Mean-field theory of an electron solvated in molten salts

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A mean-field, microscopic theory of an excess electron solvated in a molten salt is presented. Starting with the grand partition function of the system, we reformulate the problem to evaluate a mean field induced by charges and calculate self-consistently the electron density distribution. We obtain a Poisson–Boltzmann equation for the mean-field and Schrödinger equation for the electron wave functions with a potential dependent on the mean field and a local density of melt. We also derive expressions for electron–ion correlation functions. We demonstrate that the mean field is weak in molten salts and can be analytically evaluated in the Debye–Hückel limit. Using a simple variational treatment, we calculate energetic and structural properties of a solvated electron for a wide range of alkali halide melts. These properties are mainly determined by the polaron effect, while the repulsion between the electron and ion cores leads to a remarkable variance of the properties. The results obtained are in good agreement with path-integral simulations and experimental data on the maximum of the absorption spectrum of an electron solvated in these melts. © *2000 American Institute of Physics.* [S0021-9606(00)51107-6]

I. INTRODUCTION

The behavior of a solvated electron in various media has been the focus of attention for the last few decades.[1–4] Recent progress in computing technique and numerical simulations based on path-integral methods has stimulated interest in the problem. Polaron and semicontinuum models[5] of a solvated electron allow to treat the solvated electron behavior with regard to the effects of cavity formation and polaron tails. Modern RISM-polaron (reference interaction site model)[6,7] and mean-field[8,9] theories are a good tool to calculate equilibrium properties of an electron solvated in nonpolar[8,10–12] and dipolar hard-sphere solvents,[9,13] molten salts,[14] and water[15,16] with regard to the microscopic structure of solvent and electron–solvent interactions. The models require extensive numerical computations.

Special attention is given to an electron solvated in molten salts and metal–molten–salt solutions.[17–21] Structural and thermodynamic properties of molten salts are thoroughly studied numerically and experimentally.[22] Dramatic concurrence of long-range Coulomb attraction and short-range repulsion effects are revealed there. Occurrence of striking phenomena such as nonmetal–metal transitions, bipolaron formation[23,24] in the systems sends researchers to investigate them time and again.

In this paper, we develop a statistical theory of an electron solvated in molten salt, starting with the grand partition function for the coupled electron–Coulomb–liquid system.

Using path integral field formalism, we reformulate the problem to evaluate a mean-field induced by charges and calculate self-consistently the electron density distribution for the ground and first excited states of an excess electron. As a result, we derive nonlinear differential equations deter-mining the electron density distribution and the mean field, and correlate them with the RISM-polaron treatment using integral RISM-like equations. We show that for the systems under consideration the Debye screening is strong and the mean field is weak, which enables us to evaluate the mean field in the Debye–Hückel limit. We apply the method to calculate equilibrium energetic and structural properties of the solvated electron for a wide group of alkali halide melts. Of special interest is the evaluation of the absorption spectrum of a solvated electron, since there are a lot of data on this spectrum in the molten salts.[25–27] Using a simple variational treatment we consider the influence of the Coulomb attraction and short-range repulsion between the electron and ions on the behavior of the solvated electron.

The paper is organized as follows. In Sec. II we describe the model, considering the grand partition function of the system. In Sec. III using a path-integral field treatment, we reduce the problem to the evaluation of a mean field induced by charges, which is determined by a Poisson–Boltzmann equation, and self-consistent calculations of electron wave functions determined by a Schrödinger equation. Section IV deals with an analytical evaluation of the mean field, obtained in the Debye–Hückel limit. Numerical results and discussions are presented in Sec. V, where we use the data obtained to calculate the maximum of the absorption spectrum of an electron solvated in various alkali halide molten salts. There, we also compare the results obtained with the available numerical and experimental data. Appendixes A and B include several of mathematical steps omitted from the main text.

II. STATEMENT OF THE PROBLEM

Let us consider an excess electron in a molten salt. Ions interacting with the electron are a source of a potential. The

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detailed study of the potential field is very difficult. But we can treat this field as a disordered one, use a self-averaging procedure, and calculate electron characteristics via thermodynamic and structural parameters of the molten salt.

We start the statistical treatment of an electron dissolved in a molten salt, considering the grand partition function of the system Ξ. We use the system of units for which $\hbar = m = e = 1$. For simplicity, we suppose that chemical potentials of ions (μ_+, μ_-) as well as their masses (M_+, M_-) are equal, i.e., $\mu_+ = \mu_- = \mu$ and $M_+ = M_- = M$, while ion charges are equal to ± 1, considering the molten salt as a symmetric 1-1 electrolyte. Then, the grand partition function Ξ can be written as the functional integral depending on the ion configuration $\mathbf{R}^{\{N\}}$ and the electronic path $r(\tau)$

$$\Xi = \sum_{N \geqslant 0}^{\infty} \frac{[(2\pi M)^{-3/2} \beta^{3/2} V \exp(\beta\mu)]^N}{N!} \int D[\mathbf{r}(\tau)]$$

$$\times \int d\mathbf{R}^{\{N\}} \exp[-Q],$$

$$Q = \left[\beta U_{ii} + \int_0^\beta d\tau \left[\frac{\dot{\mathbf{r}}^2(\tau)}{2} + \sum_i^N u_\pm(\mathbf{r}(\tau) - \mathbf{R}_{i\pm}) \right] \right], \quad (1)$$

where $U_{ii}(\mathbf{R}^{\{N\}})$ denotes the ion–ion interaction potential, $u_\pm(\mathbf{r} - \mathbf{R}_{i\pm})$ is the electron–ion potential, V is the volume of the system, β is the inverse temperature, R_{i+} (or R_{i-}) is the coordinate of ith positive (or negative) ion.

To reveal the effects of short- and long-range forces, we decompose the ion–ion potential into the Coulomb part $u_q(\mathbf{R}) = R^{-1}$ and the short-range component $U_s(R)$ as a hard-sphere potential

$$U_{ii}(\mathbf{R}^{\{N\}}) = U_s(\mathbf{R}^{\{N\}}) + \frac{1}{2} \sum_{i \neq j} \pm u_q(\mathbf{R}_{i\pm} - \mathbf{R}_{j\pm}). \quad (2)$$

The signs in Eqs. (1) and (2) depend on the signs of interacting charges.

