Analysis of electron behavior in liquids, based on the use of the dispersion relations

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An analysis of the main physical characteristics of thermalized excess electrons in liquids and glasses is carried out. The analysis is based on the use of nonmodel formulas for the optical constants and the photoionization cross section that arise from the dispersion relations, the virial theorem, and various sum rules. The obtained expressions are used to analyze experimental data pertaining to electrons in polar solutions. It is established that optical transitions in such systems correspond to excitation into the continuous spectrum and that the initial electron state is localized at atomic distances by a short-range effective interaction.

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1. INTRODUCTION

Let us first enumerate those basic facts of the history of the investigation of thermalized electrons in liquids that are necessary for the understanding of the formulation of the present problem. (For detailed information and references, see[1,2].) The hypothesis of a separate "solution" of electrons was first put forward at the beginning of the present century to explain the distinctive properties of the solutions of alkali metals in ammonia. The following stage of the investigations is connected with the discovery at the beginning of the 1960's of a localized electron state in water and, subsequently, in many other polar liquids. Below we shall denote such a state by e_s^-. In the course of the indicated investigations various techniques—in particular, optical and radiospectrometric ones—were developed which have made the accumulation of vast empirical information possible. The most important characteristic of the absorption spectra of the e_s^-, which is that their general form, usually a single wide asymmetric peak of the form shown in Figs. 1 and 2, does not change appreciably when substantial changes are made in the various parameters, was elucidated. Thus, in the case of water the absorption band of the e_s^- preserves its form in the temperature range of from -4 to 360 °C, i.e., even when we go over to supercritical conditions. Further, e_s^- transitions into a "conduction band" having a sharp lower boundary and responsible for a relatively small loss were reliably established.

Recently, excess electrons with the same optical and other characteristics as in polar solvents were discovered in nonpolar liquids: hydrocarbons and liquified inert gases. Similar formations have also been observed in congealed glasses. It became clear that localized electron states with identical optical properties form in materials that are completely different in their dielectric characteristics. On the other hand, in liquids that are similar in their dielectric properties the e_s^- sometimes differ sharply and may be entirely absent in one of them. At the same time, there are indications that the properties of the e_s^- are connected with the local characteristics of the medium and, especially, its microscopic disorder.[3]

The theoretical description of the e_s^- was begun by Ogg,[4] who introduced the model of cavities (bubbles) with impenetrable walls, in which the electrons are enclosed. In recent years the Ogg theory has been revived in a new form in a number of descriptions of electron states in liquified inert gases.[5] Davydov and Beigen[6,7] developed the qualitative stage of e_s^- theory by applying Landau and Pekar's ideas about polarons in ionic crystals, and were, as a result, able to account for the position of the light-absorption band of e_s^- in ammonia.

The sharp rise in the number of papers began in the 1960's, after the universal character of the e_s^- had become apparent and the suggestion had been made that the e_s^- play important roles in diverse physical, chemical, and biological phenomena. This growth was also connected with the growth of interest in the theory of electron states in disordered media. The papers[1,8] by Jortner *et al.* should be mentioned in this connection. In the papers of these authors the e_s^- is described with the aid of a one-electron Schrödinger equation with a centrally symmetric potential, called the Landau potential:

$$V(r)=-\frac{\beta e^2}{a}\theta(a-r)-\frac{\beta e^2}{r}\theta(r-a),\qquad \theta(r)=\begin{cases}1, & r>0\\ 0, & r<0\end{cases}\tag{1}$$

where a is the radius of the cavity and $\beta=\varepsilon_\infty^{-1}-\varepsilon_0^{-1}$ is the difference between the inverse optical and static di-

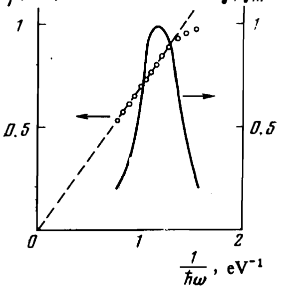

FIG. 1. The spectral characteristics of e_s^- in ammonia.[20] The continuous curve represents the absorption spectrum; the points, the function $\varphi=(1-mc/Ae^2\int_0^\omega\gamma_s d\omega')^{2/5}$. According to the formula (13), the points should, in the φ, $(\hbar\omega)^{-1}$ coordinate system, lie along a straight line in the region $\omega\to\infty$.

