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Energy-density relationships for the treatment of ion solvation within density-functional theory

Renato R. Contreras and Fernando Mendizabal
Departamento de Quimica, Centro de Mecanica Cuantica Aplicada, Facultad de Ciencias, Universitad de Chile, Casilla 653 Santiago, Chile

Arie J. Aizman
Departamento de Quimica, Universidad Tecnica Federico Santa Maria, Casilla 110-V, Valparaiso, Chile

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Useful energy-density relationships, connected with the embedding of singly charged postive or negative atomic ions in polar solvents, are developed. The insertion of the atomic charged system into the polarizable host is modeled through successive isoelectronic processes at the nucleus, involving a varying nuclear charge. In this way, the controversial procedure of selecting appropriate ionic radii, involved in the calculation of solvation energies through the Born formula, is avoided and replaced by integration in $[0,\infty]$. The approximate expressions, derived from a variational procedure proposed by Levy [J. Chem. Phys. **68**, 5298 (1978); **70**, 1573 (1979)], are reformulated within the nuclear-transition-state model. The classical reaction field expression for the insertion energy is recovered. The quality of the approximations made are discussed within the frame of the Kohn-Sham formulation of density-functional theory.

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INTRODUCTION

The electronic properties of charged atoms and molecules embedded in polar liquids have usually been described in terms of the electrostatic potential of the privileged subsystem, in the field of a polarizable effective medium. Under the assumption that we may have accurate electron densities at hand, the description of electrostatic potentials becomes highly sensitive to the choice of ionic radii. For instance, within the Born formulation [1], despite the apparent simplicity of the mathematical expression giving the electrostatic solvation energy, there exists no physically meaningful model to justify the empirical adjustments of ionic radii [2–4].

A more consistent examination of atomic electrostatic potentials revealed that it is impossible to have a uniform criterion to select appropriate ionic radii, to be used within a Born-like calculation of solvation energies [5,6]. This conclusion is obtained by using some exact relationships between electron density and electrostatic potentials derived in the context of density-functional theory [7,8]. Starting from Poisson equation, it is quite simple to show that the electrostatic potentials for anions and cations display different functional behavior, with respect to the radial variable $\mathbf{r}$. In the case of singly charged negative atomic ions, the electrostatic potential $V(\mathbf{r})$ displays a minimum at a critical finite value r^*, $0<r^*<\infty$. Moreover, the r^* values were in close agreement with the crystallographic ionic radii for a series of anions [8].

Estimates of ionic radii for cations may be obtained from a simple Thomas-Fermi-Dirac model [8,9]. The use of this simplified representation of an atomic system indicates that there may be a radial distance r_μ at which the chemical potential μ is equal to the negative of the electrostatic potential $V(\mathbf{r})$, which is produced at r_μ by a nucleus of charge Z and electrons of the ion. Here, again, the ionic radii obtained by this procedure were in close agreement with the Pauling ionic radii for a series of cations [8].

In summary, the Poisson equation and density-functional theory provide a firm physicochemical ground to define ionic radii for anions and cations, respectively, which can be used in the context of Born formulation of electrostatic solvation free energy. There remains, however, the problem of being forced to use different mathematical criteria for the selection of ionic radii in both cases.

In this work we propose an approximate theory of ion solvation that uses the electrostatic potential at the nucleus as the basic variable. In this way, anions and cations may be treated within a unified formalism. This procedure avoids the problem of selecting ionic radii since all integrations are performed over $[0,\infty]$.

The paper is organized as follows: In Sec. (I) we present the charging model based on a Noyes-like cycle and the variational formulation of the insertion energy. In Sec. II the resulting expression of the electrostatic solvation energy is reformulated within the framework of the nuclear-transition-state (ZTS) model. In Sec. III the quality of the approximations made is tested and discussed in the context of the Kohn-Sham version of density-functional theory. Our conclusions are presented in Sec. IV.

