Absorption spectrum of a solvated electron in a polar disordered medium

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We use a path integral method to develop a theory which enables us to calculate the statistical operator for a solvated electron in a molecular disordered system in terms of the density correlation functions of the surrounding medium. With this method we determine the effective potential and free energy surface as functions of the molecular microstructure of the medium. This, in turn, makes it possible to evaluate the shape of the absorption spectrum, its maximum, and its width. We give for a classical polar liquid a qualitative study of the effect of the state of the medium (its temperature, pressure, and ion density) on the absorption maximum and the width of the absorption band. The estimates obtained agree with the experimental data.

1. INTRODUCTION

There is at present a vast amount of experimental data on the absorption spectra of solvated electrons in various molecular media.[1,2] The existing theory (see Refs. 3 and 4 and also the review of Ref. 5) enables us to calculate this absorption spectrum if we know some characteristics of the vibrational spectrum of the medium and the electron state. One basically assumes in that case that the vibrations are harmonic.

However, for disordered systems the experimental determination or the theoretical calculation of the vibrational spectrum of the medium meet with considerable difficulties. This relates, first of all, to materials with complex molecular structure and a high degree of molecular disorder (as an example we mention glasses, polymer melts, and so on). The behavior of such disordered media is statistical and can be described by a set of correlation functions. A classical liquid can also be considered a topologically disordered system[6] whose local microstructure is determined by the density correlation functions. In a number of cases (see, e.g., the review of Ref. 7 about molecular liquids) there exist well developed methods which enable one to calculate these correlation functions numerically or analytically.

The basic idea of the present paper is rather general and consists in finding, by using a statistical formulation, a connection between the shape of the absorption spectrum of a solvated electron and the density correlation functions of the surrounding medium. Attempts to determine this connection have been made many times in the case of a solvated electron (see Ref. 8 and references given there). However, we shall use a special technique, namely the path integral method.[9] This technique enables us to calculate directly the statistical operator and thereby to determine the various equilibrium and kinetic characteristics of the electron state.

The light absorption process is determined by the dynamic behavior of two interacting subsystems: the electron state and the molecular medium in which the electron resides. In the general case it is necessary to study a chain of coupled equations of the Bogolyubov–Born–Green–Kirkwood–Yvon type.[10] We consider a more simplified situation and assume that the surrounding medium follows the change in the state of the electron adiabatically.

In the second part of the paper we consider the statement of the problem and obtain the basic relations connecting the probability for absorption and the statistical operator of the initial and final electron states. In the third part we derive the basic relations which determine the way the statistical operator depends on the density correlation functions of the medium. In the fourth part we find the connection between the effective potential for the solvated electron and the molecular microstructure of the surrounding medium. In the same part of the paper we obtain equations which determine the ground state and the first excited electron state in this potential. Different possible shapes of the absorption spectrum are studied in the fifth part of the paper. To demonstrate the possibilities of the method we give in the sixth part of the paper a qualitative study of the effect of the state of a classical polar liquid, its temperature, pressure, and ion density, on the absorption maximum and the absorption line width. We also give there a comparison of the results obtained and the experimental data. At the end of the paper we present the conclusions and a brief discussion of the results. The Appendix contains the derivation of some important formulas.

2. STATEMENT OF THE PROBLEM

We assume that the characteristic relaxation time of the electron state is considerably longer than the relaxation time of the surrounding medium, i.e., that the electron is in a state of equilibrium or quasiequilibrium with the medium.

As the surrounding medium we consider a uniform molecular fluctuating medium of classical particles with an interaction energy U.

We introduce the equilibrium density correlation functions of the medium, χ_n, which are defined as follows:[10]

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$$\chi_1(\mathbf{R})=\frac{1}{N}\int d\mathbf{R}_2\dots\int d\mathbf{R}_n\exp[-\beta U(\mathbf{R},\mathbf{R}_2,\dots,\mathbf{R}_n],$$

$$\chi_1(\mathbf{R}')\chi_1(\mathbf{R})+\chi_2(\mathbf{R},\mathbf{R}')$$

$$=\frac{1}{N(N-1)}\int d\mathbf{R}_3\dots\int d\mathbf{R}_n \qquad (1)$$

$$\times\exp[-\beta U(\mathbf{R},\mathbf{R}',\mathbf{R}_3\dots,\mathbf{R}_n].$$

Here $\chi_1(\mathbf{R})$ denotes the average density of the medium, whereas $\chi_2(\mathbf{R},\mathbf{R}')$ is the density–density correlation function, which is related to the structure factor, $\chi_{ss'}\propto S_{ss'}$.This correlation function can be determined from molecular modeling; for simple liquids one can obtain information about the behavior of this function from experiments.[7]

