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# Electron bound states of a dielectric sphere

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We have calculated the energy levels for an electron just outside the surface of a dielectric sphere. The electron is bound by dispersion forces which depend on the dimensions of the sphere (or droplet) and on the inner potential of the material of the sphere. Some comments as to relevance of these bound levels to experiments are made.

## I. INTRODUCTION

In a recent paper, Armbruster *et al.*<sup>1</sup> have reported the observation of free negatively charged water clusters of the form  $(\text{H}_2\text{O})_n^-$ . They suggest that the electrons are bound to a permanent dipole potential. Such a potential has been shown theoretically to have bound states.<sup>2</sup> We describe here an alternate model whereby an electron may be bound to a cluster of neutral molecules, which may well describe the larger molecular clusters observed by Armbruster *et al.* The model considers only the optical dielectric constant of the cluster and the resulting electrodynamic interaction. It disregards any contribution from any permanent electric dipole moments.

The problem of electron binding to an isolated dipole has a long history. It has been shown that either a point dipole of moment  $0.639ea_0$  or a finite molecular dipole of moment  $ea_0$  can bind an electron ( $a_0$  is the Bohr radius).<sup>3</sup> Clusters of dipoles may also have bound states.<sup>4</sup> Nevertheless, there have been few reliable observations of dipole binding except possibly for strongly dipolar molecules such as HCl and HF.<sup>5</sup> We propose that the model to be described provides an alternate explanation of the observed electron trapping.

It is well known that an electron can be bound to a planar dielectric such as the surface of liquid helium.<sup>6</sup> The electron is attracted to the liquid-vapor interface by the classical image potential. The surface presents a substantial repulsive barrier  $V_0$  to the penetration of the electron into the liquid. The electron is then trapped in the resulting potential well which runs parallel to the surface. A hydrogenlike series of weakly bound states is found. The energy spectrum and mutual interactions of these "external" electrons have been extensively studied.<sup>7</sup> There are also electron states *internal* to the bulk fluid. These states are "bubble" states: the electron resides in a large (20 Å in liquid He) cavity in the fluid.<sup>8</sup> We consider here the model of the electron bound to a neutral dielectric sphere. We disregard any contribution which might come from a permanent electric dipole moment. The sphere could be composed of He atoms,  $\text{H}_2\text{O}$  molecules, or any other polarizable species.

We find the interaction of an electron with a sphere of finite radius to be sufficiently strong to bind an electron. There are two major contributions to the potential. One is the induced polarization and the other is the inner potential of the sphere  $V_0$ . We describe the induced polarization by the classical model of an image

potential<sup>6,9</sup> cutoff, at  $r_1$ , near the surface of the dielectric. An electron outside the sphere radius  $a$  sees a potential  $\phi(r)$  given by

$$\phi(r) = -\frac{(1-\epsilon)e^2}{4\pi\epsilon_0 r} \sum_{n=1}^{\infty} \frac{n}{[(\epsilon+1)n+1]} \left(\frac{a}{r}\right)^{2n+1}, \quad r > r_1$$

$$= \phi(r_1), \quad a < r < r_1.$$

An electron which penetrates the sphere sees an inner potential  $V_0$  which is the energy at the bottom of the conduction band in the dielectric.  $V_0$  may be positive (+1.0 eV) as in liquid He,<sup>8</sup> near zero as in  $\text{H}_2\text{O}$ ,<sup>10</sup> or negative (-0.65 eV) as in Xe.<sup>11</sup> An electron interior to the sphere also sees a repulsive potential<sup>9</sup> from the surface produced by the polarization of the sphere by the presence of the electron. That potential inside the sphere is represented by  $\Phi(r)$  and has the form

$$\Phi(r) = \frac{e^2(\epsilon-1)}{4\pi\epsilon_0 a} \sum_{n=0}^{\infty} \frac{(n+1)}{[(\epsilon+1)n+1]} \left(\frac{r}{a}\right)^{2n}, \quad 0 \leq r < r_0$$

