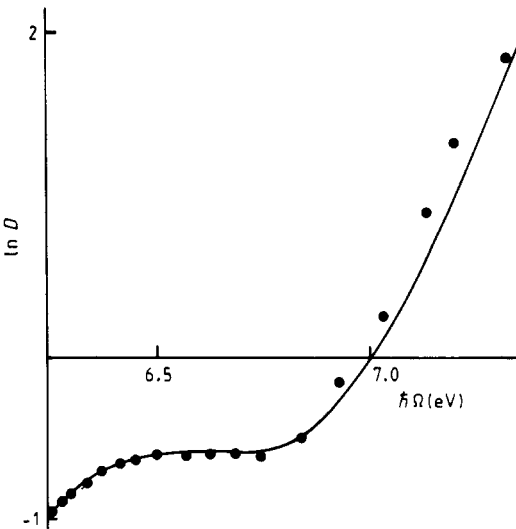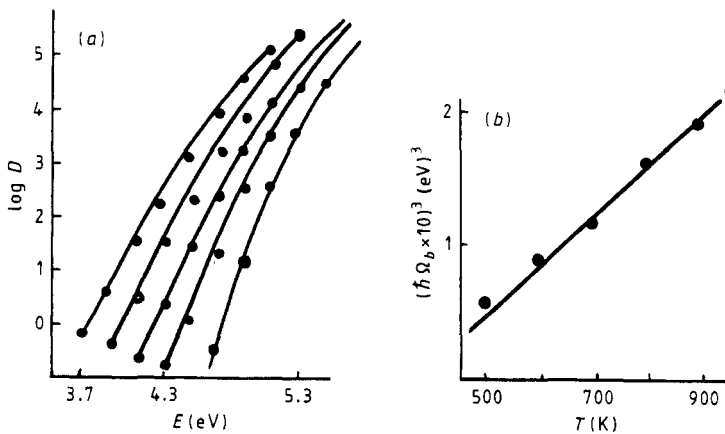

Figure 2. The optical density D against photon energy $\hbar\Omega$. Points show the data of Mahr for the absorption of pure KCl at 300 K. The curve corresponds to the present theory using equations (20) and (21).

The physical sense of these equations (23) describing an absorption may be interpreted as follows. The behaviour of absorption at the frequencies $\Omega_f \sim \Omega_b$ is defined by the fact that, near the threshold, the accessible final phase volume is less than the phase volume accessible for the non-interacting particle. Transition is possible only in the direction where the projection of the polarisation field is zero and which, accordingly, conforms to the zero mean classical kinetic energy of electron pulsing. The threshold law is no longer three dimensional and as a result there appears a region at $\Omega_f \sim \Omega_b$ linear in Ω_f, instead of the usual cross section proportionality of production of $\Omega_f^{3/2}$ (Brodsky and Tsarevsky 1981). In contrast, further growth of absorption with increasing Ω_f, involving an increase in the accessible final phase volume, turns out to be faster than that for the particle not bound with phonons. Obviously such a behaviour cannot be obtained when only the Stark-type initial level shift in a phonon field is considered, and the electron matrix elements of the optical transition are taken constant. It should also be noted that an account of the first non-vanishing order in the Stark-type energy shift always leads to 'repulsion' of the lower levels and levels closer to it. In other words, it can in no way explain the shift of the absorption maximum to the red side with increasing temperature, observed in the conditions of strong coupling, though it can be interpreted in the framework of the theory developed under conditions of sufficiently strong coupling. At the same time, with a rather weak coupling where an inequality inverse to (19) is fulfilled, equations (17) and (18) actually lead to the shift of the absorption maximum to the blue side with increasing temperature. The exponential damping at $\Omega_f < 0$ is in agreement with the tunnelling at favourable values of the phonon field coordinates. The corresponding expression is close to that for the empirical Urbach law for optical transitions in semiconductors, though it somewhat differs from it analytically. In particular, as in Dow and Redfield (1972) the energy $\hbar\Omega_f$ enters into the exponent to the power $\frac{3}{2}$ and not linearly, as is stated in the Urbach rule. The results obtained in § 3 can be compared qualitatively with optical transitions in semiconductors with the condition that the initial level $-\varkappa^2/2m$ conforms to an extremely narrow valence band and the continuous spectrum conforms to a conduction band. It is most essential in this comparison to describe the transition from the