In our case the state of the electron can be described by a statistical operator $\rho(\mathbf{r}(t),\chi_1,\chi_2,\dots)$ that depends on the electron coordinate $\mathbf{r}(t)$ and the correlation functions of the medium. The probability $W(\omega)$ for the absorption of light can be written as an integral over the time t of a product of the statistical operators ρ_{in} of the initial and ρ_f of the final state,

$$W(\omega)=\frac{d^2}{\hbar}\int_{-\infty}^{+\infty}\frac{1}{Z_{\text{in}}(\beta)}\rho_{\text{in}}\left(\beta-\frac{it}{\hbar}\right)$$

$$\times\exp(-i\omega t)\rho_f\left(\frac{it}{\hbar}\right)dt. \qquad (2)$$

Here ω is the frequency of the absorbed light, d is the matrix element of the electron–photon interaction for the transition from the initial to the final state, and β is the reciprocal temperature. In the aforementioned relation $Z_{\text{in}}=\rho_{\text{in}}(\beta)$ is the partition function for the initial state of the electron.

In the general case the probability for absorption includes summation over all initial and final electron states. However, we retained only one term of the sum in (2), namely, the one characterizing the transition from the ground state to the lowest excited state of the electron. As a rule, notwithstanding this simplification, this enables us to determine rather well the absorption maximum, and in a number of cases to estimate the absorption line width as well.

We note that the states of the electron and the medium are correlated and connected by certain general relations that determine the free energy surfaces of the initial and final electron states. The problem of determining the effect of the medium on the absorption spectrum consists in evaluating the integral (2), taking into account the fact that the states of the electron and the surrounding medium are correlated.

We define the free energy F_{in} of the initial and F_f of the final state as

$$\theta F_f(\theta)=-\ln\rho_f(\theta),$$
$$(\beta-\theta)F_{\text{in}}(\beta-\theta)=-\ln\rho_{\text{in}}(\beta-\theta), \qquad (3)$$

where $\theta=it/\hbar$ is a complex variable. Equation (2) can then be transformed into a complex integral of the form

$$W(\omega)=d^2\int_{-i\infty}^{i\infty}\exp[-\delta F(\theta,\omega)d\theta, \qquad (4)$$

where δF denotes the expression

$$\delta F(\theta,\omega)=[(\beta-\theta)F_{\text{in}}(\beta-\theta)+\theta(F_f(\theta)-\hbar\omega)]$$
$$-\ln Z_{\text{in}}(\beta).$$

To calculate the probability for the absorption of light it is necessary to evaluate the electron statistical operator in a molecular fluctuating medium for the complex variable θ, and to determine the free energy surfaces of the initial and the final states of the electron.

3. EFFECT OF CORRELATIONS OF THE MEDIUM ON THE STATISTICAL OPERATOR

We can write the statistical operator, ρ of a solvated electron in a medium of classical particles as the usual configurational integral over the particle coordinates $\mathbf{R}_n$ and a path integral over the electron coordinate,

$$\rho\propto\int d\mathbf{R}_1\dots\int d\mathbf{R}_n\exp[-\beta U(\mathbf{R}_1,\dots\mathbf{R}_n)]$$

$$\times\int D[\mathbf{r}]\exp[-S(\mathbf{r},\mathbf{R}_1,\dots,\mathbf{R}_n)]. \qquad (5)$$

In this form S denotes the action for the electron

$$S(\mathbf{r},\mathbf{R}_1,\dots\mathbf{R}_n)=\int d\theta\left[\frac{m}{2}\dot{\mathbf{r}}(\theta)^2+\sum_s u_s(\mathbf{r}(\theta)-\mathbf{R}_s)\right]. \qquad (6)$$

In Eq. (6), m is the electron mass and u_s is the pairwise potential of the interaction of the electron with the sth particle in the medium (the index indicates that this potential may differ for different kinds of particles if the medium contains several kinds of particles). We note that this potential can be estimated from the scattering by an individual atom.

