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Density functional study of polarons and bipolarons in polar liquids

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The density functional theory of polarons and bipolarons in a polar liquid is presented. Starting from the grand partition function, we have developed a microscopic model and derived the free-energy functional of the system in which the electrons are treated within the Kohn-Sham formalism, while the solvent via the integral equations theory. The case of our approach concerns with the free-energy functional corresponding to the mean spherical approximation and the extended point dipole model. We have calculated different properties for a polaron and a singlet bipolaron formation and their variations caused by changes in temperature, density, and polarity of the solvent. The obtained results are in agreement with available experimental data and simulations.

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I. INTRODUCTION

Excess electrons forming polaron and bipolaron states in polar liquids are an object of intensive theoretical investigation and computer simulation[1–6]). Numerous experimental techniques have been developed and extensive experimental evidence on the behavior of solvated electrons in various media has been accumulated.[7,8] Excess electrons solvated in polar liquids provide a simple example of mixed quantum and classical systems, which exhibit a large number of various effects and are can conveniently be studied by quantum statistical methods. Such a mixed quantum-classical system is suitable to demonstrate the potential of various simulation methods such as quantum molecular dynamics, the path integral method, and a variety of hybrid schemes. At present there are a lot of examples of such calculations of excess electrons in water clusters,[9] ammonia,[10–12] and ionic solutions.[13–16] These studies have shown that excess electrons in polar liquids can reveal quite intriguing properties such as polaron and bipolaron formations, multielectron clustering. Generally these models treat the electrons by the density functional theory (DFT), whereas the solvent effects are simulated by molecular dynamics (MD) or Monte Carlo (MC) tools. However, these hybrid methods, being more realistic, require simulation of huge numbers of solvent configurations and high computational efforts.

In this work we have applied the DFT to investigate excess electrons in a polar liquid. Density functional theory (DFT) was proven to be a powerful tool for studying atoms and molecules by a works on the electronic structure of various molecular complexes.[17–19] Recent developments of numerical schemes based on the DFT (Refs. 20,21) have demonstrated that the density functional language is able to provide calculations with an accuracy comparable with the *ab initio* ones. From another hand, the density functional treatment is widely used to investigate the behavior of classical inhomogeneous systems.[22–24] The application of DFT to molecular liquids[25–27] indicates that the DFT is very promising to treat many-body problems correlated to solvation phenomena. Recently the DFT approach has been implemented to calculate a microscopic structure of solvent[28,29] and both the examples have demonstrated the DFT results to be in a good agreement with molecular simulations, and that the theory reliably accounts for the pair correlation functions and the free energy of solvation.

We will use a scheme based on self-consistent calculations of the Kohn-Sham equations for an electron density coupled with the integral equations for the solvent. The integral equations theory yields a detailed information about solute-solvent interactions in terms of correlation functions, but does not require huge computational costs. Using the mean spherical approximation, the extended point dipole and the reference interaction models we will evaluate the chemical potentials of the solvent and solute and derive the final relations for the electron and solvent densities. We consider the low concentration limit when correlations between electrons are small. In this case we will calculate the electron characteristics such as the electron mean radius, electron energy, and the chemical potential for a polaron and a singlet bipolaron formation. Variations of these characteristics caused by changes in temperature, density, and polarity of the solvent will also investigated.

II. FORMALISM

A. Density functional treatment of the electronic subsystem

We consider a system consisting of N_e excess electrons and N classical solvent particles, whose distribution depends not only on their coordinates $\mathbf{R}^{\{N\}}=\{\mathbf{R}_1,\mathbf{R}_2,\ldots,\mathbf{R}_N\}$ but also on the orientations (Euler angles) $\mathbf{w}^{\{N\}}=\{\mathbf{w}_1,\mathbf{w}_2,\ldots,\mathbf{w}_N\}$ of their dipole momenta $\mathbf{m}$. In the statistical approach the system consisting of interacting classical particles and electrons is described by the grand partition function Ξ given by

$$\Xi=\langle\langle\exp[-\beta(H-\mu_e N_e-\mu N)]\rangle_e\rangle_S, \qquad (1)$$

where the symbols $\langle\cdots\rangle_e$ and $\langle\cdots\rangle_S$ denote the averages over electronic and solvent degrees of freedom respectively, H is the Hamiltonian of the system, μ_e and μ are the chemical potentials of electrons and solvent particles, while β is the inverse temperature. We write the Hamiltonian of the system as

$$H = T + U_{ee}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_{N_e}) + \sum_{im}^{N_eN} u_{ec}(|\mathbf{r}_i-\mathbf{R}_m|,\mathbf{w}_m) + \frac{1}{2}\sum_{mk}^{N} u_{cc}(|\mathbf{R}_m-\mathbf{R}_k|,\mathbf{w}_m\mathbf{w}_k). \tag{2}$$

The first term in the right side of Eq. (2) is the kinetic energy of electrons, the second one is the contribution due to electron–electron interactions, while the third and the fourth terms are the electron-solvent and solvent-solvent potentials which we assume that are pairwise.

In principle, the average over electronic degrees of freedom requires the knowledge of the N_e-electron wave function $\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_{N_e})$, however, the DFT approach[30] reduces the problem to the calculation of the electron density

$$n_e(\mathbf{r}) = \int |\Psi(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_{N_e})|^2 \mathbf{d}\cdot\mathbf{r}_2,\ldots,\mathbf{d}\cdot\mathbf{r}_{N_e},$$

$$N_e = \int n_e(\mathbf{r})\mathbf{d}\cdot\mathbf{r}. \tag{3}$$

The latter is needed to minimize the energy functional

$$F_e[n_e] = T[n_e] + \frac{1}{2}\int\int d\mathbf{r}d\mathbf{r}'\frac{n_e(\mathbf{r})n_e(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{\mathrm{xc}}[n_e] + V_{ec}[n_e] = E_{ee}[n_e] + V_{ec}[n_e], \tag{4}$$

where $V_{ec}[n_e] = \Sigma_m \int n_e(\mathbf{r})u_{ec}(|\mathbf{r}-\mathbf{R}_m|,\mathbf{w}_m)\mathbf{d}\cdot\mathbf{r}$ is the contribution due to solvent particles and $E_{\mathrm{xc}}[n_e]$ is the exchange-correlation energy. There are several approximate expressions for $E_{\mathrm{xc}}[n_e]$ including the local one[30] which is given by

$$E_{\mathrm{xc}} = \int n_e(\mathbf{r})[\epsilon_x(\mathbf{r}) + \epsilon_c(\mathbf{r})]\mathbf{d}\cdot\mathbf{r}. \tag{5}$$

The explicit expression for $\epsilon_x(\mathbf{r})$ is usually written as $\epsilon_x(\mathbf{r}) = n_e(\mathbf{r})^{1/3}$, while accurate approximations for $\epsilon_c(\mathbf{r})$ are obtained by fitting of quantum MC calculations.[31]

