

Mean-field treatment of polarons in strong electrolytes

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Using variational estimates for the grand partition function, we have developed a microscopic theory of an excess electron in an ionic liquid at high ion concentrations. We have derived the free-energy functional for the electron and have calculated electron energies for the ground and the first excited states as well as electron-ion correlation functions versus thermodynamic parameters of liquid and parameters of electron-ion potentials. We have found that the energetic characteristics of solvated electron are mainly determined by the Coulomb interaction which gives birth to polaronlike states, while ion cores have a pronounced quantitative effect on these characteristics. The local solvent structure around the excess electron is determined by the mean field induced by ions. Using the method developed we have calculated polaron characteristics in molten salts, such as the maximum of the absorption spectrum and its variations caused by changes in temperature, density, and composition of the electrolyte. The data obtained are in agreement with experiments and computer simulations.

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I. INTRODUCTION

Excess electrons in ionic liquids have been the subject of considerable studies [1–6]. Interest in such systems is caused by the fact that they exhibit a wide variety of electric and magnetic properties due to dramatic competition between long-range Coulomb attractions and short-range repulsion effects. Metal-ammonia solutions as well as molten salts are real objects where striking phenomena such as nonmetal-metal transitions, formation of bipolarons are observed [2–4,7]. Excess electrons in such liquids provide a simple example of mixed quantum and classical systems, which exhibit a large number of various effects and are conveniently studied by quantum statistical methods. By now extensive evidence has been accumulated on structural and thermodynamic properties of these liquids [8].

Path integral simulations have provided the basis for the study of excess electrons in such systems [9–14]. According to the data of these simulations, an excess electron forms a localized polaronlike state in the solutions at low concentration of metals. But the local structure and the behavior of the polaron state differ significantly from those of similar formations in solids [15].

Another way to treat excess electrons in liquids is based on integral equations (IE) [16–23]. The IE provide a microscopic description of liquids as well as an accurate account of peculiarities of electron-solvent interactions. The implementation of these methods has been facilitated by special numerical algorithms and powerful computers.

Recently we have developed a semianalytical theory of an electron dissolved in molten salts [24,25], which reduces the problem to an evaluation of a mean field induced by charges and a self-consistent calculation of the electron density distribution. We have calculated equilibrium energetic properties and evaluated the absorption spectrum of the excess electron for a wide range of alkali halide melts in the case

when the mean field is negligible. Here we extend our approach to strong electrolytes and investigate polarons in liquids consisting of ions and dipoles. The influence of changes in temperature, density or composition of electrolyte on the polaron characteristics will also be studied.

The paper is organized as follows. In Sec. II starting from the grand partition function we state the problem and describe the system under consideration. In Sec. III we use variational estimates of the electron path integral and field transformation to evaluate the grand partition function of the system and derive the free-energy functional of the electron. We will derive analytical relations for polaron characteristics with the use of an asymptotic analysis (Sec. IV A). Results of our numerical calculations and their application to localized electron states in molten salts are presented in Sec. IV B, and discussed in Sec. IV C.

II. DESCRIPTION OF THE SYSTEM

Let us consider an ionic liquid with excess electrons dissolved there. We suppose the number of the electrons to be small so that we can ignore electron-electron interactions and restrict ourselves to a single-electron problem. The liquid is assumed to consist of ions with charges Z_+ and Z_- , respectively, and dipolar particles with dipole momentum \mathbf{d} . In the case under consideration the averaged density of dipoles $n_{0\mathbf{d}}$ is supposed to be considerably smaller than the corresponding densities of anions n_{0-} and cations n_{0+} .

In the statistical treatment an ensemble of classical particles interacting with an excess electron is described by the grand partition function Ξ , which can be written as the functional integral depending on the solvent configuration and the electron path $\mathbf{r}(\tau)$:

$$\Xi = \sum_{N \geq 0} \frac{z_a^N}{N!} \int D[\mathbf{r}(\tau)] \int d\mathbf{R}^{[N]} \exp[-\beta(U_{ss} + T + U_{e+} + U_{e-} + U_{e\mathbf{d}})], \quad (1)$$

where we use the system of units for which $\hbar = m = e = 1$, β stands for the inverse temperature, and z_a stands for the ac-

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tivity of solvent particles, assumed to be the same for all the solvent particles. Coordinates of anions $\{\mathbf{R}_-\}$, cations $\{\mathbf{R}_+\}$, and dipoles $\{\mathbf{R}_d\}$ as well as dipole orientations (Euler angles) $\{\omega_d\}$ determine a configuration $\mathbf{R}^{(N)}$ of solvent particles.