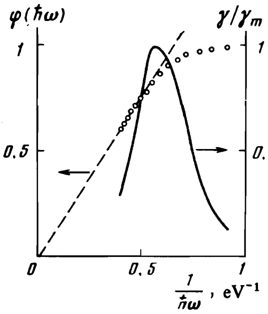

FIG. 2. As in Fig. 1, but for e_s^- in water at 25 °C.[19]

electric constants. The optical absorption was computed in these papers as $1s$–$2p$ transitions.

It became clear at the end of the 1960's and the beginning of the 1970's that the experimental data that were rapidly being accumulated, especially on the optical manifestations of e_s^-, were qualitatively not in agreement with the theoretical estimates. There appeared a whole stream of refining calculations in which elements of modern polaron theory were used, a more detailed description of the interactions with the nearest molecules (which, as it turned out, play a central role) was considered, and an effective mass with a complicated dependence on the external conditions was introduced.[2] The majority of the above-enumerated calculations were based on far-reaching model concepts with vaguely defined regions of applicability and a considerable number of adjustable parameters. Dissatisfaction with the results led to the development of an alternative direction: the application of the methods of quantum chemistry, in which an additional orbital in a cluster of solvent molecules is calculated on a computer by the self-consistent field method. The most significant results were obtained by Byakov, Klyachko, and Ovchinnikov in[9]. Here, in contrast to the majority of the investigations carried out in this direction, the influence of the polar medium on the energetics of the e_s^- was also taken into account. It follows from the results obtained in[9] that the ground state of the e_s^- in water is localized over a region of atomic dimensions and that it is predominantly made up of the $1s$ state. Calculations, with the aid of quantum-chemistry methods, of the more delocalized excited states cast, however, considerable doubt on the degree of validity of this result.

Of particular importance in connection with the undefined state of the theory is the analysis of the properties of the e_s^-, based on theoretical relations connecting different experimental characteristics and derived with as few model considerations as possible. In the present paper we consider the results obtainable from sum rules and the virial theorem. We consider the sum rules in Sec. 2 on the basis of definite generalizations of the applications of dispersion relations in the theory of condensed media, generalizations that are accomplished in a manner analogous to the way similar results in high-energy physics are obtained. A comparison with the experimental data is directly carried out in Secs. 2 and 3, using as examples electrons in polar solutions, for which the authors had the most extensive experimental data at their disposal.

2. SUM RULES AND THE VIRIAL THEOREM

Sum rules have long been used in nuclear and atomic spectroscopy.[10] Recently, new sum rules for the optical constants of condensed media were derived with the aid of a union of the dispersion relations and the so-called superconvergence rules. The use of the sum rules in the analysis of the e_s^- turns out to be especially effective for the following two reasons. First, in many cases the excess electron's entire absorption spectrum, which ends in the near-ultraviolet region or at even lower frequencies, is experimentally known. Often, this spectrum overlaps little with the fundamental absorption band of the solvent, and has a sharp threshold.1) The indicated circumstance is a direct consequence of the fact that the binding energy of the e_s^- (and, consequently, the characteristic absorption frequencies) is substantially smaller than the binding energies of the electrons of the medium. As a result, there arises the possibility of the application of the sum rules for the perturbations of the optical constants of the medium upon the introduction of the excess electron. The system under consideration is, apparently, that object in which the new optical sum rules and their further generalizations mentioned at the beginning of this section can most effectively be used. Second, into the sum rules enter the characteristics of only the ground state, which is important for the theoretical analysis, since there is at present almost no reliable information about the excited states of the e_s^-.

