# Addendum to "Electron structure of a dipole-bound anion confined in a spherical box": The case of a finite dipole

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We investigate the problem of an electron placed in the potential of a finite dipole and confined by an impenetrable prolate spheroidal box. The critical cage sizes at which successive bound states are ionized as the box becomes smaller are found to be the roots of associated Legendre functions of complex order. We find the asymptotic behavior for a large cage. The lowest few roots are computed numerically. Comparison is made with the case of an electron bound by an ideal dipole plus short-range repulsion, confined in a spherical box.

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## I. INTRODUCTION

The formation and structure of dipole-bound anions, i.e., the binding of electrons to highly polar molecules is presently of considerable theoretical and experimental interest (see, e.g., [1–5]). The wave functions describing these anions are much more diffuse than those of more tightly bound conventional "valence" anion. Fermi and Teller [6] were the first to predict, within the Born-Oppenheimer (bo) approximation, that a dipole should bind an electron only if the dipole moment is larger than 1.625 D (Debye). Higher dipole moments are required for the existence of two or more dipole bound states with binding energy above 1 meV. Such higher excited states were observed experimentally [2].

In view of the very diffuse nature of dipole-bound states, it is evident that such an anion will be particularly sensitive to environmental effects. The possibility of the existence of dipole-bound states on an impurity in a quantum dot is also intriguing [7]. If the quantum dot is sufficiently small, boundary effects due to confinement are expected to become important. In a previous paper [8], we explored such effects in a simple model of an electron in a potential of an ideal dipole plus inner repulsive core, confined by a spherical box. Here, we extend the study of such effects to the case of an electron bound by a finite dipole consisting of two opposite charges and confined in a prolate spheroidal box.

The model of an atom or a molecule confined to a box has proved to be a useful model for simulating the effect of neighboring atoms in many physical situations. There has been considerable interest in the confined hydrogen atom [9–14], with applications to pressure effects, quantum dot impurities, and atoms caged in $C_{60}$. Investigations have been also carried out for the hydrogen molecular anion inside hard and soft spherical and prolate spheroidal boxes [15–17]. Our present study is closely related to the latter, corresponding to considering two opposite nuclear charges (a finite dipole) instead of identical ones ($H_2$ molecule).

In confined systems, as one decreases the size of the confining box, one expects the various bound states to ionize one by one until some minimum cage size is reached, below which there are no bound states. It is particularly interesting to compute the critical sizes at which ionization of the $n$th bound state takes place. This has been done for the confined hydrogen atom [9–12] and the case of a spherically confined electron in the field of an ideal dipole [8]. In these cases one speaks of critical cage radii. From knowing these critical radii/sizes it is immediate to obtain the number of bound states for any given box size. Our aim is to compute the critical cage sizes for the model suggested here.

## II. MODEL

As described above, we envisage an electron bound by a finite dipole created by two opposite charges $+q$ and $-q$ at positions $\boldsymbol{R}_1=(0,0,a/2)$ and $\boldsymbol{R}_2=(0,0,-a/2)$ separated by a distance $a$. The dipole moment is $D=qa$. The whole system is placed in a confining, impenetrable, prolate spheroidal box. This geometry enables separation of variables and analytical solution of the problem.

Within the Born-Oppenheimer approximation, the Schrödinger equation is

$$\left(-\frac{\hbar^2}{2m_e}\nabla-\frac{eq}{|\boldsymbol{r}-\boldsymbol{R}_1|}+\frac{eq}{|\boldsymbol{r}-\boldsymbol{R}_2|}-E\right)\Psi=0. \tag{1}$$

The boundary condition due to confining, to be specified exactly below, involves the length $b$ of the major axis of the spheroidal box. Dimensional analysis shows that only two independent dimensionless quantities can be constructed. These may be chosen as

$$\alpha=\frac{2m_eeD}{\hbar^2}=2\frac{D}{ea_0} \quad \text{or} \quad D=\alpha\times 1.271 \text{ D}, \tag{2}$$

where $a_0$ is the Bohr radius and

$$R=\frac{b}{a}. \tag{3}$$

It is therefore sufficient to solve the problem for $a=a_0$. Then, for any other $a$ (and the same ratio $R$), the energy eigenvalues scale as $(a_0/a)^2$. This may be compared with the hydrogen atom problem, for which a natural length scale (the Bohr radius) exists, while here it is only the introduction of the distance between the nuclei which brings a typical length scale into the problem. It may also be compared with

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the ideal dipole model considered in Ref. [8]. An ideal dipole does not introduce a length scale, and it was necessary to introduce there an additional repulsive core potential with its own length scale. From now on we shall use atomic units, i.e., $\hbar = e = m_e = 1$. We put $a = a_0 = 1$.