$$= \Phi(r_0) \quad r_0 \leq r < a.$$

In Eq. (2) we have again cut off the image potential near

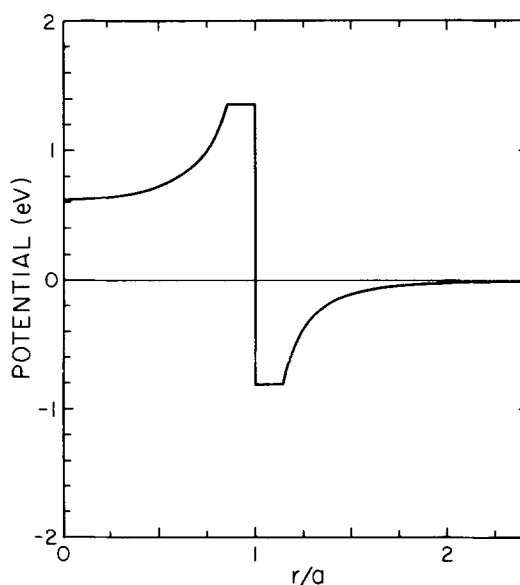


FIG. 1. Potential seen by an electron in the neighborhood of a dielectric sphere. The sphere radius is  $a$ . For  $r < a$  the potential is  $\Phi + V_0$  [Eq. (2)] and for  $r > a$ , the potential is  $\Phi$  [Eq. (1)].

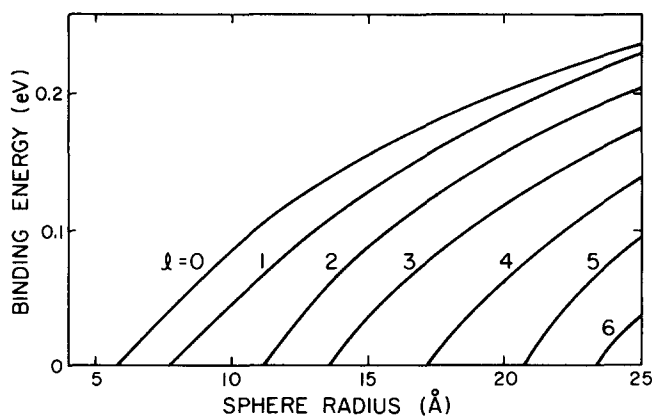


FIG. 2. Binding energy  $-E_B$  as a function of sphere radius  $a$ . The other parameters are:  $\epsilon = 1.76$ ,  $b = 1.5$  Å, and  $V_0 = 0$ . The  $l$  values are indicated on each curve. Note that as the sphere size increases new states appear.

the surface of the dielectric. The total potential for  $r < a$  is, of course,  $V_0 + \Phi(r)$ . Note that  $\Phi(0) > 0$ . A typical potential is shown in Fig. 1.

The image potential model breaks down for small distances from the surface of the dielectric for a variety of reasons. In order to avoid the unphysical divergence of the image potential at the surface, we have cut off the potential at some distance  $b (= r_1 - a = a - r_0)$  from the surface of the dielectric (both inside and outside). The surface thickness is therefore  $2b$ , and is a parameter of the calculation. Values of  $2b$  should be close to a molecular diameter.

The details of the calculation are presented in the following section and the results and discussion are in Secs. III and IV.

## II. COMPUTATIONS

With the potential defined in Eqs. (1) and (2), and shown in Fig. 1 the radial part of the Schrödinger equation is as follows, for a wave function  $r\psi$ ,