The first term $U_{ss}(\mathbf{R}^{(N)})$ in (1) is the interaction potential between solvent particles, the second term $T = \int_0^\beta r^2(\tau) d\tau / 2\beta$ is the kinetic energy of the electron, and the terms U_{ej} ($j = +, -, \mathbf{d}$) are the corresponding electron-ion and electron-dipole interactions. These terms can be written as the sum of potentials u_{ej} between an electron and a solvent particle with coordinate $\mathbf{R}_{ij} : (j = +, -, \mathbf{d})$:

$$U_{ej} = \frac{1}{\beta} \int_0^\beta d\tau \sum_i^{N_j} u_{ej}(\mathbf{r}(\tau) - \mathbf{R}_{ij}). \quad (2)$$

The potentials u_{ej} are not local in the general case. However for our treatment we will use a pseudopotential approximation [26,27] and decompose the electron-ion and electron-dipole potentials into short- and long-range parts: $u_{ej} = u_{esj} + u_{lj}$. Since the typical size r_e of the electron density distribution exceeds greatly the typical size of changes in the short-range components, we characterize the short-range electron-anion and electron-dipole components $u_{esj}(r < a_j)$ only by the parameters $a_j : (j = -, \mathbf{d})$ and do not consider details of electron-ion and electron-dipole potentials at small distances. The electron-cation potential u_{e+} presents the Coulomb attraction at large distances and differs from it at distances less than a_+ . This parameter takes into account the influence of metallic cores. We suppose that the corresponding long-range potentials $u_{lj}(\mathbf{r})$ are proportional to the Coulomb interaction $u_q(r) \equiv 1/r$. Using the three-component vector $\mathbf{u}_l(\mathbf{r}\omega) = (u_{l+}, u_{l-}, u_{l\mathbf{d}})$ we can write $\mathbf{u}_l(\mathbf{r}) = \mathbf{z}u_q(r)$, where $\mathbf{z}(\mathbf{r}\omega) = (Z_+ \equiv 1 - a_+^2 \nabla^2 / 4\pi, Z_-, Z_{\mathbf{d}} \equiv \mathbf{d}\nabla)$ is the vector of generalized charges.

In the similar manner we decompose the interaction potential $U_{ss}(\mathbf{R}^{(N)})$ into the long-range pairwise interaction U_l determined by charges of solvent particles and the short-range repulsion component $U_s : U_{ss}(\mathbf{R}^{(N)}) = U_s(\mathbf{R}^{(N)}) + U_l(\mathbf{R}^{(N)})$. For our consideration the details of the short-range potential $U_s(\mathbf{R})$ is not sufficient either, we take into account only the fact that this potential is pairwise and restricted by a size $\sigma_j : (j = +, -, \mathbf{d})$.

III. THEORY

To evaluate (1) we should calculate the path integral over the electron coordinate $\mathbf{r}(\tau)$. A simple way for estimating the path integral is its variational treatment by the Green's function $G(\mathbf{r}, \mathbf{r}') = \sum_i \phi_i(\mathbf{r}') \phi_i(\mathbf{r}) \exp(-\beta W_i)$ (where W_i and ϕ_i is the total energy and the wave function of i th electron state). Using these variational estimates we have found [25] that when the ground electron state is dominant, the functionals depending on the electron path are replaced by the averaged potentials expressed as

$$\langle U_{ej}(\mathbf{R}) \rangle = \int U_{ej}(\mathbf{r} - \mathbf{R}) \phi_0^2(\mathbf{r}) d\mathbf{r}, \dots (j = +, -, \mathbf{d}), \quad (3)$$

where symbols $\langle \dots \rangle$ denote averaging over the electron density distribution $\phi_0^2(r)$. Thus, we reduce the problem to an evaluation of the grand partition function in an external field induced by an excess electron, which includes short- and long-range components depending on the electron density distribution.

