Effect of Overscreening on the Localization of Hydrated Electrons

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The problem of the ground state of hydrated electron is revisited with a focus on the effects due to nonlocal dielectric response of water. The standard variational analysis is performed. It takes into account – in addition to nonlocal polarization of nuclear modes – the electron repulsion from the closed shells of water molecules, a possibility to form a cavity around the electron and the interaction of the hydrated electron with the high frequency electronic degrees of freedom of water. The classical dielectric continuum limit, shown for a reference, gives the ground state hydration energy that is 2.5 times smaller than the experimental value. The situation alters dramatically if one accounts for the nonlocal dielectric response of water. If one takes literally the existing MD simulation data for the static wave-vector dependent dielectric response function (with an "over-screening" resonance at $k \sim 3\,\text{Å}^{-1}$), the hydration energy becomes 3 times larger than the experimental one. Thus, an over-screening may have a dramatic effect on the formation of the hydrated electron. For a reduced height of the "over-screening peak", the ground state energy reduces to the measured value. At the same time, over-screening enhances the localization of electrons. The undamped resonance gives rise to an unphysically small localization radius. A reduced resonance, that provides the correct ground stage energy, is better in this respect but it still gives very compact localization: 2/3 of the Bohr radius. It is thus concluded that either the defect structure of water around the electron suppresses the resonance, or the models of bulk water, which predict a high peak in the response function, are inadequate. The study paves the way to future molecular or phenomenological multi-order parameter models, in which the density and polarization of molecular dipoles and charge density distributions of the solvated electron are considered

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on the same footing. Such models might reveal the reduction of over-screening near the excess electron.

1. Introduction

Electron solvation in dielectric solvents, particularly in aqueous environments, has been a focus of intensive research for many years [1–12]. Experimental work has provided energetic and spectroscopic [2–6, 8, 10, 11] and, more recently, dynamic information [13–16] on electron hydration. Theoretical approaches to this issue have relied on continuum dielectric theories [1, 7, 9, 12] and more recently on numerical simulations based on mixed quantum-classical descriptions [17, 18]. Recently, *ab-initio* calculations on relatively small electron water systems were reported [19].

While numerical simulations of quantum and classical solvation are very important for providing detailed information on the energetics and dynamics of solvation processes, linear response theories based on continuum dielectric models of solvation remain useful for providing a good qualitative, and sometime semi-quantitative picture of dielectric solvation. Thus, variants of the Born theory of solvation are often used as first estimates of solvation free energies of classical ions. The corresponding theory for electron solvation is based on calculating the free energies solvation as sums of kinetic and electrostatic terms

$$W = E_{\mathrm{K}} + E_{\mathrm{es}} \tag{1}$$

$$E_{\mathrm{es}} = \left(\frac{1}{2} \langle \psi | e\Phi | \psi \rangle \right)_{\mathrm{solvent}} - \left(\frac{1}{2} \langle \psi | e\Phi | \psi \rangle \right)_{\mathrm{vacuum}} \tag{2}$$

$$E_{\mathrm{K}} = -\frac{1}{2} \langle \psi | \nabla^2 | \psi \rangle = \frac{1}{2} \int \mathrm{d}r |\nabla \psi(\mathbf{r})|^2 \,, \tag{3}$$

where ψ is the wave function of the electron and $\langle ... \rangle$ stands for the ground state averaging, e is the electron charge and Φ is a solution of the Poisson equation

$$\nabla^2 \Phi = -\frac{4\pi}{\varepsilon} \rho(\mathbf{r}) \tag{4}$$

and $\rho(\mathbf{r})$ is the charge density

$$\rho(\mathbf{r}) = e|\psi|^2 \,. \tag{5}$$

In Eq. (2), $(\ )_{\mathrm{solvent}}$ and $(\ )_{\mathrm{vacuum}}$ denotes results obtained using the given ε, and $\varepsilon = 1$, respectively. According to the Poisson equation

$$\langle \psi | \Phi | \psi \rangle = -\frac{\varepsilon}{4\pi} \int \mathrm{d}^3 r \, \Phi \nabla^2 \Phi = \frac{1}{2\pi^2 \varepsilon} \int \mathrm{d}^3 \mathbf{k} \frac{|\rho(\mathbf{k})|^2}{k^2} \,, \tag{6}$$

where $\rho(\mathbf{k}) = \int \mathrm{d}^3 \mathbf{r} \, \mathrm{e}^{-i\mathbf{k}\cdot\mathbf{r}} \rho(\mathbf{r})$.