Equation (1) is separable in prolate spheroidal coordinates. Let $r_1$ and $r_2$ be the distances of the electron from the nuclei. The prolate spheroidal coordinates are $(\lambda, \mu, \phi)$ with $\lambda = (r_1 + r_2)/a$ and $\mu = (r_1 - r_2)/a$, where we have $1 \leqslant \lambda < \infty$ and $-1 \leqslant \mu < 1$. $\phi$ is azimuthal coordinate. For large $r_1, r_2$ the coordinates $\lambda, \mu$ behave, in spherical coordinates, like $2r/a$, $\cos(\theta)$, respectively. In this sense $\lambda$ is a "radial" coordinate and $\mu$ an "angular" coordinate. The confining box is defined by the surface $\lambda = R$, where the constant $R > 1$ is the spheroid's major axis in units of $a$.

We put

$$\Psi(r, \theta, \phi) = F(\lambda)\Theta(\mu)e^{im\phi}. \tag{4}$$

Transforming Eq. (1) into prolate spheroidal coordinates and effecting the separation of variables, we obtain the following equations:

$$\frac{d}{d\lambda}\left[(\lambda^2 - 1)\frac{dF}{d\lambda}\right] + \left[\frac{1}{2}E\lambda^2 - A_{pm} - \frac{m^2}{\lambda^2 - 1}\right]F = 0, \tag{5}$$

and

$$\frac{d}{d\mu}\left[(1 - \mu^2)\frac{d\Theta}{d\mu}\right] + \left[-\frac{1}{2}E\mu^2 + \alpha\mu + A_{pm} - \frac{m^2}{1 - \mu^2}\right]\Theta = 0, \tag{6}$$

where $A_{pm}$ is the separation constant. The index $p$ specifies the number of nodes of the angular function $\Theta$. The radial function $F$ must be finite at $\lambda = 1$. The boundary condition due to the confining box is $F(R) = 0$.

### III. CRITICAL CAGE SIZES

With no confinement, the solutions of the above equations give both discrete, bound states, and continuum, unbound states. Bound states exist only if $D > 1.625$ D. When we add confinement all states become discrete. However, states with positive energy will be ionized as soon as the impenetrable wall potential is replaced with a more realistic finite potential wall. We are interested here in finding the critical major axis length $R$ at which bound states are ionized. For such $R$ we have $E = 0$.

We now note that Eq. (6) with $E = 0$ is exactly the same as the angular equation appearing in the problem of an electron bound by an ideal dipole, see Eq. (7) of Ref. [8]. Therefore, we can use the same method as there to find $A_{pm}$. For $m = 0$, a graph of the separation constant $A_{10}$ corresponding to the angular function with no nodes appears in Fig. 1 of Ref. [8].

Now consider the radial Eq. (5). For the unconfined problem (no box), it is known (as shown in Ref. [18]) that a bound state solution of Eq. (5) with $E < 0$ exists only for $A_{pm} < -\frac{1}{4}$. This condition then provides the value of the critical dipole for binding through the dependence of the separation constant on the dipole moment. The same condition is therefore necessary (but not sufficient) for the existence of bound states with confinement (whose effect is always to raise the energy of any given state).

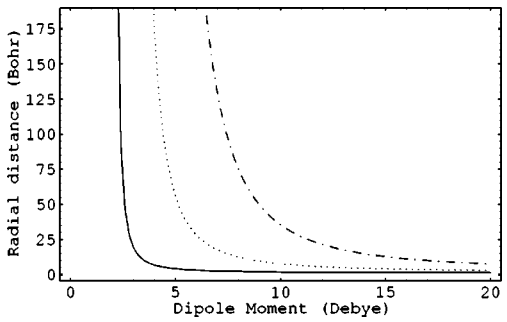


FIG. 1. The first three critical cage major axis lengths as a function of the dipole moment strength, for the azimuthal quantum number $m = 0$. They scale as $a/a_0$ with the dipole length $a$.