Representing the electron density by the one-electron wave functions, i.e., $n_e(\mathbf{r}) = \Sigma_i \phi_i^2(\mathbf{r})$, the minimization of Eq. (4) results in the Kohn-Sham equations

$$\left[-\frac{1}{2}\nabla^2 + u_{\mathrm{ext}} + \int \frac{n_e(\mathbf{r}')\mathbf{d}\cdot\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} + u_{\mathrm{xc}}(\mathbf{r}) - \epsilon_i\right]\phi_i(\mathbf{r}) = 0, \tag{6}$$

where $u_{\mathrm{xc}}(\mathbf{r}) = \delta E_{\mathrm{xc}}/\delta n_e$ is the exchange-correlation contribution and $u_{\mathrm{ext}} = \Sigma_m u_{ec}(|\mathbf{r}-\mathbf{R}_m|,\mathbf{w}_m)$ is the external potential depending on the equilibrium configuration of solvent particles, which can be found through the evaluation of the grand partition function

$$57\Xi = \left\langle \exp\left[-\beta\left(\frac{1}{2}\sum_{mk}^{N} u_{cc} + V_{ec}[n_e] - \mu N\right)\right]\right\rangle_S \times \exp[-\beta(E_{ee} - \mu_e N_e)]. \tag{7}$$

Thus, the next step of our study requires the estimation of the average over solvent degrees of freedom and the derivation of the total free-energy functional. We note that the electron density $n_e(\mathbf{r})$ serves in Eq. (7) as a source inducing the external potential V_{ec} in a classical liquid. Therefore, following Percus' idea[32] we can apply the DFT in the classical domain and perform the complete evaluation of the grand partition function.

B. Total free-energy functional

To derive the total free-energy functional we should consider the electron-solvent interactions in more details. In the general case, the electron-solvent potential includes long-range attractive and short-range repulsive parts and can assumed to be

$$u_{ec}(r,\mathbf{m}) = u_{es}(r) + \boldsymbol{m}\cdot\boldsymbol{\nabla}u_q, \tag{8}$$

where we denote the Coulomb potential as u_q. The short-range and long-range parts differently affect the solvent. The first leads to a cavity formation (solvophobic effect), while the second one causes a polarization and orientational rearrangement of the solvent. These interactions, together with similar interactions between solvent particles, result in a redistribution of solvated particles.

Dividing the solvent-solvent potential u_{cc} into short-range (u_{ss}) and long-range parts, we can rewrite the solvent functional as

$$E_{\mathrm{solv}}[n_s\mu] = \sum_{mk}^{N}\frac{u_{cc}}{2} + V_{ec} - \mu N = n_s^* \frac{(u_{ss} + \mathbf{m}\cdot\mathbf{T}\cdot\mathbf{m})}{2} * n_s + n_e^*(u_{es} + \mathbf{m}\cdot\boldsymbol{\nabla}u_q) * n_s - \mu * n_{s.} \tag{9}$$

Here, $\mathbf{T}(\mathbf{r}-\mathbf{r}')$ is the rank-2 tensor of dipolar interactions

$$\mathbf{T}(\mathbf{r}) \equiv \frac{\mathbf{3r}\cdot\mathbf{r}}{r^5} - \frac{\mathbf{I}}{r^3}, \tag{10}$$

and $\mathbf{I}$ is the rank-2 unit tensor. In Eq. (9) the asterisk corresponds to the convolution integration

$$a*b \equiv \int a(\mathbf{R}_1,\mathbf{w}_1)b(\mathbf{R}-\mathbf{R}_1,\mathbf{w}-\mathbf{w}_1)\mathbf{d}\cdot\mathbf{R}_1\cdot\mathbf{d}\cdot\mathbf{w}_1, \tag{11}$$

while $n_s(\mathbf{R}) = \Sigma_j^N \delta(\mathbf{R}-\mathbf{R}_j)$ is the generalized density of solvent particles.

Our task is to find the functional dependence of $E_{\mathrm{solv}}[n_s]$ and to calculate $n_{es}(\mathbf{R}\cdot\mathbf{w}) \equiv n_s(\mathbf{R},\{V_{ec}\})$ in a solvent subjected to the external field V_{ec}. To provide it we should average the solvent energy $E_{\rm solv}$ over solvent degrees of freedom. Of course, the formal expression (9) does not simplify the averaging procedure, because of the requirement data of the explicit expression of $n_s(\mathbf{R})$ or the introduction of some approximations for the Jacobian $J(n_s\mathbf{R})$ of the transformation from **R**-variables to n_s—variables. Nevertheless, the bilinear relation (9) between $E_{\rm solv}$ and n_s allows us to perform these approximations with a physical reasoning.

First, we note that polarization induced by the electrons in the liquid gives a main contribution to solvation energy, see Eq. (9). Therefore, evaluating the polarization effects, we can estimate the dominant term in (9). For this purpose, we transform the solvent dependent part of the grand partition function into the path integral over the field intensity **E** induced by the charges (see Appendix A). Then it is possible to evaluate the path integral by the saddle point method

$$\begin{aligned}\exp[-\beta\Omega_{\rm solv}]&=\langle\exp[-\beta E_{\rm solv}]\rangle_s\\&\propto\int D[\mathbf{E}]\exp[-\beta S(\mathbf{E},\mu)]\\&\approx\exp[-\beta S(\mathbf{E}_m,\mu)],\end{aligned}\tag{12}$$

where $\mathbf{E}_m$ is the mean-field intensity. The saddle point method determines the mean-field from the condition

$$\frac{\partial S(\mathbf{E}=\mathbf{E}_m)}{\partial\mathbf{E}}=0.\tag{13}$$

Performing simple manipulations, we express $\mathbf{E}_m$ in terms of n_{es} and μ (see Appendix A) and derive the relation for the solvent functional $\Omega_{\rm solv}[n_{es},\mu]$:

$$\begin{aligned}\Omega_{\rm solv}=S_m[\mathbf{E}_m(n_{es}),\mu]=&-\frac{1}{2}\mathbf{P}(n_{es})^*\mathbf{T}^*\mathbf{P}(n_{es})\\&-\beta^{-1}n_0f(n_{es})^*\left[1+\frac{1}{2!}n_0h_{ss}^*f(n_{es})\right].\end{aligned}\tag{14}$$

$\mathbf{P}(n_{es})$ is the polarization of the liquid related to the solvent density

$$\mathbf{P}(\mathbf{R})=\int\mathbf{m}(\mathbf{w})n_{es}(\mathbf{R}\cdot\mathbf{w})\mathbf{d}\cdot\mathbf{w},\tag{15}$$

n_0 is the averaged solvent density, and $h_{ss}(R)$ is the short-range total correlation function of the pure solvent

$$\begin{aligned}n_0^2[1+h_{ss}(|\mathbf{R}-\mathbf{R}'|)]=\Bigg\langle&\langle\delta(|\mathbf{R}-\mathbf{R}_1|)\delta(|\mathbf{R}'-\mathbf{R}_2|)\\&\times\exp\left[-\frac{\beta}{2}\sum_{mk}^{N}u_{ss}(|\mathbf{R}_m-\mathbf{R}_k|)\right]\Bigg]\Bigg\rangle_S,\end{aligned}\tag{16}$$

f denotes the Mayer function

$$f(n_{es},\mu)=\exp[-\beta(u_{ec}^*n_e+\mathbf{m}\cdot\mathbf{T}^*\mathbf{P}-\mu)]-1.\tag{17}$$

