

# POLARON STATES IN UNCHARGED MOLECULAR CLUSTERS

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A continual model for the cluster of polar molecules is studied. Based on the assumption of the polaron nature of solvated electron, the authors describe experimental data on the  $\text{Na}(\text{H}_2\text{O})_n$  and  $\text{Na}(\text{NH}_3)_n$  cluster ionization.

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## 1. Introduction

Progress in experimental studies of molecular clusters allows recognition of the microscopic nature of electron solvation in condensed media of polar molecules. Currently, experimental data are available on electron photodetachment from charged clusters of water  $(\text{H}_2\text{O})_n^-$  and ammonia  $(\text{NH}_3)_n^-$  [1] and on ionization energy of neutral clusters  $\text{Na}(\text{H}_2\text{O})_n$  and  $\text{Na}(\text{NH}_3)_n$  with sodium impurities [2]. Charged ammonia clusters are found only at  $n \geq 35$ . In contrast, water clusters retain an excessive electron at a virtually arbitrary number of molecules. The data on neutral clusters are available for water at  $n \leq 20$  and for ammonia at  $n < 35$ . The experiments on electron photodetachment from neutral ammonia clusters show that their electron is solvated and its energy tends to the electron energy in solution as the number of molecules increases. As distinct from ammonia clusters, the electron energy in a neutral water cluster becomes constant at  $n \geq 4$ , like that in a hydrated electron.

The above experimental data represent rich material for successive understanding of these phenomena in the framework of a common mathematical model. According to the conventional approach, the bound electron state in a polar medium is conditioned by local polarization of dipole moments of medium molecules, induced by the proper electron itself. Based on the concept of self-consistent electron state and polar continual medium, mathematical models of an excess

electron in the cluster were constructed [3,4]. The model in [4] assumed no cavity formation for the electron. The calculations confirmed the critical size of the charged cluster and had good agreement with experiments. The critical cluster size was found to relate closely to the surface electron state observed experimentally. This surface state of the excess electron in the cluster was first predicted in the quantum molecular dynamics calculation [5].

An attempt to calculate the neutral cluster was undertaken in [2] based on solving the one-electron linear Schrödinger equation with a model potential. It allows one to describe satisfactorily the electron state in a neutral cluster only at  $n \leq 4$ . According to [4], a greater number of cluster molecules causes two-center localization of independent cation and electron. In the present work, to model the neutral cluster, we develop an approach based on the Pekar polaron theory [6] and the works [4,7-9] solving the nonlinear Schrödinger equation. As we show below, the available experimental data can be described within the concept of one-center localization of a cation-electron pair in the cluster.

## 2. Mathematical model

A cluster of polar molecules represents a dielectric polarizable sphere  $\Omega$  of radius  $R$  in vacuum. An alkali metal cation corresponds to the point charge  $Ze$  in the sphere center. The effective surface charge at the cluster boundary is zero. The electron states in the cluster

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are considered the states of a polaron bound by the acceptor potential. The electron is quantized and has certain effective mass  $m = \mu m_0$ , where  $m_0$  is the electron mass in vacuum,

$$\frac{\hbar^2}{2m} \Delta \psi(\mathbf{r}) + e \left( \frac{Ze}{\varepsilon_0 |\mathbf{r}|} + \frac{e}{\tilde{\varepsilon}} \int_{\Omega} \frac{|\psi(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + a \right) \psi(\mathbf{r}) + W \psi(\mathbf{r}) = 0, \quad (1)$$

$$\int_{R^3} |\psi(\mathbf{r})|^2 d\mathbf{r} = 1, \quad (2)$$

$$\tilde{\varepsilon}^{-1} = \varepsilon_{\infty}^{-1} - \varepsilon_0^{-1}, \quad (3)$$

where  $\varepsilon_0$ ,  $\varepsilon_{\infty} = n^2$ , and  $\tilde{\varepsilon}$  are respectively the static, high-frequency ( $n$  is the refractive index), and effective dielectric constants in the cluster. Outside it, in vacuum,  $\varepsilon_0 = \varepsilon_{\infty} = 1$  and  $\tilde{\varepsilon} = 0$ . Inside the cluster the quantity  $a$  takes on a certain constant value governed by continuity of the whole potential at the cluster boundary, while  $a$  is zero outside the cluster. Thus, the polarization potential induced by the distributed electron charge vanishes at this boundary.