The sum rules used below can be divided into two groups. Let us first discuss the sum rules of the first group, which are often called "f-sum rules" in the literature. These rules follow from the well-known Kramers–Kronig relations for the real $n(\omega)$ and imaginary $k(\omega)$ parts of the complex refractive index of a medium without an n-type conductivity2):

$$n(\omega)-1=\frac{2}{\pi}\mathrm{P}\int_0^\infty\frac{\omega' k(\omega')}{\omega'^2-\omega^2}d\omega',\qquad k(\omega)=-\frac{2\omega}{\pi}\mathrm{P}\int_0^\infty\frac{n(\omega')-1}{\omega'^2-\omega^2}d\omega',\tag{2}$$

where P is the principal-value symbol. Besides (2) we use the natural assumption that in the high-frequency limit the medium behaves like a free-electron gas[15]:

$$n(\omega)-1\to-\frac{1}{2}\frac{\omega_p{}^2}{\omega^2}=-\frac{1}{2}\frac{4\pi Ne^2}{m\omega^2},\qquad \omega\to\infty,\tag{3}$$

where N is the total number of free electrons in a unit volume. Concerning $k(\omega)$, it is assumed that as $\omega\to\infty$ the value of $k(\omega)$ tends to zero faster than ω^{-2}:

$$k(\omega)=o(\omega^{-2}),\quad \omega\to\infty.\tag{4}$$

Analysis of the relations (2)–(4) as $\omega\to\infty$ leads, along with many others, to the following relations:

$$\begin{gathered}\int_0^\infty \omega k(\omega)\,d\omega={}^1/_4\,\pi\omega_p{}^2,\\ \int_0^\infty \omega k(\omega)[n(\omega)-1]d\omega=0,\qquad \int_0^\infty[n(\omega)-1]d\omega=0.\end{gathered}\tag{5}$$

The second relation in (5) can be derived with the aid of the well-known formula[15]

$$\int_0^\infty \omega\,\mathrm{Im}\,\varepsilon(\omega)\,d\omega={}^1/_2\,\pi\omega_p{}^2,\qquad \varepsilon(\omega)=[n(\omega)+ik(\omega)]^2.\tag{6}$$

The first two relations in (5) are also valid in a conducting medium. Since the quantity $n(\omega)-1$ is positive at low, and negative at high, energies, it follows from the union of these two relations, when the positiveness of $k(\omega)$ is taken into account, that any change in $k(\omega)$ at high energies should be accompanied by a change in $k(\omega)$ at low energies, and vice versa. This conclusion is completely analogous to the conclusion about the connection between low- and high-energy asymptotic forms of amplitudes in high-energy physics.[16] The last relation in (5), like the formula (6), gets modified in the presence of conduction electrons because of the appearance of a pole[15] in $\varepsilon(\omega)$ at $\omega=0$. In this case we can obtain the formula

$$\int_0^\infty [(n-1)^2-k^2]\,d\omega=-2\pi^2\sigma(0), \tag{7}$$

where $\sigma(0)$ is the zero-frequency conductivity. The formula (7) follows at once from the fact that, after the pole has been separated out, $n(\omega)-1$ and $k(\omega)$ become related through the norm-preserving Hilbert transformation.

Upon the introduction into the system of excess electrons, $n(\omega)$ and $k(\omega)$ are replaced respectively by $n(\omega)+\Delta n(\omega)$ and $k(\omega)+\Delta k(\omega)$. Combining the relations (5) and (7), we obtain for the optical constants before and after the introduction of the electrons the following formulas:

$$\begin{gathered}\int_0^\infty \omega\Delta k\,d\omega=\pi^2N_se^2/m, \qquad \int_0^\infty \Delta n\,d\omega=0,\\ \int_0^\infty [2\Delta n(n-1)-2\Delta kk+(\Delta n)^2-(\Delta k)^2]\,d\omega=-2\pi^2\sigma(0).\end{gathered} \tag{8}$$

The most useful of the relations (8) is the first relation, into which enters the excess-electron concentration N_s, since, in view of the rapid decrease of $\Delta k(\omega)$, the integration is virtually restricted to within a relatively narrow frequency interval. The second relation in (8) obtains in the absence of n-type conductivity both before and after the introduction of excess electrons. The third relation can be derived if we postulate the appearance of n-type conductivity upon the introduction of excess electrons into the dielectric. These last two relations can be used to control the agreement between the results and the verification of the possibility of the appearance, along with localized electron states, of conduction electrons in systems in which the lifetimes of the excess electrons are very short, and the direct measurement of the conductivity is difficult.3)

The above-given relations can be verified in diverse dynamical model calculations. In particular, they are obtainable in the electron gas model from the relation[17]

$$\varepsilon_L^{-1}(\omega,\mathbf{k})=1+\frac{4\pi e^2}{k^2}F_L(\omega,\mathbf{k}) \tag{9}$$

on account of the general properties of $F_L(\omega,\mathbf{k})$, the Fourier transform of the averaged—over the ground state—retarded commutator of two density operators.