Eq. (1) is used in a variational context: the energy W is minimized with respect to ψ. For the simple choice of a $1S$ trial function

$$\psi(\mathbf{r}) = \sqrt{\frac{1}{8\pi a^3}} \exp\left(-r/2a\right) \tag{7}$$

minimization with respect to the localization radius a yields an estimate, often considered as an upper bound, for the ground state energy E and the localization radius. Eqs. (2) and (3) imply that E is measured relative to the ground state energy in vacuum, so it can be regarded as the hydration energy. The values obtained, $E = -1.32$ eV and $a = 1.18$ Å, are about half the actual (i.e. experimentally observed) values.

While the results of the simplest dielectric continuum model are not unreasonable, the model itself is grossly oversimplified. First, the use of a position independent dielectric response is questionable because the Pauli repulsion of the water molecules from the excess electron depletes the water density near the center of the hydrated electron (numerical simulations support this intuitive expectation). Second, this repulsive short distance interaction was not taken into account in the total energy calculation. Finally, the formulation outlined above was written in terms of a homogeneous, local dielectric constant ε. However the relevant distance scale implies that non-local effects should not be disregarded. For these reasons, a re-examination of these issues is desirable. There was recently a revival of activity aimed at determining the true form of the non-local dielectric function of water by means of statistical theory and molecular dynamics computer simulations [20–22]. In the present work we evaluate the solvation energy, applying a model dielectric function that represents the results of these calculations, while at the same time accounting also for short range, non-electrostatic contributions [23] to the electron–water interaction.

2. The non-local dielectric response of water

Non-local electrostatics describes linear response in a homogeneous and isotropic medium by the relation

$$\mathbf{D}_\alpha(\mathbf{r}) = \int d\mathbf{r}' \varepsilon_{\alpha\beta}(\mathbf{r} - \mathbf{r}') \mathbf{E}_\beta(\mathbf{r}') \qquad (\alpha, \beta = x, y, z) \tag{8}$$

between components of the electrostatic field vector $\mathbf{E}$ and the electric displacement vector $\mathbf{D}$, where $\varepsilon_{\alpha\beta}(\mathbf{r})$ is the static nonlocal dielectric tensor. In Fourier-space this equation relates the longitudinal (in $\mathbf{k}$) components of the $\mathbf{E}$ and $\mathbf{D}$ fields

$$\mathbf{D}_{\|}(\mathbf{k}) = \varepsilon(\mathbf{k})\mathbf{E}_{\|}(\mathbf{k}), \tag{9}$$

where the longitudinal static dielectric function is given by

$$\varepsilon(\mathbf{k}) = \sum_{\alpha\beta} \frac{k_\alpha k_\beta}{k^2} \int d\mathbf{k}_\| e^{-i\mathbf{k}(\mathbf{r}-\mathbf{r}')} \varepsilon_{\alpha\beta}(\mathbf{r}-\mathbf{r}') . \tag{10}$$

The following functional form for the non-local dielectric function represents fairly well a broad class of theoretical and simulation results [24]

$$\frac{1}{\varepsilon(k)} = \frac{1}{\varepsilon_\infty} - \left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_s} \right) f(k)$$

$$f(k) = \left[\frac{1-c}{1+\lambda_1^2 k^2} + \frac{c(1+l^2 k^2)}{(1+\lambda_2^2 k^2)(1+l^2 k^2) - L^2 k^2} \right] , \tag{11}$$