I. THE CHARGING MODEL AND THE VARIATIONAL FORMULATION OF SOLVATION ENERGY

Our working hypothesis states that it is possible to develop a unified model of solvation for anions and cations, if the classical Born charging process [1] is replaced by a Noyes-like charging process [10]. This last model represents the immersion of a charged atom into a liquid solution through a three-step hypothetical cycle: (a) In the gas phase, an ion is converted into a neutral isoelectronic species by removing or adding a nuclear charge unity, (b) the resulting neutral system is added to the liquid solution, and (c) the original charged atomic system is restored by the process opposite to that described in (a). If the nonelectrostatic (cavitation) energy contribution [step (b)] is neglected, the electrostatic solvation energy reduces to the sum of contributions (a) and (c). These successive isoelectronic processes may be represented, for the immersion of a charged monoatomic ion say, A^+, by the cycle described in Fig. 1, where X is an auxiliary isoelectronic neutral system.

According to the cycle shown in Fig. 1, we may write the insertion energy variation as follows:

$$\Delta E_{\text{ins}}(Z+1,Z+1)=\Delta E_a^0(Z+1,Z)+\Delta E_b(Z,Z)+\Delta E_c(Z,Z+1)\ , \tag{1}$$

where $\Delta E_a^0(Z+1,Z)$ represents the total-energy variation for the isoelectronic charge *in vacuum*, $\Delta E_b(Z,Z)$ represents the total-energy variation associated with the insertion of the neutral isoelectronic species into the polar liquid, and $\Delta E_c(Z,Z+1)$ denotes the total-energy variation for the isoelectronic process opposite to step (a), in the presence of the polarizable medium. This last quantity not only differs by an opposite sign from $\Delta E_a^0(Z+1,Z)$ but also contains the polarization effect due to the electrostatic interaction with the medium. Moreover, if we are interested only in the electrostatic contributions to $\Delta E_{\text{ins}}(Z+1,Z+1)$, the quantity $\Delta E_b(Z,Z)$, representing the work required to form the hole in the polarizable host where the ion will be embeded, may be neglected to give

$$\Delta E_{\text{ins}}(Z+1,Z+1)=\Delta E_a^0(Z+1,Z)+\Delta E_c(Z,Z+1) \tag{2}$$

in the sense that, hereafter, ΔE_{ins} will be considered as an electrostatic energy variation.

From the above charging model, we may derive an expression for ΔE_{ins} applying the variational theorem. Consider the isoelectronic pair (A^+,X) *in vacuum*, with Hamiltonians $\hat{H}_A^0$ and $\hat{H}_B^0$, which differ in external potentials $\hat{v}^0(\mathbf{r})$. In this particular case [step (a) of Noyes cycle in Fig. 1], $\hat{H}_A^0$ and $\hat{H}_B^0$ have different nuclear charges.

For such isoelectronic changes in atoms, Levy [11,12] has proposed the approximate relationship

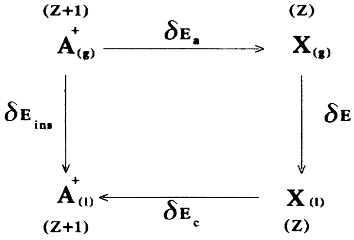


FIG. 1. Hypothetical thermodynamic cycle modeling the Noyes charging process, to achieve the insertion of an arbitrary singly positive charged atom from gas to solution phase.

$$\Delta E_a^0=E_X^0-E_A^0=\int d\mathbf{r}\,\delta\hat{v}^0(\mathbf{r})\rho_{\text{av}}^0(\mathbf{r})\ , \tag{3}$$

where

$$\rho_{\text{av}}^0(\mathbf{r})=\tfrac{1}{2}[\rho_X^0(\mathbf{r})+\rho_A^0(\mathbf{r})] \tag{4}$$

is Levy's average electron density [12], defined in terms of the one-electron densities $\rho_X^0(\mathbf{r})$ and $\rho_A^0(\mathbf{r})$, and $\delta\hat{v}^0(\mathbf{r})$ represents the difference between the electron-nuclear attraction operators of the isoelectronic pair (A^+,X) *in vacuum*. Since Levy's expression (3) was derived for an isolated atomic system, we can immediately identify it with the first term of Eq. (2).