To describe electron–ion interaction, we use a simple local pseudopotential. For the interaction between the electron and a negative ion, the pseudopotential $u_{e-}(r)$ includes the Coulomb part $u_q(r)$ and the hard-sphere repulsion component $u_{es}(r < d_-)$, the latter takes into account the excluded volume effect

$$u_{e-}(\mathbf{r}) = u_q(r) + u_{es}(r). \quad (3)$$

On the other hand, the electron–cation potential $u_{e+}(r)$ being purely Coulomb attraction at large distances can be modeled by the constant $u_{e+}(r < d) = u_{e+}(d)$, where the cut-off distance d is an adjustable parameter

$$u_{e+}(r \geqslant d) = -u_q(r), \quad u_{e+}(r < d) = u_{e+}(d). \quad (4)$$

A similar form of the electron–cation pseudopotential are commonly used in computer simulations.[14,18–21,28]

To find the grand partition function Ξ, we should calculate the complicated multidimensional integrals in Eq. (1), and then evaluate the series over N. Various statistical methods can be used for this purpose. In principle, we can consider a molten salt with an excess electron as an ensemble of classical ions in an external field. The source of the field is an excess electron. Therefore, the problem can be reduced to

an evaluation of the grand partition function for a symmetric electrolyte in an external field. Then we should calculate self-consistently the electron density distribution which induces the external field.

III. MEAN-FIELD APPROXIMATION

In view of the above treatment, we reformulate (1), using the standard field-theoretic approach.[29,30] As a result, the grand partition function can be written as the path integral over the electric field Ψ induced by charges (see Appendix A)

$$\Xi = \Xi_0 \int D[\mathbf{r}(\tau)] \int D[\Psi] \exp[-\beta\Omega\{\Psi, \mathbf{r}(\tau)\}],$$

$$Q = T_e + (\Psi - u_e) * \frac{u_q^{-1}}{2} * (\Psi - u_e) - \beta^{-1} A(\Psi, \mathbf{r}(\tau)). \quad (5)$$

Here Ω is the thermodynamic potential of the system, T_e is the kinetic energy of the electron, the long-range component of the external field induced by the electron is

$$u_e(\mathbf{R} - \mathbf{r}) = \frac{1}{2\beta} \int_0^\beta [u_q(\mathbf{R} - \mathbf{r}(\tau)) - u_{e+}(\mathbf{R} - \mathbf{r}(\tau))] d\tau,$$

and $u_q^{-1} = \frac{1}{4}\pi\Delta(\mathbf{r})$ is the operator inverse to the Coulomb interaction $u_q(r)$. The symbol ''$*$'' denotes the convolution integration: $y * x \equiv \int x(\mathbf{R}) y(\mathbf{R} - \mathbf{R}_1) d\mathbf{R}_1$.

The last term in Eq. (5) reflects the changes in the distribution of ions, caused by the electric field $\Psi(R)$. It can be written in terms of the average ion density ρ and the total correlation function $h_s(r)$ of hard spheres (see Appendix A) as

$$A(\Psi, r(\tau)) = \rho * f_q + \frac{\rho^2}{2!} f_q * h_s * f_q + \cdots, \quad (6)$$

where f_q is the generalized Mayer function of the electron in the mean field

$$f_q(\mathbf{R}, \mathbf{r}(\tau)) = \frac{1}{2} \left(\exp[\beta\Psi(\mathbf{R})] + \exp\left[-\beta\Psi(\mathbf{R}) - \int_0^\beta u_{es}(\mathbf{r}(\tau)) d\tau \right] - 2 \right). \quad (7)$$

Thus, we should evaluate path integrals over electron path $\mathbf{r}(\tau)$ and over a classical field $\Psi(R)$. Below, we will show that the path integral over the electric field includes a large parameter $\beta\alpha \gg 1$ (where α^{-1} characterizes the averaged electron radius). Therefore, the saddle point method can be used to calculate the path integral over the electric field. The saddle point determines the mean-field $\tilde{\Psi}(R)$ as

$$\left. \frac{\partial\Omega}{\partial\Psi} \right|_{\Psi = \tilde{\Psi}} = 0. \quad (8)$$

We will derive the explicit expression for $\tilde{\Psi}$ in Sec. IV, and calculate it analytically, using various relations between the mean-field and electron–ion correlation functions.

The integral over electron path can be estimated by a trial action S_0. Using Jensen's inequality, we find

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$$\Xi \geqslant \int D[\mathbf{r}(\tau)]\exp[-S_0]\exp(\langle S_0 - \beta\Omega\rangle_{S_0})$$

$$\equiv \exp[-\beta\Omega_{ef}], \tag{9}$$

where symbols $\langle S_0 - \beta\Omega\rangle_{S_0}$ denote averaging with the use of trial action S_0

$$\langle S_0 - \beta\Omega\rangle_{S_0} \equiv \int D[\mathbf{r}(\tau)](S_0 - \beta\Omega)\exp[-S_0]. \tag{10}$$

Equation (9) determines the effective thermodynamic potential Ω_{ef}. If the trial action S_0 depends on a parameter α, the upper bound of estimate (9) can be found by searching the extremum of the effective thermodynamic potential Ω_{ef} with respect to α. The latter yields a set of nonlinear algebraic equations relating the parameter α and parameters of Ω_{ef}. This method of electron path integral was used in RISM-polaron theory for the quadratic trial action.[6,7] Another way for estimating Eq. (9) is its variational treatment by the electron density matrix $\varrho(\mathbf{r},\mathbf{r}')$ related to the Green's function $G(\mathbf{r},\mathbf{r}') = \Sigma_i \phi_i(\mathbf{r}')\phi_i(\mathbf{r})\exp(-\beta W_i)$[31,32] (where W_i and ϕ_i is the total energy and wave function of ith electron state). These variational estimates lead to a Schrödinger equation for $\phi_i(\mathbf{r})$, and allow to find the states of an excess electron which does not form chemical bonds.