where ε_∞ and ε_s are the optical and the static dielectric constants respectively, taken in the calculation below to be 2 and 80. The other parameters, c, λ_1, ℓ and L are chosen to fit the numerical simulation results. Such a representative set [24], $c = 0.3$, $\lambda_1 = 2.83$, $\lambda_2 = 0.19$, $l = 2.13$ and $L = 2.3135$ will be taken
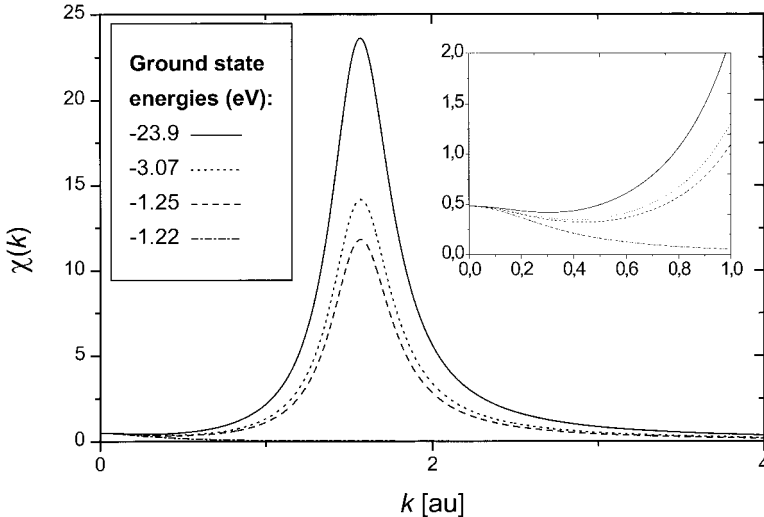
Fig. 1. The wave-vector dependence of response functions, which lead to the indicated values of the ground state energy of hydrated electron. The inset is a blow up of the small wave-vector domain. The functions are given by Eq. (11) with parameters fixed as presented in the text, except for c which is varied to show different ground state energies. For the curves from top to the bottom $c = 0.3, 0.18, 0.15, 0$, respectively. The $c = 0$ curve corresponds to the pure Lorentzian approximation. A moderate variation of the peak height leads to dramatic change in the ground state energy for the reason clarified in Figs. 3 and 4.

as a starting point in our calculations, though other options will also be considered. Fig. 1 shows the functional form of the resulting dielectric susceptibility function

$$\chi(k) = 1 - \frac{1}{\varepsilon(k)} , \qquad (12)$$

which is the quantity that determines the response of the medium polarization to the external field.

Before applying electrostatics, whether local or nonlocal, we must consider the timescales involved. At issue is the question how the solvent response is reflected in the Schrödinger equation. We make the standard assumption that the solvent nuclear motion is much slower than the characteristic time associated with the solvated electron, so that the nuclear motion responds to the fully developed electron wavefunction. In contrast, the solvent electronic response is assumed to be fast relative to the solvated electron motion, so it screens the *local* solvent-electron interaction potential. The solvation energy therefore contains contributions from interactions with both fast and slow environmental modes, but they should be calculated in different ways, as discussed below. In view of this perspective we rewrite the response function, Eqs. (11) and (12) as

$$\chi(k) = \chi_{\infty}(k) + \chi_{n}(k) , \qquad (13)$$

where

$$\chi_{\infty}(k) = 1 - \frac{1}{\varepsilon_{\infty}} \qquad (14)$$

is the contribution due to the fast electronic polarization of the medium, while

$$\chi_{n}(k) = \left(\frac{1}{\varepsilon_{\infty}} - \frac{1}{\varepsilon_{s}} \right) f(k) \qquad (15)$$

is due to the slow nuclear motion. These two components of the dielectric response contribute differently to the electrostatic part of the solvation energy, as described below.

3. Solvation energy

The solvation energy W for an electron is the energy taken ($W > 0$) or released ($W < 0$) when the electron is transferred from a free, zero momentum, plane wave state (uniform density) to a localized state in the dielectric continuum. The simple theory that leads to Eq. (1) associates two terms, kinetic energy and electrostatic potential energy, with this transition. Here we consider a more general picture which takes into account also the short-range repulsion between the excess electron and the cores of the water atoms. This short range repulsion

may lead to the formation of a cavity-like structure, which we take here simply as a sphere of radius R. This implies also a surface tension contribution to the overall energy. The radius R and the parameters that define the trial ground state electron wavefunction are treated as variational parameters to be determined by energy minimization. The energy to be minimized is then written as the sum

$$E = E_{\rm K} + E_{\rm es} + E_{\rm R} + E_{\rm S} + E_{\rm VP} \tag{16}$$

of kinetic, electrostatic, Pauli-repulsion, surface and volume-pressure energies, respectively.