The variation of the solvent functional $\Omega_{\rm solv}$ with respect to the chemical potential μ gives the expression for the solvent density $n_{es}(\mathbf{R}\cdot\mathbf{w})$:

$$\begin{aligned}\frac{\delta\Omega_{\rm solv}}{\delta\mu(\mathbf{R}\cdot\mathbf{w})}&=n_{es}(\mathbf{R}\cdot\mathbf{w})=n_0[1+h_{es}(\mathbf{R}\cdot\mathbf{w})]\\&=n_0[1+n_0f(n_{es})^*h_{ss}][f(n_{es})+1].\end{aligned}\tag{18}$$

Thus, combining Eqs. (17) and (18), we can express μ *via* n_{es} and find the required relation for $\Omega_{\rm solv}[n_{es}]$. Unfortunately, expression (18) is nonlinear, and its inversion can be performed only by additional approximations. For example, transforming Eq. (18) as

$$\begin{aligned}\mu-\beta^{-1}\ln(h_{es}+1)]-u_{ec}^*n_e\approx\mathbf{m}\cdot\mathbf{T}^*\mathbf{P}(n_{es})+h_{ss}^*(n_{es}-n_0)\\=-C_2^*(n_{es}-n_0),\end{aligned}\tag{19}$$

where $C_2(\mathbf{R}\cdot\mathbf{w})$ is the function depending only on the parameters of the pure solvent, we immediately obtain

$$\Omega_{\rm solv}[n_{es}]=\frac{1}{2}n_0h_{es}^*C_2^*n_0h_{es}-\beta^{-1}(n_{es}-n_0)^*1.\tag{20}$$

With the use of the conventional relations between the thermodynamic potential and the free energy

$$F[n_e,n_{es}]-\mu N=\Omega_{\rm solv}+E_{ee},\tag{21}$$

we result in the final formula for the total free-energy functional

$$\begin{aligned}F[n_e,n_{es}]=T[n_e]+\frac{1}{2}n_e^*u_q^*n_e+E_{\rm xc}[n_e]+n_e^*u_{ec}^*n_{es}\\+\beta^{-1}n_{es}^*[\ln(h_{es}+1)-1]\\-\frac{\beta^{-1}}{2}n_0h_{es}^*C_2^*n_0h_{es}.\end{aligned}\tag{22}$$

In the classical limit this expression reduces to the well known free-energy functional obtained in the hypernetted chain (HNC) approach. Therefore, the function $C_2(\mathbf{R}\cdot\mathbf{w})$ is related to the second derivative of the functional with respect to n_{es} and can be written in terms of the equilibrium density susceptibility $X(\mathbf{R}-\mathbf{R}_1\cdot\mathbf{w}-\mathbf{w}_1)=\langle\delta n_s(\mathbf{R}\cdot\mathbf{w})\delta n_s(\mathbf{R}_1\cdot\mathbf{w}_1)\rangle$ of the pure solvent

$$\begin{aligned}C_2(\mathbf{R}-\mathbf{R}_1\cdot\mathbf{w}-\mathbf{w}_1)&=\frac{-\delta^2\beta F}{\delta n_{es}(\mathbf{R}\cdot\mathbf{w})\delta n_{es}(\mathbf{R}_1\cdot\mathbf{w}_1)}\Big|_{n_{es}\to n_0}\\&=\frac{\delta(\mathbf{R}-\mathbf{R}_1)}{n_0}-X^{-1}.\end{aligned}\tag{23}$$

The minimization of the free-energy functional with respect to n_e leads to the Kohn-Sham equations (6) with the external potential $u_{ext}=u_{ec}^*n_{es}$. The solvent density n_{es} results from the extremum of the functional with respect to n_{es} and is given by

$$n_{es}(\mathbf{R}\cdot\mathbf{w})=n_0[1+h_{es}(\mathbf{R}\cdot\mathbf{w})]$$
$$=n_0\exp[-\beta(u^*_{ec}n_e+h_{es}-X^{-1}*h_{es})]. \quad (24)$$

Thus, the complete DFT formalism of excess electrons in polar liquids includes the self-consistent calculation of both n_{es} and n_e via Eqs. (6) and (24). The last relation for n_{es} can be written as an integral equation, so the calculation of the solvent density can be performed in the framework of the integral equations theory.[35–38]

An alternative treatment can be provided by a variational approach. Using a chosen basis set for $n_{es}(R)=\{\gamma_i f_{si}(R)\}$ and $n_e(R)=\{\alpha_i f_{ei}(R)\}$, we can minimize the total free energy functional with respect to the variational parameters γ_i and α_i, and derive a set of nonlinear algebraic equations for γ_i and α_i. Of course, the accuracy of the method strongly depends on the choice of the basis set, especially for n_{es}. However, the accurate account of the asymptotic behavior of solvent density n_{es} at small and large distances yields the results comparable with direct solutions of the integral equations.

C. Integral equations

Introducing a new function $c_{es}(\mathbf{R}\cdot\mathbf{w})$, which satisfies the integral equation:

$$n_0h_{es}(\mathbf{R}\cdot\mathbf{w})=X*c_{es}$$
$$=\int\int X(\mathbf{R}-\mathbf{R}_1,\mathbf{w}-\mathbf{w}_1)c_{es}(\mathbf{R}_1,\mathbf{w}_1)\mathbf{d}\cdot\mathbf{R}_1\mathbf{d}\cdot\mathbf{w}_1. \quad (25)$$

We rewrite Eq. (24) in the form

$$h_{es}(\mathbf{R}\cdot\mathbf{w})=n_0\exp[-\beta(u^*_{ec}n_e+h_{es}-c_{es})]-1. \quad (26)$$

The former relation is the molecular Ornstein-Zernike equation, while Eq. (26) is the HNC closure.[38] Thus, we note that formula (19) corresponds to the HNC treatment. In the general case Eq. (25) requires six-dimensional integration that can be hardly carried out, even numerically, without additional simplifications. A simple way for solving Eqs. (25),(26) is to expand h_{es}, c_{es}, and X in spherical harmonics and consider only several terms of this expansion. For instance, linearization with respect to the dipole orientations leads to the mean spherical approximation (MSA).[38]

An alternative way to avoid the integration over angles is to use the averaged solvent density $n_{av}(\mathbf{R})=\langle n_{es}(\mathbf{R}\cdot\mathbf{w})\rangle_{\mathbf{w}}$ and the averaged chemical potential $\mu_{\mathrm{av}}(\mathbf{R})f=\langle\mu(\mathbf{R}\cdot\mathbf{w})\rangle_{\mathbf{w}}$. Integrating Eq. (19) over dipole orientations, we find

$$\mu_{av}(\mathbf{R})=\langle\mu(\mathbf{R}\cdot\mathbf{w})\rangle_{\mathbf{w}}\approx\beta^{-1}\ln(h_{av}+1)]+u^*_{es}n_{av}$$
$$+h^*_{ss}(n_{av}-n_0), \quad (27)$$

and, consequently the averaged solvent density can be found explicitly:

$$n_{av}(R)=n_0[\mathrm{cotanh}(\beta mE_m)-(\beta mE_m)^{-1}]$$
$$\times[1+n_0f^*_{es}h_{ss}]\exp[-\beta u^*_{es}n_e], \quad (28)$$

where $A(R)=\beta mE_m$ and $f_{es}=\exp[-\beta u^*_{es}n_e]-1$. When the mean field intensity is estimated as $E_m(R)=4\pi\int_0^R n_e(x)x^2dx/\epsilon R^2$ and short-range repulsive effects are ignored, the expression (28) corresponds to the point dipole treatment.[33] A similar model was used in Ref. 34 to evaluate optical spectra of an excess electron in amorphous ice and water.