We assume that the ground electron state is not degenerate and dominant, i.e., $\beta|W_0 - W_i| \gg 1$, and restrict ourselves to only the consideration of the ground wave function $\phi_0(\mathbf{r})$ of the electron (the evaluation of the first excitation will be obtained below). Then, the averaging $\langle\cdots\rangle_{S_0}$ changes into averaging over the electron density distribution $\phi_0^2(r)$. As a result of this procedure the potentials depending on the electron path change to averaged potentials (see Appendix B), i.e., $u_{es} \to \langle u_{es}\rangle \equiv u_{es}*\phi_0^2$, $u_e \to \langle u_e\rangle \equiv u_e*\phi_0^2$, i.e.,

$$\Omega_{ef} = T_e + (\tilde{\Psi} - \langle u_e\rangle)*\frac{u_q^{-1}}{2}*(\tilde{\Psi} - \langle u_e\rangle)$$

$$- \beta^{-1}A(\tilde{\Psi}, \langle u_{es}\rangle). \tag{11}$$

Then, the upper bound of Eq. (9) can be obtained by the extremum

$$\frac{\partial\Omega_{ef}}{\partial\phi_0} = 0. \tag{12}$$

The extremum results in the nonlinear Schrödinger equation

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

where $V_{ef}(\mathbf{r},\{\phi_0\})$ is the self-consistent effective potential for an excess electron in liquid

$$V_{ef}(\mathbf{r},\{\phi_0\}) = s*(\tilde{\Psi} - \langle u_e\rangle) + u_{es}*\rho(1 + \rho h_s*f_q)$$

$$\times \exp[-\beta(\Psi + \langle u_{es}\rangle)]/2, \tag{14}$$

here we introduce the switching function $s = u_q^{-1}*u_e$ determining the influence of cation core. For our choice of u_{e+} the Fourier transform of the switching function is $s(k) = (1 + \sin(kd)/kd)/2$, where d is the cut-off distance [when d

$\to 0$, $s(k) \to 1$]. The first and the second terms of Eq. (14) correspond to the short- and long-range components of the effective potential V_{ef}.

We can also define electron–ion correlation functions $g_{e-}(\mathbf{r})$ and $g_{e+}(\mathbf{r})$, determining the probability for anion or cation to occur at distance $\mathbf{r}$ from the center of electron localization

$$g_{e+}(\mathbf{r}) = \frac{\delta\Omega_{ef}}{\delta\langle u_{e+}\rangle} = (1 + \rho h_s*f_q)\exp[\beta\tilde{\Psi}], \tag{15}$$

$$g_{e-}(\mathbf{r}) = \frac{\delta\Omega_{ef}}{\delta\langle u_{e-}\rangle} = (1 + \rho h_s*f_q)\exp[-\beta\tilde{\Psi} - \beta\langle u_{es}\rangle]. \tag{16}$$

Using these functions, we express the effective potential as:

$$V_{ef} = \rho(u_{e+}*g_{e+} + u_{e-}*g_{e-})/2. \tag{17}$$

Thus, the problem of an excess electron in a molten salt is reduced to computation of mean field $\tilde{\Psi}$, and to self-consistent evaluation of the ground electron function $\phi_0(r)$, depending on the parameters of molten salt via the electron–ion correlation functions.

To calculate the mean field, we rewrite Eq. (8) as the Poisson–Boltzmann equation

$$u_q^{-1}*(\tilde{\Psi} - \langle u_e\rangle) = \rho_{ef}(r) = \rho(g_{e+} - g_{e-})/2, \tag{18}$$

where $\rho_{ef}(r)$ is the effective density of charges. The latter can be transformed into the integral equation

$$\tilde{\Psi} = \langle u_e\rangle - \rho_{ef}*u_q, \tag{19}$$

which is similar to the Ornstein–Zernike equation. It relates the mean field and the electron–ion correlation functions depending on this field via Eqs. (15) and (16). Relation (19) is nonlinear and can be calculated only numerically, but we can find an analytical solution to Eq. (19) in the Debye–Hückel limit when the mean field is small.

IV. EVALUATION OF THE MEAN FIELD IN THE DEBYE–HÜCKEL LIMIT

We symmetrize the generalized Mayer function f_q by the shift $\hat{\Psi} = \tilde{\Psi} + \langle u_{es}\rangle/2$ and expand the thermodynamic potential Ω_{ef} taking into account only the terms whose order is lower than the second one with respect to $\hat{\Psi}$. As a result, we arrive at the expression for the thermodynamic potential

$$\Omega_{ef} = T_e + (\hat{\Psi} - \langle\hat{u}_e\rangle)*\frac{u_q^{-1}}{2}*(\hat{\Psi} - \langle\hat{u}_e\rangle)$$

$$- \beta\frac{\rho}{2}(1 + \rho h_s*f_{es})\hat{\Psi}*(1 + f_{es})\hat{\Psi} + \Omega_s, \tag{20}$$

where we also use the shifted external field $\langle\hat{u}_e\rangle = \langle u_e + u_{es}/2\rangle$, while Ω_s and f_{es} are the relevant quantities arising from short-range electron–ion repulsion

$$\Omega_s = -\rho\beta^{-1}\left(f_{es} + \frac{\rho}{2}f_{es}*h_s*f_{es}\right),$$

$$f_{es} = \exp[-\beta\langle u_{es}\rangle/2] - 1. \tag{21}$$

We introduce the quantities: $z(k)\hat{\Psi}(k)=\int(1+\rho h_s*f_{es})$ $\times\exp[-\beta\langle u_{es}\rangle/2+i\mathbf{k}\mathbf{r}]\hat{\Psi}(\mathbf{r})d\mathbf{r}$, $\hat{s}(r)=\hat{u}_e*u_q^{-1}$ and the inverse Debye radius $æ=(4\pi\rho\beta)^{1/2}$. Then we find the formal explicit expression for the Fourier transform of the mean field

$$\hat{\Psi}(k)=\frac{4\pi\hat{s}(k)\phi_0^2(k)}{k^2+æ^2z(k)}. \tag{22}$$

Note that when the excess electron is considered to be a point charge, i.e., $\hat{s}(k)=\phi^2(k)=z(k)=1$ the mean field takes the Debye–Hückel form: $\hat{\Psi}(r)=\exp[-ær]/r$. Since the thermodynamic potential (20) is quadratic with respect to the mean field, the path integral over field $\hat{\Psi}$ can be analytically evaluated, resulting in the final expression for the effective thermodynamic potential

$$\Omega_{ef}=T_e+\Omega_s-\frac{1}{\pi}\int\frac{\hat{s}^2(k)æ^2z(k)\phi_0^4(k)dk}{k^2+æ^2z(k)}. \tag{23}$$

