POLARON STATES OF ELECTRONS IN CLUSTERS

N.K.Balabaev and **V.D.Lakhno**

Institute of Mathematical Problems of Biology, Russian Academy of Sciences, *Pushchino, Moscow Oblast 142292*

Exact spherical-symmetric solutions to polaron equations are found for a cluster. It is shown that there are two different types of the solutions, corresponding to two different ground states. One of them describes electron localization inside the cluster, while the other is for the state in which electron density is mainly distributed outside the cluster. There is a critical cluster size below which the localized states are absent. At the critical point a bifurcation of solutions takes place. For water clusters the energy of interior electron states falls' into the observed range of experimental data.
PACS: 71.+x, 71.38.+i

1. Introduction

Extended electron states in globular proteins were considered in [1-3]. The use of the simplest model of "dielectric cavity" enabled us to explain quantitatively the IR-absorption band for metalloproteins in the range of charge transfer transitions [1, 2] and the long-range electron transfer in biomacromolecules [3].

Here we use the model developed for proteins to consider extended electron states in molecular dusters. The main suggestion of our treatment is that the clusters containing even a few molecules, ***n*~10**, are considered as continuum which can be polarized by an excess electron interacting with the medium. In polar media this mechanism form the polaron state, where the electron has no chemical bounds with a single molecule. In polar liquids these states can arise without formation of a cavity, where the electron is trapped. Thus, polarization interaction does not break the cluster and can be described by the polaron model. Another point in favor of the polaron model is that the characteristic dimension of wave function for the excess electron can exceed the cluster size (for instance, in a water cluster [4]).

2. Model

Describing of electron states in a cluster, we treat the cluster as continuum. For definiteness sake we consider a water cluster in vacuum as volume **Ω** with dielectric constant ***ε***, confined by surface ***S***. As it follows from electrostatics, any charge in vacuum should be attracted to this region. Thus, the electron in vacuum is trapped by the region with a higher dielectric constant and forms a bound electron state.

Equations for the electron in a polar medium with the local dielectric permittivity depending on space coordinates take on the form

$$\frac{h^2}{2m}\Delta_r \Psi(r) + e\Pi(r)\,\Psi(r) + W\Psi(r) = 0, \tag{1}$$

$$div\left[\tilde{\varepsilon}(r)\,grad\left(\Pi(r)\right)\right] + 4\pi e\left|\Psi(r)\right|^2 = 0, \tag{2}$$

where ***m*** and ***e*** are the effective mass and charge of the electron, ***W*** and **Ψ(r)** are its energy and normalized wave function; $\tilde{\varepsilon}$ ***(r)*** is the effective dielectric constant, introduced by Pekar,

$$\tilde{\varepsilon}^{-1}(r) = \varepsilon_{\infty}^{-1}(r) - \varepsilon_{0}^{-1}(r),$$

where ε_{∞}**(r)** and ε_{0} **(r)** are the high-frequency and static dielectric permittivities ***T***, respectively. These equations coincide with Pekar's equations for polaron [5] in a homogeneous medium when the effective

permittivity is a constant. Below, we consider the case when ε is constant in the region **Ω**, occupied by the cluster, and is zero outside it. That is, potential **Π(*r*)** in (1) is determined by equations

$$\Delta_r \Pi(r) + \frac{4\pi e}{\tilde{\varepsilon}} |\Psi(r)|^2 = 0, \qquad r \in \Omega, \tag{3}$$

$$\Pi(r) = 0, \qquad r \not\subset \Omega. \tag{4}$$

At the surface ***S***

$$\Pi(r)\Big|_{r \in S} = 0 \tag{5}$$

and the electron wave function **Ψ** with its first derivatives are continuous.