Problem (1), (2) is nonlinear in the wave function  $\psi(\mathbf{r})$  and the electron energy  $W$ . At  $R=0$  equation (1) transforms to an ordinary equation for the atomic hydrogen electron. At  $R=\infty$  the problem transforms to that of the  $F$ -center in a homogeneous polar medium [8]. The case of  $Z=0$  corresponding to the charged cluster is considered in [4]. The case of  $Z=1$  corresponds to the neutral cluster. Hereafter,  $Z$  is considered a continuous parameter of the model.

Expression (3) for the effective dielectric constant is derived by Pekar [6] in the double adiabatic approximation: the electron motion is much faster than dipole orientational oscillations of medium molecules, but slower than characteristic oscillations of internal electron states of medium atoms. When studying the model properties,  $\tilde{\varepsilon}$  is considered as a parameter.

Below we present the spherically symmetrical electron states in problem (1), (2), which correspond to the concept of a one-center cation and electron localization in the cluster.

### 3. Solution method

The solution method is based on the approach used in [4, 7-9]. Following [9], the spherically symmetrical solutions to the Schrödinger equation (1) are found by solving the boundary problem

$$\begin{cases} \xi'' + \left( \frac{\eta}{x} - 1 \right) \xi = 0, & 0 < x < x_R; & \xi'' + \left( \frac{\hat{q}}{x} - 1 \right) \xi = 0, & x > x_R; \\ \eta'' + \frac{\xi^2}{x} = 0, & & & \end{cases} \quad (4)$$

$$\xi(x) \in C^1(0, \infty), \quad \xi(0) = \xi(\infty) = 0, \quad \eta(0) = \frac{\hat{q}}{\varepsilon_0}, \quad \eta(x_R) = \hat{q}. \quad (5)$$

Here the electron energy is expressed via the integral of solution to problem (4), (5), as

$$|W| = \frac{2m_0 e^4}{\hbar^2} \frac{\mu}{\tilde{\varepsilon}^2} \Gamma^{-1}, \quad \Gamma = \int_0^{\infty} \xi^2(x) dx.$$

The eigenparameters  $\hat{q}$  and  $x_R$  of problem (4), (5) are the dimensionless cation charge and cluster radius. The relevant dimensional values depend on the solution as

$$Z = \frac{\hat{q}}{\tilde{\varepsilon}} \Gamma^{-1}, \quad R = \frac{\hbar^2}{2m_0 e^2} \frac{\tilde{\varepsilon}}{\mu} \Gamma x_R.$$

Differential equations (4) represent nonlinear "polaron" equations on the interval  $(0, x_R)$  and a linear equation of a hydrogen atom on the interval  $(x_R, \infty)$ .

Let us consider the method of solving the boundary problem (4), (5). By substituting the variables  $\xi' = \rho\xi$ , the equation for  $\xi$ , linear and homogeneous at  $x > x_R$ , is reduced to the Riccati equation

$$\rho' + \rho^2 + \hat{q}/x - 1 = 0.$$

Solution of this equation with the initial condition  $\rho(\infty) = -1$  defines a one-parametric family of the solutions  $\xi(x)$  exponentially decreasing at infinity. Thus, the boundary condition  $\xi(\infty) = 0$  can be numerically transferred to the cluster boundary. We consider two boundary conditions at  $x = x_R$  as equations in two unknowns  $\xi'(0)$  and  $\eta'(0)$  having no initial data at the left. Such a solution method is called shooting. To find a family of solutions corresponding to the same physical charge  $Z$ , let us take three equations: two boundary conditions at  $x = x_R$  and the condition  $\hat{q}\Gamma^{-1} = \text{const}$  in the four unknowns  $\{\xi'(0), \eta'(0), \hat{q}, x_R\}$ . In general, the latter define a curve in four-dimensional space, which can be numerically reproduced by the CURVE code [10] based on an algorithm of moving along a curve.