We consider the vector $\mathbf{n}(\mathbf{R}\omega) = (n_+, n_-, n_{\mathbf{d}})$ of generalized densities

$$n_j(\mathbf{R}) = \sum_i^{N_j} \delta(\mathbf{R} - \mathbf{R}_{ij}), \dots (j = +, -, \mathbf{d}), \quad (4)$$

and introduce 3×3 matrices \mathbf{U}_s and \mathbf{H}_s , whose components are the respective short-range interaction potentials between solvent particles, and the total correlation functions caused by these interactions:

$$n_{0+} n_{0j} [1 + H_{sij}] = \sum_N^\infty \frac{z^N}{\Xi(N-2)!} \int \exp[-\beta U_{sij}] d\mathbf{R}^{(N-2)}. \quad (5)$$

Then, using the Hubbard-Stratonovich transform [28,29], we rewrite the grand partition function as the path integral over the scalar fields (Φ, Ψ) induced by charges:

$$\begin{aligned} \Xi &= \Xi_0 \int D[\Psi \Phi] \exp[-\beta Q], \\ Q &= T + \Phi \mathbf{l} * (\mathbf{n}_0 - \mathbf{n}) - \frac{1}{8\pi} \int [\nabla(\Psi - \langle u_q \rangle)]^2 d\mathbf{R} \\ &\quad - \beta^{-1} \mathbf{n}_0 \cdot \left[\mathbf{I} + \frac{1}{2!} \mathbf{n}_0 \cdot \mathbf{f} * \mathbf{H}_s \right] * \mathbf{f}, \end{aligned} \quad (6)$$

where \mathbf{I} is 3×3 diagonal unit matrix, while \mathbf{l} is the three-component unit vector, $\langle \mathbf{u}_{es} \rangle = (\langle u_{es+} \rangle, \langle u_{es-} \rangle, \langle u_{es\mathbf{d}} \rangle)$, $\mathbf{n}_0 = (n_{0+}, n_{0-}, n_{0\mathbf{d}})$, the symbol \cdot denotes a scalar production: $\mathbf{a} \cdot \mathbf{b} = \sum_{ij}^3 a_i(\mathbf{R}) b_j(\mathbf{R})$, while the symbol $*$ corresponds to the convolution integration:

$$\mathbf{a} * \mathbf{b} \equiv \sum_{ij}^3 \int a_i(\mathbf{R}\omega) b_j(\mathbf{R} - \mathbf{R}_1, \omega - \omega_1) d\mathbf{R}_1 d\omega_1. \quad (7)$$

In relation (6) we also introduce the vector \mathbf{f} of generalized Mayer functions, whose components are written as

$$f_j(\mathbf{R}\omega) = \exp[\beta(Z_j \Psi + \Phi - \langle u_{esj} \rangle)] - 1. \quad (8)$$

The free-energy functional (6) has a simple meaning. The second term in (6) corresponds to the contributions caused by changes in the averaged density of the electrolyte. The third term is the electrostatic energy of the system, while the last term in (6) reflects the changes in the distribution of solvent particles, caused by the influence of an excess electron, fluctuation potential $\Phi(\mathbf{R}\omega)$, and electric field $\Psi(\mathbf{R})$. The short- and long-range contributions in (6) are separated in the explicit form, which allows us to obtain simple analytical estimates for the free-energy functional.

The saddle point method can be used to estimate the path integral over fields $\Psi(\mathbf{R})$ and $\Phi(\mathbf{R})$. It determines the mean-field $\Psi_m(\mathbf{R})$ and fluctuation potential $\Phi_m(\mathbf{R}\omega)$ as extrema $\partial Q/\partial\Psi(\Psi=\Psi_m)=0$ and $\partial Q/\partial\Phi(\Phi=\Phi_m)=0$.

The first extremum results in the Poisson–Boltzmann (PB) equation:

$$\Delta(\Psi_m - \langle u_{mq} \rangle) = 4\pi \sum_j \int Z_j n_{0j} g_{ej} d\omega, \quad (9)$$

where $g_{ej}(\mathbf{R}\omega)$ are the corresponding electron-anion, -cation, and -dipole correlation functions, determining the probability for the relevant solvent particle to have an orientation ω and coordinate \mathbf{R} with respect to the center of electron localization. These correlation functions are written in the vector form as

$$\mathbf{g}_e(\mathbf{R}\omega) = [\mathbf{I} + \mathbf{n}_0 \cdot (\mathbf{f} + \mathbf{I})^* \mathbf{H}_s] \cdot (\mathbf{f} + \mathbf{I}). \quad (10)$$

Note that the electron-solvent correlation functions satisfy certain conditions. Making the Fourier transform of (9), expanding the result in power series of the wave vector k , we find various momentum conditions. The zero-momentum condition yields the local neutrality relation

$$1 = 4\pi \sum_j \int \int Z_j n_{0j} g_{ej}(\mathbf{R}\omega) d\mathbf{R} d\omega. \quad (11)$$