Figure 3. (a) The optical density D against photon energy $\hbar\Omega$ for the absorption of I^- in KCl. Points show the data of Mahr. Curves correspond to the present theory using equations (20) and (21) for, from left to right, $T = 900, 800, 700, 600, 500$ K. (b) Temperature dependence of the parameter Ω_b deduced from (a).

exponential absorption law to the power law in the framework of a unique formula, observed experimentally with increasing frequency.

The curve in figure 1 shows a comparison of theoretical and experimental results for the temperature shift for the optical absorption of a solvated electron in methanol and water. As an example of threshold range analysis of optical transitions in semiconductors we choose the KCl system, investigated by Mahr (1963). As can be seen from figure 2, the theory can describe the complex behaviour of the experimental curve in the whole threshold range. Figure 3 shows the comparison of the theory with Mahr's results concerning the optical absorption of I^- in KCl near the red edge of the absorption band below the threshold of exciton creation. As can be seen from figure 3(b), the relation $\Omega_b^3 \sim T$ is in agreement with experimental results. Note that the smooth maximum just below the threshold at ≈ 6.5 eV in figure 2 is associated with phase-volume relations and has the same nature as the cusps in cross sections near thresholds in scattering theory (see Newton 1966).

It is obvious that there is an analogy between the above expressions and formulae of the theory of phase transitions of the second kind, the phonon field playing the role of the coordinate-dependent order parameter in the effective Ginzburg–Landau Hamiltonian and the threshold value corresponding to the phase transition point.

Appendix 1

In the case where $U(x)$ is approximated by a potential proportional to $\delta^3(x)$ the Green function $\mathcal{Y}_e(\tau_1, x_1; \tau_2, x_2|\gamma b)$ with γ as the parameter defining the force of interaction, is presented in the form

$$\mathcal{Y}_e(\tau_1, x_1; \tau_2, x_2|\gamma b) = \mathcal{Y}_e^0(\tau_1, x_1; \tau_2, x_2|\gamma b)$$

$$+ \int_0^\beta d\tau' d\tau'' \, \mathcal{Y}_e^0(\tau_1, x_1; \tau', 0|\gamma b)$$

$$\times T(\tau', \tau''|\gamma b) \mathcal{Y}_e^0(\tau'', 0; \tau_2, x_2|\gamma b). \tag{A1.1}$$

Here the quantity $T(\tau', \tau''|\gamma b)$ is to be determined. (A1.1) is written out proceeding from the structure of iterative series for a T matrix, each of its summands containing the delta function $\delta^3(x)$ at the edges. To find $T(\tau', \tau''|\gamma b)$ we use the operator equality:

$$\frac{\partial \hat{\mathcal{Y}}_e}{\partial \gamma} = -\hat{\mathcal{Y}}_e \frac{\partial \hat{\mathcal{Y}}_e^{-1}}{\partial \gamma} \hat{\mathcal{Y}}_e = -\hat{\mathcal{Y}}_e \frac{\partial \hat{\mathcal{Y}}_e^{0-1}}{\partial \gamma} \hat{\mathcal{Y}}_e. \tag{A1.2}$$

Substituting (A1.1) into (A1.2) we obtain

$$\frac{\partial T^{-1}}{\partial \gamma} = -\frac{\partial}{\partial \gamma} \mathcal{Y}_e^0(\tau_1, 0; \tau_2, 0|\gamma b). \tag{A1.3}$$