The explicit expressions for $g_{e\pm}$ are easily obtained if we consider the zero- and the first- order terms over the mean field in Eqs. (15) and (16) and use expression (22). As a result, we find the Fourier transform of the effective electron–solvent potential $V_{ef}(k)$ including the repulsive short-range (V_s) and attractive long-range (V_l) components

$$V_{ef}(k)=V_l+V_s=-\frac{\hat{s}^2(k)æ^2z(k)\phi_0^2(k)}{k^2+æ^2z(k)}\cdot\frac{4\pi}{k^2}+\frac{\rho}{2}$$
$$\times[(1-\hat{s})u_qg_{e+}+u_{es}g_{e-}]. \tag{24}$$

As is seen $V_s(k\to0)=V_0=$const, while $V_l(k\to0)=-4\pi/k^2$.

For qualitative estimates we will characterize the ground electron state by a single parameter α related to the mean electron radius $r_e=\langle r^2\rangle^{1/2}\sim\alpha^{-1}$. Note that the expansion in series of $\hat{\Psi}$ is correct when $\beta\hat{\Psi}\ll1$. For our estimate (22) we have $\beta\hat{\Psi}(0)\approx\phi^2(0)/\rho+\cdots\propto\alpha^3/\rho$ which is small in view of our assumption that the solvated electron does not form chemical bonds. Point out that in the systems under consideration $r_e\approx3$ Å while $æ\approx7.5$ Å^{-1}, i.e., $r_eæ\gg1$ and the effective thermodynamic potential (23) represents the zero- and the first-order terms of the expansion in series of $(r_eæ)^{-1}$. Our numerical calculations show that the consideration of the second order term in Eq. (23) changes the results by less than 1%, therefore, for estimates we can use the simplified thermodynamic potential

$$\Omega_{ef}=T_e+\Omega_s-\frac{1}{\pi}\int\hat{s}^2(k)\phi_0^4(k)dk, \tag{25}$$

where we separate different effects of electron–ion interactions. The second term in Eq. (25) results from the excluded volume effect similar to the F-center formation, while the third term is determined by the Coulomb interaction modified by cation–core effect. Thus our problem is reduced to evaluation of Eq. (25) which can be transformed to the calculation of a Schrödinger equation with the corresponding self-consistent potential. In this paper we will obtain varia-

tional estimates of Eq. (25) using simple trial wave functions for the ground and first excited electron states.

Using a simple trial wave function $\phi_0(\mathbf{r})=\phi_0(\alpha r)$ for the electron ground state, we reduce the evaluation of the grand partition function to the search for the extremum

$$\frac{\partial\Omega_{ef}}{\partial\alpha}=0.$$

This extremum for the simplified thermodynamic potential (25) yields the nonlinear algebraic equation for α

$$\alpha=C_1[1+f(\alpha d)]+\frac{C_2\rho}{\beta\alpha^4}\left[1+\frac{\pi\rho\sigma^3}{3}(1+C_3\sigma\alpha)\right], \tag{26}$$

where C_1, C_2, and C_3 are constants depending on the type of the wave function chosen, while $f(\alpha d)$ is a function determining the influence of cut-off distance d, and σ is the hard-sphere diameter of ions. To evaluate analytically the excluded volume we use the steplike approximation for $h_s(r)$: $h_s(r<\sigma)=-1$, $h_s(r\geq\sigma)=0$, and $f_{es}(r)$: $f_{es}(r<r_e)=-1$ and $f_{es}(r\geq r_e)=0$.

For the known self-consistent effective electron–solvent potential we can calculate the first excited electron state in the potential. Using a simple trial wave function for the first excited electron state $\phi_1(\alpha_1\mathbf{r})$ depending on parameter α_1, we also reduce the problem to the search for the extremum

$$\frac{\partial\tilde{\Omega}_{ef}}{\partial\alpha_1}=0,$$
$$\tilde{\Omega}_{ef}(\alpha,\alpha_1)=T_e+V_{ef}(\{\phi_0\})*\phi_1^2. \tag{27}$$

Thus for simple variational estimates we can find the extremum of $\Omega_{ef}(\alpha)$ and then the extremum of $\tilde{\Omega}_{ef}(\alpha,\alpha_1)$, and using these data calculate energetic and structural characteristics of an excess electron in various molten salts.

To complete the mean-field study we will correlate our results with those obtained within the RISM-polaron theory[6,7] based on the solution to the corresponding integral equations. For this purpose we consider the quantities

$$C_{e\pm}=-f_{es}-\beta(1+f_{es})u_{e\pm}, \tag{28}$$

which play the role of the electron–ion direct correlation functions. Then again taking into account only the terms whose order is lower than the second one with respect to $\hat{\Psi}$ and evaluating analytically the quadratic path integral over the electric field, we result in the effective electron functional

$$\beta\Omega=\beta T_e+\frac{\rho}{2}*(C_{e+}+C_{e-})$$
$$+\frac{\beta^{-2}}{2}\int_0^\beta d\tau\int_0^\beta d\tau' U(\mathbf{r}(\tau')-\mathbf{r}(\tau)), \tag{29}$$

where $U(\mathbf{r})=\Sigma_{ij}C_{ei}*\chi_{ij}*C_{ej}$ is the influence functional potential and $\chi_{ij}(\mathbf{r}-\mathbf{r}')$ is the density–density correlation function of the electrolyte, which is related to the total correlation function h_{ij} of the symmetric electrolyte: $\chi_{ij}(\mathbf{r})=\rho\delta(\mathbf{r})+\rho^2h_{ij}(\mathbf{r})$. This effective electron functional is the starting point of the RISM-polaron treatment.[6,7] The electron–ion correlation functions derived by us can also be