Our approach can be extended to the case of molecular liquids and a discrete structure of charge distribution of solvent molecules. For this purpose we introduce a vector $\mathbf{Q}=\{q_1,q_2,\ldots,q_j\}$ for the site charges (j is the number of sites of a solvent molecule) and a vector for the solvent densities $\mathbf{n}_s(\mathbf{R})\equiv\{n_{s1},n_{s2},\ldots,n_{sj}\}$, whose components are the respective electron-site density distributions. Then, repeating our derivation for the vector quantities we obtain the relation for the free energy (see Appendix B):

$$F_{3DRISM}[n_e,n_{es}]=T[n_e]+\frac{1}{2}n^*_eu^*_qn_e+E_{\mathrm{xc}}[n_e]+n^*_e\mathbf{u}^*_{ec}\mathbf{n}_s$$
$$+\beta^{-1}\sum_j n^*_{sj}[\ln(h_{sj}+1)-1]$$
$$-\frac{\beta^{-1}}{2}n_0\mathbf{h}^*_s\mathbf{C}^*_2n_0\mathbf{h}_s, \quad (29)$$

where the convolution includes also a summation over all the site components, $h_{si}+1=n_{si}/n_{s0}$, n_{s0} is the averaged density of the respective site component, $\mathbf{u}_{ec}(\mathbf{R})=\{u_{e1},\ldots,\mathbf{u}_{ej}\}$ is the vector of electron-site interactions, while $\mathbf{C}_2$ becomes a matrix, whose elements are equal to

$$C_{2ij}(R)=\frac{\delta_{ij}\delta(R)}{n_0}-X^{-1}_{ij}. \quad (30)$$

In the classical limit, the free-energy functional reduces to that derived by the reference interaction site model[39] extended to the three-dimensional case.[40,41] The equilibrium susceptibility $\mathbf{X}(R)$ also becomes a matrix, whose elements are intramolecular (ω_{ij}) and intermolecular (h_{ij}) molecular correlation functions of the pure solvent

$$X_{ij}(R)=\omega_{ij}(R)+n_0h_{ij}(R). \quad (31)$$

The minimization of the functional yields a set of three-dimensional integral equations

$$n_0\mathbf{h}_s(\mathbf{R})=\mathbf{X}*\mathbf{c}_s, \quad (32)$$

with the respective HNC closure between $\mathbf{h}_s(\mathbf{R})$ and $\mathbf{c}_s(\mathbf{R})$.

III. RESULTS

A. Single electron problem

The situation is very simplified when concentration of excess electrons is so low that the correlations between electrons can be ignored. In this case the Kohn-Sham equations (6) reduce to the Schrödinger equation for a single electron in the self-consistent potential $u_{ext}=u^*_{ec}n_{es}$, and the solution to the problem requires the calculation only of the wave function for the electron ground state. The electron forms a spherically symmetrical polaron state and hence the consideration of excess electrons in polar liquids becomes similar to that for classical spherical ions. As a result, excess electrons can be treated on the basis of the ion-dipolar theory.[42]

In this case as for an ion in a dipolar liquid[43] the expansion of the electron-solvent correlation function includes only two terms, i.e., $h_{es}(\mathbf{R}\cdot\mathbf{w})=h_{000}(R)+h_{011}(R)\theta_{011}$. The spherically symmetrical part $h_{000}(R)$ of the electron-dipole correlation function is found by the solution to the integral equation

$$h_{000}(R)=c_{000}(R)+4\pi n_0\int h_{ss}(|\mathbf{R}-\mathbf{r}|)c_{000}(r)\mathbf{d}\cdot\mathbf{r}, \tag{33}$$

with the closure

$$c_{000}(R>R_c)=0, \quad h_{000}(R<R_c)=\exp[-\beta u^*_{es}n_e]-1. \tag{34}$$

The latter is slightly different from that for classical ions where $h_{000}(R<R_c)=-1$ and is a consequence of the quantum behavior of excess electrons. Apart from it, due to the quantum effects the interaction of the excess electrons with the solvent particles becomes weak and the short-range part $h_{000}(R)$ of the solvent density can be approximated as

$$h_{000}(R)\approx[1+h^*_{ss}f_{es}]\exp[-\beta u^*_{es}n_e]-1. \tag{35}$$

The numerical calculations have indicated[44] that the approximate expression (35) for $h_{000}(R)$ is rather close to that obtained by the direct solution to Eq. (33).

The situation with the angular dependent part of the electron-dipole correlation function is more complicated and requires the integral equation for $h_{011}(R)$. But the latter can be rewritten with the use of the Baxter factorization[42] as

$$J_{011}(R)=Q_{es}(R)+24\xi\int_0^{\sigma}J_{011}(|R-r|)Q_{ss}(r)r^2dr, \tag{36}$$

where σ is the hard core diameter of solvent particles. In this expression $J_{01}(R)$ is the function related to $h_{011}(R)$, i.e. $J_{011}(R)=2\pi R\int_R^\infty h_{011}(t)dt$, ξ is the parameter found from Wertheim's MSA solution,[45] while $Q_{es}(r)$ and $Q_{ss}(r)$ are the respective Baxter functions.[46] The closure to this equation is similar to Eq. (34):

$$c_{011}(R>R_c)=\beta m/R^2,$$

$$h_{011}(R<R_c)=\beta m e^*(R)/R^2\exp[-\beta\tilde{u}^*_{es}n_e], \tag{37}$$

where $e^*(R)=4\pi\int_0^R n_e(x)x^2dx$ is the effective charge enclosed of the sphere of radius R, and $\tilde{u}_{es}$ is a short range repulsive potential at small distances.

Concerning with the electron density, we should note that the accurate treatment requires numerical solution to the Schrödinger equation with the self-consistent potential. An alternative way is to use a variational approach. In the previous papers[47] we have numerically solved the Schrödinger equation for an excess electron in electrolytes by the COLSYS package.[48] Our results have indicated that the difference between the solutions found by the variational approach and that found numerically does not exceed several percents and not influences sufficiently the accuracy of calculated electron characteristics. Therefore, for quantitative treatment of excess electrons we have used the Gaussian trial function

$$n_e(r)=\left(\frac{2\alpha^2}{\pi}\right)^{3/2}\exp[-2\alpha^2r^2], \tag{38}$$

where α is a single variational parameter characterizing the electron density. Using this approximation we have calculated electron characteristics in a polar liquid by the two ways.

In the first case we treat the solvent density by the variational method and approximate it as

$$n_s(R)=n_0\left[\operatorname{cothan}\left(\frac{\beta\gamma m e^*}{R^2}\right)-\left(\frac{R^2}{\beta m\gamma e^*}\right)\right]\times[1+n_0 f^*_{es}h_{ss}]\exp[-\beta u^*_{es}n_e], \tag{39}$$

γ is a variational parameter. This approximation is an extension of the point dipole treatment (28) and takes into account the long-range behavior of the polarization in a polar liquid and the short-range effects such as the cavity formation and the saturation of the polarization. Below we refer to it as the extended point dipole (EPD) model. Then, using approximations (38),(39) and varying the free-energy functional (22) with respect to the variational parameters we obtain nonlinear algebraic equations for α and γ and easily find the electron characteristics *versus* thermodynamic and structural parameters of the solvent.