#### 4. Properties of the model

The nonlinear boundary problem at each set of the parameters  $\{\hat{q}, x_R, \epsilon_0\}$  exhibits multiple solutions, qualitatively different in the number of nodes  $\xi(x)$ . Figure 1 displays the first two solutions in physical variables: the electron density distributions and corresponding potentials. As is seen from the figure, the ground-state electron (curve 1) is virtually localized inside the cluster, while the first excited state (curve 2) is strongly diffusive: the electron density distribution extends far beyond the cluster.

Figure 2 shows the projections of some curves found numerically according to the above method. Every curve defines a family of solutions to the initial nonlinear Schrödinger equation at fixed values of all parameters except for the cluster radius.

As a possible dependence of electron energy on the cluster radius, Fig. 3 shows several families of solution. At  $Z = 0$ , there are reproduced the results for the charged cluster [4], demonstrating its critical size. At arbitrary small  $Z$ ,

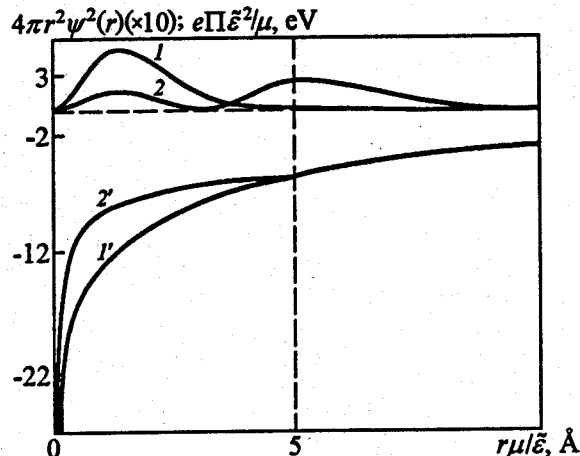


Figure 1. Electron density distributions (1, 2) and the potentials (1', 2') corresponding to ground (1, 1') and excited (2, 2') electron states in the cluster at  $Z\tilde{\epsilon} = 2$  and  $\epsilon_0 = 20$ . The dashed line is the cluster boundary.

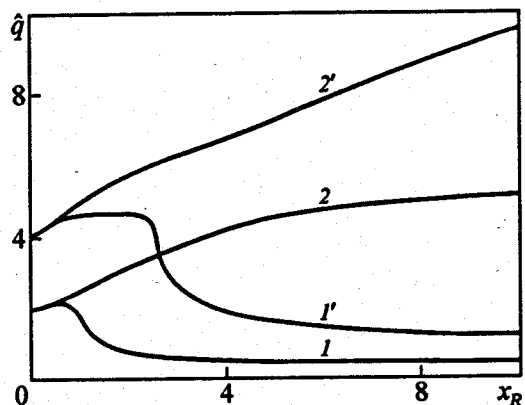


Figure 2. Dimensionless charge  $\hat{q}$ -radius  $x_R$  relation furnishing  $Z\tilde{\epsilon} = 0.1$  along curves 1, 1' and  $Z\tilde{\epsilon} = 2.0$  along curves 2, 2' at  $\epsilon_0 = 20$ . Calculations 1, 2 and 1', 2' correspond to the zero and first modes of wave functions,  $q = 2, 4, \dots$  are the eigenvalues of hydrogen atom dimensionless equation (4).

an S-shaped dependence of energy on radius appears due to formation of a weakly bound hydrogen-like electron state at the cluster. Within a certain radius range three electron states coexist, differing by the electron density distribution in the cluster (Fig. 4). Note that the values  $Z\tilde{\epsilon} < 1$  for the neutral cluster in vacuum are not physical.