To complete mean-field evaluations, let us consider the contribution made by the fluctuation potential. Using (10) we obtain from the extremum of the free energy

$$\int \mathbf{g}_e \cdot \mathbf{n}_0 d\omega = \mathbf{n}_0 \cdot \mathbf{I} = n = \text{const}, \quad (12)$$

which implies that the averaged density of the electrolyte is constant. This relation results in that the logarithmic term $\propto \int d\mathbf{R} \ln(\int \mathbf{n}_0 \cdot \exp[\beta \mathbf{z} \Psi - \beta \langle \mathbf{u}_{esj} \rangle]) d\omega / \beta$ arises in the free-energy functional. A similar path-integral treatment of the fluctuation potential was considered in Ref. [30] for binary electrolytes. In the absence of dipolar interactions the fluctuation potential is short-range, since according to (12) $\Phi(R \rightarrow \infty) \propto \beta \sum Z_i n_{0i} \Psi^2$. Hence the account of the potential yields small corrections to the free-energy functional, and weakly affects the electron density distribution. However, for point dipoles this term provides long-range orientation correlations and the potential should be carefully treated for the correct account of these correlations.

The upper bound of (6) can be obtained by the extremum $\delta \ln \Xi / \delta \phi_0 = 0$ leading to the Schrödinger equation

$$\left[-\frac{\Delta}{2} + V_{ef}(\mathbf{r}) - W_0 \right] \phi_0(r) = 0, \quad (13)$$

where $V_{ef}(\mathbf{r})$ is the effective potential for an excess electron. Using the expression for the electron-solvent correlation functions we rewrite the effective potential as

$$V_{ef}(\mathbf{r}) = \sum_j \int \int Z_j n_{0j} u_{ej}(\mathbf{R} - \mathbf{R}_1, \omega - \omega_1) \times g_{ej}(\mathbf{R}\omega) d\mathbf{R}_1 d\omega_1. \quad (14)$$

Thus, we should solve self-consistently the set (9), (10), (12), and (13). For the known self-consistent effective potential $V_{ef}(\mathbf{r})$ we can calculate the first excited electron state, evaluate the transition energy $\Delta W = |W_0 - W_1|$ between the ground and the first excited electron state and estimate the maximum absorption spectrum of an excess electron.

IV. RESULTS

A. Asymptotic analysis

Note that the PB equation can easily be solved in the Debye–Hückel (DH) limit. Using (9) we find the Fourier transform of the mean field in the case of point ions:

$$\Psi_{\text{DH}}(k) = \frac{[4\pi - a_+^2 k^2] \phi_0^2(k)}{k^2 + \kappa_D^2}, \quad (15)$$

where $\kappa_D^2 = 4\pi\beta \sum Z_i^2 n_{0i}$ is a square of the inverse Debye radius. Therefore, the relative field contribution into the free energy of an excess electron should be proportional to the parameter $(r_e \kappa_D)^{-2}$. The typical mean electron radius $r_e = \langle r^2 \rangle^{1/2}$ approximates $\approx 2-3 \text{ \AA}$ [1]. Thus, in the case of strong electrolytes there exists a small parameter $(r_e \kappa_D)^{-1} \ll 1$. Taking into account this fact we rewrite the free energy of excess electron in the form

$$Q(\Psi_m, \Phi_m, \phi_0) = F_0(\phi_0) + F_{\text{DH}}(\Psi_m, \Phi_m, \phi_0) + F_N(\Psi_m, \Phi_m, \phi_0), \quad (16)$$

which presents an expansion in series of the parameter $(r_e \kappa_D)^{-2}$: $F_0(\phi_0)$ is the field-independent part, F_{DH} is the DH contribution, and F_N is a residue determined by high order field-dependent terms.

The zero-order contribution F_0 can be approximated [24] as

$$F_0(\phi_0) \approx T + \int \int \left[a_+^2 \delta(|\mathbf{r}_1 - \mathbf{r}|) - \frac{1}{2|\mathbf{r}_1 - \mathbf{r}|} \right] \times \phi_0^2(\mathbf{r}_1) d\mathbf{r}_1 \phi_0^2(\mathbf{r}) d\mathbf{r} + \frac{4\pi\rho}{3\beta} r_e^3. \quad (17)$$