In the second case we have calculated the solvent and the electron densities within the MSA approach by solution to integral equations (35) and (36) in the way similar to that in Ref. 42. As indicated previously[44] the short-range repulsive pseudopotential $u_{es}(r)$ can be characterized by a single scattering length L and approximated as a delta function, but then the effective short-range potential $\widetilde{u_{es}}(r)$ differs from the pure repulsive part $u_{es}(r)$ due to the contribution of attractive forces at small distances. Therefore, we use the approximation $\widetilde{u_{es}}(r)=4\pi L^*\delta(\mathbf{r})$, where L^* is an effective scattering length which can be found in a self-consistent manner. If we know L^* and hence the data on $h_{011}(R<R_c)$, we can calculate $J_{011}(R>R_c)$ by the trapezoidal rule and then calculate the correlation function $h_{011}(R>R_c)$ by the following relation:

$$h_{011}(R>R_c)=\frac{dJ_{011}(R)}{2\pi R dR}-\frac{J_{011}(R)}{2\pi R^2}. \tag{40}$$

Thus, we have two expressions for $h_{011}(R<R_c)$ and $h_{011}(R>R_c)$, hence the parameter L^* can be found by equating both the expressions at $R=R_c$. In our calculations (see below) we have $L^*\approx 0.5$–$0.7L$ that indicates the validity to use the single scattering length approximation.

We have calculated the polaron characteristics such as its kinetic (T) and total (E_t) energies in the ground state as well

TABLE I. Parameters of a polaron and a singlet bipolaron solvated in polar liquid.

	model	T(eV)	E_p(eV)	E_t(eV)	μ_e(eV)	r_e(Å)
		polaron				
Simulation	(Ref. 50)	2.2	-5.0	-2.8	-2.2	2.1
	(Ref. 42)	1.8	-3.6	-1.8		2.4
Theory	MSA(this work)	1.33	-5.57	-4.24	-1.13	2.5
	EPD(this work)	1.58	-5.79	-4.21	-0.91	2.3
	MSA (Ref. 42)	1.8	-3.6	-1.8		2.2
	RISM (Ref. 49)	1.84	-6.08	-4.26	-0.96	2.9
		singlet bipolaron formation				
Simulation	(Ref. 9)	4.05	-16.4	-7.71	-1.57	2.6
Theory	MSA(this work)	2.34	-10.62	-9.67	-2.27	2.7
	EPD(this work)	3.17	-11.38	-9.88	-2.00	2.5

as the potential energy E_p of electron-solvent interactions and the mean polaron radius r_e under the conditions corresponding to water at temperature equal to 300 K, $m=2.347$ D, $\sigma=3.15$ Å, $n_0\sigma^3=1.05$, $L=5.54$ a.u., and $R_c=0.5\sigma+0.81r_e$. Our results as well as other calculations by integral equations,[42,49] and simulations[50] are presented in Table I. All the methods yield similar results, although our calculations are more close to the RISM-polaron model[49] and predict a more weak localization of the electron than that obtained by simulations. Note that the absolute values of the polaron energies are very sensitive to the details of the short-range pseudopotential, and only the data on the chemical potential of the polaron are available from the experiment, which indicates that $\mu_e\approx-1.6$ eV.[51] Our estimate of the chemical potential is also close to that obtained by the RISM-polaron theory[49] and comparable with the experimental value.

We have also investigated changes in the polaron characteristics caused by variations of solvent parameters. Figure 1 demonstrates the influence of the solvent polarity on the electron energy, radius, and the chemical potential. As it is seen, the total polaron energy and the chemical potential rise and become positive as the dipole moment of solvent particles decreases. When this dipole moment is rather small the electron behavior is completely determined by short-range repulsion as was found earlier by the integral equation theory[42] and simulations.[52]

In contrast to it a decrease in the solvent density leads to an increased mean polaron radius and an increased total energy (Fig. 2). Although the chemical potential increases at high densities (Fig. 2) our calculations indicate that it exhibits a nonmonotonic behavior versus the solvent density. This is due to the fact that both the repulsive and attractive contributions to the chemical potential decrease as the solvent density decreases but at a high solvent density the changes in the repulsive contribution is dominant and, as a result, the chemical potential decreases.

Figure 3 depicts the temperature dependence of the chemical potential and the energies of the polaron. Both our models predict that all the values rise at increased temperature. These result contradicts the RISM-polaron the chemical calculations,[49] which indicate a small decrease (~ 0.1 eV) in potential and the total energy of the electron and a nonmonotonic behavior for the potential energy. We think that this discrepancy of our calculations could be

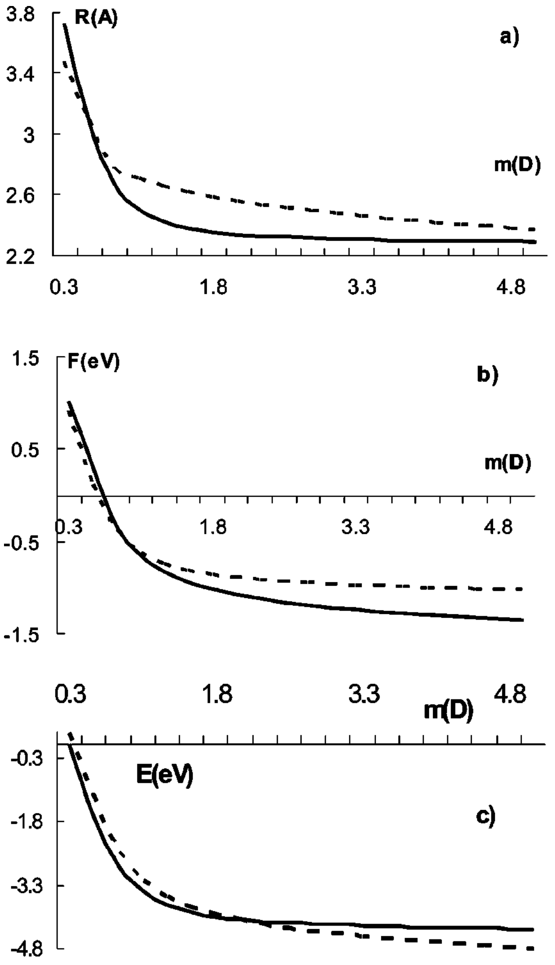

FIG. 1. The polaron characteristics versus the solvent polarity: (a) the mean radius, (b) chemical potential, and (c) the total polaron energy. The solid curve corresponds to the EPD model, while the dashed one to the mean spherical approximation.