Consider now the systems A^+ and X in the field of a polarizable medium, with Hamiltonians

$$\hat{H}_X=\hat{H}_X^0+\hat{H}_X^{\text{int}} \tag{5}$$

and

$$\hat{H}_A=\hat{H}_A^0+\hat{H}_A^{\text{int}}\ , \tag{6}$$

where $\hat{H}_A^0$ and $\hat{H}_X^0$ are the Hamiltonians of the isoelectronic pair (A^+,X) *in vacuum* and $\hat{H}_A^{\text{int}},\hat{H}_X^{\text{int}}$ the corresponding interaction Hamiltonians representing the electrostatic interaction with the polarizable environment. Using the fact that $\hat{H}_A^0$ and $\hat{H}_X^0$ differ in external potentials [i.e., $\Delta\hat{H}^0=\delta\hat{v}^0(\mathbf{r})$], subtraction of Eqs. (5) and (6) yields

$$\hat{H}_X=\hat{H}_A+\delta\hat{v}^0(\mathbf{r})+\Delta\hat{H}^{\text{int}} \tag{7}$$

and

$$\hat{H}_A=\hat{H}_X-\delta\hat{v}^0(\mathbf{r})-\Delta\hat{H}^{\text{int}}\ , \tag{8}$$

with

$$\Delta\hat{H}^{\text{int}}=\hat{H}_X^{\text{int}}-\hat{H}_A^{\text{int}}\ . \tag{9}$$

If Ψ_X and Ψ_A are eigenstates of $\hat{H}_X$ and $\hat{H}_A$, respectively, then by the variational theorem, we obtain from Eqs. (7) and (8)

$$E_X<\langle\Psi_A|\hat{H}_A+\delta\hat{v}^0(\mathbf{r})+\Delta\hat{H}^{\text{int}}|\Psi_A\rangle \tag{10}$$

and

$$E_A<\langle\Psi_X|\hat{H}_X-\delta\hat{v}^0(\mathbf{r})-\Delta\hat{H}^{\text{int}}|\Psi_X\rangle\ . \tag{11}$$

If we neglect, in accordance with Eq. (2), the interaction of the neutral species X with the polarizable environment (i.e., $\langle\Psi_X|\Delta\hat{H}^{\text{int}}|\Psi_X\rangle=0$), we obtain the following approximate relationships:

$$E_A\approx E_X-\int d\mathbf{r}\,\delta\hat{v}^0(\mathbf{r})\rho_A(\mathbf{r})-\langle\Psi_A|\Delta\hat{H}^{\text{int}}|\Psi_A\rangle \tag{12}$$

and

$$E_X\approx E_A+\int d\mathbf{r}\,\delta\hat{v}^0(\mathbf{r})\rho_X(\mathbf{r})\ . \tag{13}$$

An additional comment with regard to Eqs. (12) and (13) is worth making. Equations (12) and (13) are not exact because, in addition to the neglect of the interaction contribution of the neutral X system with the polarizable environment, there are the variational errors δ_A and δ_X associated with the expectation values E_A and E_X, respectively. Since we are interested in the energy difference $\Delta E=E_A-E_X$ and because the errors δ_A and δ_X are always positive, it follows that the errors in the energy difference will in general compensate.

Addition of Eqs. (12) and (13) yields

$$\langle \Psi_A | \Delta \hat{H}^{\mathrm{int}} | \Psi_A \rangle = -\int d\mathbf{r}\, \delta\hat{v}^0(\mathbf{r}) \delta\rho(\mathbf{r}) \ , \tag{14}$$

where

$$\delta\rho(\mathbf{r}) = [\rho_A(\mathbf{r}) - \rho_X(\mathbf{r})] \ . \tag{15}$$

According to the Hohenberg-Kohn theorem, $\delta\rho(\mathbf{r})$ given in Eq. (15) never vanishes because $\rho_A(\mathbf{r})$ and $\rho_X(\mathbf{r})$ are determined by different external potentials [13]. Moreover, $\delta\rho(\mathbf{r})$ represents the electronic polarization contribution due to the isoelectronic change under the influence of the external electrostatic field.

On the other hand, subtraction of Eqs. (12) and (13) yields

$$[E_A - E_X] = -\int d\mathbf{r}\, \delta\hat{v}^0(\mathbf{r}) \rho_{\mathrm{av}}(\mathbf{r}) - \tfrac{1}{2} \langle \Psi_A | \Delta \hat{H}^{\mathrm{int}} | \Psi_A \rangle \ , \tag{16}$$

where $\rho_{\mathrm{av}}(\mathbf{r})$ is an average electron density equivalent to that introduced in Eq. (4), but this time defined in terms of the one-electron densities of the isoelectronic pair (A^+, X), in the presence of an external electrostatic field.