It depends only on two dimensionless parameters $a_+^* = a_+ / r_e$ and $\Gamma = \rho \beta^{-1} r_e^4$. The first parameter takes into account the influence of metallic cores, while the second one corresponds to the F -center formation. The zero-order contribution (17) has been investigated by us for the case when $a_+^* = 0$ and $\Gamma = 0$ [24], and at finite values of a_+^* and Γ corresponding to conditions in various molten salts [25]. We have found that properties of an excess electron are mainly determined by the Coulomb interactions resulting in the polaron formation. However, the short-range contributions caused by the F -center formation and the ion-core effect lead

to a remarkable variance of the equilibrium electron characteristics. The calculated energy of a solvated electron agrees with the data found by path-integral simulations [14], while the calculated transition energy $\Delta W = |W_0 - W_1|$ is in good agreement with the experimental data [31–33] on the maximum of the absorption spectrum of an electron solvated in alkali-halide melts. The characteristics of an excess electron depend weakly on temperature and concentration, since $\Gamma \ll 1$ under appropriate conditions.

The above analysis can be improved by the account of high-order terms in (16). Using (15) to estimate this contribution, i.e., $F_N \approx \langle F_N \rangle_{\text{DH}}$, we immediately obtain the approximated expression for electron-ion correlation functions

$$g_{e+}(r) \approx \exp[\beta \Psi_{\text{DH}}(r)], \quad (18)$$

$$g_{e-}(r) \approx \exp[-\beta(a_+^2 \phi_0^2(r) + \Psi_{\text{DH}}(r))].$$

The temperature dependence of solvent density is an origin of the similar dependence of the correlation functions. This results in a linear correlation between the maximum of the absorption spectrum and the thermal expansion coefficient, which was experimentally found in Ref. [33]. Using these correlation functions we can also calculate the coordination numbers of anions and cations:

$$N_{e\pm} = 4\pi n_{0\pm} \int_0^{r_e+r_{\min}} g_{e\pm}(r) r^2 dr. \quad (19)$$

Under conditions typical for molten KCl we obtain $N_+ \approx 3.5$.

Another important peculiarity of (18) is the explicit dependence of the electron-cation correlation function on the parameter a_+ . According to (15) and (18), electron localization on a cation decreases as a_+ rises. Under certain conditions $g_{e+}(0)$ becomes less than unity, as a result of which results an atomlike state transforms into the F -center-like state of excess electron. Such transition is numerically found in Ref. [14] by path integral simulations.

As indicated above, dipolar interactions lead to long-range orientation correlations. This can result in the formation of various localized electron states. One of them is the electron surrounded by an oscillating ion atmosphere. Another formation arises when the electron is embedded into a cluster of oriented dipoles. The coexistence of the states and their structural transitions is a very interesting problem,

TABLE I. The mean radii and the electron energies for the ground and the first excited polaron state calculated by various approximations of Ψ_m and by the COLSYS method.

Method of solution	r_0 (Å)	r_1 (Å)	$-W_0$ (eV)	$-W_1$ (eV)
$\Psi_m = \Psi_{\text{DH}}$	2.824	3.888	3.185	1.385
$\Psi_m \propto A \sin(\pi r/2\sigma)$, $A=0$	2.688	3.817	3.299	1.342
$\Psi_m \propto A \sin(\pi r/2\sigma)$	2.504	3.724	3.466	1.466
$\Psi_m \propto A \sin(\pi r/2\sigma)$, $\sigma=0$	2.459	3.694	3.500	1.46
COLSYS	2.318		3.62	

which will be considered elsewhere. Leaving aside this question, we consider here only the concentration range at which dipoles do not produce any structural changes. In this case their influence can be estimated by the perturbation theory. Expanding in relation (9) the term proportional to concentration of dipoles into a power series in $\Psi_m(\mathbf{R})$ we have

$$\Psi_{\text{DH}}(k) = \Psi_{\text{DH}}(k, n_{0d}=0) [1 - 3y k^2 / \kappa_D^2], \quad (20)$$

where $y = 4\pi\beta n_{0d} d^2 / 9$. Therefore the presence of dipoles results in an additional screening of polaron. According to (20), the increase in the concentration of dipoles decreases the mean field, and hence the energy and the mean radius of the excess electron also decrease, the latter leads to enhanced transition energy ΔW in the case under consideration.

Finally we investigate the effect of asymmetry of electrolyte, i.e., $Z_+ + Z_- \neq 0$. Introducing the asymmetry factor $dZ = |Z_+ + Z_-| / |Z_-|$, we find that the change in the inverse Debye radius is proportional to this factor, i.e., $\kappa_D^2 \propto (1 + dZ)^2$. Hence, the increase in the asymmetry of the electrolyte composition decreases the parameter $(r_e \kappa_D)^{-1}$ and all the electron characteristics tend to the limiting values determined by the zero-order contribution.