In (A1.3) we have introduced the quantity $T^{-1}(\tau_1, \tau_2|\gamma b)$ determined from the equation

$$\int_0^\beta d\tau \, T^{-1}(\tau_1, \tau|\gamma b) T(\tau, \tau_2|\gamma b) = \frac{2\pi}{\beta} \delta\left(\sin \frac{2\pi}{\beta}(\tau_1 - \tau_2)\right). \tag{A1.4}$$

Applying the value of T^{-1} at $\gamma = 0$ obtained from the well known expression of the

theory of potential scattering, from (A1.3) and (11) we obtain

$$T^{-1}(\tau_1, \tau_2 | \gamma b) = -\frac{\mathrm{i} 2m}{(2\pi)^3 \beta} \exp\left[-\frac{e^2}{2mv} \sum_{q,q'} \int_{\tau_1}^{\tau_2} \mathrm{d}\tau \left(y(\boldsymbol{q}, \tau) \right. \right.$$

$$\times y(\boldsymbol{q}', \tau) - \frac{1}{\beta} \int_0^\beta y(\boldsymbol{q}, \tilde{\tau}) y(\boldsymbol{q}', \tilde{\tau}) \, \mathrm{d}\tilde{\tau}$$

$$\left. \left. + 2y(\boldsymbol{q}, \tau) \frac{1}{\beta} \int_0^\beta y(\boldsymbol{q}', \tilde{\tau}) \, \mathrm{d}\tilde{\tau} \right) \right]$$

$$\times \int \mathrm{d}^3 p \sum_s \left(\left\{ \frac{1}{p^2 - 2m[(2s+1)\mathrm{i}\pi/\beta + \tilde{\mu}]} \right. \right.$$

$$\left. - \left[\left(p - \frac{e}{v^{1/2}} \sum_q \frac{\boldsymbol{q}}{q} \tilde{y}(\boldsymbol{q}, \tau_1) \right)^2 + \varkappa^2 \right]^{-1} \right\}$$

$$\times \exp\left(-\frac{(2s+1)}{\beta} \mathrm{i}\pi(\tau_1 - \tau_2) \right.$$

$$\left. \left. - \frac{e}{mv^{1/2}} \sum_q \int_{\tau_2}^{\tau_1} \frac{\boldsymbol{q}\boldsymbol{p}}{q} \tilde{y}(\boldsymbol{q}, \tilde{\tau}) \, \mathrm{d}\tilde{\tau} \right) \right)$$

$$= -\mathrm{i} \frac{2m}{\beta(2\pi)^3} \exp\left[-\frac{e^2}{2mv} \sum_{q,q'} \frac{\boldsymbol{q}\boldsymbol{q}'}{qq'} \int_{\tau_1}^{\tau_2} \mathrm{d}\tau \left(y(\boldsymbol{q}, \tau) y(\boldsymbol{q}', \tau) \right. \right.$$

$$\left. \left. - \frac{1}{\beta} \int_0^\beta y(\boldsymbol{q}, \tilde{\tau}) y(\boldsymbol{q}', \tilde{\tau}) \, \mathrm{d}\tilde{\tau} + 2y(\boldsymbol{q}, \tau) \frac{1}{\beta} \int_0^\beta y(\boldsymbol{q}', \tilde{\tau}) \, \mathrm{d}\tilde{\tau} \right) \right] \tag{A1.5}$$

$$\times \left[2m\left(-\frac{\partial}{\partial \tau_1} + \tilde{\mu} \right) + \varkappa^2 + \frac{e^2}{v} \sum_{q,q'} \frac{\boldsymbol{q}\boldsymbol{q}'}{qq'} \tilde{y}(\boldsymbol{q}, \tau_1) \tilde{y}(\boldsymbol{q}', \tau_1) \right]$$