On further allowing for the fact that optical absorption is appreciable even at low concentrations of the e_s^- (when their interaction can be neglected) and the fact that the dipole approximation is adequate for the computation of the optical transitions, we obtain additional sum rules for the directly measurable quantity $\gamma_s(\omega)$, the molar e_s^--extinction factor:

$$\gamma_s(\omega)=\frac{2\omega\Delta k(\omega)}{cN_s}6.02\cdot10^{20}\ln 10\left[\frac{\text{liter}}{\text{mole-cm}}\right]. \tag{10}$$

Since similar rules are actively used in spectroscopy,[10] we give them without derivation:

$$\begin{gathered}S_{-1}=\int_0^\infty \gamma_s(\omega)\,\omega^{-1}\,d\omega=A\frac{2}{3\hbar c}\frac{\Delta\langle P^2\rangle}{N_s},\\ S_0=\int_0^\infty \gamma_s(\omega)\,d\omega=A\frac{e^2}{mc},\\ S_1=\int_0^\infty \gamma_s(\omega)\,\omega\,d\omega=A\frac{1}{3c\hbar}\frac{\Delta\langle J^2\rangle}{N_s},\\ A=2\pi^2 6.02\cdot10^{20}\ln 10.\end{gathered} \tag{11}$$

In the formulas (11) the quantities $\Delta\langle P^2\rangle$ and $\Delta\langle J^2\rangle$ correspond to the changes in the mean values of the polarization and current-density operators for the system upon the introduction of N_s excess electrons into the medium. In the simplest potential models

$$\frac{\Delta\langle P^2\rangle}{N_s}=e^2\langle R_s^2\rangle, \qquad \frac{\Delta\langle J^2\rangle}{N_s}=2e^2\left\langle\frac{p^2}{2m}\right\rangle m^{-1}, \tag{11'}$$

where $\langle R_s^2\rangle$ determines the square of the density distribution, and $\langle p^2/2m\rangle$ denotes the kinetic energy, of the e_s^-. The formula (11) for S_0 can be derived from the first relation in (5), it being significant that it contains no parameters with the exception of the universal constants.

To conclude the general analysis of the sum rules, let us use the fact that the functional form of the high-frequency behavior of γ_s is known. In the case when the initial state of the excess electron is localized, this quantity coincides up to a numerical coefficient with the total dipole-transition cross section, whose asymptotic behavior is well known. As a result, we obtain for the intermediate (when $\omega\gtrsim E_i$) asymptotic form

$$\gamma_s(\omega)\to B\omega^{-7/2}, \tag{12}$$

where the quantity B, which does not depend on ω, is determined by the form of the matrix element. This allows us to limit the integration domain in (11), choosing a cutoff frequency ω_0 lying outside the fundamental absorption band. In particular, from the sum rule for S_0 we find

$$\int_0^{\omega_0}\gamma_s(\omega)\,d\omega-A\frac{e^2}{mc}=-\frac{2}{5}B\omega_0^{-5/2}. \tag{13}$$

Relations of the type (13), which are equivalent to the so-called sum rules with finite energies in high-energy physics,[16,17] are useful for the verification of the agreement between the results. Similar relations can be derived with the aid of threshold formulas and the introduction of some lower cutoff frequency. However, we shall not touch upon the question of the threshold behavior here, since it has been considered from a somewhat different point of view in[2,26].