B. Numerical calculations

To verify our asymptotic analysis we have investigated numerically free-energy functional (6) and the Schrödinger equation (13) together with the PB equation (9). Both the differential equations were solved self-consistently using the COLSYS package [35]. Table I and Fig. 1 present the results found under the conditions $\beta = 281$, $\rho = 2.27 \times 10^{-3}$, $a_+^2 = 10$, and $a_-^2 = 32$, $n_{0d} = 0$ (all of the parameters are in

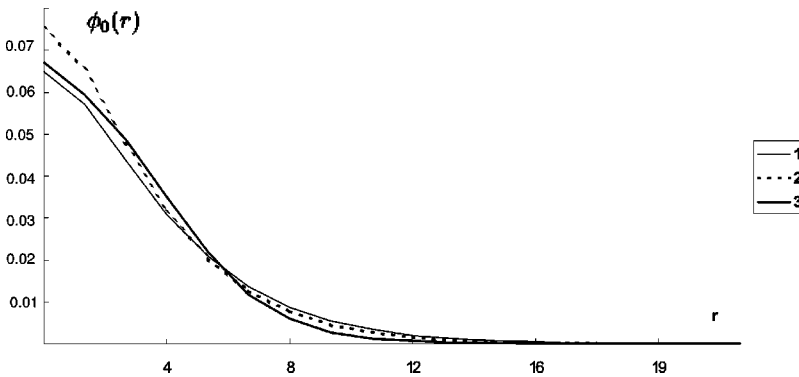


FIG. 1. Distance dependence of the electron wave function $\phi_0(r)$ for the ground state in molten NaCl calculated in the DH limit (1), by variational estimates (2), and by the COLSYS procedure (3); all the values are in atomic units.

atomic units). They show that the polaron state is strongly localized under these conditions.

The free-energy functional was also evaluated by simple variational estimates. We used trial hydrogenlike functions for electron wave functions of the ground and the first excited states:

$$\begin{aligned}\phi_0(r) &= \sqrt{\frac{\alpha^3}{7\pi}}(1 + \alpha r)\exp(-\alpha r), \dots \phi_1(\mathbf{r}) \\ &= \sqrt{\frac{\alpha_1^5}{\pi}}r \cos \Theta \exp(-\alpha_1 r),\end{aligned}\quad (21)$$

where α_i ($i=0,1$) are varying parameters, r and Θ are the absolute value and the angle of the radius vector, respectively. Such a choice of trial functions provides correct asymptotic behavior of electron wave functions at $r \rightarrow 0$. Taking into account relation (15), we approximate the mean field as

$$\Psi_m(r) = \frac{4\pi A \sin(\pi r/2\sigma) \phi_0^2(\alpha r)}{\kappa_D^2 r}, \quad (22)$$

where A and σ are varying parameters. We also considered two limiting cases (22): $A=0$, which corresponds to the zero-order contribution (17) and the case $\sigma=0$, while A/σ is finite, which ignores the oscillations of ionic atmosphere around the polaron. Thus considering the free-energy functional $F(A, \alpha, \sigma)$, we calculated its extrema, found $g_{e\pm}(r)$, then calculated $V_{ef}(r)$, and evaluated W_1 . The electron energies (W_0, W_1) and the mean electron radius (r_e) found under the same conditions are listed in Table I. As is seen, all the approximations yield similar values, which are close to the data obtained by numerical integration of differential equations. The difference in W_0 found by the variational estimate and obtained by the COLSYS treatment is less than 3%. Figure 1 plots the comparison of the electron wave functions for the ground state obtained by variational estimates at $A=0$ and $\sigma=0$, and the data obtained by the COLSYS method. The data obtained in various ways are a good agreement.

The choice of the varying parameter σ weakly affects the data obtained except the case when the electron forms a hydrogenlike state strongly localized on cation (see below). Taking into account this fact, we performed the subsequent analysis by variational estimates supposing σ to be equal to the mean ion distance. To reveal the influence of short-range interactions, we calculated the dependencies of (W_0, W_1) on a_- . This parameter characterizing the influence of an anion core weakly affects the energy W_0 (Fig. 2). The dependence of the energy on this parameter is mainly determined by changes in the fraction of the electron density [$1 - q(r < r_e)$], localized inside the electron cavity: $W_0 \propto \rho a_- [1 - q(r < r_e)]$. However the transition energy $\Delta W = |W_0 - W_1|$ depends on a_- stronger due to the fact that the first excited state is more extended, and the fraction of electron density inside the cavity is higher than that for the ground state. For comparison we also depict in Fig. 2 the dependen-