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transformed into the integral form. Taking into account that the Fourier transform $\phi_0^2(k)$ is related to the average inter-polymer correlation function $\omega(k)$,[33] i.e.,

$$\phi_0^2(k) \simeq \omega(k) = \beta^{-1} \int_0^\beta \omega(k,\tau) d\tau, \tag{30}$$

and considering only the zero- and first-order terms, we arrive at

$$g_{ei} = 1 + h_{ei} = 1 + \sum_j \omega * C_{ej} * \chi_{ij} / \rho. \tag{31}$$

Various closures can be used to complete Eq. (31). Our treatment corresponds to the mean spherical approximation for which $C_{e\pm}(r>r_e) = -\beta u_\pm$ and $g_{e\pm}(r<r_e) = 0$. Another widely used closure is based on the hypernetted chain approximation (HNC) for which

$$g_{e\pm} \simeq \exp[\pm \beta \hat{\Psi}]. \tag{32}$$

Substituting expression (22) for $\hat{\Psi}$ in this equation and taking into account that

$$\rho_{ef}(k) = -\frac{\mathscr{æ}^2 z(k)}{k^2 + \mathscr{æ}^2 z(k)} \hat{s}(k) \phi_0^2(k)$$

$$\simeq \rho \sum_i h_{ij}(k) C_{ei}(k) \phi_0^2(k), \tag{33}$$

we result in the closure

$$g_{ei} \simeq \exp\left[-\beta\langle u_{ei}\rangle + \left\langle \sum C_{ei} * \rho h_{ij} \right\rangle \right], \tag{34}$$

which is derived in Ref. 15 by the optimized perturbation theory.

Thus we see three ways to calculate structural and energetic properties of the solvated electron, namely, to obtain variational estimates by solving nonlinear algebraic equations [Eqs. (26) and (27)], to calculate the coupled Schrödinger and the Poisson–Boltzmann differential equations [Eqs. (13) and (18)], and to solve linear integral equation [Eq. (31)] with various closures together with variational treatment of the effective electron functional (29). The first way is the simplest one and does not require extensive computations, we will use it to study the behavior of an excess electron in alkali halide melts.

V. RESULTS AND DISCUSSIONS

The case when the short-range components of u_{e+} and u_{e-} are ignored (polaron limit) is studied in Ref. 34. There the electron behavior is described by the polaron effective functional

$$\Omega_{ef} = T_e - \frac{1}{\pi} \int \phi_0^4(k) dk. \tag{35}$$

Note that in the polaron limit the electron kinetic (T_e), potential (Π), and total W_0 energies satisfy the virial theorem

$$|T_e| : |W_0| : |\Pi| = 1 : 3 : 4. \tag{36}$$

Expressing the polaron functional via the parameter α we find $\Omega_{ef} \propto \alpha^2 - C\alpha$. The extremum of the functional yields

$\alpha = \alpha_0 =$ const and $\Omega_{ef} = -C\alpha_0/2$, the latter results in the large parameter $\beta\alpha_0 \gg 1$ of the saddle point approximation (8). As is seen from the relations, the electron energy and the electron mean radius are independent of the parameters of molten salt. The correlation function $g_{e+}(r)$ obtained in the polaron limit[34] at small distances $g_{e+}(r\to 0) \simeq 1 + \phi_0^2(r)\rho^{-1}$ is close to that found by the RISM-polaron theory.[14] The ratio between the relevant electron energies found by path-integral simulations[18] is also close to that given by Eq. (35) and only slightly changes as the cut-off radius d varies.

Therefore, we conclude that the Coulomb interactions resulting in the self-consistent polaronlike state make the main contribution to the behavior of an electron solvated in molten salt. But the polaron treatment yields rather a simplified picture of the behavior of the solvated electron. In particular, the polaron limit does not allow one to consider short-range repulsion effects or the effects of finite size of ions. The polaron model cannot explain the variance of energetic and structural properties of the solvated electron as the ion size changes.

To investigate the behavior of the solvated electron with the account of the excluded volume and cation core effects by variational estimates for the extrema of $\Omega_{ef}(\alpha), \tilde{\Omega}_{ef}(\alpha,\alpha_1)$, we use various types of the wave functions for the ground and the first excited electron states. The best estimate is obtained for the hydrogenlike functions

$$\phi_0(r) = \sqrt{\frac{\alpha^3}{7\pi}} (1 + \alpha r)\exp(-\alpha r), \tag{37}$$

$$\phi_1(\mathbf{r}) = \sqrt{\frac{\alpha_1^5}{\pi}} r \cos\Theta \exp(-\alpha_1 r), \tag{38}$$

where r and Θ are the absolute value and the angle of the radius-vector, respectively. Note that in the polaron limit the difference between the electron energies obtained by the exact solution to the Schrödinger equation and that found by variational estimate using Eqs. (37) and (38) is less than 1%.

First, we examine the influence of cation core, ignoring the hard-sphere repulsion of negative ion, i.e., $u_{es} \equiv 0$. Initially we determine the cut-off distance from the experimental data on the first ionization potentials for alkali metals, namely, Li(5.39 eV), Na(5.14 eV), Cs(3.89 eV), K(4,339 eV), Rb(4,176 eV) by searching the extremum with the hydrogenlike potential, using the trial wave function in the form (37). The resultant values are listed in Table I, they are slightly different from that found by local pseudopotential method.[35]

The extrema yield the nonlinear equations for α and α_1, which we present here in the explicit form by expanding in series of αd

$$\alpha = 0.49972 - 8.129 \cdot 10^{-2}(\alpha d)^2 + 1.466 \cdot 10^{-2}(\alpha d)^4$$

$$- 3.01 \cdot 10^{-3}(\alpha d)^6 + 7.9 \cdot 10^{-4}(\alpha d)^8$$

$$- 3.8 \cdot 10^{-4}(\alpha d)^{10} + \cdots, \tag{39}$$

TABLE I. Salt parameters [temperature T, mean ion diameter σ (Ref. 37), density ρ (Ref. 36), cut-off radius d] and calculated total energies and mean radii of the ground and first excited electron states in various molten akali halides.