Kinetic energy

For the spherically symmetric wavefunction expected for the ground state, Eq. (3) reduces to

$$E_{\rm K} = \frac{1}{4\pi^2} \int\limits_{0}^{\infty} {\rm d}k \cdot k^4 |\psi(k)|^2 \,, \tag{17}$$

where

$$\psi(k) = \psi(\mathbf{k}) \equiv \int {\rm d}\mathbf{r}\, e^{-i\mathbf{k}\cdot\mathbf{r}} \psi(\mathbf{r}) = \int\limits_{0}^{\infty} {\rm d}r \cdot r^2 \frac{\sin(kr)}{kr} \psi(r)\,. \tag{18}$$

Electrostatic energy

As discussed above, the electrostatic solvation energy should be estimated differently for the slow (nuclear) and the fast (electronic) part of the solvent response, and is therefore written as a sum of the corresponding contributions

$$E_{\rm es} = E_{\rm es}^{\rm (n)} + E_{\rm es}^{\rm (el)}\,. \tag{19}$$

Consider first the nuclear response, which is assumed slow enough relative to the excess electron timescale, so that it responds to the fully developed excess electron charge density. In the first approximation, which neglects the presence of a cavity in the solvent structure, one may use the Dogonadze–Kornyshev equation [25, 26] for the corresponding contribution to the electrostatic energy. In the spherically symmetric case

$$E_{\rm es}^{\rm (n)} = -\frac{1}{\pi} \int_{-\infty}^{\infty} {\rm d}k\, \chi_{\rm n}(k) [\rho(k)]^2 \,, \tag{20}$$

where

$$\rho(k) = \int_0^\infty dr \cdot r^2 \frac{\sin(kr)}{kr} \rho(r) \tag{21}$$

and $\rho(\mathbf{r})$ is given by Eq. (5).

The presence of a cavity breaks both homogeneity and isotropy. We can still get a relatively manageable description by adopting the "cut-out" approximation [27, 28]

$$\chi_{\alpha\beta}^{(n)}(\mathbf{r}, \mathbf{r}') = \chi_{\alpha\beta}^{(n)}(\mathbf{r} - \mathbf{r}')\theta(r - R)\theta(r' - R), \tag{22}$$

where θ is the usual step function, $\theta(x) = 0$ for $x < 0$ and $\theta(x) = 1$ for $x > 0$. In the spherically symmetric case this leads to [28]

$$E_{es}^{(n)} = -\frac{1}{\pi} \int_0^\infty dk \chi_n(k) [\rho(k) - \Delta\rho(k)]^2, \tag{23}$$

where

$$\Delta\rho(k) = \frac{R}{\pi} \int_0^\infty dk' \rho(k') F(kR, k'R) \tag{24}$$

and

$$F(u, v) = \frac{\cos(u + v) - \cos(u - v)}{uv} + \frac{\sin(u + v)}{u + v} + \frac{\sin(u - v)}{u - v}. \tag{25}$$

Consider now the contribution of the dielectric response of the medium electrons. Since we assume that it is fast relative to the excess electron timescale, we take it as a part of the excess electron Hamiltonian, a contribution to the position dependent potential. In the absence of a cavity we take this potential to be of the Born-like form:

$$V_{el}(\mathbf{r}) = -\frac{e^2}{2\xi} \left(1 - \frac{1}{\varepsilon_\infty}\right); \quad r \gg R, \tag{26}$$

where ξ is a correlation length of the medium electronic polarization, to be specified below. When there is a cavity, we keep this form far outside the cavity. Well inside the cavity the solvent contribution to the electron energy should be smaller, and we assume the form

$$V_{el}(\mathbf{r}) = -\frac{e^2}{2(\xi + R)} \left(1 - \frac{1}{\varepsilon_\infty}\right); \quad r \ll R. \tag{27}$$