In many cases the water duster presents closely-packed water molecules, and is quasi-spherically shaped. In our calculations we conceive the model of the cluster as an uncharged homogeneous sphere of radius ***R*** with an effective dielectric permittivity $\tilde{\varepsilon}$. In this case the set of differential equations (1) and (3)-(5) for a spherically symmetrical solution is rewritten as

$$\frac{h^2}{2m} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \psi(r) \right) + e\Pi(r)\Psi(r) + W\Psi(r) = 0, \tag{6}$$

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \Pi(r) \right) + \frac{4\pi e}{\tilde{\varepsilon}} |\Psi(r)|^2 = 0, \quad r \le R, \tag{7}$$

$$\Pi(r) = 0, \quad r \ge R. \tag{8}$$

The corresponding boundary conditions are

$$\begin{aligned} &\Psi'(0) = \Psi(\infty) = 0, \quad \Pi'(0) = \Pi(R) = 0, \\ &\Psi(R+0) = \Psi(R-0) = 0, \quad \Psi'(R+0) = \Psi'(R-0). \end{aligned} \tag{9}$$

The set of equations (6)-(9) with normalizing condition

$$4\pi \int_0^\infty \Psi^2(r) r^2 \, dr = 1, \tag{10}$$

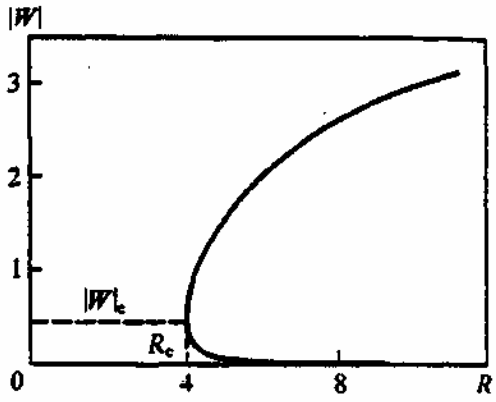

Figure 1. Dependence of the energy $|W|$ of ground electron state on the cluster radius ***R***.

Energy is given in $\tilde{\varepsilon}^{-2}\mu$ eV units, and radius in $\mu^{-1}\tilde{\varepsilon} \cdot \mathring{\text{A}}$.

determines electron wave function Ψ, electron energy W, and total energy I_F, determined by the functional

$$I_F[\Psi, \Pi] = \frac{h^2}{2m} \int (\nabla \Psi)^2 d^3 r - e \int_\Omega \Psi^2 \Pi d^3 r + \frac{\tilde{\varepsilon}}{8\pi} \int_\Omega (\nabla \pi)^2 d^3 r. \quad (11)$$

We note that equations (6)-(9) can be derived directly by variation in functional (11) over wave function $\Psi(R)$ and potential $\Pi(R)$ with regard to normalization condition (10).

3. Solutions for the ground state

The set of equations (6)-(9) can be numerically integrated. Here algorithm for solution is similar to that presented in [1] and will be published elsewhere.

Figure 1 shows the dependence of ground state energy $|W|$ on cluster radius R. As it follows from the figure, bound electron states are absent in clusters with a dimension less than the critical size $R_c \approx 4.091\, \mu^{-1}\tilde{\varepsilon} \cdot \mathring{A}$, where $\mu = m/m_0$ and m_0 is the free electron mass. If $R > R_c$, there are two different types of ground states. The branch over $|W|_c$ in Fig. 1 corresponds to the states in which the electron is localized within the duster. The branch below this critical energy corresponds to the "surface" states of the

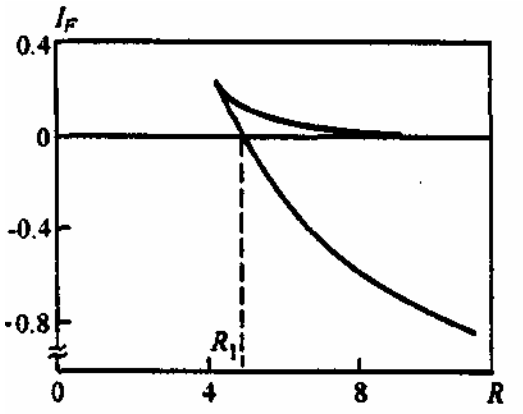

Figure 2. Dependence of the total electron energy on the cluster radius.
(The same units as in Fig. 1)

electron. For such states the electron is outside the cluster. The point $R = R_c$ *is* the bifurcation one, where branching the solutions takes place.