The dimensionality of the integral (5) is very large, and the main problem in evaluating this integral lies in judiciously reducing this dimensionality while preserving all interesting physical properties of the system. we study.

Most importantly, we note that the statistical operator can be transformed to

$$\rho\propto\int D[\mathbf{r}]\exp[-S_{\text{eff}}(\mathbf{r})], \qquad (7)$$

where the effective action S_{eff} depends only on the electron coordinate and the correlation functions of the medium,

$$S_{\text{eff}}(\mathbf{r})=\int d\theta\frac{m}{2}\dot{\mathbf{r}}(\theta)^2-\sum_s\int\chi_s(\mathbf{R})f_s(\mathbf{r}(\theta)-\mathbf{R})d\mathbf{R}$$

$$+\frac{1}{2}\sum_{ss'}\int d\mathbf{R}\int d\mathbf{R}'f_s(\mathbf{r}(\theta)-\mathbf{R})f_{s'}$$

$$\times(\mathbf{r}(\theta)-\mathbf{R}')\chi_{ss'}(\mathbf{R},\mathbf{R}')+A(\chi_3,\dots,\chi_n). \qquad (8)$$

Here $\chi_s \equiv \chi_1$ is the average density of the particles of the sth kind and the density-density correlation functions $\chi_{ss'}$ are defined simply.

In Eq. (8), $f_s(\mathbf{r}(\theta)-\mathbf{R})$ is the generalized Mayer function for an electron,

$$f_s(\mathbf{r}(\theta)-\mathbf{R})=\exp\left[-\int u_s(\mathbf{r}(\theta)-\mathbf{R})d\theta\right]-1. \tag{9}$$

Equations (8) and (9) determine the effect of the surrounding medium on the statistical operator of the electron in terms of the density correlation functions of the medium.

In the general case, we can retain in Eq. (8) correlations of those orders that we need. However, in many practical cases we can neglect higher correlations in (8), i.e., assume that $A=0$ and that the medium is described by a Gaussian distribution of the density fluctuations. This is the standard method to reduce the dimensionality of a system in statistical physics.[10]

By neglecting all non-pairwise correlations, we have thus reduced the dimensionality of the configurational integral to a calculation of ordinary double integrals.

4. EFFECTIVE POTENTIAL FOR A SOLVATED ELECTRON

The next step consists in evaluating the statistical operator of an electron with the effective action (8). An estimate of this statistical operator can be obtained by the trial action method.[9] For a localized state of the electron it turns out to be possible to obtain by the trial action method an effective Schrödinger equation that determines the state of the electron in a molecular medium. We note that the way given below to obtain such an equation is analogous to the optimum fluctuation method.[11]

Using a trial action S_0 we can estimate the statistical operator as follows

$$\rho \geqslant \rho_0 \exp(\langle S_0 - S_{\mathrm{eff}} \rangle s_0) \equiv \exp[-\beta F(S_0)], \tag{10}$$

where

$$\langle S_0 - S_{\mathrm{eff}} \rangle s_0 = \int (S_0 - S_{\mathrm{eff}}) \exp(-S_0) D[\mathbf{r}]. \tag{11}$$

Equation (10) is valid for any real S_0, but the estimate (10) for the statistical operator will be optimal if we choose the parameter S_0 such that the right-hand side of (10) is a maximum. To do this we interchange the integration over space and the path integral. The problem reduces to evaluating $\langle f_s \rangle$ and $\langle f_s f_{s'} \rangle$.For a localized state of the electron we can evaluate the generalized Mayer function if we know the wave function of the electron for some trial action.