The possible dependencies (Fig. 3) of electron energy on the cluster size can be explicitly inter-

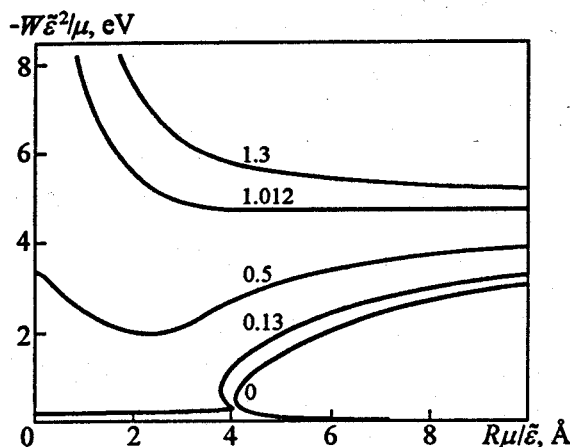


Figure 3. Dependencies of the ground electron energy state on the cluster radius at  $Z\tilde{\epsilon}$  indicated at curves and  $\epsilon_0 = 80$  for water. The calculation at  $Z = 1$  and  $\tilde{\epsilon} = 1.012$  qualitatively corresponds to the constant ionization potential of  $\text{Na}(\text{H}_2\text{O})_m$  clusters. The value  $\mu = 0.7$  quantitatively conforms to the hydrated electron energy 3.17 eV [2].

preted within the model. The electron motion is controlled by two competing factors: a bond with positive charge and a self-consistent interaction with medium polarization. As the cluster radius increases, the bond contributes less to the electron energy due to screening of charge potential by the polar region, while the interaction does more. Therefore, the electron energy can vary nonmonotonically.  $Z\tilde{\epsilon}$  can increase due to the charge  $Z$  increase (bond strengthening) or due to  $\tilde{\epsilon}$  increase (weakening the feedback in electron-polarization interaction).

The electron energy  $W$  at greater  $R$  is well approximated by the linear dependence

$$W \frac{\tilde{\epsilon}^2}{\mu} = A(\epsilon, Z\tilde{\epsilon}) + B(\epsilon, Z\tilde{\epsilon}) R^{-1} \frac{\tilde{\epsilon}}{\mu}. \quad (6)$$

In particular, at  $Z = 0$ , the values  $A$  and  $B$  are independent of  $\epsilon$  and  $\tilde{\epsilon}$ . Relationship (6) can be used to derive a dimensional cluster equation for the real physical system. Then the parameters  $\mu$  and  $\tilde{\epsilon}$  of polaron state should be preassigned as well as the dielectric constant  $\epsilon$ . Assuming  $\mu$  to be independent of the polar region size (at least in large clusters), we conclude from (6) that electron energy variation with cluster radius is qualitatively defined by the  $\tilde{\epsilon}$ , while  $\mu$  merely normalizes the asymptotic energy value. Therefore,

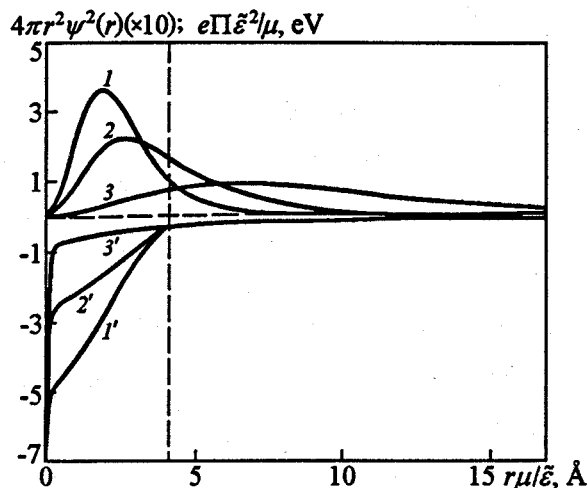


Figure 4. Electron density distributions ( $1-3$ ) and the potentials ( $1'-3'$ ) relevant to internal ( $1, 1'$ ), surface ( $2, 2'$ ), and external ( $3, 3'$ ) electron states in the cluster at  $Z\tilde{\epsilon} = 0.1$  and  $\epsilon_0 = 20$ . Dashed line is the cluster boundary.

effective parameters are unambiguously found by comparing (6) with the dimensional cluster equation approximating experimental data.