Substitution of Eq. (14) into Eq. (16) yields

$$\begin{aligned} [E_A - E_X] &= \Delta E_c(Z, Z+1) \\ &= -\int d\mathbf{r}\, \delta\hat{v}^0(\mathbf{r}) \rho_{\mathrm{av}}(\mathbf{r}) + \tfrac{1}{2} \int d\mathbf{r}\, \delta\hat{v}^0(\mathbf{r}) \delta\rho(\mathbf{r}) \ . \end{aligned} \tag{17}$$

Finally, combination of Eqs. (2), (3), and (17) yields the desired general expression. Namely,

$$\begin{aligned} \Delta E_{\mathrm{ins}}(Z+1, Z+1) = {} & \int d\mathbf{r}\, \delta\hat{v}^0(\mathbf{r}) [\rho_{\mathrm{av}}^0(\mathbf{r}) - \rho_{\mathrm{av}}(\mathbf{r})] \\ & + \tfrac{1}{2} \int d\mathbf{r}\, \delta\hat{v}^0(\mathbf{r}) \delta\rho(\mathbf{r}) \ . \end{aligned} \tag{18}$$

II. REACTION FIELD FORMULATION OF ΔE_{ins} WITHIN THE NUCLEAR-TRANSITION-STATE MODEL

It is interesting to note that Eq. (18) may be easily interpreted within the framework of reaction field theory [14]. For instance, the second term of Eq. (18) represents the electronic polarization contribution that accounts for the solute screening cloud induced by the external (reaction) field: It may be interpreted as the response of electrons moving under the influence of an effective potential including the reaction field effect. A completely equivalent interpretation has been established by Norskov and Lang [15] with regard to the second term of Eq. (18), from a second-order perturbation-theory approach, in the study of atomic impurities in solids. To reinforce the above argument, we must show that the first term of Eq. (18) corresponds to the ion-solvent electrostatic interaction energy.

We shall develop here a simple methodology for the computation of ΔE_{ins}, in terms of the electrostatic potential at nucleus V_0. Within this framework, we will show that the first term of Eq. (18) represents, in the context of reaction field theory, the ion-solvent interaction energy.

We start by reiterating that the insertion of an atomic ion into a polar liquid is being described in terms of successive isoelectronic processes that take place *in vacuum* and in the presence of a polarizable environment. Within this model, the energy changes are written as a function of a varying nuclear charge. It seems then natural to express the energy associated with the isoelectronic changes using the Hellmann-Feynman (HF) theorem. Consider, for instance, the energy change from Z_A to Z_X. Using the integrated form of the HF theorem, we obtain [16]

$$\Delta E(Z_A, Z_X) = \int_{Z_A}^{Z_X} \int d\mathbf{r}' dZ \frac{\rho(\mathbf{r}', Z)}{|\mathbf{r} - \mathbf{r}'|_{\mathbf{r}=0}} \ . \tag{19}$$

Application of the mean value theorem yields

$$\begin{aligned} \int_{Z_A}^{Z_X} \int d\mathbf{r}' dZ \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|_{\mathbf{r}=0}} &= [Z_X - Z_A] \int d\mathbf{r}' \frac{\rho(\mathbf{r}', Z^*)}{|\mathbf{r} - \mathbf{r}'|_{\mathbf{r}=0}} \\ &= [Z_A - Z_X] V_0^* \ , \end{aligned} \tag{20}$$

where $\rho(\mathbf{r}, Z^*)$ is the electron density for some nuclear charge Z^* such that $Z_X < Z^* < Z_A$ and

$$V_0^* = -\int d\mathbf{r}' \frac{\rho(\mathbf{r}', Z^*)}{|\mathbf{r} - \mathbf{r}'|_{\mathbf{r}=0}} \tag{21}$$

is the electrostatic potential at a nucleus with an intermediate charge between Z_A and Z_X. This method for calculating $\Delta E(Z_A, Z_X)$ is called the ZTS model [17]. Within this model, the energy variation associated with the work of removing a nuclear charge unity in an isoelectronic process may be directly obtained for atoms, from a self-consistent-field (SCF) wave function computed for the atomic charge $Z^* = \frac{1}{2}(Z_A + Z_X)$ [18].