$$\times \int \mathrm{d}^3 p \sum_s \left(\exp\left(-\frac{(2s+1)}{\beta} \mathrm{i}\pi(\tau_1 - \tau_2) + \frac{e}{mv^{1/2}} \sum_q \frac{\boldsymbol{q}\boldsymbol{p}}{q} \int_{\tau_2}^{\tau_1} \tilde{y}(\boldsymbol{q}, \tilde{\tau}) \, \mathrm{d}\tau \right) \right.$$

$$\left. \times \left\{ \left[p^2 - 2m\left(\frac{2s+1}{\beta} \mathrm{i}\pi + \tilde{\mu} \right) \right] \left[\left(p - \frac{e}{v^{1/2}} \sum_q \frac{\boldsymbol{q}}{q} \tilde{y}(\boldsymbol{q}, \tau_1) \right)^2 + \varkappa^2 \right] \right\}^{-1} \right)$$

$$\tilde{\mu} = \mu - \frac{e^2}{2mv} \sum_{q,q'} \frac{\boldsymbol{q}\boldsymbol{q}'}{qq'} \left(\int_0^\beta y(\boldsymbol{q}, \tilde{\tau}) y(\boldsymbol{q}', \tilde{\tau}) \, \mathrm{d}\tilde{\tau} \right.$$

$$\left. - \frac{1}{\beta} \int_0^\beta y(\boldsymbol{q}, \tilde{\tau}) y(\boldsymbol{q}', \tilde{\tau}') \, \mathrm{d}\tilde{\tau} \, \mathrm{d}\tilde{\tau}' \right).$$

In (A1.5) we have performed a shift in the integration variable p. It is essential that the derivative of the summand with the reciprocal length of scattering $\varkappa > 0$ in the first expression of (A1.5) for T^{-1} with respect to γ is zero. The $y(\boldsymbol{q}, \tau_1)$-dependent addition, cancelled by the shift of variable p, is introduced into the denominator of this summand (which makes the integral taken over p converging at $p \to 0$) to simplify further calculation. In what follows we use an approximation satisfying (11), assuming that the values of $\exp(-\varkappa^2/2mT)$ and $\mathrm{e}^{\mu/T}$ tend to zero. In such an approximation for the

integral entering into (A1.5), for instance, at $-1/2T \le \tau_1 - \tau_2 \le 1/2T$ with the help of (10) we have

$$\frac{2m}{\beta(2\pi)^3} \int d^3p \sum_s \left(\exp\left(-\frac{(2s+1)}{\beta} i\pi(\tau_1 + \tau_2) + \frac{e}{mv^{1/2}} \sum_q \frac{qp}{q} \int_{\tau_2}^{\tau_1} \tilde{y}(q, \tilde{\tau}) d\tilde{\tau} \right) \right.$$

$$\left. \times \left\{ \left[p^2 - 2m\left(\frac{2s+1}{\beta} i\pi + \tilde{\mu} \right) \right] \left[\left(p - \frac{e}{v^{1/2}} \sum_q \frac{q}{q} y(q, \tau_1) \right)^2 + \varkappa^2 \right] \right\}^{-1} \right)$$

$$\approx \exp\left[\left(\mu + \frac{\varkappa^2}{2m} \right)(\tau_1 - \tau_2) + \frac{e^2}{2mv} \sum_{q,q'} \frac{qq'}{qq'} \right.$$

$$\left. \times \int_{\tau_2}^{\tau_1} \tilde{y}(q, \tau) \tilde{y}(q', \tau) d\tau \right] \mathscr{I}(\tau_1, \tau_2) \tag{A1.6}$$

$$\mathscr{I}(\tau_1, \tau_2) = -\frac{\theta(\tau_1 - \tau_2)}{(2\pi)^3} \int d^3p \exp\left[-\frac{\varkappa^2 + p^2}{2m}(\tau_1 - \tau_2) \right]$$

$$\times \left[\left(p - \frac{e}{v^{1/2}} \sum_q \frac{q}{q} \tilde{y}(q, \tau_1) \right)^2 + \varkappa^2 \right]^{-1}$$