We introduce a trial action S_0 with a potential V_0, which determines a set of electron wavefunctions ϕ_n with energies E_n,

$$\left[\frac{-\hbar^2}{2m}\Delta + V_0(\mathbf{r}) - E_n\right]\phi_n(\mathbf{r})=0. \tag{12}$$

Using a two-level approximation and considering only the ground state ϕ_{in} and the first excited state ϕ_f of the electron we obtain (see Appendix) an estimate of the Mayer functions for the initial $f^{(\mathrm{in})}$ and final $f^{(f)}$ states of the electron,

$$\begin{aligned}\langle f_s^{(\mathrm{in})}(\beta)\rangle &= \exp\left[-\beta\int \phi_{\mathrm{in}}^2(\mathbf{r})u_s(\mathbf{r}-\mathbf{R})d\mathbf{r}\right]-1,\\ \langle f_s^{(f)}(\beta)\rangle &= \exp\left[-\beta\int \phi_f^2(\mathbf{r})u_s(\mathbf{r}-\mathbf{R})d\mathbf{r}\right]-1.\end{aligned} \tag{13}$$

The functional free energy can be expressed as

$$\begin{aligned}F_{\mathrm{in}}(\beta) = {} & \int \frac{\hbar^2}{2m}(\nabla\phi_{\mathrm{in}}(\mathbf{r}))^2 d\mathbf{r}\\ & -\frac{1}{\beta}\int d\mathbf{R}' \int d\mathbf{R} \sum_{ss'} f_s^{(\mathrm{in})}(\beta) C_{ss'}\\ & \times(\mathbf{R},\mathbf{R}',f_s^{(\mathrm{in})}(\beta)),\end{aligned} \tag{14}$$

where

$$\begin{aligned}C_{ss'}(\mathbf{R},\mathbf{R}',f_{s'}^{(\mathrm{in})}(\beta)) = {} & \chi_s(\mathbf{R})\delta_{ss'}\delta(\mathbf{R},\mathbf{R}')\\ & +\tfrac{1}{2}\chi_{ss'}(\mathbf{R}',\mathbf{R})f_{s'}^{(\mathrm{in})}(\beta).\end{aligned} \tag{15}$$

For the final state we obtain a similar expression for the functional with the appropriate substitution of $f^{(f)}$ for $f^{(\mathrm{in})}$.

We have thus reduced the path integral (7) to an ordinary functional of the energy that depends on the wavefunction ϕ of the electron, the potential $u(\mathbf{r}-\mathbf{R})$ of the interaction of the electron with a single particle, and the correlation functions χ_s and $\chi_{ss'}$ of the medium.

The best estimate of the partition function is determined by the optimum choice of S_0, ϕ_{in}, and ϕ_f. This leads to the problem of finding the extremum of the free energy functional F, which yields the effective Schrödinger equation for the ground state and excited state wave functions of the electron,

$$\left[\frac{-\hbar^2}{2m}\Delta + V_{\mathrm{eff}}(\mathbf{r},\phi) - E_n\right]\phi_n(\mathbf{r})=0, \tag{16}$$

$$\begin{aligned}V_{\mathrm{eff}}(\mathbf{r}) = {} & \int d\mathbf{R} \int d\mathbf{R}' \sum_{ss'} [1+f_s^{(\mathrm{in})}(\beta)]\\ & \times C_{ss'}(\mathbf{R},\mathbf{R}',2f_{s'}^{(\mathrm{in})}(\beta))u_s(\mathbf{r}-\mathbf{R}).\end{aligned} \tag{17}$$

This Schrödinger equation has a simple physical interpretation. The electron induces fluctuations in the density of the medium and locally changes the average density of the medium, after which the electron is self-localized in these local fluctuations. This mechanism is similar to the mechanism for forming a fluctuon.[12]

Equation (17) determines a self-consistent potential for the electron that is in complete equilibrium in a molecular medium. The long-range and short-range parts of the potential are the same as the result of the continuous and semicontinuous theories of the self-consistent field for a solvated electron,[13] and the effective potential can be written in the form

$$V_{\mathrm{eff}} = V_0\theta(|\mathbf{r}_p - \mathbf{r}|) + U_p(\mathbf{r})\theta(|\mathbf{r}-\mathbf{r}_p|). \tag{18}$$

Here $\Theta(r)$ is the Heaviside step function, r_p is the radius of the well, and V_0 the depth of the well, which is determined by the parameters of the medium in a complicated way, but in the classical limit as $\beta\to 0$ we find

$$V_0=-\beta u_0^2\rho S(0)r_p^{-3}, \tag{19}$$

where we have $u_0=\int\tilde{u}(\mathbf{r})d\mathbf{r}$; $\tilde{u}$ is the short-range part of the potential of the interaction of the electron with the particles of the medium, $\rho=\Sigma_s\chi_s$ is the average density, and $S(0)$ is the Fourier component of the structure factor for $k=0$.