It is convenient to use these limiting behaviors together with a switching function that will bridge between these two response regimes. Thus we write

$$V_{el}(\mathbf{r}) = V_{el}(r) = -\frac{e^2}{2\xi}\left(1 - \frac{1}{\varepsilon_\infty}\right)S(r, \xi, R)\,, \tag{28}$$

so that $S \to 1$ when $r \ll R$ and $S \to \xi/(\xi + R)$ when $r \gg R$. The exact form of S makes little difference to the computed energy. We have used the form

$$S(r, \xi, R) = 1 - \left(1 - \frac{\xi}{\xi + R}\right)\frac{1 - \tanh[(r - R)/\xi]}{1 + \tanh[R/\xi]}\,, \tag{29}$$

which has the desired limiting behavior. The corresponding contribution to the solvation energy is the expectation value

$$E_{es}^{(el)} = \int d\mathbf{r}\, V_{el}(\mathbf{r})|\psi(\mathbf{r})|^2 = 4\pi \int_{-\infty}^{\infty} dr\, r^2 V_{el}(r)|\psi(r)|^2 \tag{30}$$

Cavity formation energy

For the surface energy [1, 29] we use the simplest form

$$E_S = 4\pi R^2 \gamma\,, \tag{31}$$

where γ is the surface tension. In general γ may depend on the surface curvature so that $\gamma = \gamma(R)$, but we disregard this dependence. The surface tension of water at room temperature is 72 erg/cm^2. In atomic units ($\gamma = 4.64 \cdot 10^{-5}$) we have

$$E_S = 5.83 \cdot 10^{-4} R^2\,.$$

The hydrostatic pressure term,

$$E_{PV} = (4\pi/3)R^3 P\,. \tag{32}$$

For $P = 1$ atm in au

$$E_{PV} = 1.66 \cdot 10^{-8} R^3\,.$$

For water both terms are much smaller than the other energy terms discussed above. They were included into the calculation in order to check the limiting case of nonpolar liquids, but for water their effect is negligible; the free energy functional E is dominated by other terms. For this reason one should not be concerned about the possible violation of the macrosopic law (Eq. 31) for microscopic values of the radius.

Short range repulsion

To account for the Pauli repulsion of the excess electron from the cores of the water oxygens [30–35], we add a constant positive potential V_R between the

electron and the solvent outside the cavity. This makes a positive contribution to the solvation energy:

$$E_R = V_R \int_R^\infty d\mathbf{r} |\psi(\mathbf{r})|^2 . \tag{33}$$

The parameter V_R can be estimated from the repulsive part of the electron–water pseudopotential by a coarse-graining procedure that takes into account the water density. If, for example, this interaction was written in the form of a Harrison pseudopotential [32, 36], $u \cdot \delta(\mathbf{r} - \mathbf{r}_i)$, where $\mathbf{r}_i$ is the position of the water molecule, then $V_R = un$ where n is the number density. Using a number suggested by Badiali and co-workers [33], $u = 15$ au, this leads to $V_R \cong 0.9$ au. Lower estimates comprise $V_R = 0.15$ au [37].

To complete our model we must specify the length parameter ξ (Eqs. (26) and (27)). In the absence of a cavity:

$$E_{es}^{(el)} + E_R = \left[V_R - \frac{e^2}{2\xi} \left(1 - \frac{1}{\varepsilon_\infty} \right) \right] \int d\mathbf{r} |\psi|^2 = V_R - \frac{e^2}{2\xi} \left(1 - \frac{1}{\varepsilon_\infty} \right) = V_0 . \tag{34}$$

V_0 represents the solvation energy of a "hot, dry" electron. For such a fast electron the cavity did not have time to form, and only the faster, electronic degrees of freedom of the medium could respond to it. V_0 is therefore identified with the "bottom of electronic conduction band". For water, using $V_R = 0.15$ au and the observed value $V_0 \cong -0.037$ au $(= -1 \text{ eV})$, this leads to $\xi \cong 1.34$ au for the correlation length ξ that appears in Eqs. (26)–(29). Shorter values for ξ are obtained for the upper estimate $V_R = 0.9$ au.

