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ELECTRON STATES COUPLED BY A POLAR DIELECTRIC SPHERE

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Electron states on a polarizable dielectric sphere in vacuum are studied numerically. The electron energy and affinity are found depending on the sphere radius. Two types of surface states are shown to exist.

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For the states of an excessive electron coupled by the cluster containing a great number of molecules, such a cluster can be simulated by a dielectric sphere. This model was first used in [1] to calculate electron states in a water cluster. The electron was believed to interact with a sphere of the dielectric constant ϵ_∞ corresponding to a high-frequency limit for the analyzed medium. The case with a positive charge at the sphere center was considered in [2]. These data were applied to calculate the energy of coupled electron states in neutral clusters of polar and nonpolar molecules.

The model considered in [1,2] is used widely for calculating the electron states in nonpolar clusters, in particular, those consisting of inert gas atoms [3–8]. However, that model is inapplicable to polar clusters, for example, of water or ammonia, although it was originally employed. There electron localization inside the polar cluster is caused by a polarization inertial component, and the interaction with the dielectric sphere is controlled by the effective dielectric constant $\tilde{\epsilon}$ defined by formula $\tilde{\epsilon}^{-1} = \epsilon_\infty^{-1} - \epsilon_0^{-1}$, where ϵ_0 is the static constant.

A consistent description of the interaction between an electron and a polar dielectric sphere is based on the polaron model, first used in [9] for electron states in $(NH_3)_n$ clusters. By analogy with a volume medium, the electron localized in such a cluster is assumed to form a vacuum cavity inside it. The critical analysis [10] of experimental data array on negatively charged ammonia clusters does not confirm this assumption.

The calculation of electron states in the polar dielectric sphere, based on the polaron model with no vacuum cavity describes satisfactorily the experimental data on photoionization of negative water and ammonia clusters (see [11]).

Despite the progress achieved, the model of [11] calls for correction containing the potential image outside the sphere and a probable nonzero average potential caused by short-range interaction inside the sphere. The consideration of these factors yields more accurate stability criteria for electron surface and internal states. Furthermore, other states are possible as will be shown below.

In this work we restrict ourselves to weakly polar clusters, where the condition $(\epsilon_\infty - 1)/\epsilon_\infty \ll 1$ is satisfied. Among them there are such clusters as $(NO_2)_n$, $(N_2O)_n$, $(NO)_n$, and $(CO)_n$. We consider the charged clusters as dielectrically polarized spheres containing an excessive electron.

Equations of coupled electron states in the field of such a dielectric sphere are analogous to those considered in [11],

$$\frac{\hbar^2}{2m}\Delta\Psi(\mathbf{r}) + \left[e\Pi(\mathbf{r}) + V(\mathbf{r}) - W\right]\Psi(\mathbf{r}) = 0, \quad (1)$$

$$\Delta\Pi(\mathbf{r}) + \tilde{\epsilon}^{-1} 4\pi e|\Psi(\mathbf{r})|^2 = 0, \quad (2)$$

where $\Psi(\mathbf{r})$ is the electron wavefunction; $\Pi(\mathbf{r})$ is the potential induced by the inertial polarization component; and e, m, and W are the electron charge, mass, and energy.

As distinct from [11], Schrödinger equation (1) contains the potential $V(\mathbf{r})$ of interaction between the electron and the high-frequency polarization of the sphere, induced by the electron. According to [3–8], this potential is given by

$$V(r) = -V_0, \quad r < R, \tag{3}$$

$$V(r) = V(R+a), \quad R < r < R+a, \tag{4}$$

$$V(r) = \frac{e^2(\epsilon_\infty - 1)}{4(\epsilon_\infty + 1)}\left[\frac{2R}{r^2 - R^2} + \frac{1}{r}\ln\left(\frac{r-R}{r+R}\right)\right], \quad r > R + a. \tag{5}$$

Figure 1 shows profiles of the potentials $U(r) = e\Pi(r) + V(r)$ and electron density $r^2\Psi^2(r)$ at $V_0 = 0$, cluster radius $R = 10\mu\tilde{\epsilon}^{-1}$(Å) (where $\mu = m/m_0$ and m_0 is the free electron mass), potential cutoff parameter $a = r\mu\tilde{\epsilon}^{-1}$(Å), and dimensionless charge $\tilde{\epsilon}(\epsilon_\infty - 1)/4(\epsilon_\infty + 1) = 0.14$ for three types of solutions to (1) and (2), corresponding to possible electron ground states in the cluster. Solution *1* corresponds to internal states, when the electron is almost totally localized inside the cluster. Solutions *2* and *3* are internal and external surface states, respectively. As is evident from Fig. 1, the electron density of state *2* has two maxima, while states *1* and *3* are characterized by one maximum. This difference is retained also in the limit of great radii. Thus, state *2* is intermediate between states *1* and *3*.

