CONDENSED MEDIA

Delocalized States of Excess Electrons in Clusters

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Abstract – The functional of the total energy of an excess electron in a cluster of polar molecules is used to find spherically symmetrical solutions corresponding to the extremal functional values. The problem is solved in the continual approximation. There exist two different types of solutions corresponding to two types of states. Solutions of one type describe an electron localized within the cluster, while those of the other correspond to the state in which the electron density is mainly distributed outside of it. The cluster is shown to have a critical size at which the two solutions coalesce. The smaller clusters do not have states with electrons localized within them. For clusters of n water or ammonia molecules, the energies of localized states corresponding to various n values are in close agreement with experimental values. Estimates of the number of molecules necessary for the formation of bound polaron states also agree with available experimental data.

According to modern views, a solvated electron does not belong to a particular molecule but participates in collective interactions with many atoms of the polar medium. This in turn implies (see review [1]) that starting with a certain size, clusters containing the same molecules as those of the polar medium should also interact with excess electrons. A study of the dependence of the properties of an excess electron in a cluster on the cluster size should shed light on the patterns of electron solvation in condensed media. Thanks to progress in experimental techniques, precision measurements of the energy of binding of excess electrons with small water and ammonia clusters comprising n molecules were performed over a wide range of cluster sizes: $n = 2, 6, 7$, and $11 - 69$ for water and $n = 41 - 1100$ for ammonia [2, 3]. At the same time, there is still no consistent theory satisfactorily describing the observed phenomena.

In this work, excess electrons in clusters are treated in terms of the polaron model based on a continual description of the medium and on representing a cluster of polar molecules by a dielectric sphere in the vacuum. We proceed from the consistent polaron theory developed by Pekar [4] and the results obtained in our works on extended electron states in polar media [5, 6] and globular proteins [7, 8].

MATHEMATICAL MODEL

Clusters are treated using the continual model. Let Ω be the region occupied by a cluster (a sphere of radius R). According to Pekar [4], the total energy functional for the excess electron that strongly interacts with the polar medium can then be written as

$$I_F[\Psi, \Pi] = \frac{\hbar^2}{2m}\int (\nabla\Psi)^2 d^3\mathbf{r}$$
$$- e\int_\Omega \Psi^2 \Pi d^3\mathbf{r} + \frac{\bar\varepsilon}{8\pi}\int_\Omega (\nabla\Pi)^2 d^3\mathbf{r}, \quad (1)$$

where $\Psi(\mathbf{r})$ is the normalized wave function of the electron, $\Pi(\mathbf{r})$ is the potential of medium polarization; m and e are the effective mass and charge of the electron, respectively; $\bar\varepsilon$ is the effective dielectric constant of the medium given by $\bar\varepsilon^{-1} = \varepsilon_\infty^{-1} - \varepsilon_0^{-1}$, where ε_∞ and ε_0 are the high-frequency and static medium permittivities; and $\hbar$ is the Planck constant. On the right-hand side of (1), the integration is over the whole space in the first term and over region Ω in the two others.

To find the extremal values of electron energy and electron wave functions, functional (1) should be varied independently with respect to Ψ and Π under the condition of the normalization of wave function Ψ. After necessary transformations and the introduction of dimensionless variables, the problem of finding the extrema corresponding to spherically symmetrical wave functions reduces to the boundary-value problem

$$y'' + \frac{2}{x}y' + y(z-1) = 0,$$
$$z'' + \frac{2}{x}z' + y^2 = 0 \quad (2)$$

with the boundary conditions

$$y'(0) = z'(0) = 0;$$
$$(X_R + 1)y(X_R) + X_R y'(X_R) = 0; \quad z(X_R) = 0, \quad (3)$$

where X_R is the dimensionless radius of the cluster.

The dimensionless variables are related to the initial ones as follows:

$$r = \hbar(2m|W|)^{-0.5}x;$$

$$\Psi = |W|\,(e\hbar)^{-1}\,(m\bar{\varepsilon}/2\pi)^{0.5}y; \quad \Pi = |W|e^{-1}z. \tag{4}$$

Electron energy W is found from the condition of wave function normalization:

$$|W| = 2me^4\hbar^{-2}\bar{\varepsilon}^{-2}\Gamma^{-2}, \quad \text{where} \quad \Gamma = \int_0^\infty y^2(x)x^2dx. \tag{5}$$