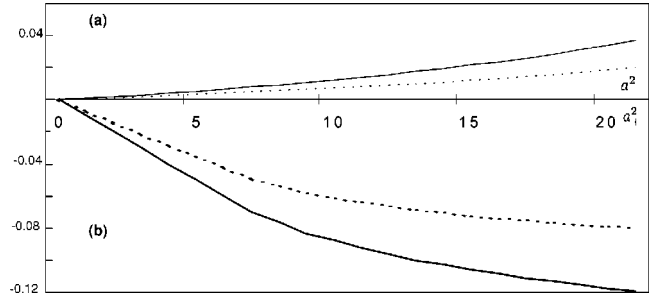


FIG. 2. Changes in the absolute value of the ground electron energy $|\delta W_0|$ (solid lines), and the transition energy $\delta \Delta W$ (dashed lines) versus the square of anion-core (a) and cation-core (b) parameters under the conditions $\beta=294$, $\rho=2.37 \times 10^{-3}$, $n_{0d}=0$, while $a_+=3.01$ (a), and $a_-=4.18$ (b). All the values are in atomic units.

cies of the electron energy W_0 and the transition energy $\Delta W = |W_0 - W_1|$ on the parameter a_+ . These dependencies are close to those obtained in Ref. [25]. As a_+ increases, the energy W_0 decreases, while $\Delta W = |W_0 - W_1|$ increases in a similar manner.

We have applied our method to calculate the characteristics of polaron states in molten salts. The data on temperature-dependent densities of the melts were taken from Ref. [36]. For ion radii we used values obtained by Abramo *et al.* [37]. The cation-core parameter a_+ was extracted from the data obtained by pseudopotential calculations for electron-metal interactions in liquid metals [26]. The cation parameter was calculated as $a_+^2 = 2\pi \int [u_q(r) + u_{e+}(r)] r^2 dr$, where $u_{e+}(r)$ is the electron-cation potential found in Ref. [26]. For the anion-core parameter we used $a_-^2 = 19$ a.u. Table II lists the calculated transition energies and the mean radii as well as their experimental values and the values obtained by the mean spherical approximation (MSA) [38]. As is seen our calculations are in good agreement with the MSA theory as well as with the experimental data. However we have obtained more localized electron states than those calculated in Ref. [38]. The difference between our data and experimental values is less than 5%. The extraordinary situation is only for LiCl. In this case the electron is mainly localized on cation, the electron state is weakly affected by surrounding ion atmosphere and strongly depends on small changes in a_+ and σ . The experimental situation is not clear for this case too. A broad absorption band was observed in Ref. [39]. We suppose that the polaronlike state is metastable in this case and the electron forms a hydrogenlike state on a cation.

We have also studied the effect of temperature on the electron state. The calculations confirmed our asymptotic analysis. According to our calculations, there is a direct correlation between the temperature dependencies of the electron mean radius and the energy. They are caused by the same effect, i.e., temperature dependence of the electrolyte density. In the case of NaCl our numerical estimates yield $\partial \Delta W / \partial T \approx -1 \times 10^{-4}$ eV/K, while the experimental value is much higher $\partial \ln(W_{\max}) / \partial T \approx -7.1 \times 10^{-4}$ eV/K [40]. The difference between our results and the experimental data may be explained by the fact that we used transition energy

TABLE II. Calculated and experimental values of the transition energy ΔW (eV) and the mean radius r_e (Å) for the polaron in various molten salts.

		LiCl	NaCl	KCl	RbCl	CsCl
		Theory				
This work	ΔW	2.36	1.666	1.219	1.105	0.997
	r_e	2.066	2.579	3.077	3.241	3.414
[38]	ΔW	2.22	1.69	1.33	1.22	1.06
	r_e	3.24	3.31	3.46	3.51	3.70
		Experiment				
	ΔW	2.26 [39]	1.68 [32]	1.29 [32], 1.33 [41]	1.18 [41]	1.08 [32], 1.01 [33]
	r_e			3.5 ± 0.4 [34]		

$\Delta W = |W_0 - W_1|$ instead of W_{\max} , but the latter should include the contribution related to the reorganization of the medium, which determines temperature dependence of the absorption maximum.