	T (K)	σ (Å)	ρ (10^{-2} Å^{-3})	d (Å)	r_0 (Å)	r_1 (Å)	$-W_0$ (eV)	$-W_1$ (eV)
LiF	1210	1.74	8.15	1.58	2.29	4.53	3.91	2.41
LiCl	953	2.19	4.15	1.58	2.56	4.68	3.78	2.33
LiBr	889	2.24	3.39	1.58	2.63	4.72	3.73	2.31
LiI	801	2.47	2.71	1.58	2.71	4.78	3.69	2.29
NaF	1370	1.97	5.37	1.69	2.40	4.64	3.78	2.35
NaCl	1160	2.43	3.07	1.69	2.61	4.77	3.68	2.29
NaBr	1100	2.55	2.62	1.69	2.67	4.80	3.65	2.28
NaI	1007	2.61	2.12	1.69	2.75	4.85	3.60	2.25
KF	1220	2.30	3.80	2.16	2.63	4.98	3.40	2.20
KCl	1126	2.69	2.37	2.16	2.80	5.07	3.35	2.16
KBr	1087	2.86	2.08	2.16	2.85	5.10	3.33	2.15
KI	1030	3.05	1.72	2.16	2.93	5.14	3.30	2.13
RbF	1150	2.38	3.20	2.28	2.82	5.12	3.31	2.15
RbCl	1075	2.80	2.15	2.28	2.87	5.16	3.26	2.12
RbBr	1042	2.98	1.91	2.28	2.92	5.19	3.25	2.11
RbI	994	3.09	1.60	2.28	2.99	5.23	3.22	2.10
CsF	1054	2.62	2.77	2.51	2.85	5.27	3.16	2.08
CsCl	991	2.99	1.90	2.51	2.99	5.33	3.11	2.05
CsBr	981	3.15	1.68	2.51	3.03	5.35	3.10	2.05
CsI	971	3.28	1.39	2.51	3.09	5.39	3.08	2.03

$$14\alpha(m+1)-(20m^5+106m^4+392m^3+196m^2+56m+7)$$
$$+2(\alpha d)^2(10m^5+45m^4)-11/9(\alpha d)^4(2m^6$$
$$+16m^5-7m^4)+2/35(\alpha d)^6(m^8+8m^7+58m^6$$
$$-54m^5)-2{,}8\cdot10^{-2}(\alpha d)^8(m^8+8m^7-32m^6$$
$$-4m^5)-1{,}1\cdot10^{-3}(\alpha d)^{10}(5m^{12}+40m^{11}+140m^{10}$$
$$+280m^9+368m^8+424m^7+144m^6-18m^5)+\cdots$$
$$=0, \qquad\qquad (40)$$

where $m=\alpha_1/\alpha$. The computation of these equations differs from the solution to the exact transcendent equations only by several percents at $d \lesssim 2.3$ Å.

Figure 1 plots the results of the calculations: the dependencies of the total and potential energies for the ground (W_0, P_0) and first excited (W_1, P_1) electron states on the cut-off radius d. Figure 2 depicts the mean radii for the first (r_1) and the ground (r_0) electron states versus the cut-off distance d. They increase as the distance rises. For KCl, our

estimate yields $r_e \simeq 3.4$ Å, while the path integral and RISM-polaron calculations result in a smaller value $r_e \simeq 3.2$ Å.[14]

We use the difference $\Delta W = |W_0 - W_1|$ to estimate the maximum of the absorption spectrum (Fig. 3). It is evident that it decreases as the cut-off radius rises. In Fig. 3 we also present the experimental data on the maximum of the absorption spectrum[25-27] and the results corresponding to the polaron limit. We see that our estimates accounting only the cut-off distance effect correctly describe the changes in the maximum of the absorption spectrum but underestimate the absolute value for K- and Na-ions.

The consideration of short-range component $u_{es}(r)$ results in the formation of a vacancy of the type of F-center. We calculate the structural and energetic properties of the solvated electron in alkali halide melts by searching the extremum for thermodynamic potentials (25) and (27). The excluded volume effect results in a stronger localization of the solvated electron leading to a decrease in the electron mean radius r_e by 15%–20%. Table I lists the data on the electron total energies for the ground and the first excited states. The
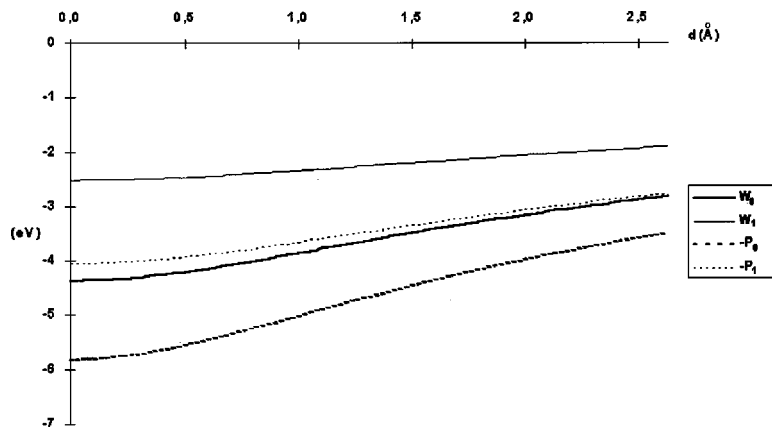

FIG. 1. Dependencies of the total and the potential energies for the ground (W_0, P_0) and first excited (W_1, P_1) electron states on the cut-off radius d.
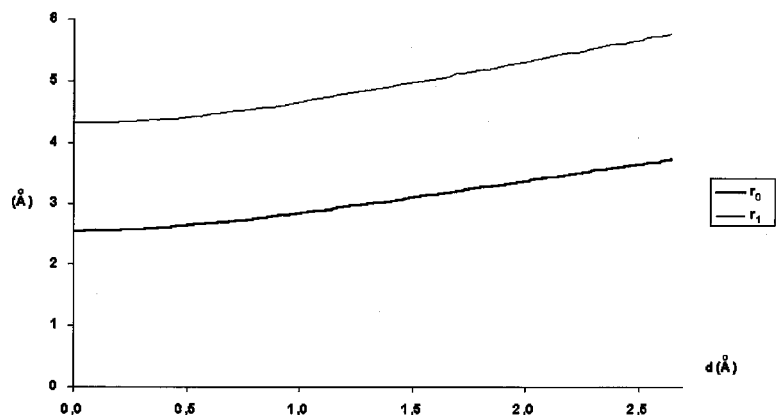
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FIG. 2. The mean radii of the ground (r_0) and the first excited (r_1) electron states versus the cut-off distance d.