Let us emphasize that the formula (13) for $k(\omega)$ cannot be derived in its general form, since, in contrast

Substance	$\tilde{\gamma}_s \cdot 10^{-4}$, liter/mole-cm		Mean distribution radius (in Å)	References
	Experiment	Theory		
Water, 25 °C	1.84 ± 0.36	2.3 ± 0.2	2.2	[19]
Ammonia	4.92 ± 0.14	5.4 ± 0.3	3.3	[20]
Tetrahydrofuran	4.0	4.0	...	[22]
Methyltetrahydrofuran	3.9	3.9	...	[22]
Diethyl ether*	3.5	3.5	...	[22]

*) The total oscillator strength determined in[22] for absorption by e_s^- in these substances turned out to be equal to 1.0 ± 0.05; therefore, the same values are given in the "Theory" column as in the "Experiment" column.

to the formula (3) for $n(\omega)$, the asymptotic form of $k(\omega)$ for $\omega \to \infty$ depends on the characteristics of the initial state.

Let us begin the direct use of the above-given formulas with the determination, with the aid of the expression (11) for S_0, of the extinction factor at the peak of the optical-absorption band for a number of substances. In the table we give the results obtained when the optical-absorption curves were analyzed with the aid of the formula

$$\tilde{\gamma}_s = A\frac{e^2}{mc}\left[\int\limits_0^\infty \frac{D_s}{\tilde{D}_s} d\omega\right]^{-1}, \tag{14}$$

(where $\tilde{\gamma}_s$ and $\tilde{D}_s$ are respectively the extinction factor and the optical density at the point of maximum absorption) arising from (11). For comparison, we present data obtained in conventional measurements, which require an independent determination of the concentration by chemical methods. It follows from the table that the sum rules (11) can be used in many cases with sufficient reliability, their use being restricted only by the spectral data available in the frequency range in question. Figures 1 and 2 show the general shape of the optical-absorption curves and their analysis with the aid of the formula (13).

The expression for S_0 can clearly be used with a sufficiently high—for many applications—accuracy to determine the extinction factor and, consequently, the e_s^- concentration from only the optical absorption data. Notice that the expression (11) for S_0 has already been used[21–23] to verify the correctness of the determination of the coefficient of e_s^--extinction in a number of solvents.

From the formulas (11) we can further find the values of the various physical characteristics of the e_s^-. In particular, from the expression for S_{-1} we obtain the value of the mean radius of the charge density distribution in the initial state. The results obtained are also represented in the table. Notice that the values for the e_s^- radius in water and ammonia are in agreement with the independently obtained experimental estimates for the kinetic collision radius of the e_s^-.[1]

It is of interest to compare the expression (11) for S_1 with the model theories in which the electron is assumed to be described by a one-particle Hamiltonian $H(r)$ with some centrally-symmetric potential well.

Let us consider the case, mentioned in the Introduction, of the Landau potential (1). From the generalized virial theorem[24] we have for the initial state

$$0 = \left\langle i \left| \left[-i\hbar\left(\frac{\partial}{\partial r} + \frac{1}{r}\right) r, H \right] \right| i \right\rangle = 2i\hbar \left\langle i \left| \frac{p^2}{2m} - \frac{\beta e^2}{2r}\theta(r-a) \right| i \right\rangle. \tag{15}$$

It follows from (15) that the energy E_i satisfies the equality

$$E_i = \langle i|H|i\rangle = -\left\langle i \left| \frac{p^2}{2m} \right| i \right\rangle - \frac{\beta e^2}{a}\langle i|\theta(a-r)|i\rangle. \tag{16}$$

For $a = 0$ the formula (15) goes over into the usual virial theorem for the Coulomb potential. The last term in (16) characterizes that portion of the electron density that is concentrated in the "cavity" defined by $r < a$, since $\langle i|i\rangle = 1$. We find with the aid of the formula (11) for S_1 that for water at 25 °C $\langle i|p^2/2m|i\rangle \approx 2.6$ eV. According to (16), $|E_i| \geqslant 2.6$ eV in the model with a potential of the type (1), and in water e_s^- should appreciably absorb light with quantum energy higher than 2.6 eV, which is at variance with direct experiment and the fact that the sum rule for S_0 is exhausted without such absorption.