$$\times \exp\left[\frac{e}{mv^{1/2}} \sum_q \frac{qp}{q} \int_{\tau_2}^{\tau_1} \tilde{y}(q, \tilde{\tau}) d\tilde{\tau} \right.$$

$$\left. -\frac{e^2}{2mv} \sum_{q,q'} \frac{qq'}{qq'} \int_{\tau_2}^{\tau_1} y(q, \tilde{\tau}) y(q', \tilde{\tau}) d\tilde{\tau} \right]$$

$$= \begin{cases} 0 & \text{provided } \tau_1 - \tau_2 \ne 0 \\ \infty & \text{provided } (\tau_1 - \tau_2) \to 0 \end{cases} \qquad \text{when } \exp(-\varkappa^2 \beta / 2m) \to 0.$$

At $\tau_1 = \tau_2$ the divergence is delta-function-like and one should bear in mind that below only the integrals of the derivative $\partial \mathscr{I} / \partial \tau_1$ multiplied by smooth functions of τ_1 enter into the calculations. In addition, due to properties of the Fourier series of jump functions, the value of $\theta(\tau_1 - \tau_2)$ at $\tau_1 = \tau_2$ should be assumed equal to $\frac{1}{2}$. To support the above statement on the character of singularity and to elucidate the coefficient of the corresponding δ function we consider the integral displaying the structure of $\mathscr{I}(\tau_1, \tau_2)$ in the vicinity of $\tau_1 - \tau_2 \approx 0$:

$$\int d\tau \frac{1}{(2\pi)^3} \int d^3p \exp\left(-\frac{(p-B)^2 + \varkappa^2}{2m} \tau \right) [(p-B)^2 + \varkappa^2]^{-1} = -\frac{m}{4\pi\varkappa}. \tag{A1.7}$$

From (A1.5)–(A1.7), after periodic continuation with respect to $\tau_1 - \tau_2$, it follows that in the approximation used the T matrix $T(\tau_1, \tau_2|b)$ is written in the form of (12).

To elucidate these approximations we present a precise T matrix in the absence of interaction with the field $b(q, \tau)$ in the form

$$T(s_1, s_2|0) = -\delta_{s_1, s_2} \frac{2\pi i}{m} \left\{ \left[2m\left(\frac{2s_1 + 1}{\beta} i\pi + \mu \right) \right]^{1/2} + \varkappa \right\}^{-1}$$

$$= \delta_{s_1, s_2} \frac{1}{m^2} \left(\frac{2\pi\varkappa}{\varkappa^2/2m + \mu + (2s_1 + 1)i\pi/\beta} \right.$$

$$\left. - \int d^3p \frac{1}{(p^2 + \varkappa^2)(p^2/2m - \mu - (2s_1 + 1)i\pi/\beta)} \right). \tag{A1.8}$$

In this case the adopted approximation corresponds to omitting the second summand in (A1.8) which describes the effect of a delta-function-like potential on the s state of the continuous spectrum. When equation (11) is satisfied, such states are not populated, and the transition from the initial s state of a discrete spectrum in a dipole approximation is forbidden. Hence the expressions obtained at $\gamma = 0$ turn into exact results for the zero-radius potential.

Appendix 2

To perform functional integration over δy in (14) we use the formula

$$
\frac{1}{Z_0} \int \delta y(\boldsymbol{q}, \tau)[1; y(\boldsymbol{q}, \tau) y(\boldsymbol{q}', \tau')] \exp\left(-\tfrac{1}{2} \sum_{\tilde{q}\tilde{q}'} \int_0^\beta \mathrm{d}\tilde{\tau}\,\mathrm{d}\tilde{\tau}'\, y(\boldsymbol{q}, \tilde{\tau}) \right.
$$

$$
\left. \times \hat{K}^{-1}(\tilde{\boldsymbol{q}}, \tilde{\tau}; \tilde{\boldsymbol{q}}', \tilde{\tau}') y(\tilde{\boldsymbol{q}}', \tilde{\tau}') \right) = \left| \frac{\det \hat{K}_0^{-1}}{\det \hat{K}^{-1}} \right|^{1/2} [1; K(\boldsymbol{q}, \tau; \boldsymbol{q}', \tau')]. \qquad \text{(A2.1)}
$$