Within this framework, it is possible to show that the first term of Eq. (18) represents the electrostatic ion-solvent interaction energy, in terms of the ZTS potential at nucleus V_0^*. Under the approximation

$$\rho(\mathbf{r}, Z^*) \approx \rho_{\mathrm{av}}(\mathbf{r}) \ , \tag{22}$$

the use of the definition given in Eq. (4) together with Eqs. (18), (20), and (21) allows us to write the first term of Eq. (18) in terms of V_0^* as follows:

$$\begin{aligned} \int d\mathbf{r}\, \delta\hat{v}^0(\mathbf{r}) [\rho_{\mathrm{av}}^0(\mathbf{r}) - \rho_{\mathrm{av}}(\mathbf{r})] &= [Z_X - Z_A][V_0^* - \bar{V}_0^*] \\ &= \Delta E_{\mathrm{int}}[\delta\rho(\mathbf{r})] \ , \end{aligned} \tag{23}$$

which is the reaction field expression of the ion-solvent electrostatic interaction energy [14], expressed in terms of V_0^* and $\bar{V}_0^*$, the electrostatic potential at the nucleus of a pseudoatom having a fractional nuclear charge, *in vacuum* and in the presence of the external electrostatic field induced in the solvent. As expected, the interaction energy is a functional of the induced electron density $\delta\rho(\mathbf{r})$.

We shall now show that the insertion energy may be cast into a form completely equivalent to the Born formula. This may be easily done by using the well-known relationship between the electrostatic ion-solvent interaction energy and the electronic polarization energy [14,19]. Namely,

$$\Delta E^{\mathrm{pol}}[\delta\rho(\mathbf{r})] = -\tfrac{1}{2} \Delta E_{\mathrm{int}}[\delta\rho(\mathbf{r})] \ . \tag{24}$$

From Eqs. (23) and (24) we get

$$\tfrac{1}{2}\int d\mathbf{r}\,\delta\hat{v}^0(\mathbf{r})\delta\rho(\mathbf{r}) = -\tfrac{1}{2}[Z_X - Z_A][V_0^* - \hat{V}_0^*]\ . \qquad (25)$$

Finally, combination of Eqs. (18), (23), (24), and (25) yields the desired final result. Namely,

$$\Delta E_{\text{ins}}(Z+1, Z+1) = \tfrac{1}{2}[Z_X - Z_A][V_0^* - \bar{V}_0^*]\ . \qquad (26)$$

If we define the ZTS reaction field potential

$$\Phi_R^*[\delta\rho(\mathbf{r})] \equiv [V_0^* - \bar{V}_0^*]\ , \qquad (27)$$

then the agreement of ΔE_{ins} with the classical reaction field (RF) expression of Born solvation energy is complete. Namely,

$$\Delta E_{\text{ins}}(Z+1, Z+1) = \tfrac{1}{2}\Delta Z \Phi_R^*[\delta\rho(\mathbf{r})]\ . \qquad (28)$$

In summary, a general expression giving the solvation energy of singly positive or negative charged atomic ions has been presented. The formulation introduces the electrostatic potential at the nucleus of a nuclear-transition-state system having a fractional nuclear charge Z^*. Expression (28), which gives the solvation energy, is completely equivalent to the reaction field version of the Born formula. However, in the present approach, ΔE_{ins} appears completely independent of the ionic radii. This aspect of the model is really important and very promising, since it permits the calculation of the insertion energy without making any reference to the partition of the space into a quantum region containing the solute, and a classical region representing the solvent. The absence of boundaries in the representation of the solute-solvent system leads directly to integration over $[0, \infty]$, thereby avoiding the introduction of empirical ionic radii in the calculation of solvation energies. In other words, the polarization of the environment appears naturally into the formalism, as a response to the coupling between the solute electron density and the external electrostatic perturbation.