corresponding mean radii for alkali–halide melts are also presented in the table. The data on temperature-dependent densities of the melts were taken from Ref. 36. For ion radii we use data obtained by Abramo *et al.*[37] The change in the used ion radii by 10% changes the found data by less than 1%. We have examined the temperature dependence of the absorption maximum, taking into account only the temperature dependence of salt density. It provides the correct shift of ω_{max} versus temperature, but yields the results qualitatively different from available experimental data. We believe that the use of more accurate data on the structural properties of salt, i.e., $h_s(r)$ can offset this disadvantage.

Figure 4 plots the comparison of the calculated maximum of the absorption spectrum by our theory and within the RISM-polaron treatment,[19,20] and available experimental data.[25–27] As is seen, our estimate is in a good agreement with the experimental data. The variational estimates and experimental data differ by 10%–15% for Na- and Cs ions. The difference between the theory and the experiment may result from insufficient consideration of the cation core effect.

Thus, starting with the exact grand partition function of the system we have derived nonlinear deferential equations determining the mean-field and the electron density distribution. Using the simple variational treatment we have examined the behavior of the solvated electron in molten salts. We conclude that our simple variational treatment provides cor-

rect estimates of structural and energetic characteristics of an excess electron in alkali halide melts. We have found that the properties of the solvated electron are mainly determined by the polaron effect, while the short-range effects such as the F-center formation and the cation–core effect leads to a remarkable variance of the equilibrium electron characteristics.

Although we have considered a simplified case, i.e., a symmetric 1-1 electrolyte, our treatment can be extended to the dipolar liquids, ion–dipole mixtures and metal–molten–salt solutions. A similar treatment was also used to study an electron solvated in a disordered medium[31] and liquid helium.[32] Therefore, the above treatment is rather general and can be applied to a wide range of problems dealing with an excess quantum particle in spatially disordered media. The main criterion of the theory is that the number $\tilde{N}$ of environmental particles interacting with the excess electron be large, i.e., $\tilde{N} \propto \rho \alpha^{-3} \gg 1$. Otherwise we should use quantum-chemical methods.

APPENDIX A: PATH-INTEGRAL TREATMENT OF THE GRAND PARTITION FUNCTION

We introduce the generalized charge density $\rho_q(\mathbf{r})$ and the generalized ion densities $\rho_{\pm}(\mathbf{r})$, respectively
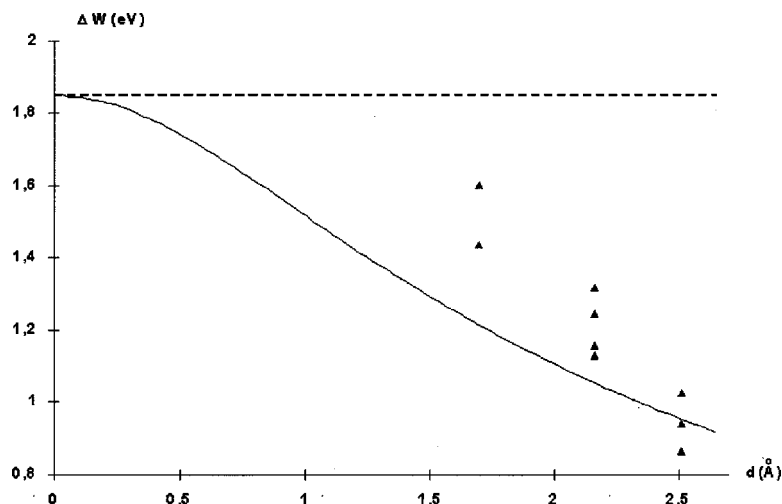

FIG. 3. Difference ΔW vs the cut-off radius d, the symbols correspond to the experimental data on the maximum of the absorption spectrum (Ref. 25–27), while the horizontal line—to the polaron limit.
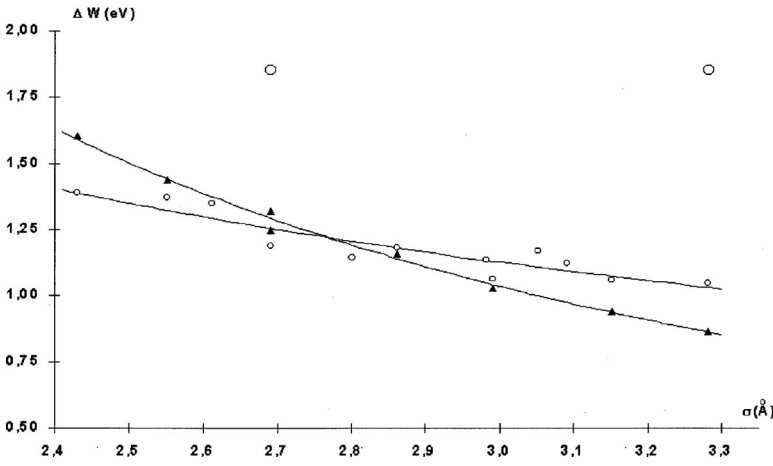
FIG. 4. The calculated (circles) and the experimental data (Refs. 25–27) (triangles) on the maximum of the absorption spectrum in molten salts, solid lines present the spline approximation of the data, large circles correspond to the data obtained by the RISM-polaron theory (Refs. 19 and 20).

$$\rho_{\pm}(\mathbf{r}) = \sum_{i}^{N/2} \pm \delta(\mathbf{r} - R_{i\pm}), \quad \rho_q(\mathbf{r}) = \rho_+(\mathbf{r}) + \rho_-(\mathbf{r}).$$
(A1)