In turn, U_p is the polarization part of the effective potential, which is defined as

$$U_p(\mathbf{r})=\left(1-\frac{1}{\epsilon}\right)\int\frac{\phi_{\rm in}(\mathbf{R})^2}{|\mathbf{r}-\mathbf{r}|}d\mathbf{R}. \tag{20}$$

The whole discussion given above can also be repeated for electron states in partial equilibrium with the medium and, in particular, for the case in which the electron polarization is not in equilibrium with the electron configuration and it is necessary to eliminate it from Eqs. (13) to (17); this is the adiabatic (polar) approximation. The difference between the adiabatic and the self-consistent treatments of the state of a solvated electron were discussed in Ref. 14. In the simplest case one can take this difference into account by replacing the factor $c=1-(1/\epsilon)$ by the Pekar factor $c_{\rm eff}=(1/\epsilon_\infty)-(1/\epsilon)$, where ϵ_∞ and ϵ are the high- and the low-frequency dielectric constants of the medium.

5. SHAPE OF THE ABSORPTION SPECTRUM

We can obtain an estimate such as (10) for the statistical operator $\rho(\theta)$ for a complex variable θ if we analytically continue the functions $F_{\rm in}(\theta)$ and $F_f(\theta)$ into the complex domain. As a result we get for the integrand of (4)

$$\delta F(\theta,\omega)=\theta[E_{\rm in}-E_f-\hbar\omega-E_r^{(1)}]+\sum_{n=2}^{\infty}\theta^n\frac{E_r^{(n)}}{\beta^{n-1}}. \tag{21}$$

We shall see below that $E_r^{(n)}$ is a reorganization energy. Although it is not especially difficult to get general expressions for these quantities, we restrict ourselves because of the unwieldiness of these expressions to the limiting case of high temperatures, $\beta\to 0$. In Eq. (21), we can then retain only the term with $n=2$ in the sum,

$$\begin{aligned}E_r^{(1)}&\equiv E_r^{(2)}\equiv E_r\\&=\int d\mathbf{r}\int d\mathbf{r}'[\phi_{\rm in}^2(\mathbf{r})-\phi_f^2(\mathbf{r})]\\&\quad\times[\phi_{\rm in}^2(\mathbf{r}')-\phi_f^2(\mathbf{r}')]V(\mathbf{r},\mathbf{r}'),\end{aligned} \tag{22}$$

$$\begin{aligned}V(\mathbf{r},\mathbf{r}')=\beta\int d\mathbf{R}\int d\mathbf{R}'\sum_{ss'}u_s(\mathbf{r}-\mathbf{R})u_{s'}(\mathbf{r}'-\mathbf{R}')\\\times[\tilde{\chi}_s(\mathbf{R})\delta_{ss'}\delta(\mathbf{R},\mathbf{R}')+\tilde{\chi}_{ss'}(\mathbf{R},\mathbf{R}')].\end{aligned}$$

We carry out the analysis of Eqs. (21) and (22) similarly to what was done in Ref. 4. Depending on the parameter $\tilde{S}\equiv E_r\beta$, two limiting cases can be realized:

1. $\tilde{S}\gg 1$ (strong coupling and major reorganization of the medium).

The integral (4) can then be estimated by the steepest descent method. In that case the largest contribution to (4) comes from the vicinity of the saddle point and the shape of the spectrum is Gaussian:

$$W=W_{\max}\exp\left[-\frac{\hbar^2(\omega_{\max}-\omega)^2}{\Delta^2}\right], \tag{23}$$

where

$$W_{\max}=2\sqrt{\pi}\frac{d^2}{\hbar\Delta},\quad \hbar\omega_{\max}=E_f-E_{\rm in}+E_r,\quad \Delta^2=\frac{4E_r}{\beta}. \tag{24}$$

Here $\omega_{\max}$ and Δ denote the frequency of the absorption maximum and the halfwidth of the absorption line.

2. $\tilde{S}\ll 1$ (weak coupling and a minor change in the state of the medium when light is absorbed).