According to (A2.1) one should define the Green function $K(\boldsymbol{q}, \tilde{\tau}; \boldsymbol{q}', \tilde{\tau}')$ satisfying the periodicity conditions and the following equation (the function $K_0(\boldsymbol{q}, \tilde{\tau}; \boldsymbol{q}', \tilde{\tau})$ should satisfy the same equation with $e = 0$):

$$
\sum_{q''} \left[\frac{\varepsilon}{4\pi} \left(-\frac{\partial^2}{\partial \tau^2} + \omega^2 \right) \delta_{qq''} K(\boldsymbol{q}'', \tilde{\tau}; \boldsymbol{q}', \tilde{\tau}') \right.
$$

$$
+ \frac{e^2}{2mv} \frac{\boldsymbol{q}\boldsymbol{q}''}{qq''} \tfrac{1}{2} \theta(\tfrac{1}{2}\tau^2 - \tilde{\tau}^2) \left(K(\boldsymbol{q}'', \tilde{\tau}; \boldsymbol{q}', \tilde{\tau}') \right.
$$

$$
\left. \left. - \frac{2}{\tau} \int_{-\tau/2}^{\tau/2} K(\boldsymbol{q}'', \tilde{\tau}''; \boldsymbol{q}', \tilde{\tau}')\, \mathrm{d}\tilde{\tau}'' \right) \right]
$$

$$
= \delta_{qq'} \frac{2\pi}{\beta} \delta\left(\sin\left(\frac{2\pi}{\beta} (\tilde{\tau} - \tilde{\tau}') \right) \right). \qquad \text{(A2.2)}
$$

We shall search for the function $K(\boldsymbol{q}, \tilde{\tau}; \boldsymbol{q}', \tilde{\tau}')$ as follows:

$$
K(\boldsymbol{q}, \tilde{\tau}; \boldsymbol{q}', \tilde{\tau}') = K_0(\tilde{\tau}, \tilde{\tau}') \left(\delta_{qq'} - \frac{3}{vv_q} \frac{\boldsymbol{q}\boldsymbol{q}'}{qq'} \right)
$$

$$
+ \frac{3}{vv_q} \frac{\boldsymbol{q}\boldsymbol{q}'}{qq'} \tilde{K}(\tilde{\tau}, \tilde{\tau}') \qquad \text{(A2.3)}
$$

$$
K_0(\tilde{\tau}, \tilde{\tau}') = \frac{2\pi}{\varepsilon\omega} \frac{\cosh \omega(1/2T - |\tilde{\tau} - \tilde{\tau}'|)}{\sinh(\omega/2T)}.
$$

We use a formula which is verified on transition from a discrete space to a continuous one:

$$
\frac{1}{v} \sum_{q''} \frac{\boldsymbol{q}\boldsymbol{q}''}{qq''} \frac{\boldsymbol{q}''\boldsymbol{q}'}{q''q'} = \frac{\sqrt{q}}{3} \frac{\boldsymbol{q}\boldsymbol{q}'}{qq'} \qquad \text{(A2.4)}
$$

where v_q is the volume of the momentum space cell. With the help of (A2.4) after substituting (A2.3) into (A2.2) we obtain for $\tilde{K}(\tilde{\tau}, \tilde{\tau}')$ the equations and boundary conditions