Figure 2 presents the dependence of total electron energy I_F (according to (11)) on cluster radius R. The branch of lower total energy I_F corresponds to the bound electron states, while the branch of higher I_F corresponds to the surface electron states. According to the figure, for cluster with radius R less than $R_1 = 4.85\, \mu^{-1}\tilde{\varepsilon} \cdot \mathring{A}$ the positive total energy corresponds to both bound and surface states. Thus, the two states are metastable within the interval (R_c, R_1). When $R > R_1$, the inner electron localization becomes energetically preferable. The figure also shows that the surface states are metastable at any cluster radius. Both the surface and the inner states are self-consistent for the electron and the cluster. They coexist and are separated by a potential barrier.

Figure 3 depicts the solutions for inner (1) and outer (2) states near the critical cluster size. Vertical line on the figure denotes cluster radius $R = 4.5\, \mu^{-1}\tilde{\varepsilon}$. In this case for solution 1 the probability of the electron to be inside the cluster is 0.95 and outside is 0.05, and for solution 2 it is 0.62 and 0.38 respectively. At critical cluster size $R = R_c$ the two solutions merge, and the probability for the electron to be inside the cluster is 0.82, and outside is 0.18.

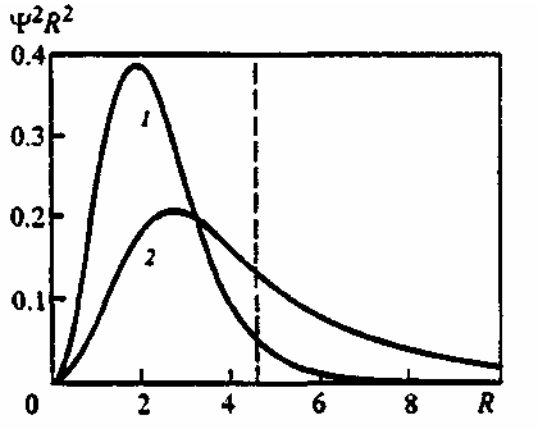

Figure 3. Spherically symmetrical solutions of equations (6)-(9) for $\boldsymbol{R} = 4.5\,\mu^{-1}\tilde{\varepsilon}\cdot\mathring{\mathrm{A}}$. Curve 1 is for the inner state, while curve 2 for the outer one, vertical line denotes the cluster radius.

We plot curve $\boldsymbol{W(R^{-1})}$ in Fig.4, as calculated by solutions for inner electron states in the cluster. But for narrow region of small $\boldsymbol{R}$, the calculated dependence can be easily approximated by a function linear in $\boldsymbol{R^{-1}}$,

$$W = -4.43\,\frac{\mu}{\tilde{\varepsilon}^2} + \frac{14.4}{\tilde{\varepsilon}}\,\frac{1}{R}, \tag{12}$$

where $\boldsymbol{W}$ is the electron energy in eV, and $\boldsymbol{R}$ is the cluster radius in angstroms. As $\boldsymbol{R \to \infty}$, $\boldsymbol{W \to -4.43\,\mu\tilde{\varepsilon}^{-2}}$, which coincides with the polaron energy in a homogeneous polar medium [6].

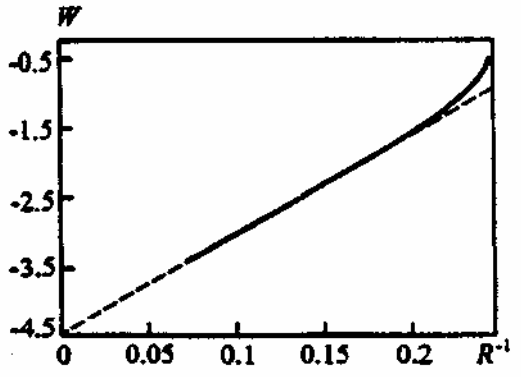

Figure 4. Dependence of the inner electron state energy $\boldsymbol{W}$ on $\boldsymbol{R^{-1}}$ (solid line) and its linear approximation (dashed line). Energy is given in eV, and inverse radius in $\mu\tilde{\varepsilon}^{-1}\cdot\mathring{\mathrm{A}}^{-1}$ units.