In this case it is necessary to take the whole integration range into account; the main contribution comes from the region with large $|{\rm Im}\theta|$, for which the function $\delta F(\theta)$ is linear in θ. The shape of the absorption spectrum will be that of a Lorentzian,

$$\begin{aligned}W&=W_{\max}\frac{\Delta_l^2}{[\hbar^2(\omega_{\max}-\omega)^2+\Delta_l^2]},\\W_{\max}&=2\frac{d^2}{\hbar\Delta_l},\quad \Delta_l=\frac{\pi\tilde{S}}{\beta}.\end{aligned} \tag{25}$$

A detailed analysis of Eq. (21) shows that the terms dropped from the sum do not qualitatively change the situation for those limiting cases, and only lead to a certain asymmetry of the absorption line for $\omega>\omega_{\max}$ and $\omega<\omega_{\max}$.

6. EFFECT OF THE STATE OF THE MEDIUM ON THE ABSORPTION MAXIMUM AND THE ABSORPTION LINE WIDTH

In the general case one must carry out the calculation of the absorption spectrum numerically by solving the Schrödinger equation (16) and subsequently calculating the parameters of the spectrum. To demonstrate the possibilities of the proposed method we give in this part of the paper qualitative estimate of the effect of the medium (temperature, pressure, ion density, and so on) on the absorption maximum and the width of the Gaussian absorption spectrum for a solvated electron in a classical polar liquid.

We note above all that for a pure Coulomb potential we have

$$\hbar\omega_{\max}=\tfrac{3}{4}|E_{\rm in}|=\tfrac{3}{8}|U|=\int V_{\rm eff}(\mathbf{r})\phi_{\rm in}(\mathbf{r})^2d\mathbf{r}. \tag{26}$$

Here U is the potential of the electron in its ground state. The last equality in the foregoing relation is obtained using the virial theorem. For a polaron potential we can find similarly that $\hbar\omega_{\max}=\frac{3}{8}C|U|$ where $C\simeq 1$ is a numerical coefficient of order unity. The short-range forces lead to some reduction in this coefficient, $C\simeq 0.5$ to 1, but for a rough estimate we can put $C=1$ and determine the effect of the medium on the absorption maximum through its effect on the potential energy.

We write the reorganization energy as

$$E_r=E_r^0+\frac{ce^2}{2}\int d\mathbf{r}\int d\mathbf{r}'\times\frac{[\phi_{\text{in}}^2(\mathbf{r})-\phi_f^2(\mathbf{r})][\phi_{\text{in}}^2(\mathbf{r}')-\phi_f^2(\mathbf{r}')]}{|\mathbf{r}-\mathbf{r}'|}, \tag{27}$$

where E_r^0 is the reorganization energy connected with the change in the effective potential in the well; one can estimate this energy to be

$$E_r^0\propto\frac{1}{2}V_0\left[1-\int d\mathbf{r}\phi_{\text{in}}^2(\mathbf{r})\phi_f^2(\mathbf{r})\right]. \tag{28}$$

The main role in the reorganization energy is played by the second term in Eq. (27) for strongly polar media.

6.1. Influence of the temperature

We note that the temperature-dependence of the dielectric constant is weak, and numerical results[15] show that this dependence does not cause a shift in the absorption maximum. Neglecting this dependence, we find that

$$\frac{d\hbar\omega_{\max}}{dT}\sim 0.375\frac{dV_0}{dT}\sim -0.375\frac{V_0}{T}. \tag{29}$$

In this last estimate we neglected the weak temperature dependence of the density and the well radius. Substituting $V_0\sim 1$–2 eV, we find $d\hbar\omega_{\max}/dT\sim -14$–28. According to Ref. 1, the experimental data fall in this range.

For the halfwidth of the absorption band we get a square-root dependence on the temperature which has been studied several times experimentally and theoretically:

$$\frac{d\Delta}{dT}\propto\sqrt{\frac{E_r}{T}}. \tag{30}$$

6.2. Influence of the pressure

Proceeding similarly, we find the way the shift in the absorption maximum depends on the pressure P:

$$\frac{d\hbar\omega_{\max}}{dP}=0.375\left(\frac{V_0}{\rho}\frac{d\rho}{dP}+\frac{U_p}{c}\frac{dc}{dP}\right). \tag{31}$$

For highly polar liquids with $\epsilon\geqslant 10$, the last term does not give more than 10 percent and the behavior of the shift will be basically determined by the pressure dependence of the density. This correlation was noted experimentally in Ref. 16.