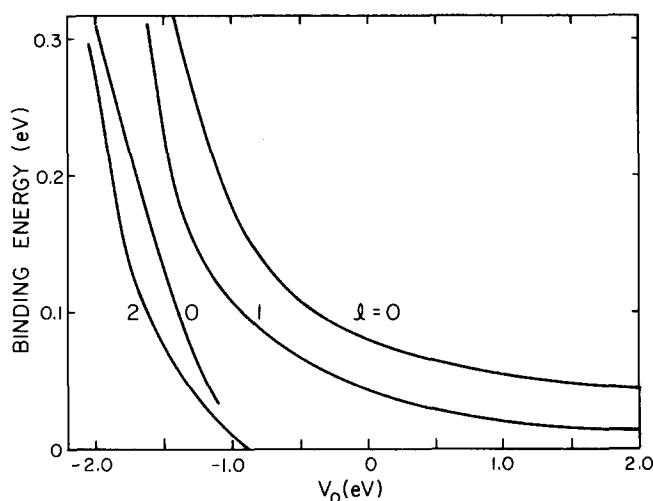


FIG. 4. Binding energy  $-E_B$  as a function of the inner potential  $V_0$ . Note that in this figure negative values of  $V_0$ , more than one level is found for  $l = 0$  states. The other parameters are  $\epsilon = 1.76$ ,  $b = 1.5$ , and  $a = 10$  Å.

Equations (3) and (4) were solved using a fourth order Runge-Kutta routine. The wave functions were integrated inward from  $r = 10a$ .

$$-\frac{\hbar^2 d^2 \psi}{2m_a r^2} + \left[ \frac{l(l+1)\hbar^2}{2mr^2} + \phi(r) \right] \psi = E \psi, \quad r > a, \quad (3)$$

$$-\frac{\hbar^2 d^2 \psi}{2m_a r^2} + \left[ \frac{l(l+1)\hbar^2}{2mr^2} + V_0 + \Phi(r) \right] \psi = E \psi, \quad r < a. \quad (4)$$

## III. RESULTS

A number of bound states for a variety of dielectric spheres have been found with binding energies in excess of room temperature thermal energies. We first consider the application of the model to  $H_2O$ . The values of  $\epsilon$ ,  $b$ , and  $V_0$  were chosen to be, therefore, 1.78, 1.5 Å and 0 eV, respectively. The variation of binding energy  $-E_B$  with sphere size  $a$  is shown in Fig. 2. It should be noted that there is a minimum sphere size for the existence of a bound state. Higher angular momentum states require a larger sphere for binding. For a sphere of given radius there is the possibility of more than one bound state.

We now consider the variation of each of the parameters so as to indicate the behavior of the model. If we then choose a given state, say  $l = 0$ , and a given radius, say  $a = 10$  Å, we find the variations with  $b$ ,  $\epsilon$ , and  $V_0$  shown in Figs. 3, 4, and 5. The binding energy decreases as the cutoff distance increases. However, states bound more strongly than  $kT$  persists until  $b$  exceeds 2 Å, for the other parameters chosen. The binding energy varies approximately linearly with dielectric constant. It may be seen in Fig. 5 that as the inner potential  $V_0$  increases the binding energy decreases. This is a result of the wave function being forced to zero at the surface of the sphere as  $V_0$  tends to infinity. Consequently the amplitude of the wave function is small in the region of the most attractive

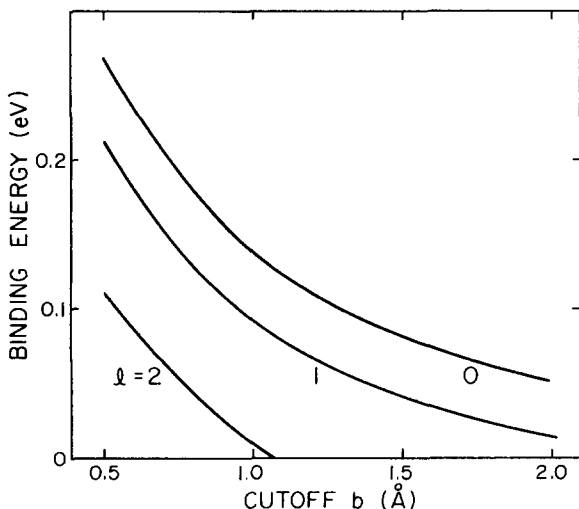


FIG. 3. Binding energy  $-E_B$  function of image potential cutoff  $b$ . Both internal and external potentials are cut off at the same distance  $b$  from the surface. The other parameters are  $\epsilon = 1.76$ ,  $V_0 = 0$ , and  $a = 10$  Å.