4. Comparison with experimental data

There is a set of papers devoted to charged clusters. Bowen et al. reviewed in [7, 8] the experimental data on photodetachment energy of the electron in water clusters $(H_2O)\,\overline{n}$ for a wide range of $\boldsymbol{n = 2\ldots69}$. In this case when $\boldsymbol{n \geq 11}$ the energy is well approximated by the linear dependence on $\boldsymbol{n^{-1/3}}$,

$$W_{\exp} = -3.30 + 5.73 n^{-1/3}\,(eV). \tag{13}$$

We assume that duster size $\boldsymbol{R}$ relates to number of molecules $\boldsymbol{n}$ as $\boldsymbol{R = R_S\, n^{1/3}}$, where $\boldsymbol{R_S}$ is an effective cluster radius. If we require that (12) should be equivalent to (13), we receive relation between $\boldsymbol{R_S}$, $\boldsymbol{\mu}$, and $\tilde{\varepsilon}$. For water at room temperature the optical dielectric constant is $\boldsymbol{\varepsilon_\infty = 1.77}$ and the static dielectric

constant is $\varepsilon_0 = 80$, hence the effective dielectric constant is $\tilde{\varepsilon} \equiv \varepsilon_0 \varepsilon_\infty / (\varepsilon_0 - \varepsilon_\infty) \approx 1.81$. Theoretical expression (12) and experimental one (13) coincide when $R_S = 1.40$ Å and $\mu = 2.44$. We note that calculated radius R_S is slightly less than the effective radius $R_S = 1.48$ used by Newton [9].

Experimental data on photodetachment energy of the electron for ammonia cluster $(NH_3)\bar{n}$ are listed in [8] for a wide range of $n = 41 \ldots 1100$. These data are well approximated as

$$W_{exp} = -1.25 + 2.63 n^{-1/3} (eV). \qquad (14)$$

In this case, comparing (14) and (12), we get relation $R_S = 5.5 \tilde{\varepsilon}^{-1}$ and $\mu = 0.28 \tilde{\varepsilon}^2$. Taking for liquid ammonia the optical dielectric constant $\varepsilon_\infty = 1.77$ at $T = -33^oC$ and the static dielectric constant $\varepsilon_0 = 22$, we find $\tilde{\varepsilon}_0 = 1.92$, therefore, $R_S = 2.85$ Å and $\mu = 1.04$.

Let us estimate for water and ammonia critical cluster size R_c, at which polaron states form. and R_1, which separates the metastable and stable polaron states, i.e., when $I_F(R_1) = 0$ (see Fig. 2). For water we calculate $R_c = 3.03$ Å and $R_1 = 3.6$ Å, which lead to $n_c = 11$ and $n_1 = 17$. In the case of ammonia, we get $R_c = 7.85$ Å and $R_1 = 9.3$ Å, for which $n_c = 21$ and $n_1 = 35$, respectively. These estimates are in good correlation with experimental data for ammonia [7, 8].

This work was supported by the Russian Foundation for Basic Research (Project Code 95-04-11432a).

REFERENCES

1. Balabaev N.K., Lakhno V.D., et al. *J. Mol. Elec-inn.* 1990, **6**, 155.
2. Balabaev N.K. and Lakhno V.D. Laser Applications in Life Sciences. Proc. SPIE. Eds. Akhmanov S.A.et al. 1991, Vol. **1403**, p. 478.
3. Chuev G.N. and Lakhno V.D. *J. Theor. Biol.* 1993, **163**, 51.
4. Barnett R.N., Landman V., et al. *Phys. Rev. Lett.* 1987, **59,** 811.
5. Pekar S.I. *Zh. Eks. Teor. Fiz.* 1946, **16**, 41; 335 *(Sov. Phys.-JETP).*
6. Balabaev N.K. and Lakhno V.D. *Teor. Mat. Fiz.* 1980, **45,** 139.
7. Coe J.V., Lee G.H., et al. J. *Chem. Phys.* 1990. **92,** 3980.
8. Lee G.H., Arnold S.T., et al. *Z. Phys. D* 1991 **20**, 9.
9. Newton M. *J. Phys. Chem.* 1975, **79**, 2795.