It can be seen from the sum rules (11) that the asymmetry and width of the e_s^- spectrum are, to a large extent, determined by the characteristics of the initial state. Apparently, it is precisely to this circumstance that the good agreement between the calculations carried out in[9] and the experimental total light-absorption characteristics is due, since the initial state was most accurately found there. If there is a distribution over the initial states that is given by a normalized (to unity), possibly temperature-dependent distribution function, $\rho(i, T)$, then we should, for example, for S_1 write

$$S_1 = \int\limits_0^\infty \gamma_s(\omega)\,\omega\, d\omega = A\frac{2e^2}{3mc\hbar}\int \left\langle i \left| \frac{p^2}{2m} \right| i \right\rangle \rho(i, T)\, d(i). \tag{17}$$

Instead of averaging over the ensemble, we can average over time. Then it is not difficult to show with the aid of the well-known Gell-Mann–Feynman theorem that in the adiabatic approximation and for a linear electron-phonon coupling there is virtually no averaging to be performed in (17). In any case from the experimental fact that the e_s^- spectrum is stable with respect to changes in the external conditions we can conclude that fluctuations make only a small contribution to the mean characteristics of the e_s^-.

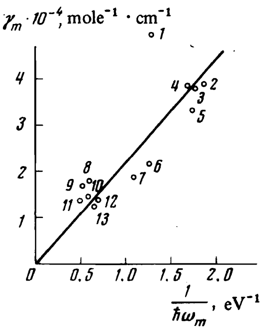

FIG. 3. The coefficients of extinction of a solvated electron in different substances at the absorption peak: 1) ammonia, 2) diethyl ether, 3) methyltetrahydrofuran, 4) tetrahydrofuran, 5) dimethoxyethane, 6) 1, 3-propylene diamine, 7) ethylene diamine, 8) water, 9) methyl alcohol, 10) ethyl alcohol, 11) ethylene glycol, 12) isopropyl alcohol, 13) propyl alcohol. The straight line corresponds to the ω-dependence of $\tilde{\gamma}_s$, determined by the formula (18).

3. DISCUSSION OF THE RESULTS

From the above-performed analysis we can draw two basic conclusions about the physical nature of the e_s^-, conclusions which must be taken into account in the construction of any dynamical theory. In the first place, the optical transitions of the e_s^- are, in the majority of cases, transitions from localized states into the continuum. A similar conclusion has been reached before in independent papers,[2,3,26,28] but only as some hypothesis.

In the second place, the effective (possibly many-particle) interaction, which gives rise to the localization of the e_s^-, is a short-range interaction. The localization diameter turns out to be equal to atomic dimensions, i.e., of the order of 1 Å. The last conclusion is especially important for the analysis of the polaron models of the e_s^-. In this connection it is worth noting the fact that the most important characteristics of the absorption spectrum of the e_s^- are well described by the formulas of the zero-radius-potential theory.[24] In this case for the cross section for photoabsorption with a transition from the 1s state into the continuum we obtain the following expression[25]:

$$\sigma(\omega)=\frac{16\pi e^2}{3mc}\frac{2k_0}{1-k_0\rho_0}\left(\frac{k}{k^2+k_0^2}\right)^3, \tag{18}$$

where $E_i = -\hbar^2 k_0^2/2m$ is the binding energy and $k=(k_0^2 + 2m\omega/\hbar)^{1/2}$ is the wave number of the electrons after absorbing a light quantum. The expression (18) also takes into account the corrections corresponding to the so-called effective radius in the initial state, which radius is denoted by ρ_0.

Figure 3 shows some experimental data and a straight line corresponding to the maximum of the expression (18) for $\rho_0 = 0$. If the experimental errors for the substances indicated in Fig. 3, except ammonia, are taken into account,[4] then the experimental values for the extinction coefficient $\tilde{\gamma}_s$ are in good agreement with the dependence (18). The experimental-error exceeding deviation for ammonia can, in accord with the independently-obtained data on the expansion of the solutions, be connected with the relatively large dimensions of the initial e_s^- state. In this case, in order to obtain agreement with experiment, we must introduce for ρ_0 a finite value that, for ammonia, should be equal to $\rho_0 \approx 1-2$ Å. For the remaining substances indicated in Fig. 3, we should obviously have $\rho_0 < 1$ Å. Notice that in the Coulomb-well model the location of the absorption peak corresponding to the 1s–2p transition does not, in contradiction to experiment, depend on the value of the quantum energy $\hbar\bar{\omega} = \frac{3}{4}\beta$Ry at the maximum of the band, which arises as a result of the broadening of the absorption line.