III. ZTS ELECTRON DENSITY IN THE PRESENCE OF AN EXTERNAL FIELD

The basic assumption leading to Eq. (28) is represented by approximation (22), which relates Levy's average electron density with the corresponding ZTS electron density. It is important to emphasize that the average electron density approximates the transition density in the integral HF theorem, which is an exact expression for isoelectronic changes *in vacuum* [12]. However, it is not obvious that such an approximation still holds for ions in the presence of a perturbing external electrostatic field. In order to test the quality of approximation (22) for isoelectronic changes in atomic ions coupled to an external field, it is necessary to determine the corresponding electron density. The Kohn-Sham (KS) formulation of density-functional theory [20] appears to be a suitable procedure to achieve this objective.

When an atomic ion is under the influence of an additional external spin-independent potential $v_{\text{ext}}(\mathbf{r})$, produced, for instance, by a polarizable environment, the effective energy of the atomic ion becomes

$$E[\rho(\mathbf{r})] = E[\rho^0(\mathbf{r})] + \int d\mathbf{r}\,\rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r})\ . \qquad (29)$$

The $E[\rho^0(\mathbf{r})]$ functional is minimized by the ground-state density of the isolated system $\rho^0(\mathbf{r})$. The $E[\rho(\mathbf{r})]$ functional is minimized by a new density $\rho(\mathbf{r})$ which differs from $\rho^0(\mathbf{r})$ by an amount $\delta\rho(\mathbf{r})$:

$$\rho(\mathbf{r}) = \rho^0(\mathbf{r}) + \delta\rho(\mathbf{r})\ . \qquad (30)$$

Following the KS prescription, the density $\rho(\mathbf{r})$ may be obtained from a set of electronic orbitals $\phi_i(\mathbf{r})$ as

$$\rho(\mathbf{r}) = \sum_{\epsilon_i < \mu} |\phi_i(\mathbf{r})|^2\ , \qquad (31)$$

where the summation is done over all the bound states having monoelectronic energies ϵ_i lower than the chemical potential μ.

The $\phi_i(\mathbf{r})$ orbitals are solutions of the eigenvalue equation (in atomic units):

$$[-\tfrac{1}{2}\nabla_i^2 + v_{\text{eff}}(\mathbf{r})]\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})\ , \qquad (32)$$

where the effective potential $v_{\text{eff}}(\mathbf{r})$ is also a functional of the density and is given by

$$v_{\text{eff}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta\epsilon_{xc}[\rho]}{\delta\rho(\mathbf{r})}\ . \qquad (33)$$

The third term of Eq. (33) is the electronic Hartree potential, whereas the fourth one represents the exchange-correlation potential. This last term is usually obtained from a model exchange-correlation energy functional $\epsilon_{xc}[\rho]$. To a first-order approximation, the effective KS potential compatible with the electron density $\rho(\mathbf{r})$ given in Eq. (30) may be written as

$$v_{\text{eff}}(\mathbf{r}) = v_{\text{eff}}^0(\mathbf{r}) + \delta v_{\text{eff}}(\mathbf{r})\ , \qquad (34)$$

where $v_{\text{eff}}^0(\mathbf{r})$ is the sum of the external potential $v(\mathbf{r})$, the electronic Hartree potential, and the exchange-correlation potential. The quantity $\delta v_{\text{eff}}(\mathbf{r})$ may be obtained from a RF model, and it will depend, to a first-order approximation, on the induced electron density $\delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho^0(\mathbf{r})$. If a linear-response model [21] is assumed for simplicity, the reaction-field-induced electron density becomes

$$\delta\rho(\mathbf{r}) = [\epsilon^{-1} - 1]\rho^0(\mathbf{r})\ . \qquad (35)$$

This simplified model of electronic polarization may be used within a KS-like formalism to determine the electron density $\rho(\mathbf{r})$. For instance, if we place the model within the Hartree-Fock-Slater X_α approximation [22], the exchange-correlation potential reduces to

$$\frac{\delta\epsilon_{xc}[\rho]}{\delta\rho(\mathbf{r})} = v_{X\alpha}^0(\mathbf{r})\ , \qquad (36)$$

with

$$v_{X\alpha}^0(\mathbf{r}) = -\tfrac{3}{2}\alpha \left[\frac{3}{\pi}\rho(\mathbf{r})\right]^{1/3} = C(\alpha)[\rho(\mathbf{r})]^{1/3}\ . \qquad (37)$$