Is the particular choice of ξ important? We see that at fixed V_0 the repulsion of the electron from the medium is strongly compensated by the "attraction" to the fast electronic polarizability. Thus, if the cavity radius is small, the last equality in Eq. (34) implies that the choice of V_R and ξ is insignificant because in this case they enter into the total solvation energy only through this combination. In our calculations we find that this is always the case.

This concludes our (admittedly heuristic) approach to the estimate of the ground state energy of the solvated electron. Next we consider the choice of a trial function and its consequence.

4. The trial function

In the calculations reported below we have considered the following trial function

$$\psi(\mathbf{r}) = \sqrt{\frac{1 + 4q^2 a^2}{8\pi a^3}} \frac{\sin(qr)}{qr} e^{-r/2a} . \tag{35}$$

For $q = 0$ this becomes the S wave-function Eq. (9) considered above, however we have allowed more freedom in the variational procedure in order to examine the possibility that, due to the strong medium response associated with the resonance of non-local susceptibility at finite k (see Fig. 1), the ground state wave-function may "wish" to display more structure. Such an option gives a chance to enhance the integrand in Eq. (23) and, thus, lower the energy.

From Eq. (35) we obtain the following expression for the kinetic energy

$$E_K(a, b) = \frac{1 + 4q^2a^2}{8a^2} \tag{36}$$

and the following expressions for the charge density and its Fourier transform:

$$\rho(r) = \frac{1 + 4q^2a^2}{8\pi a^3} \frac{\sin^2(qr)}{q^2 r^2} e^{-r/a} \tag{37}$$

$$\rho(k) = \left[1 + \frac{1}{4q^2a^2}\right] \frac{2\arctan(ak) - \arctan[a(k+2q)] - \arctan[a(k-2q)]}{2ak} \tag{38}$$

Also, E_R of Eq. (33) can be evaluated analytically, resulting in

$$E_R = V_R e^{-R/a} \frac{1}{4q^2a^2} [1 + 4q^2a^2 + 2qa\sin(2qR) - \cos(2qR)] \tag{39}$$

and E_S and E_{PV} are given by Eqs. (31) and (32). The rest of the energy terms, $E_{es}^{(n)}$ (Eqs. (23)–(25)) and $E_{es}^{(el)}$ (Eqs. (28)–(30)) are to be evaluated numerically.

The exponentially decaying form of the trial function Eq. (35) is probably not the best choice in the presence of a cavity. However, in all cases discussed below the cavity radius is found to be negligibly small. This provides and aposteriori justification of the choice Eq. (35).

5. Results and discussion

The variational procedure is defined in terms of the variables a and q that determine the wavefunction, and the cavity radius R. For the minimal values of these parameters we may calculate the ground state hydration energies. Next we present some results of this procedure.

Fig. 1 shows the shape of the response function, Eq. (11) for several values of the parameter c that determines the intensity of the overscreening resonance. $c = 0.3$ is the value determined in the simulations of Ref. [24]. $c = 0.18$ yields a solvation energy of ~ 3 eV, of the order of the experimental value. $c = 0$ represents the Lorentzian approximation that was applied to the problem of localized state of solvated electrons in [12, 38, 39] (with no cavity effects
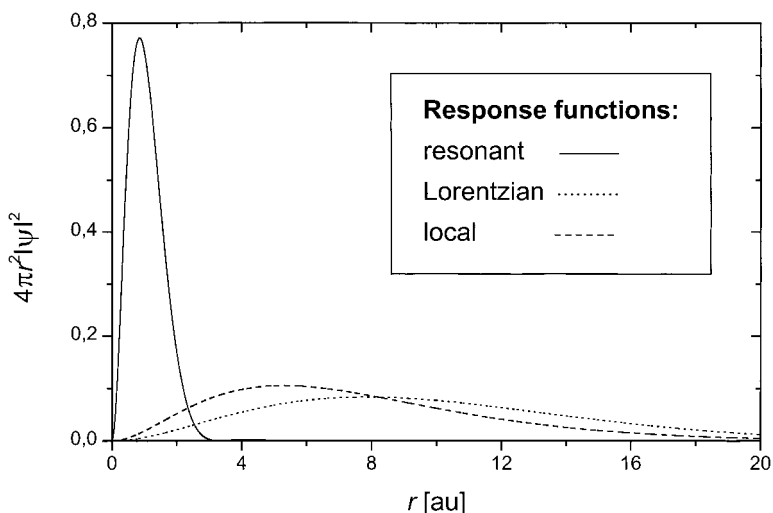
Fig. 2. The radial distribution of the excess electron density, shown for three response functions: the resonant response function ($c = 0.18$, that provides the observed value of the ground state energy, at the fixed set of the rest parameters discussed in the text), the classical (local) dielectric continuum model ($\lambda_1 = 0$), and the Lorentzian approximation ($c = 0$). The resonant case exhibits much more compact electron localization, as compared to the classical limit. For the Lorentzian model, the wave-function is more delocalized than in the classical case, because of reduced ability of the nuclear polarization to respond to the field of the excess electron [12, 38].