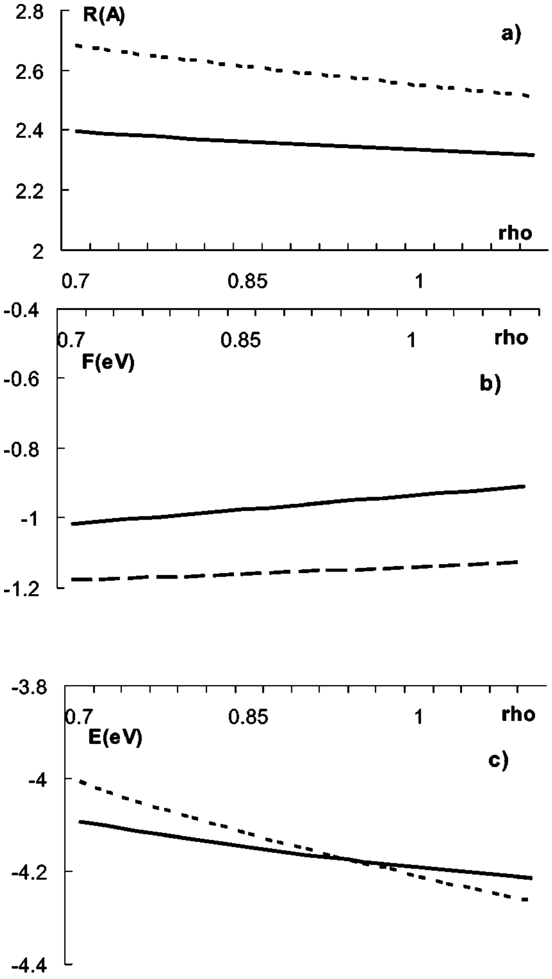

FIG. 2. The polaron characteristics versus the solvent density. Same key as in Fig. 1.

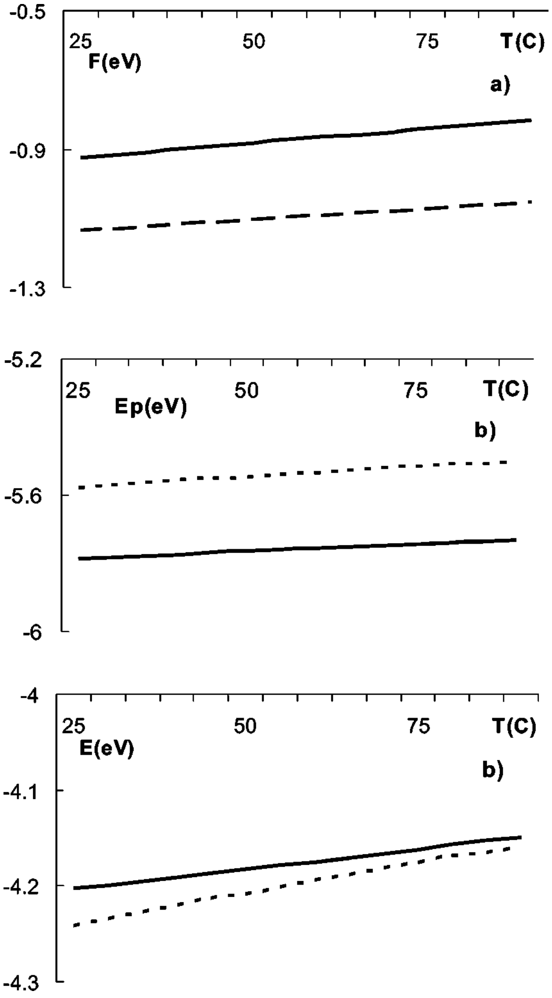

FIG. 3. The polaron characteristics versus temperature of the solvent. Same key as in Fig. 1.

eliminated by anaccurate account of temperature-dependent solvent density (for the EPD model) or using as an input as in Ref. 49.

B. Bipolaron formation

Our theory is able to treat multielectron states. For instance, we have applied the method to estimate characteristics of a singlet bipolaron formation, which arises due to coupling of two electrons with opposite spins. In this case the electron density is obtained by solving Kohn-Sham equations (6). Following Ref. 31, we approximate the local exchange and correlation energies as

$$\epsilon_x(\mathbf{r}) = -\frac{C_p}{r_s(\mathbf{r})}, \quad \epsilon_c(\mathbf{r}) = \frac{\beta_0}{1+\beta_1 r_s(\mathbf{r})^{1/2} + \beta_2 r_s(\mathbf{r})}, \tag{41}$$

where $r_s(\mathbf{r})$ is the averaged radius coupled with electron density, i.e., $r_s(\mathbf{r}) = [n_e(\mathbf{r})/4\pi]^{-1/3}$. Since the electron density distribution is spherical for singlet bipolarons, we can use the simplified variational evaluations for $n_e(r)$ with trial function (38), whose variational parameter is found by the minimization of the total free-energy functional (22), while the solvent density is calculated by the solution of the MSA integral equations (33) and (36).

Table I lists various bipolaron characteristics obtained under the conditions identical to that for the polaron and the data on simulations obtained in Ref. 9 by the hybrid DFT/MD method. To verify our results we have evaluated these characteristics within the extended point dipole model (Table I). We have also calculated the variations of bipolaron characteristics caused by changes in the solvent parameters such as the strength of dipole moment of solvent particles (Fig. 4) and density of solvent (Fig. 5). All trends revealed for a single solvated electron remain also for the bipolaron formation. The mean bipolaron radius and the total bipolaron energy rise at an decreased solvent density and dipole moment of solvent particles. As for a single solvated electron all the methods yield similar results, although the theory underestimates the absolute values of the kinetic energy and the chemical potential. The MSA calculations predict more weak localization than that obtained in simulations and within the EPD model. We think these effects to be a consequence of the use of the simplified short-range pseudopotential for electron-solvent interactions.

Using the MSA and EPD model we have estimated the

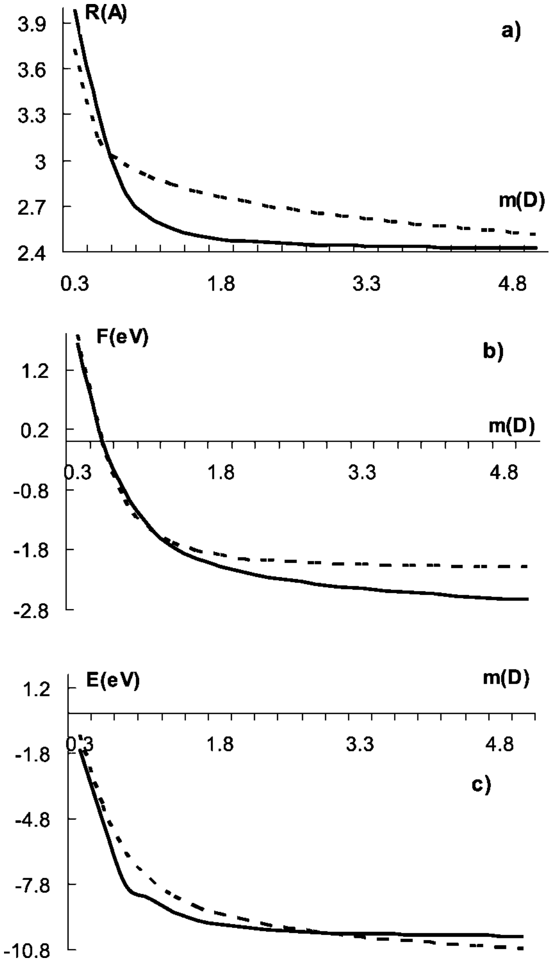

FIG. 4. The characteristics of a singlet bipolaron solvated in a polar liquid versus the solvent polarity: (a) the mean radius, (b) chemical potential, and (c) the total bipolaron energy. The solid curve corresponds to the EPD model, while the dashed one to MSA.

stability of the singlet bipolaron formation with respect to the decay into two polarons. The criterion of the stability implies that the chemical potential μ_b of the bipolaron is lower than that for two polarons, i.e., the bipolaron binding energy ΔF_b is negative

$$\Delta F_b = \mu_b - 2\mu_e < 0. \tag{42}$$

Both the models predict the singlet bipolaron formation to be stable, although the MSA calculations yield the extremely low value for ΔF_b equal to 0.002 eV, the EPD model results in $\Delta F = 0.15$ eV, while the estimates obtained in simulations[9] provide the value $\Delta F_b = 0.6$ eV . The MSA calculations indicate also that the bipolaron formation is not stable at $m > 2.54$ D and $n_0\sigma^3 < 1.02$ (see Figs. 4 and 5), however, the EPD model predicts the bipolaron to be stable in the whole range of the studied solvent parameters. Our verification of the MSA model have demonstrated that the low value of ΔF results from that the obtained data on the chemical potential are rather sensitive to the using value of the cutoff radius R_c. The appropriate choice of the cutoff radius can eliminate this discrepancy without sufficient changes in other bipolaron characteristics (see Fig. 6).