Combination of Eqs. (21) and (33)–(37) yields

$$\delta v_{\text{eff}}(\mathbf{r}) = \Phi_R^*(\mathbf{r}) + \delta v_{X\alpha}^0(\mathbf{r})\ , \qquad (38)$$

with

$$\Phi_R^*(\mathbf{r})=[1-\epsilon^{-1}]V_0^* \tag{39}$$

and

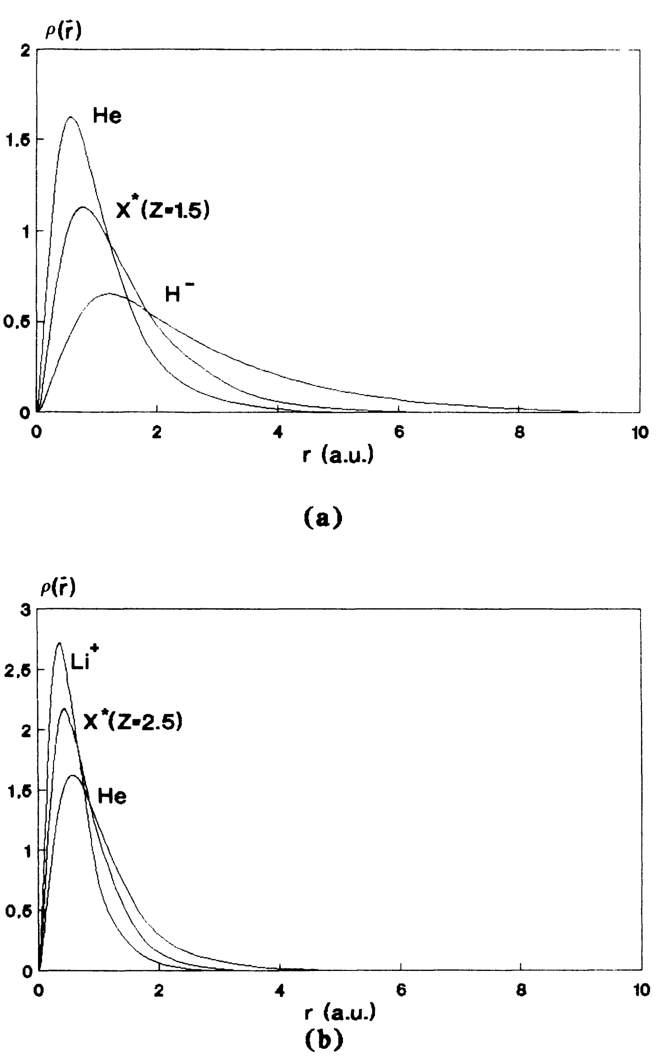
$$\delta v_{X\alpha}(\mathbf{r})=[1-\epsilon^{-1/3}]v_{X\alpha}^0(\mathbf{r}) \tag{40}$$

and the effective KS-like potential, within the X_x approximation, becomes

$$v_{\text{eff}}(\mathbf{r})=v(\mathbf{r})+[1-\epsilon^{-1}]V_0^*+[1-\epsilon^{-1/3}]v_{X\alpha}^0(\mathbf{r})\ . \tag{41}$$

Substitution of Eq. (41) into Eq. (32) yields the set of KS orbitals $\phi_i(\mathbf{r})$, which are then used to build up the electron density via Eq. (31).