taken into account). The corresponding calculated ground state energies show that even the moderate variation of the peak intensity changes the energy dramatically.

The ground state wave functions are shown in Fig. 2 for the resonance response function with $c = 0.18$, for the Lorenzian approximation, $c = 0$ and for the classical (local) response model. Though q is found to be nonzero (~ 1 au) for the resonance approximation of the medium response (c.f. Fig. 3, which shows the potential energy surface as a function of a and q), the related oscillations of the electron density are too small to be seen on these graphs. For the classical continuum and the Lorentzian models the variational procedure yields $q = 0$, as expected.

Fig. 3 shows the solvation energy, Eq. (16), as a function of the wavefunction parameters a and q. The computed energy surfaces have two minima: one for zero q and one for a nonzero q. The latter becomes more stable at a critical intensity of the response function peak as determined by the parameter c. Fig. 4, which shows the localization radius a as a function of this parameter, reflects the "transition" which takes place at the critical value $c \approx 0.16$.

For the case $c = 0.18$ which corresponds to a calculated ground state energy of the order observed experimentally, the resulting localization radius is
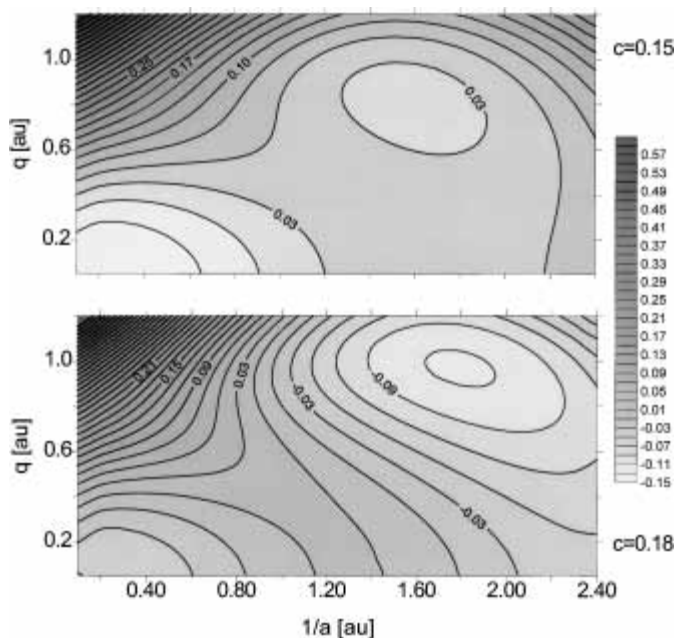
Fig. 3. Contour maps of the total energy [au] as a function of the inverse localization radius a^{-1} and the oscillation wave-number q. The maps, shown for the two values of the height of the resonance of the response function (which differ by only 20%) show a remarkable behavior. There are two minima of different depth, for zero and nonzero q. The nonzero q minimum goes together with a much stronger localization (larger $1/a$). For the case of $c = 0.15$ (the lower resonance peak) the well at $q = 0$ is deeper. For $c = 0.18$ (the higher peak) the well, located $q \cong 1$ au is deeper. There should be then a critical value of c, where the transition from moderate to strong localization takes place (c.f. Fig. 4).

two thirds of the Bohr radius; for larger c values (higher peaks) it is even smaller. It would be tempting to speak of a nontrivial collective effect: "resonance compression" or "resonance localization" of the hydrated electron wavefunction, however this is not supported by computer simulations that yield a localization radius of ~ 2 Å [17, 18]. On the other hand, the pure Lorentzian approximation gives a swollen a of 5 Bohr radii, in accordance with [12, 38]. The classical continuum limit lies in between: 2.7 Bohr radii, as in the classical works on the localization of hydrated electron [1, 7, 9, 12].