$$
\left(-\frac{\partial^2}{\partial \tilde{\tau}^2} + \omega^2 \right) K(\tilde{\tau}, \tilde{\tau}') + \tfrac{1}{2}(\tilde{\omega}^2 - \omega^2)\theta(\tfrac{1}{4}\tau^2 - \tilde{\tau}^2)\left(\tilde{K}(\tilde{\tau}, \tilde{\tau}') \right.
$$

$$
\left. + \tilde{K}(-\tau, \tilde{\tau}') - \frac{2}{\tau}\int_{-\tau/2}^{\tau/2} \tilde{K}(\tilde{\tau}'', \tilde{\tau}')\,\mathrm{d}\tilde{\tau}'' \right) = \frac{2\pi}{\varepsilon}\,\delta(\tilde{\tau}' - \tilde{\tau})
$$

$$
\tag{A2.5}
$$

$$
\tilde{K}(-\tfrac{1}{2}\beta, \tilde{\tau}') = \tilde{K}(\tfrac{1}{2}\beta, \tilde{\tau}') \qquad \frac{\partial \tilde{K}}{\partial \tilde{\tau}}\bigg|_{\tilde{\tau}=-\beta/2} = \frac{\partial \tilde{K}}{\partial \tilde{\tau}}\bigg|_{\tilde{\tau}=\beta/2}
$$

$$
\tilde{\omega}^2 = \omega^2 + \frac{4\pi e^2}{3\varepsilon m}\,v_q.
$$

Let us introduce an auxiliary function $\tilde{K}_0(\tilde{\tau}, \tilde{\tau}')$, obeying (A2.5) without an integral term. The function $\tilde{K}(\tilde{\tau}, \tilde{\tau}')$ is expressed through $\tilde{K}_0(\tilde{\tau}, \tilde{\tau}')$ as follows:

$$
\tilde{K}(\tilde{\tau}, \tilde{\tau}') = \tilde{K}_0(\tilde{\tau}, \tilde{\tau}') + \frac{\tilde{\omega}^2 - \omega^2}{\tau}\int_{-\tau/2}^{\tau/2} \tilde{K}_0(\tilde{\tau}, \tau')\tilde{K}_0(\tilde{\tau}', \tau'')\,\mathrm{d}\tau'\,\mathrm{d}\tau''
$$

$$
\times \left(1 - \frac{\tilde{\omega}^2 - \omega^2}{\tau}\int_{-\tau/2}^{\tau/2} \tilde{K}_0(\tau', \tau'')\,\mathrm{d}\tau'\,\mathrm{d}\tau'' \right)^{-1}.
$$

$$
\tag{A2.6}
$$

$\tilde{K}_0(\tilde{\tau}, \tilde{\tau}')$ has the structure

$$
\tilde{K}_0(\tilde{\tau}, \tilde{\tau}') = \tfrac{1}{2}[K_1(\tilde{\tau}, \tilde{\tau}') + K_2(\tilde{\tau}, \tilde{\tau}')].
$$

For K_1 and K_2 we obtain the equations and boundary conditions

$$
K_{1,2} = \tilde{K}_0(\tilde{\tau}, \tilde{\tau}') \pm \tilde{K}_0(-\tilde{\tau}, \tilde{\tau}')\left(-\frac{\partial^2}{\partial \tilde{\tau}^2} + \omega^2 \right) K_i(\tilde{\tau}, \tilde{\tau}')
$$

$$
+ \delta_{1i}(\tilde{\omega}^2 - \omega^2)\theta(\tfrac{1}{4}\tau^2 - \tilde{\tau}^2)K_i(\tilde{\tau}, \tilde{\tau}')
$$

$$
= \frac{2\pi}{\varepsilon}[\delta(\tilde{\tau}' - \tilde{\tau}'') - (-1)^i\delta(\tilde{\tau}' + \tilde{\tau}'')] \qquad i = 1, 2
$$

$$
\tag{A2.7}
$$

$$
\frac{\partial K_1}{\partial \tilde{\tau}} = 0 \qquad \text{and} \qquad K_2 = 0 \qquad \text{at } \tilde{\tau} = 0, \beta/2.
$$