Then the exponent index Q in the grand partition function Ξ is given by

$$Q = \beta \left(T_e + u_e * \rho_q + U_{es} * \rho_- + \rho_q * \frac{u_q}{2} * \rho_q + U_s \right),$$ (A2)

here we use the notation $U_{es} = \beta^{-1} \int_0^\beta u_{es}(\mathbf{r}(\tau)) d\tau$. For the Coulomb potential $u_q(r)$, we can use the Fourier transform of an exponent with a quadratic index

$$\exp[\tfrac{1}{2}\rho_q * u_q * \rho_q] = \left\{ \int D[\Psi] \exp[-\tfrac{1}{2}\Psi * u_q^{-1} * \Psi] \right\}^{-1}$$

$$\times \int D[\Psi] \exp[-\tfrac{1}{2}\Psi * u_q^{-1} * \Psi + \rho_q * \Psi],$$ (A3)

where $u_q^{-1}(r)$ is the operator inverse to u_q. Then, Eq. (A2) becomes

$$\Xi = \Xi_0 \int D[\Psi] \exp\left[-\beta T_e - \frac{\beta}{2}(\Psi - u_e) * u_q^{-1} * (\Psi - u_e) \right]$$

$$\times I(\Psi, U_{es}, U_s),$$
(A4)

$$I(\Psi, U_{es}, U_s)$$

$$= \sum_{N \geq 0}^{\infty} \int d\mathbf{R}^{\{N\}} \frac{z^N}{N!} \prod_i^N \exp[\beta(\pm \Psi(R_{i\pm}) - U_s(\mathbf{R}^{\{N\}})$$

$$- U_{es}(\mathbf{R}_{i-})].$$

Let us introduce n-particle correlation functions $\rho_s^{(n)}(r_1, \dots r_n)$ of hard spheres

$$\rho_s^{(n)}(\mathbf{r}_1, \dots \mathbf{r}_n) = \Xi^{-1} \sum_N^{\infty} \frac{z^N}{(N-n)!}$$

$$\times \int \exp[-\beta U_s] d\mathbf{R}^{\{N-n\}}.$$ (A5)

Then, the configurational part $I(\Psi, U_{es}, U_s)$ is given by

$$I(\Psi, U_{es}, U_s) = 1 + f_q * \rho_s^{(1)} + \frac{1}{2!} f_q * \rho_s^{(2)} * f_q + \cdots$$

$$+ \frac{1}{n!} f_q * \rho_s^{(n)} * \cdots f_q.$$ (A6)

Taking into account that $\rho_s^{(1)} \equiv \rho$ and $\rho_s^{(2)} = \rho^2 + \rho^2 h_s(\mathbf{r})$ (where h_s is the total correlation function for hard spheres), and ignoring irreducible correlations whose order is higher than the second one, we arrive at

$$I(\Psi, U_{es}, U_s) = 1 + \sum_{k=1}^{\infty} (f_q * \rho)^k / k!$$

$$+ \sum_{k=2}^{\infty} \left(\frac{1}{2!} f_q * \rho^2 h_s * f_q \right)^k \bigg/ k!.$$ (A7)

Transforming it in the exponent and substituting into Eq. (A4) we result in Eq. (5).

APPENDIX B: ESTIMATES OF THE ELECTRON PATH INTEGRAL BY THE GROUND WAVE FUNCTION

First, we consider the term in Eq. (5) which is a linear functional $-\beta \Psi * u_q^{-1} * u_e$. Denoting the part $-\beta \Psi * u_q^{-1}$ independent of an electron path as C_e, we have for averaging

$$\langle \exp[C_e * u_e] \rangle_{S_0} = 1 + \left\langle C_e * u_e + \frac{1}{2!}(C_e * u_e)^2 + \cdots \right\rangle_{S_0}$$

$$= 1 + C_e * u_e * \varrho_1$$

$$+ \frac{1}{2!}(C_e * u_e) * \varrho_2 * (C_e * u_e)$$

$$+ \frac{1}{3!}(C_e * u_e) * \varrho_3 * (C_e * u_e) * (C_e * u_e)$$

$$+ \cdots,$$ (B1)

where we use ϱ_n which are the n-order density matrices of the electron subsystem.

Relation (10) means that all the n-order density matrices are expressed via the first-order electron density matrix ϱ,

i.e., $\varrho_2(\mathbf{x},\mathbf{x},\mathbf{y},\mathbf{y}) = \varrho(\mathbf{x},\mathbf{x})\varrho(\mathbf{y},\mathbf{y})$, $\varrho_3(\mathbf{x},\mathbf{x},\mathbf{y},\mathbf{y},\mathbf{z},\mathbf{z}) = \varrho(\mathbf{x},\mathbf{x}) \times \varrho(\mathbf{y},\mathbf{y})\varrho(\mathbf{z},\mathbf{z})$, etc. Using this property and bearing in mind that the electron ground state is dominant, i.e., $u_e*\varrho \sim u_e*\phi_0^2 = \langle u_e \rangle$ we have

$$\langle \exp[C_e*u_e]\rangle_{S_0} = 1 + C_e*\langle u_e \rangle + \frac{1}{2!}(C_e*\langle u_e \rangle)^2 + \cdots$$

$$= \exp[C_e*\langle u_e \rangle]. \tag{B2}$$

Similar relations also take place for the bilinear term in Eq. (5), only the first nontrivial term in the series expansion has the second order

$$\left\langle \exp\left[\frac{-\beta}{2} u_e*u_q^{-1}*u_e\right]\right\rangle_{S_0}$$

$$= 1 + \left\langle \frac{-\beta}{2!} u_e*u_q^{-1}*u_e + \cdots \right\rangle_{S_0}$$

$$= 1 + \frac{-\beta}{2!}(u_e*u_q^{-1}*u_e)**\varrho_2 + \cdots$$

$$= \exp\left[\frac{-\beta}{2}\langle u_e \rangle*u_q^{-1}*\langle u_e \rangle\right]. \tag{B3}$$

To find $\langle f_q \rangle$ we should initially expand it in series and then average linear, bilinear, and all other higher order terms. As a result, we arrive at

$$\left\langle \exp\left[-\int_0^\beta u_{es}(\mathbf{r}(\tau))d\tau\right]\right\rangle = \exp[-\beta\langle u_{es} \rangle]. \tag{B4}$$

Averaging f_q*f_q in the similar manner, we obtain Eq. (11).

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