6.3. Dependence on the ion density

The presence of ions leads to Debye screening of the polarization potential. For a strongly diluted solution, one can find that

$$U_p(\mathbf{r},n)=U_p(\mathbf{r},n=0)-\frac{e^2}{r_d}+\ldots, \tag{32}$$

where $r_d=(e^2n\beta)^{-1/2}$ is the Debye radius and n the ion density. As a result,

$$\frac{d\hbar\omega_{\max}}{dn}=\frac{1}{2}\frac{e^2}{nr_d}\propto\sqrt{\frac{1}{n}}. \tag{33}$$

This estimate correctly determines the sign of the shift in the absorption maximum when ions are added, and has been observed in experiments.[17–19] The above dependence was first obtained theoretically in Refs. 20 and 21.

For the width of the absorption band we must take into account the next terms in the expansion that are proportional to n, and as a result we find

$$\frac{d\Delta}{dn}\propto\frac{e^2}{r_d^2}\int d\mathbf{r}\int d\mathbf{r}'\phi_{\text{in}}^2(\mathbf{r})\phi_f^2(\mathbf{r}')|\mathbf{r}-\mathbf{r}'|\sim\frac{e^2r_{2p}}{r_d^2}, \tag{34}$$

where r_{2p} is the characteristic size of the excited state of the electron. This dependence also explains the asymmetry in the absorption line broadening. Since the broadening is proportional to the size of the excited state, the broadening will be larger for the higher-energy $1s\rightarrow 3p$ transition, which leads to an increase in the broadening of the whole absorption band in the short-wavelength direction. Such an asymmetry in broadening was observed experimentally in Ref. 17.

Finally we emphasize a last fact. For liquids with a significant preponderance of dipole forces we have $U\propto g$, where g is the Kirkwood factor. It follows from our considerations that the absorption maximum will be proportional to this factor. This correlation has repeatedly been noted experimentally by different authors (see the reviews in Refs. 22 to 24). A more detailed analysis[25] shows that it is roughly satisfied, which from our point of view can be explained by the influence of various effects—for instance, the influence of the short-range part of the potential of the interaction of the electron with the particles of the medium may lead to some deviations in this dependence.

7. DISCUSSION AND CONCLUSIONS

We have proposed a method that makes it possible to evaluate the effect of the molecular microstructure of the surrounding medium on the state of a quantum particle in a polar disordered medium of classical particles. Although in the present paper we have considered only an excess electron in a uniform liquid, we feel that this method can also be used to calculate electron states localized in the inhomogeneities of the medium. Quantum-mechanical or cluster calculations may then be included in the scheme for calculating the statistical operator of the quantum particle.

The method developed here is used to determine the shape of the absorption band for a solvated electron in a polar liquid. We note that this method can be applied not only for calculating optical transitions but also for any other transitions connected with charge transfer, in particular for an estimate of the electron transfer rate. In the present paper we gave a qualitative estimate of the influence of the temperature, pressure, and ion density in the liquid on the absorption maximum and the absorption line width. The estimates obtained for the shift in the maximum and the absorption line broadening agree with experimental results. These estimates show that the temperature dependence and pressure dependence of the absorption maximum is basically determined by the way the microstructure of the closest surroundings depends on the state of the medium through a change in its configuration. Such a conclusion agrees with the results of quantum-chemical calculations using a configuration model of a hydrated electron.[26] At the same time, according to our estimates the way the absorption maximum and the absorption line width depend on the ion density is determined by the Debye screening of the long-range part of the effective potential for the solvated electron. The proposed method thus allows us to take into account the influence on the absorption spectrum of both the local microstructure of the medium and the long-range part of the potential for the interaction of the electron with the medium.

We hope that this method will be useful not only for the widely studied case of an electron in a polar liquid, but also for the less trivial examples of media with a high degree of molecular disorder such as, for instance, polymer liquids or spin glasses.