The agreement of the experimental data with the formulas of the effective-radius theory constitutes further confirmation of the fact that the photoabsorption spectrum of the e_s^- corresponds to the transition of the electron into a delocalized state.[1,3,26–28]

The above-indicated principal conclusions do not exhaust the significance of the obtained results. The obtained model-free relations not only make it possible to verify the consistency of the dynamical model calculations, but also prove to be useful in the processing of experimental data, in their comparison with each other, and in the determination from the optical data of specific characteristics, such as the binding energy, the charge distribution radii, the polarizabilities, etc. Sufficiently convincing, it seems to us, examples are presented in the paper.

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[1] In principle, an additional change in the absorption band of the medium in the infrared region is possible. This change in the absorption band may be connected with both the shift in the normal-mode frequencies of the medium as a result of the interaction of the charged particle with the dipoles of the medium and the appearance near the e_s^- of new localized oscillations (of the type of the bound states of the polaron–phonon system in ionic crystals[13]). However, the authors do not know of any experimental confirmation of the existence of observable effects of this kind in the systems in question.

[2] We go into some detail here in citing these fairly simple ideas because the application of one of the sum rules for the oscillator strengths in some papers on the theory of polarons in ionic crystals[14] is connected with certain misunderstandings. This rule is sometimes derived not from the general dispersion relations for the optical characteristics of the entire medium, but from dynamical models of a particle interacting in one way or another with the medium. As a result, instead of the true electron mass, in the final formula appears some effective mass, which is, in fact, a consequence of the inadmissibility of the models used in the entire frequency range.

Notice also that the expressions given in this section are not affected by any possible spatial dispersion. Here we can cite the arguments adduced in Sec. 62 of Landau and Lifshitz's book,[15] or the fact that the obtained formulas are a consequence of the general dispersion formulas[11] for $n(\omega, \mathbf{k})$ and $k(\omega, \mathbf{k})$ with the transition to the $|\mathbf{k}| \to 0$ limit, which is equivalent to the condition, clearly fulfilled here, of applicacability of the dipole approximation in dynamical computations.

[3] In this case, however, we must measure the quantity $\varkappa(\omega)$ in a sufficiently wide frequency range, which, incidentally, is now possible if we use synchrotron radiation for the ellipsometric measurements.

[4] The experimental errors for the data given in Fig. 3 can be estimated to be, on the average, 10–20%. A more exact determination of their values from the estimates of the various experimenters—estimates which are difficult to compare—proved to be impossible.

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Investigation of free excitons in Ge and their condensation at submillimeter wavelengths

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Results are presented of an investigation of free excitons in Ge in the submillimeter wavelength range for low as well as for high excitation levels when interaction between the excitons becomes important. The free-exciton energy spectrum is discussed. It is shown that the drop radii and their concentrations can be determined by measuring the temperature dependence of the free-exciton concentration. A section of the phase diagram is obtained in the 0.5–2.8 K temperature range for the free excitons+condensate system.

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1. INTRODUCTION

The spectroscopy of excitons in Ge in the submillimeter wavelength band corresponding to their binding energy was initiated only recently. It was shown in[1–3] that these investigations can yield additional information on the energy spectrum of the excitons and their behavior in external fields, as well as on collective effects at low temperatures. In[2–5,7,8] using spectrometers with backward-wave tubes (BWT), the absorption spectrum was obtained in the 2–0.35 mm band, while in [3–5] we investigated, in addition, the photoconductivity spectra of free excitons. The energy spectrum of the excitons was constructed from a comparison of the absorption and photoconductivity spectra and from the temperature dependence of the absorption line intensity. At sufficiently high excitation levels, when the interaction between the excitons becomes appreciable in the