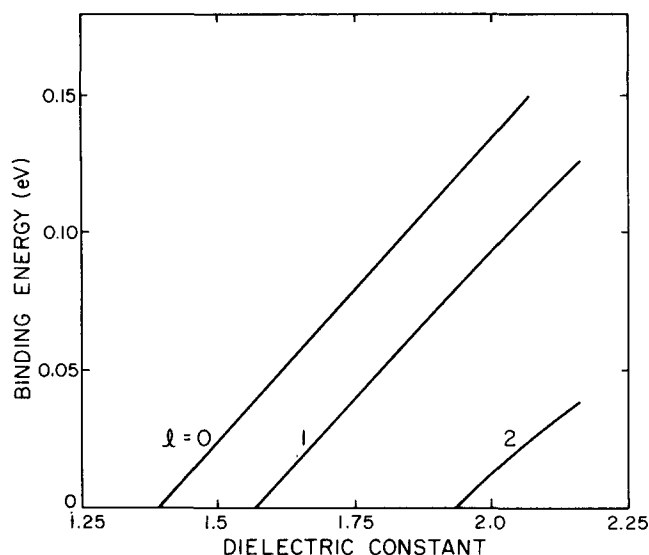


FIG. 5. Binding energy  $-E_B$  as a function of the relative dielectric constant  $\epsilon$ . The other parameters are  $V_0=0$ ,  $b=1.5$ , and  $a=10$  Å.

potential. Note that the number of bound states with  $l>0$  varies considerably with these changes in the parameters.

#### IV. CONCLUSIONS

We have demonstrated the plausibility of the trapping of an electron by a neutral dielectric sphere in the absence of permanent dipoles. There are a number of possible consequences of this conjecture. We will briefly explore several of them. An estimate of the change in the molecular binding energy  $\Delta E$  produced by the electron can be obtained as follows. We take the change in the electron binding energy with volume  $dE_B/dV$  and multiply by the volume of a single molecule

$$\Delta E = \frac{dE/dV}{4\pi r^2} \cdot \Delta V. \quad (5)$$

This yields approximately 10 meV/atom for a sphere of 5 Å radius. As the sphere size increases the change in the energy, due to the presence of the bound electron, by which the last molecule is bound to the cluster decreases rapidly to values well below  $kT$  and eventually goes to zero. The presence of this term would help to stabilize smaller clusters than would otherwise occur.

This simple, continuum model obviously cannot be directly applied to clusters containing only a few molecules. Consequently, we cannot comment on the results found by Armbruster *et al.*<sup>1</sup> near the threshold for trapping. However, this does not mean that electron-atomic polarization effects do not contribute to the binding in all cases, despite the limitations of our semiclassical model.

We suggest that our model might also apply to a variety of vapors in which mobility measurements have revealed electron localization processes at work. These include  $H_2O$  and  $NH_3$ <sup>12</sup> and also nonpolar materials such as Xe<sup>13</sup> and ethane.<sup>14</sup> The scattering cross section for a cluster will be substantially greater than its

geometric cross section even if trapping does not occur. An interesting point to consider is the changeover that must occur in  $NH_3$ , say, as the externally trapped electron becomes internally "solvated." At low densities, the interaction is most probably that described above: an electron is bound near the surface of a cluster of  $NH_3$  molecules. At high densities, the electron is known to reside within a void in the fluid: a solvated electron. At some density the electron must move from outside to inside. We have not yet determined the point at which this occurs. A recent calculation<sup>15</sup> describes the binding of a solvated electron within a cage in a finite  $H_2O$  cluster, but a direct comparison with our results has not been made. We suggest that the initial decrease in mobility observed experimentally as described increases results from the mechanism we have described and that the changeover to solvation occurs only for sufficiently large clusters near the minimum in the mobility.<sup>12</sup>

A related problem has also been discussed recently by Hernandez<sup>16</sup> in connection with some experimental results on fluid Hg reported by Hefner and Hensel.<sup>17</sup> They believe that the onset of stabilization of tiny Hg droplets by electrons, a similar effect to that discussed in this work, is responsible for an anomaly in the loss frequency dielectric constant of Hg.

#### ACKNOWLEDGMENTS

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