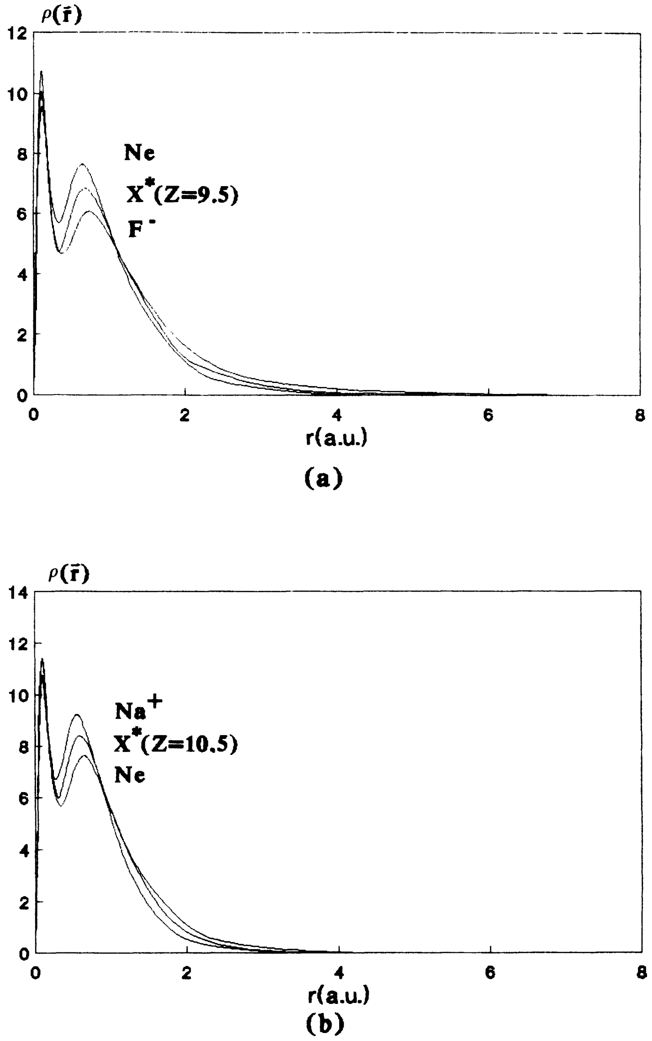
The procedure to obtain the ZTS electron density in the presence of an external electrostatic field, implemented within the X-α approximation, was used to test the quality of approximation (22). The comparison of the ZTS and Levy's average electron density was done for the following systems (using a low dielectric constant value $\epsilon=2.0$, consistent with an electronic polarization model): the $(\mathrm{H}^-,\mathrm{Li}^+)_{\mathrm{He}}$ isoelectronic pair which involves He as the neutral reference system (Fig. 2) and the $(\mathrm{F}^-,\mathrm{Na}^+)_{\mathrm{Ne}}$ isoelectronic pair, involving Ne as the neutral reference system (Fig. 3). It may be seen that in all the systems studied, the ZTS electron density is located at the midpoint between the corresponding reference densities $\rho_A(\mathbf{r})$ and $\rho_X(\mathbf{r})$.



(a)

(b)

FIG. 2. Variation of the electron density with distance from the nucleus in atomic units. The ZTS electron density in solution for (a) $Z^*=1.5$ is compared with those of He and H^- and that for (b) $Z^*=2.5$ is compared with those of He and Li^+. A high-frequency dielectric constant $\epsilon=2.0$ was used (see the text).



(a)

(b)

FIG. 3. Variation of the electron density with distance from the nucleus in atomic unis. The ZTS electron density in solution for (a) $Z^*=9.5$ is compared with those of Ne and F^- and that for (b) $Z^*=10.5$ is compared with those of Ne and Na^+. A high-frequency dielectric constant $\epsilon=2.0$ was used (see the text).

IV. CONCLUDING REMARKS

An approximate theory for the treatment of ion solvation for singly positive and negative charged atomic ions has been presented. The polarizable host has been modeled through an effective medium, and the ion-solvent interactions treated within the reaction field theory. The most relevant aspects of the proposed model are the following.

(i) The formalism uses the electrostatic potential at the nucleus as the basic property for the description of the ion-solvent interactions. This quantity is in general described more accurately than total energies for atoms. As a result, anions and cations may be treated within a unified formalism and the problem of introducing arbitrary empirical ionic radii is avoided and replaced by integration in $[0,\infty]$.

(ii) The present model may be easily implemented within a density-functional theory formulation for the self-consistent treatment of the ion-solvent interactions. Although our model was developed within a simplified scheme, where correlation effects are not included, the method is not dependent upon this approximation and may be extended to include correlation effects upon solvation.

On the other hand, some limitations are present in the proposed formalism. For instance, all the solute polarization is assumed to be electronic in nature. Orientational (temperature-dependent) effects are not introduced in the present formulation of solvation effects. However, this limitation allowed us to adopt a simple linear-response model for the representation of the induced electronic polarization through the polarization of an electron gas under the effect of an electrostatic external field. This induced electron density is to be interpreted as the response of electrons moving independently under the influence of an effective potential, including the reaction field effect.

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