APPENDIX: ESTIMATES OF THE GENERALIZED MAYER FUNCTION FOR AN ELECTRON

We obtain relations for $\langle f_s(\mathbf{r},(t)\rangle$, $\langle f_s f_{s'}\rangle$ (in what follows we omit in the equations the dependence of the generalized Mayer function for an electron on the particle coordinates of the medium). Expanding the exponent in a Taylor series, we can rewrite Eq. (9) in the following form

$$\begin{aligned}\langle f_s(\mathbf{r}(t))-1\rangle &= \int (f_s(\mathbf{r}(t))-1)\exp(-S_0)D[\mathbf{r}]\\ &= -\int_0^\beta dt\int u_s(\mathbf{r}(t))\rho(\mathbf{r};\mathbf{r})d\mathbf{r}\\ &\quad+\frac{1}{2}\int_0^\beta dt'\int_0^\beta dt\iint u_s(\mathbf{r}'(t'))u_s(\mathbf{r}(t))\\ &\quad\times\rho(\mathbf{r},\mathbf{r}';\mathbf{r}',\mathbf{r})d\mathbf{r}d\mathbf{r}'+\ldots,\end{aligned} \tag{A1}$$

where $\rho(\mathbf{r};\mathbf{r}),\rho(\mathbf{r},\mathbf{r}';\mathbf{r}',\mathbf{r}),\ldots$ are single-, two-, and multiparticle density matrices determined by the action S_0. In the general case they are related to the corresponding n-particle Green functions,

$$\rho(\mathbf{r},\mathbf{r}',\ldots;\ldots,\mathbf{r}',\mathbf{r})=\frac{G(\mathbf{r},\mathbf{r})\ldots G(\mathbf{r}',\mathbf{r}')}{\langle G(\mathbf{r},\mathbf{r})\rangle^n}+G_n, \tag{A2}$$

where $G(\mathbf{r},\mathbf{r})$ is the single-particle and G_n the n-particle Green function for Eq. (12),

$$G(\mathbf{r},\mathbf{r})=\sum_n \phi_n(\mathbf{r})\phi_n(\mathbf{r})\exp(-\beta E_n). \tag{A3}$$

If $u_s\leqslant E_{\text{in}}$, we can obtain the estimate

$$\frac{\langle\ldots\langle G_n u_s(\mathbf{r})\ldots u_s(\mathbf{r}^{(n)})\rangle\ldots\rangle}{\langle G(\mathbf{r},\mathbf{r})u_s(\mathbf{r})\rangle^n}\leqslant\left\{\sum_m\frac{\langle\phi_m u_s\phi_{\text{in}}\rangle}{|E_{\text{in}}-E_m|}\right\}^n. \tag{A4}$$

We can neglect the last term in Eq. (A2) for $u_s\ll E_{\text{in}}$. In that case the n-particle density matrix will simply be the single-particle Green function to the power n. As a result we get

$$\begin{aligned}&\langle f_s(\mathbf{r}(t))-1\rangle\\ &=-\beta\frac{\langle G(\mathbf{r},\mathbf{r})u_s(\mathbf{r})\rangle}{\langle G(\mathbf{r},\mathbf{r})\rangle}+\beta^2\frac{1}{2}\frac{\langle G(\mathbf{r},\mathbf{r})u_s(\mathbf{r})\rangle^2}{\langle G(\mathbf{r},\mathbf{r})\rangle^2}+\ldots\\ &=\exp\left(-\beta\frac{\langle G(\mathbf{r},\mathbf{r})u_s(\mathbf{r})\rangle}{\langle G(\mathbf{r},\mathbf{r})\rangle}\right)-1.\end{aligned} \tag{A5}$$

We can similarly obtain relations for $\langle f_s\, f_{s'}\rangle$.

We neglect the contribution from the excited states in (A5) when the ground state level, ϕ_{in}, E_{in} is dominant, i.e., when $\beta(E_m-E_{\text{in}})\gg 0$,

$$\frac{\langle G(\mathbf{r},\mathbf{r})u_s(\mathbf{r})\rangle}{\langle G(\mathbf{r},\mathbf{r})\rangle}=\langle\phi_{\text{in}}^2 u_s\rangle, \tag{A6}$$

whence Eq. (9) follows for $\langle f_s\rangle$.

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