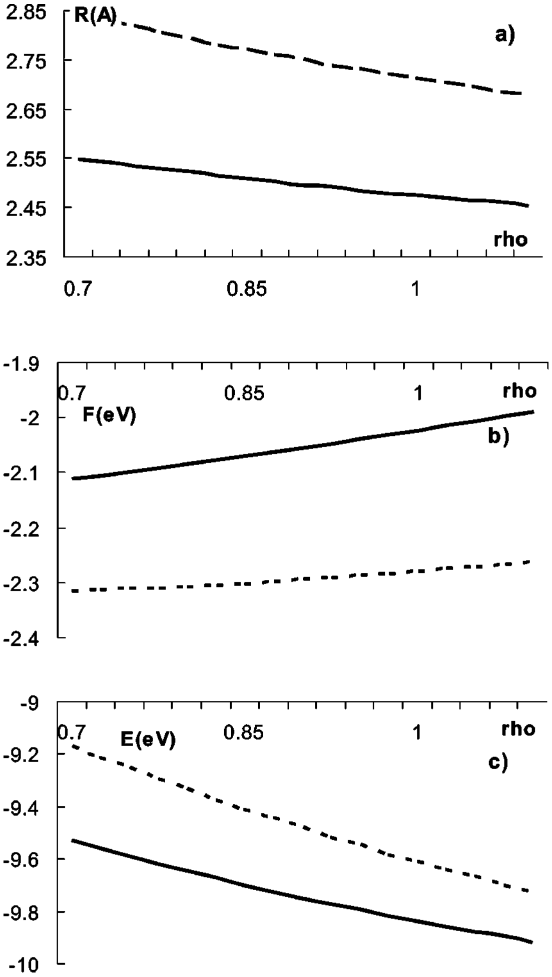

FIG. 5. The bipolaron characteristics verus the solvent density. Same key as in Fig. 4.

IV. CONCLUDING REMARKS

We have applied the density functional approach to polarons and bipolarons in polar liquids, which treats the electrons by the Kohn-Sham formalism and the solvent by the

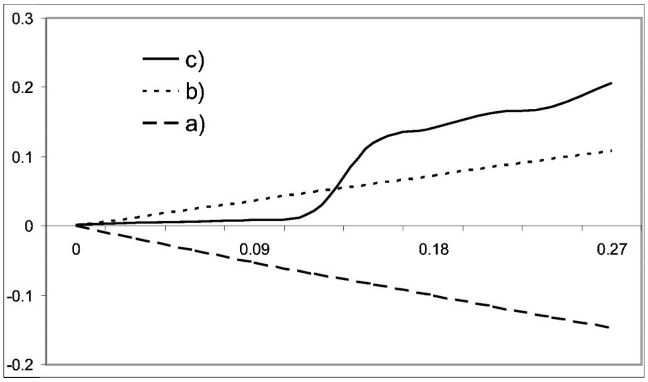

FIG. 6. Relative changes in the bipolaron characteristics versus the cutoff radius δR_c: (a) changes in the mean bipolaron radius $\delta r_b / r_b^0$, (b) the total bipolaron energy $\delta E_t / E_t^0$, and (c) in the bipolaron binding energy $\delta F_b / \mu_b^0$. All values are normalized with respect that at $R_c = 0.5\sigma + 0.81 r_b$.

integral equations theory. Note that our approach is similar to the quantum NHC method developed for liquid metals and dense plasma (see, for example, Refs. 53–56). But in contrast to the systems, where the coulomb contribution is dominant in electron-ion interactions, the short-range repulsion between electron and solvent particles has a significant effect on electron-solvent potential in our case. On the other hand we have considered only the infinitely diluted limit and ignored electron-electron contributions into the equilibrium susceptibility of the liquid. At an increased concentration of electrons our method may be improved in a manner similar to that developed for liquid metals,[56] but it requires additional approximations for the electron-electron direct correlation function.

For polar liquids we have derived the free-energy functional of the system and obtained the relations for the electron-solvent correlation function within the framework of the mean spherical approximation and the extended point dipole model. The application of these models indicates that improved closures such as the linearized HNC and the quadratic NHC (Ref. 57) are required to calculate more accurately structural properties of the solvent. Nevertheless our method can able to predict the main characteristics of polarons and bipolarons, whereas the deficiencies of the models are masked due to the diffusive distribution of the electron charge. We believe that the method can be also applied to calculate solvation not only excess electrons but also molecular ions for which the electron density is treated by the quantum DFT, while the solvent effects by integral equations method. Such investigation will be subject of our forthcoming papers.

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APPENDIX A: FIELD TRANSFORMATION OF THE GRAND PARTITION FUNCTION

Making a transformation of the solvent functional into the path integral over the electric field we should take into account the degeneration of the dipolar interactions with respect to orientations. The physical meaning of this effect is that the excess charge can induce not only a longitudinal but also a transverse electric field. Taking into account this fact, we transform Eq. (9) into a path integral over the field intensity $\mathbf{E}$. For this purpose, we use the identity

$$\exp\left[-\frac{\beta}{2}n_s^*\mathbf{m}\cdot\mathbf{T}\cdot\mathbf{m}^*n_s\right] = \int D[\mathbf{E}]\exp\left[\frac{\beta}{2}\mathbf{E}^*\mathbf{T}^{-1}{}^*\mathbf{E}-\beta n_s^*\mathbf{m}\cdot\mathbf{E}\right], \tag{A1}$$

where $\mathbf{T}^{-1}$ is the matrix inverse of the matrix of dipolar interactions and using the Hubbard–Stratonovich transform,[35,36] we find

$$\begin{aligned}\exp[-\beta\Omega_{\text{solv}}] &= \int D[\mathbf{E}]\exp[-\beta S(\mathbf{E})\\ &= \int D[\mathbf{E}]\exp\left[\frac{\beta}{2}(\mathbf{E}-n_e^*\nabla u_q)^*\mathbf{T}^{-1}{}^*(\mathbf{E}-n_e^*\nabla u_q)\right]\\ &\quad\times\langle\exp[-\beta n_s^*(\mathbf{m}\cdot\mathbf{E}+u_{es}-\mu+u_{ss}^*n_s)]\rangle_s .\end{aligned} \tag{A2}$$