From (A2.6) and (A2.7) it follows that $\tilde{K}(\tilde{\tau}, \tilde{\tau}')$ has the form

$$
\tilde{K}(\tilde{\tau}, \tilde{\tau}') = \tfrac{1}{2}(K_0(\tilde{\tau}, \tau') + K_1(\tilde{\tau}, \tau'))
$$

$$
+ \frac{2(\tilde{\omega}^2 - \omega^2)}{\tau}\left(1 - \frac{2(\tilde{\omega}^2 - \omega^2)}{\tau}\int_0^{\tau/2} K_1(\tau', \tau'')\,\mathrm{d}\tau'\,\mathrm{d}\tau'' \right)^{-1}
$$

$$
\times \int_0^{\tau/2} K_1(\tilde{\tau}, \tau')K_1(\tilde{\tau}', \tau'')\,\mathrm{d}\tau'\,\mathrm{d}\tau''.
$$

$$
\tag{A2.8}
$$

In constructing relations of determinants arising in integration over δy in (14), we apply the sequence of equalities

$$
\frac{\det \hat{K}(q, \tilde{\tau}; q', \tilde{\tau}')}{\det K_0(q, \tilde{\tau}, q', \tilde{\tau}')} = \exp\left\{ \mathrm{Sp}_{\tilde{\tau},q} \ln\left[\hat{I} + \frac{qq'}{qq'}\frac{3}{vv_q}\left(-\hat{I} + \hat{K}\hat{K}_0^{-1} \right) \right] \right\}
$$

$$
= \exp\{3\,\mathrm{Sp}_{\tilde{\tau}}[\ln(\hat{K}\hat{K}_0^{-1})]\}.
$$

$$
\tag{A2.9}
$$

The intermediate equalities are verified by expanding the logarithm in the index, using (A2.4). Note that functional integrals taken over 'even' $y(q, \tau)$ in the numerator and denominator of (14) coincide, so one should actually have only the function $K_1(\tilde{\tau}, \tilde{\tau}')$ and the corresponding 'free' function $K_0(\tilde{\tau}, \tilde{\tau}')$ determined by the first of the equations (A2.7) without the term of interaction and by the same boundary conditions as have been used for determining K_1. Differentiating (A2.9) with respect to the parameter τ, we obtain

$$\frac{\partial}{\partial \tau} \operatorname{Sp}(\ln \hat{K}^{-1} \hat{K}_0) = \operatorname{Sp}\left[\left(\frac{\partial \hat{K}^{-1}}{\partial \tau}\right) \hat{K}\right] \tag{A2.10}$$

but

$$\operatorname{Sp}\left[\left(\frac{\partial \hat{K}^{-1}}{\partial \tau}\right) \hat{K}\right] = \int d\tau' \, d\tau'' \left(\frac{\partial \hat{K}^{-1}(\tau', \tau'', \tau)}{\partial \tau}\right) K(\tau'', \tau') \tag{A2.11}$$

and, consequently,

$$\operatorname{Sp}_{\tilde{\tau}}(\ln \hat{K} \hat{K}_0^{-1}) = \frac{\varepsilon}{2\pi} (\tilde{\omega}^2 - \omega^2) \left[\int_0^{\tau/2} d\tilde{\tau} \left(K_1(\tilde{\tau}, \tilde{\tau})\right.\right.$$
$$\left.\left. - \frac{2}{\tilde{\tau}} \int_0^{\tilde{\tau}} K_1(\tau', \tilde{\tau}) \, d\tau' + \frac{1}{\tau^2} \int_0^{\tilde{\tau}} K_1(\tau', \tau'') \, d\tau' \, d\tau''\right)\right]. \tag{A2.12}$$

The expression for $K_1(\tilde{\tau}, \tau')$ is given in the text (equation (16)).

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