We have also investigate the influences of concentration of dipoles and the asymmetry of charges on the polaron characteristics. Figure 3 presents the dependencies of relative changes in W_0 , ΔW , and r_e on $c = n_{0d}/n_0$ obtained by our calculations, while Fig. 4 shows the dependencies of the same values on the asymmetry factor dZ . All the data are in good agreement with our asymptotic analysis. Note also that for high values of dZ , the situation is the same as in the case of LiCl. The polaronlike state is metastable, since there is a hydrogenlike electron state localized on a highly charged cation.

C. Concluding remarks

Combining quantum-mechanical and statistical approaches for evaluating grand-partition function of a mixed quantum-classical system, we have developed a method for treating localized electron states in ionic liquids. This method reduces the problem to self-consistent calculation of the Schrödinger and the PB equations. Due to high concentration of charged particles, which is typical for strong electrolytes, the size of electron density distribution greatly ex-

ceeds the Debye radius. This great difference in scales of interactions for quantum and classical systems allows us to provide an asymptotic analysis of the free-energy functional for the localized electrons and to calculate various electron characteristics. Comparison our results with the experimental data and numerical simulations shows that these estimates are very accurate.

We have considered only the case when the influence of dipoles on the electron state is weak and can be treated by perturbation methods. The situation in liquids with dominant dipolar interactions is more difficult due to long-range orientation correlations. The detailed mean-field treatment of an electron solvated in dipolar liquids is in progress.

The application of the method goes beyond the single-electron problem. Recently we have used the method combined with the density functional theory [42] to evaluate bipolaron states in ionic liquids [43]. For multielectron problem the approach can be combined with quantum-chemical calculations. Hirata and his colleagues have applied a similar method to calculate solvent effects on triiodide [44]. They used *ab initio* calculations to evaluate the electronic structure and RISM (reference interaction site model) equations to treat the solvent structure.

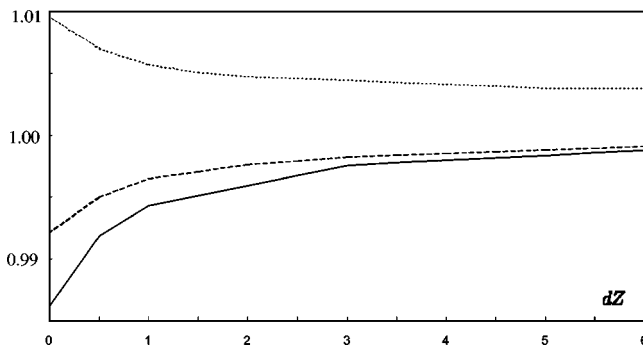


FIG. 3. Relative changes in the mean radius $\delta r_e/r_e$ (dotted line), the ground electron energy $\delta W_0/W_0$ (dashed line), and the transition energy $\delta \Delta W/\Delta W$ (solid line) caused by variation of the asymmetry parameter dZ . The unit values correspond to $dZ = \infty$.

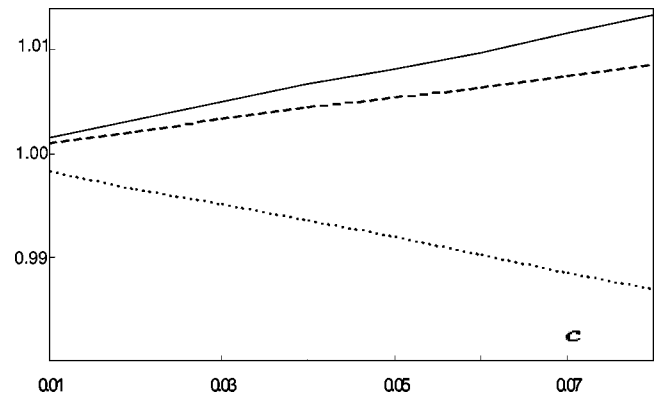


FIG. 4. Relative changes in the mean radius $\delta r_e/r_e$ (dotted line), the energy $\delta W_0/W_0$ (dashed line) of the electron ground state, and the transition energy $\delta \Delta W/\Delta W$ (solid line) versus the dipole concentration c ($a_-^2 = 10$, $\beta = 281$, $\rho = 2.27 \times 10^{-3}$, $a_+^2 = 10$).

We have restricted ourselves only to localized electron states. However, a similar RISM-polaron approach was also used by Chandler and Hsu for extended electron states in inert gases [17]. Recently Leung and Csajka have applied mean-field evaluations to reveal phase transitions between localized and delocalized electron states in metal–ammonia solutions [45]. Thus, we think the developed approach is

rather general and can be applied to a large number of problems dealing with electron states in solutions.

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