As a result, the action of Eq. (A1) can be factorized and expressed in terms of one- and two-particle irreducible correlation functions

$$\begin{aligned}S(\mathbf{E}) = &-\frac{\beta}{2}(\mathbf{E}-n_e^*\nabla u_q)^*\mathbf{T}^{-1}{}^*(\mathbf{E}-n_e^*\nabla u_q)]\\ &-\beta^{-1}n_0 f(\mathbf{E})^*\left[1+\frac{1}{2!}n_0h_{ss}^*f(\mathbf{E})\right],\end{aligned} \tag{A3}$$

where $f(\mathbf{E})$ is the Mayer function

$$f(\mathbf{E}) = \exp[-\beta(u_{es}^*n_e+\mathbf{m}\cdot\mathbf{E}-\mu)]-1. \tag{A4}$$

The extremum of the action S with respect to the field intensity yields the integral relation between the mean-field intensity and polarization

$$\mathbf{E}_m(\mathbf{R}) = n_e^*\nabla u_q + \int \mathbf{T}(\mathbf{R}'-\mathbf{R})\mathbf{P}(\mathbf{R})\mathbf{d}\cdot\mathbf{R}, \tag{A5}$$

which can be inverted into the Maxwell equation

$$\nabla\cdot\mathbf{E}_m = 4\pi n_e - 4\pi\nabla\cdot\mathbf{P}. \tag{A6}$$

Using Eqs. (A4) and (A5) we result in Eq. (14).

Ignoring short-range correlations in Eq. (A3) results in the Debye-Hückel limit. The linearization of the field dependence of the polarization, i.e., $\mathbf{P}\propto\mathbf{E}$, leads to the linearized Debye-Hückel model. We note also an additional relation between $\mathbf{P}$ and $\mathbf{E}$:

$$\mathbf{P}(\mathbf{R}) = \frac{\epsilon-1}{4\pi}\mathbf{E}, \tag{A7}$$

which serves as a definition of dielectric constant ϵ. Combining this expression with Eq. (A6) in the case when excess electrons are treated as point charges, we obtain the Clausius-Mossoti formula for the dielectric constant. Thus, various approximations can be derived with the use of Eq. (A6), the choice of the approximations being determined by the accuracy required to treat the solvent microstructure.

APPENDIX B: FREE ENERGY OF EXCESS ELECTRONS IN A MOLECULAR LIQUID

We consider the generalized solvent density $\mathbf{n}_s(\mathbf{R}) \equiv \{n_{s1}, n_{s2}, \ldots, n_{sj}\}$, whose components are determined as $n_{si}(\mathbf{R}) = \Sigma_j^N \delta(\mathbf{R}-\mathbf{R}_j-\mathbf{l}_i)$, where $\mathbf{l}_i$ is the relative position of ith site with respect to the center of a solvent molecule. Then, replacing in Eq. (9) all the scalar quantities by the corresponding vectors and write the short-range solvent-solvent interactions in the matrix form, we have

$$E_{\mathrm{solv}}[\mathbf{n}_s]=\mathbf{n}_s^*\frac{(\mathbf{U}_{ss}+\mathbf{Q}\cdot\mathbf{T}\cdot\mathbf{Q})}{2}*\mathbf{n}_s+n_e^*(\mathbf{u}_{es}+u_q\mathbf{Q})*\mathbf{n}_s-\vec{\mu}*\mathbf{n}_s. \qquad \text{(B1)}$$

Using the Hubbard-Stratonovich transform, we rewrite the solvent functional as a path integral over the scalar field Ψ with the action $S(\Psi,\mathbf{n}_s)$ equal to

$$S(\Psi,\mathbf{n}_s)=-\frac{1}{8\pi}[\nabla(\Psi-n_e^*u_q)]^2+\mathbf{n}_s^*(\mathbf{Q}\Psi+\mathbf{u}_{es}-\vec{\mu}+\mathbf{U}_{ss}^*\mathbf{n}_s)]. \qquad \text{(B2)}$$

We note that the averaging over solvent degrees of freedom includes the average over positions as well as the orientations of solvent molecules. The intra-molecular correlations caused by bonds between sites complicate the average over the orientations and, as a result, the relation for the solvent functional can not be derived analytically. One of the ways to eliminating these difficulties is to use the simple estimate

$$\langle\exp[-\beta E_{\mathrm{solv}}]\rangle_{\mathbf{w}}\approx\exp[-\beta\langle E_{\mathrm{solv}}]\rangle_{\mathbf{w}}], \qquad \text{(B3)}$$

where $\langle\cdots\rangle_{\mathbf{w}}$ means the average over orientations of solvent molecules. Under this approximation the solvent functional can be easily factorized and expressed in terms of two-particle intramolecular and intermolecular correlation functions

$$\exp[-\beta\Omega_{\mathrm{solv}}]=\int D[\Psi]\exp\left[\frac{\beta}{8\pi}[\nabla(\Psi-n_e^*u_q)]^2+\frac{n_0}{2}\mathbf{f}(\Psi)^*[\mathbf{W}+n_0\mathbf{H}_{ss}]^*\mathbf{f}(\Psi)\right], \qquad \text{(B4)}$$

where $\mathbf{f}(\Psi)$ is the vector, whose components are the Mayer functions, i.e.,

$$\mathbf{f}(\Psi)=\exp[-\beta(\mathbf{u}_{es}^*n_e+\mathbf{Q}\Psi-\vec{\mu})]-1, \qquad \text{(B5)}$$

while $\mathbf{W}$ and $\mathbf{H}_{ss}$ are the matrices, whose components are respective intramolecular and intermolecular correlations functions. The short-range intermolecular correlation functions $h_{ij}(R)$ are defined by Eq. (16), while the intramolecular ones w_{ij} by the relation

$$w_{ij}(|\mathbf{R}-\mathbf{R}'|)]=\delta_{ij}\delta(|\mathbf{R}'-\mathbf{R}|)+(1-\delta_{ij})\frac{1}{4\pi l_{ij}^2}\delta(|\mathbf{R}'-\mathbf{R}|-l_{ij}). \qquad \text{(B6)}$$

The minimization of the functional (B4) with respect to the chemical potential $\vec{\mu}$ yields the relations for solvent densities. In the vector form they are written as

$$\mathbf{n}_s=n_0[\mathbf{W}+n_0\mathbf{H}_{ss}]^*(\mathbf{f}+\mathbf{1}). \qquad \text{(B7)}$$

On the other hand, the extremum of Eq. (B4) with respect to the field gives

$$\Psi_m=n_e^*u_q+\mathbf{Q}\cdot\mathbf{n}_s^*u_q. \qquad \text{(B8)}$$

Simplifying relation (B7) between the chemical potential and the solvent density by the way similar to Eq. (19) we can write

$$\vec{\mu}-\beta^{-1}\ln(\mathbf{h}_s+\mathbf{1})]-\mathbf{u}_{ec}^*n_e\approx-\mathbf{C}_2^*(\mathbf{n}_s-\mathbf{n}_0), \qquad \text{(B9)}$$

where $\mathbf{C}_2$ is the matrix whose elements are related to the second derivative of the functional with respect to $\mathbf{n}_s$, i.e., $C_{2ij}=-\delta^2\beta F/\delta n_{si}\delta n_{ej}$. Thus, using these relations we can exclude the field and the chemical potential from Eq. (B4) and after simple manipulations to obtain the final expression for the free-energy (29) in terms of electron-site correlation functions $\mathbf{n}_s$.

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