The apparent unphysical value obtained for the localization radius for the resonance intensity parameter c that corresponds to the experimental energy deserves further study. Since the relevant range of parameters is very close to the critical transition seen in Fig. 4, small inaccuracies in the theory may account for this disparity. At the same time it is intriguing to note that the simulations of Refs. [17, 18] could possibly not see the existence of a very localized electron because the grid used in these quantum calculations was too
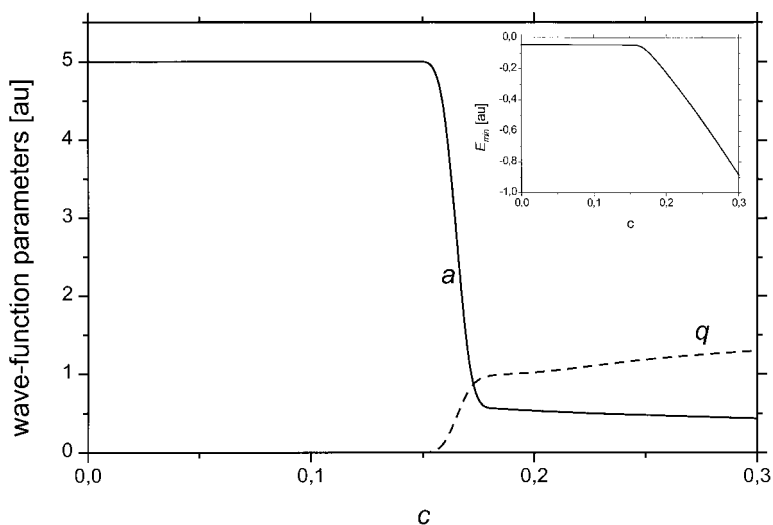
Fig. 4. The transition from a moderate to strong delocalization, following the "variation" of the parameter c that determines the resonance contribution to the nonlocal dielectric response. The transition is accompanied by the appearance of the oscillating component of the charge distribution. Calculations where made with a 0.01 step-size for c, and therefore the spline curve does not show the, presumably, abrupt character of transition. The inset shows that just where the transition occurs, the energy levels off to a plateau. This corresponds to the domain of weak resonance where its effect is negligible. [In reality c is not the parameter which can be controllably varied, but a poorly known property of the water nonlocal dielectric response].

coarse. Still, it is hard to imagine an electron localized within distances considerably smaller then intermolecular separation even in a strongly polar medium as water.

In all cases studied the cavity radius was found to be vanishingly small. The Pauli repulsion in water seems to be almost fully compensated by the electronic response of the medium, which favors the smaller cavities. It should be emphasized that the solvated electron does localize quite compactly for small enough values of the parameter c (see Fig. 4), however this localization is not accompanied by forming an appreciable cavity in the water structure. Thus, in contrast to electrons in liquid helium and other liquid rare gases [29, 32], water accommodates the hydrated electrons without forming well defined 'bubbles'. It should be noted however that molecular dynamic simulations show reduced water density in the vicinity of the hydrated electrons [40]. This does not appear in the present calculation that models the cavity as an empty bubble, but may appear in a theory where the excess electron distribution, the local water density and the local polarization are considered on the same footing.

Such a theory would hopefully harmonize the picture of the localization of a hydrated electron, "disturbed" by the current report. The main message of

this report is that the over-screening, if it exists, does have dramatic effects on electron localization. The response function obtained from molecular dynamics simulation appears to overestimate these effects. They would most likely be damped by perturbations in the water structure about the solvated electron, if such perturbations where allowed in the theory [24, 41].

Acknowledgements

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