## 5. Comparison with experiment

Figure 5 shows the calculated and experimental data for neutral ammonia clusters. The parameters are close to those chosen for the comparison with charged ammonia clusters, based on the analysis of the dimensional cluster equation [4]. As is seen from Fig. 5 in the case of neutral clusters, the calculated dependence approximates well the experimental data at small  $n$ . The calculated dependence interpolated to a condensed medium yields 1.5 eV which conforms to the energy of electron solvated by liquid ammonia [2]. The electron state in the ammonia cluster of radius 10 Å is plotted in Fig. 1.

The experimental data for water can be interpreted via Fig. 3. The dependence at which the energy is constant beginning from a certain radius, arises only at  $\tilde{\epsilon} = 1.012$ . The reasonable values  $\epsilon_\infty = 1.77$  and  $\epsilon_0 = 80$  for water provided that (3) is valid yield  $\tilde{\epsilon} = 1.81$ . At this value an agreement with the experimental data for charged clusters [4] is achieved in the framework of a dimensional equation. The value  $\tilde{\epsilon} = 1.012$  re-

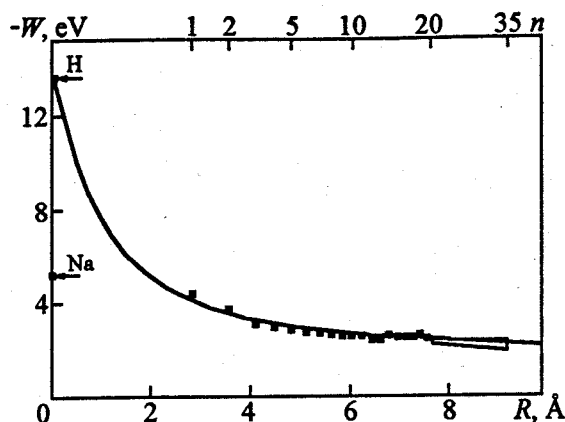


Figure 5. Dependence of the ground-state electron energy on the cluster radius at the values  $\epsilon_0 = 22$ ,  $\tilde{\epsilon} = 2$ ,  $\mu = 1$  relevant to ammonia [4]. The experimental  $\text{Na}(\text{NH}_3)_n$  cluster ionization potentials are plotted for  $n < 35$  [2]. The dot sizes correspond to experimental errors. The arrows at the ordinate axis indicate the energies of hydrogen electron and sodium 3s-electron. The upper scale is the number of cluster molecules. The relationship between the number of molecules and the cluster radius is given by  $R = R_s n^{1/3}$ , where  $R_s = 2.85 \text{ \AA}$  [4] is the effective radius of one molecule.

quires one to accept  $\epsilon_\infty = 1$ . In this case the electron oscillation frequency is close to that of inner atomic shells. Within the model we conclude that the solvated electron strongly interacts with polarization induced by it in the neutral water cluster as compared to the charged one. The experimental data on charged and neutral clusters, extrapolated to a condensed medium, yield electron energies of 3.3 and 3.17 eV, respectively [1, 2]. In spite of these close figures, the calculated electron states significantly differ. The average radii calculated by the electron density distribution are 1.7 and 3.17 Å for the charged and neutral clusters.

## 6. Discussion

Thus, we attained a quantitative agreement with the experimental data for small ammonia clusters within the continual model. The structures of the small clusters considered seem to weakly affect the solvated electron's behavior, which is shown by the absence of pronounced dimensional effects. From this viewpoint, the replace-

ment of a cluster by an effective dielectric sphere is sufficiently justified. As a whole, the problem of the model's applicability remains debatable. Comparison with experiment suggests the model is valid also beyond the initial assumptions accepted in the polaron theory [6].

An attempt to fit the experimental data for neutral and charged water clusters to the considered model shows the electron states differ significantly in such clusters. Validity of this conclusion is related to the model's applicability to hydrated electron states in the cluster.

Finally, we note that the nonmonotonic and S-shaped dependencies in Fig. 3 (corresponding to a nonphysical region of cluster parameters in vacuum) in principle can be realized if the cluster is built into a nonpolar matrix with sufficiently high dielectric constant. Possible physical consequences of these dependencies are also beyond the scope of this paper.

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