The right-side boundary condition relating y to y' at $x = X_R$ follows from the boundedness of the electron wave function, which at $x > X_R$, is described by the linear Schrödinger equation

$$y'' + \frac{2}{x}y' - y = 0. \tag{6}$$

Therefore for $x > X_R$, the solution nonincreasing at infinity can be represented in the form

$$y(x) = X_R y(X_R)x^{-1}\exp(X_R - x). \tag{7}$$

The dimensional cluster radius R is related to the dimensionless X_R value as

$$R = \hbar(2m|W|)^{-0.5}X_R \equiv \hbar^2(2me^2)^{-1}\Gamma X_R. \tag{8}$$

It follows from (8) that there exists a complex nonlinear relation between R and X_R. If the boundary-value problem [equations (2) and (3)] is solved for a given X_R value, the solution can be used to calculate first Γ and then R. We can find X_R corresponding to some cluster radius R only if the $R(X_R)$ dependence is determined numerically.

NUMERICAL SOLUTION OF THE BOUNDARY-VALUE PROBLEM

The boundary-value problem [equations (2) and (3)] was solved numerically using an approach similar to that described in Balabaev and Lakhno [5 - 8]. We will only mention the main points in order to clarify the essential features of the calculations. The task was considerably simplified by using the CURVE program [9]. The program finds a connected branch of the curve given by the system of equations $f(x) = 0$ in the n-dimensional space of points $[\dim(x) = n, \dim(f) = n - 1]$. The algorithm presupposes the existence of a starting point x_0 for which $f(x_0) \approx 0$. There should also be a subroutine for calculating function f values for given x vectors.

The principal steps of solving the boundary-value problem are as follows: (i) At $x = 0$, equations (2) have a singularity, and, at the first step, the boundary conditions on the left are shifted to a near-by point x_0 (e.g., $x_0 = 0.001$). For this purpose, the $y(x)$ and $z(x)$ solutions in the neighborhood of point $x = 0$ are

expanded in power series. These series are substituted into (2) to find relations between the expansion coefficients; it turns out that all coefficients can be expressed in terms of $y_0 = y(0)$ and $z_0 = z(0)$. (ii) The number of expansion series terms for y_0 and z_0 is chosen such that the values of the functions and their first derivatives at point $x = x_0$ have the required accuracy. (iii) The Cauchy problem is solved numerically for system (2) with various y_0 and z_0 values along the $[x_0, X_R]$ segment. The integration gives the $y(X_R) \equiv y(X_R; y_0, z_0)$ and $z(X_R) \equiv z(X_R; y_0, z_0)$ values and the values of the corresponding derivatives. The boundary-value problem (2) and (3) can be considered solved if these values satisfy conditions (3) at $x = X_R$. This is achieved step by step. (iv) For given y_0 and z_0, the Cauchy problem is solved on some segment $[x_0, x_C]$. The solution $z(x)$ intersects the x axis at some point x^*. Let us set $X_R = x^*$ and find the solution to the boundary-value problem using this X_R value. This leaves only one unsatisfied boundary condition relating $y(X_R)$ to $y'(X_R)$ at the right-hand end. (v) CURVE is used to find a curve given by one equation with two variables:

$$F(y_0, z_0) \equiv z(X_R; y_0, z_0) = 0. \tag{9}$$

The X_R value and the initial values of y_0 and z_0 at curve (9) are taken from the preceding step. The calculation of F for known argument values is described above. The obtained curve relating y_0 and z_0 at $X_R = 10$ is shown in Fig. 1. Figure 2 gives the $\varphi(y_0) \equiv (X_R + 1)y(X_R; y_0, z_0) + X_R y'(X_R; y_0, z_0)$ dependence obtained for (y_0, z_0) points of the curve shown in Fig. 1. Figure 2 shows that $\varphi(y_0)$ is zero at various curve (9) points. It follows that the corresponding y_0 and z_0 values correspond to the solutions to the boundary value problem given by (2) and (3), because all four boundary conditions (3) are satisfied at these points. (vi) Solutions to the boundary-value problem at various X_R are determined by two conditions for the corresponding Cauchy problem:

$$F_1(y_0, z_0, X_R) \equiv z(X_R; y_0, z_0) = 0,$$

$$F_2(y_0, z_0, X_R) \equiv (X_R + 1)\,y(X_R; y_0, z_0) \tag{10}$$

$$+ X_R y'(X_R; y_0, z_0) = 0.$$

We know how to determine the values of the left-hand sides in system (10); the (y_0, z_0, X_R) point satisfying (10) is also known. The curve relating these three variables can therefore be reproduced using CURVE.