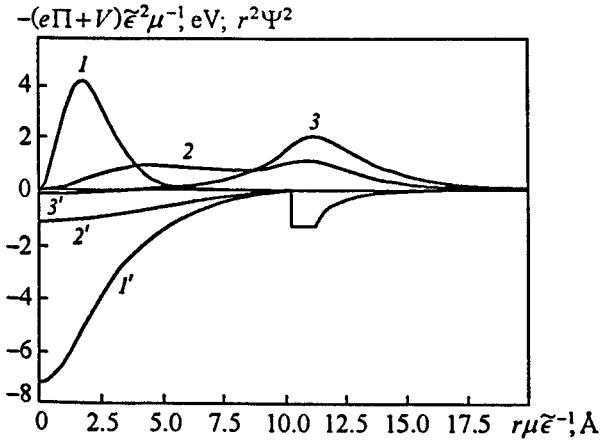

Figure 1. Profiles of potentials (*1′–3′*) and electron densities (*1–3*) of three electron states.

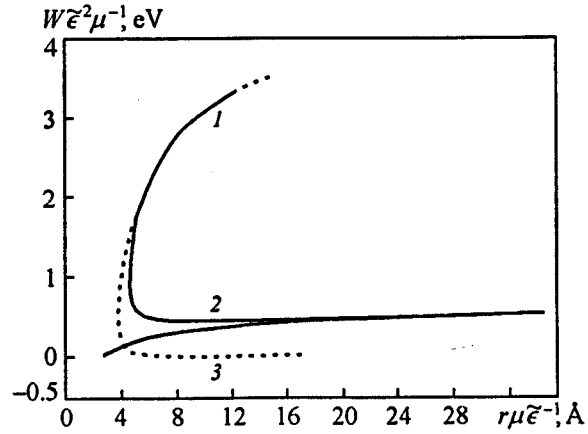

Figure 2. Electron state energies versus the cluster radius. The dashed line is calculated without image forces.

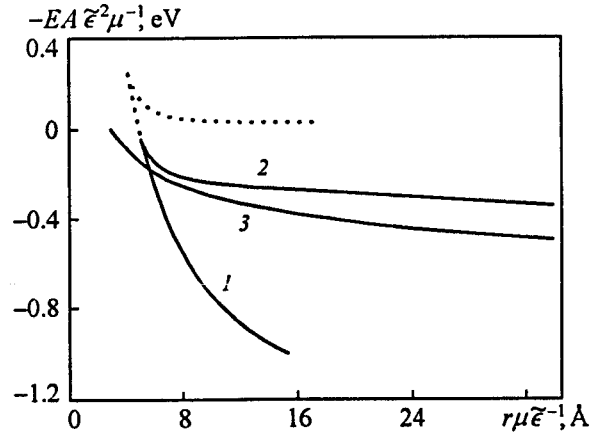

Figure 3. Electron state affinity versus the cluster radius. The dashed line is calculated without image forces.

Figures 2 to 4 display dependencies of the electron energy W for detachment from the cluster, electron energy EA of affinity to it, and radius $\langle r\rangle$ average over the electron density distribution on the cluster radius for all the three states. There the dashed line corresponds to the calculation without image forces, corresponding to [11]. Comparison of these calculations shows internal state *1* to be virtually unaffected by the

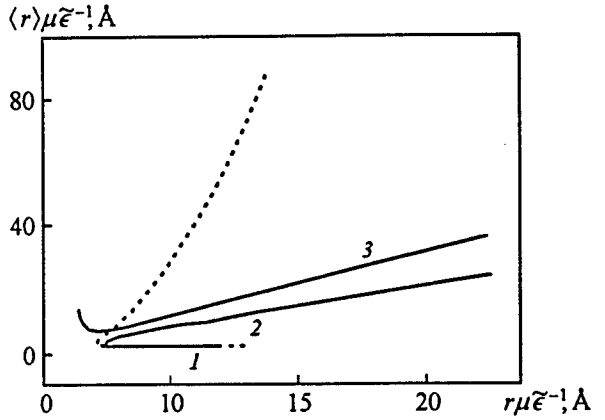

Figure 4. Average radius of electron states versus the cluster radius. The dashed line is calculated without image forces.

image potential. However, the cluster critical radius, at which the coupled polaron state arises, increases somewhat as the image potential is introduced. On the contrary, state *3* is caused by that potential and virtually does not induce cluster internal polarization. State *2* presents simultaneously polaron and surface levels.

It is noteworthy that state *2* merges by energy with state *3* (see Fig. 2) at large radii, however, judging from the electron affinity (Fig. 3) and average radius (Fig. 4), it differs considerably from the latter state. States *2* and *3* are surface since their average radii are directly proportional to the cluster radius, while the radius of state *3* is virtually equal to it. The surface state average radius calculated without the image potential (see the dashed line in Fig. 4) has a more complex (powerlike or exponential) dependency on the cluster radius, which shows up electron detachment from the cluster.

In summary, we note that if the results obtained are applied to strongly polar clusters, such as $(NH_3)_n$, then positive V_0 in ammonia clusters follows from the existence of only internal electron states in them.

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