Equations (4) and (5) make it possible to convert dimensionless variables in the solutions to the boundary-value problem (2) and (3) into dimensional ones and calculate cluster radius R, electron energy W, total energy I_F, and other physical quantities and establish relations between them.

SOLUTIONS FOR THE GROUND STATE

Figure 3 shows the dependence of the magnitude $|W|$ of the ground state energy of an electron within a cluster on cluster radius R. This dependence is indicative of

the existence of a critical cluster size $R_c \approx 4.091 \bar{\varepsilon}/\mu$ (Å), where $\mu = m/m_0$, and m_0 is the mass of the free electron. There are no bound electron states in smaller clusters. At $R > R_c$, ground states can be of two types. The branch situated above the W_c critical value corresponds to the states in which the electron is localized within the cluster; the other branch describes surface electron states. In such states, the electron mainly resides outside the cluster. The $R = R_c$ point is the bifurcation point at which the solutions branch.

The dependence of the total electron state energy in the cluster I_F on cluster radius R is shown in Fig. 4. The branch corresponding to the lower total energy values corresponds to internal (according to our terminology) states while the other branch refers to external or surface states. It follows from Fig. 4 that, for clusters with radii R below the $R_1 = 4.85\bar{\varepsilon}/\mu$ (Å) value, positive total energies correspond to both internal and external states. This means that, in the (R_c, R_1) interval, both states are metastable. When $R > R_1$, internal electron localization becomes energetically favorable. Figure 4 also shows that external states are metastable for clusters of any radius.

Both external and internal states are self-consistent states of the electron–cluster system. They coexist and are separated from each other by a potential barrier.

The wave functions corresponding to the internal and external electron states near the critical cluster radius are shown in Fig. 5. For such a cluster, the probability of the occurrence of an electron within it is 0.95 for the first solution and 0.62 for the second one. The probabilities of the occurrence of an electron outside the cluster are then 0.05 and 0.38, respectively. For the critical cluster radius $R = R_c$, the two solutions coalesce, and the probabilities of finding an electron within and outside the cluster are 0.82 and 0.18.

Figure 6 gives the dependence of electron energy W on reciprocal radius R^{-1} for the ground internal polaron state. Except for a narrow interval corresponding to small R values, the obtained dependence is closely approximated by the function linear in R^{-1},

$$W = -4.43\frac{\mu}{\bar{\varepsilon}^2} + \frac{14.4}{\bar{\varepsilon}}R^{-1}, \tag{11}$$

where the electron energy W is in eV, the cluster radius R is in Å; and $\mu = m/m_0$ is the reduced electron mass.

When R tends to infinity, W tends to $-4.43\mu/\bar{\varepsilon}^2$ eV, coinciding with the polaron energy in a homogeneous polar medium [4, 5].

Note that dependences of form (11), which relate the energy of an electron in a cluster to the cluster size, were also obtained for other models from qualitative considerations (see [1]).
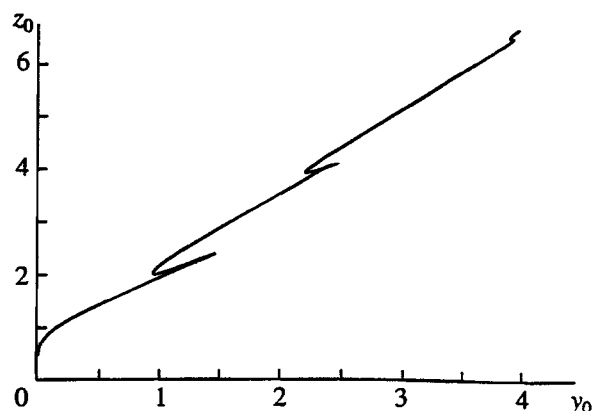

Fig. 1. Relation between y_0 and z_0 parameters ensuring fulfillment of the condition $z(X_R) = 0$ in the corresponding Cauchy problem for (2) at $X_R = 10$ (see text).
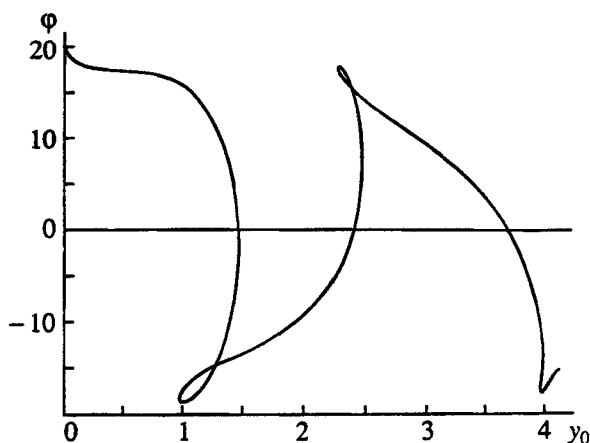

Fig. 2. The $\varphi(y_0)$ dependence for the curve shown in Fig. 1. Fulfillment of the condition $\varphi(y_0) = 0$ provides a solution to the boundary-value problem given by (2) and (3) at $X_R = 10$.
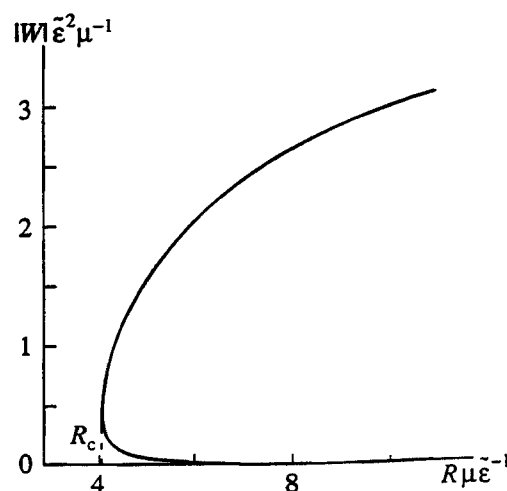

Fig. 3. Electron ground state energy in a cluster $|W|$ as a function of cluster radius R. Energy is given in eV and radius in Å.
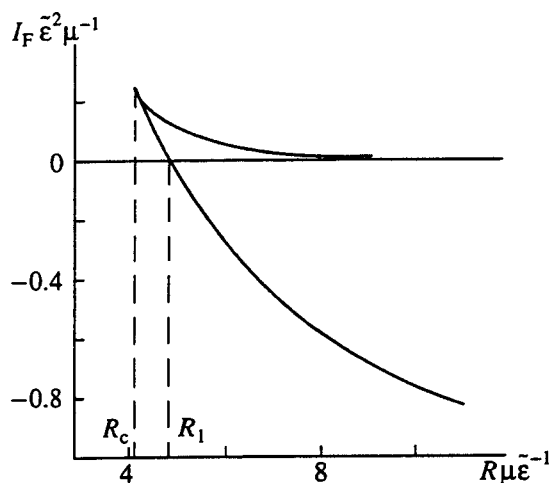
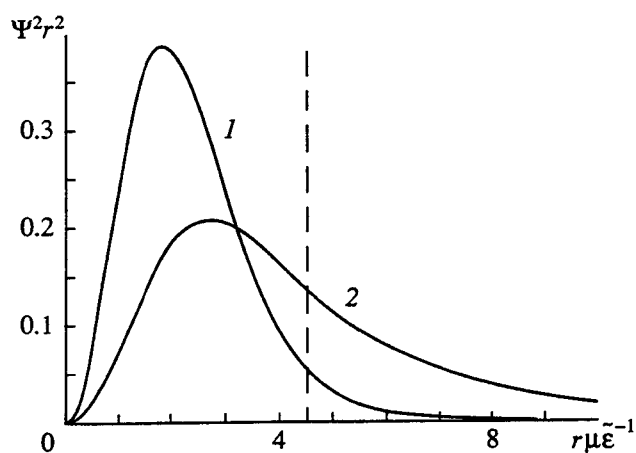Fig. 4. Total electron energy in a cluster as a function of cluster radius. Energy is in eV and radius in Å.

Fig. 5. Wave functions obtained from solutions to (2) and (3) for $R = 4.5\tilde{\varepsilon}/\mu$ (Å); (1) internal electron state and (2) external electron state. The vertical line corresponds to cluster radius $R = 4.5\tilde{\varepsilon}/\mu$.
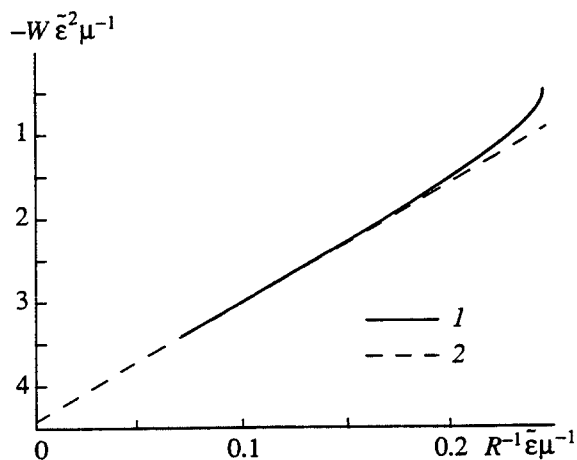

Fig. 6. (1) Dependence of internal electron state energy W on R^{-1} and (2) its linear approximation. Energy in eV and radius in Å.

COMPARISON WITH EXPERIMENT

Much work has been done on the properties of charged clusters. Coe et al. [2, 3] summarize experimental data on the energy of photodetachment of excess electrons from water and ammonia clusters, $(H_2O)_n^-$, where $n = 2 - 69$, and $(NH_3)_n^-$, $n = 41 - 1100$, where $n = 41 - 1100$. The experimental data on water clusters with $n \geq 11$ are very accurately described by the relation

$$W_{exp}, eV = -3.30 + 5.73n^{-1/3}. \qquad (12)$$

Let the cluster radius R and the number of clustered molecules n be related as $R = R_s n^{1/3}$, where R_s is the effective radius of the molecule. Dependences (11) and (12) coincide for $\mu = 0.745\tilde{\varepsilon}^2$, and $R_s = 2.52\tilde{\varepsilon}^{-1}$. The high-frequency and static permittivities of water at room temperature are $\varepsilon_\infty = 1.77$ and $\varepsilon_0 = 80$, respectively. We therefore obtain for the effective permittivity $\tilde{\varepsilon} \equiv \varepsilon_0\varepsilon_\infty/(\varepsilon_0 - \varepsilon_\infty) \approx 1.81$. Therefore, theoretical (11) and experimental (12) dependences coincide for $\mu = 2.44$ and $R_s = 1.40$ Å (note for comparison that in Newton [10], a somewhat larger R_s value of 1.48 Å was used).

Experimental data on the energy of photodetachment of an electron from ammonia clusters $(NH_3)_n^-$ for a wide range of n values, from 41 to 1100, are given in Lee et al. [3]. These data are closely approximated by the dependence

$$W_{exp}, eV = -1.25 + 2.63n^{-1/3}. \qquad (13)$$

A comparison of (13) with universal dependence (11) gives $R_s = 5.5\tilde{\varepsilon}^{-1}$ and $\mu = 0.28\tilde{\varepsilon}^{-2}$. The high-frequency and static permittivities of liquid ammonia at $-33°C$ are known to be $\varepsilon_\infty = 1.77$ and $\varepsilon_0 = 22$, respectively, whence $\tilde{\varepsilon} = 1.92$. Then $R_s = 2.85$ Å and $\mu = 1.04$, which are quite reasonable values.

Let us estimate the critical radii R_c, at which polaron states can appear, and the R_1 radii separating the region of metastable states from that of stable polaron states $[I_F(R_1) = 0$, see Fig. 4]. For water clusters, we obtain $R_c = 3.03$ Å and $R_1 = 3.6$ Å, which gives $n_c = 11$ and $n_1 = 17$. For ammonia, $R_c = 7.85$ Å and $R_1 = 9.3$ Å, which corresponds to $n_c = 21$ and $n_1 = 35$. These estimates closely agree with the existing experimental data on water and ammonia [2, 3].

PROSPECTS FOR FURTHER DEVELOPMENT OF THE THEORY

Owing to mathematical difficulties, we only considered spherically symmetrical solutions to equations (1) and (2). Combined use of the molecular dynamics and density functional techniques led Barnett et al. [11] to conclude that there exists a nonspherically symmetrical surface state of the electron, in which the major part of electron density is localized outside the cluster. There is

good reason to believe that such solutions also exist for polaron equations. Taking into account optical transitions between symmetrical and nonsymmetrical surface states can be expected to improve quantitative agreement with experimental data in the region of small n values. Specifically, it is possible that such solutions also exist in the supercritical region, where $R < R_c$. This would shed light on the nature of experimentally observed weakly bound electrons on water clusters with $n \leq 6$.

Note also that the model according to which clusters are represented by dielectric spheres interacting with electrons was used in Antoniewicz et al. [12] for calculating surface electron states and is likely to be applicable to clusters with fairly large radii. Surface-type solutions obtained in this work are only applicable to comparatively small clusters ($n \leq 10^3$). This follows from the observation that electron energies of surface states rapidly decrease in magnitude with increasing the sphere radius. Therefore starting with some definite sphere size, the frequency of electron oscillations in the potential well responsible for surface states becomes lower than the characteristic frequency of oscillations of dielectric sphere dipole moments. The use of the adiabatic approximation for describing such states ceases to be justified.

ACKNOWLEDGMENTS

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