With $E = 0$, Eq. (5) reduces to the associated Legendre equation, but for $1 \leqslant \lambda \leqslant R$ instead of the more familiar segment $[-1, 1]$. Just as for the latter, more familiar case, the requirement that $F(1)$ is finite selects as solutions the associated Legendre functions $P_{lm}$, where $A_{pm} = l(l+1)$. Because we need only consider $A_{pm} < -\frac{1}{4}$, we can define a real parameter

$$s = \sqrt{-\left(\frac{1}{4} + A_{pm}\right)}, \tag{7}$$

and then

$$l = -\frac{1}{2} + is. \tag{8}$$

Using the well-known expression of the associated Legendre functions in terms of the hypergeometric function (e.g., [19], Chap. 5), we have, for $z \geqslant 1$

$$P_{lm}(z) = \frac{\Gamma\left(\frac{1}{2} + is + m\right)(z^2 - 1)^{m/2}}{2^m \Gamma\left(\frac{1}{2} + is - m\right)\Gamma(m+1)} \times {}_2F_1\left(m + \frac{1}{2} + is, m + \frac{1}{2} - is, m + 1, \frac{1 - z}{2}\right). \tag{9}$$

For a solution which satisfies the boundary condition at the surface of the confining box, we have $P_{lm}(R) = 0$. Therefore, for a given $m$ and a dipole moment strength, the roots of $P_{lm}(z)$ with $z > 1$ define a series of critical sizes $R_1, R_2, R_3, \ldots$, corresponding to the ionization of the first, second, third, ... , bound states. For a major axis length smaller than the first root $R_1$, no bound states exist. For $R_1 < R < R_2$ there is only one bound state, etc. The three first roots for $m = 0$ and various dipole moments were computed numerically [21]. They are depicted in Fig. 1.

To examine the behavior for large cages $R \gg 1$ we use the well-known asymptotic expression for the associated Legendre functions [19]. A simple calculation gives

$$P_{lm}(z) \sim \frac{2(z^2-1)^{m/2} z^{-m}}{\sqrt{2\pi z}} \cos(s \log z + \Omega_s), \tag{10}$$

where

$$\Omega_s = \arg\left( \frac{\Gamma(is) 2^{is}}{\Gamma\left(\frac{1}{2} + is - m\right)} \right). \tag{11}$$

The roots for large cage sizes are therefore equidistant on a logarithmic scale

$$R_n = \exp\left( \frac{n\pi - \frac{\pi}{2} - \Omega_s}{s} \right), \tag{12}$$

with $n$ an integer. It is verified numerically that $R_n$ gives a good approximation to the exact $n$th root of $P_{lm}$. In principle, $n$ should be large, but in practice very good accuracy is already achieved for small $n$, as shown in Fig. 2. For $m=0$, $R_3$ as given by Eq. (12) is accurate to 0.23% for a dipole strength of 20 D, and better for smaller dipoles. We may compare this result with the critical cage radii for the case of an electron bound by an ideal dipole and confined by a spherical box [8]. For an ideal dipole with a repulsive impenetrable core of radius $a$, the critical cage radii, in units of $a$, were found to be exactly

$$R_n = \exp\left( \frac{n\pi}{s} \right). \tag{13}$$

In the present model, the dipole is of a finite length, and the cage is prolate spheroidal. For large $R$ the dipole length is small compared with the cage size, the surface $\lambda = R$ tends to a sphere, and physically one expects similar results to that of an ideal dipole. Comparing Eq. (12) with Eq. (13), it is seen that the ratio between successive critical radii is the same in the two cases, but the absolute cage size is different by a factor of $\exp(-\frac{\pi}{2} + \Omega_s/s)$. As discussed above, the parameter $s$, which depends on $m$ and the dipole strength $D$, is the same in the two models. The reason for the difference in the exponential prefactor is traced to the difference in the short range potential, which is a repulsive impenetrable core in the ideal dipole case, and the short-range potential of a finite dipole in the present case.

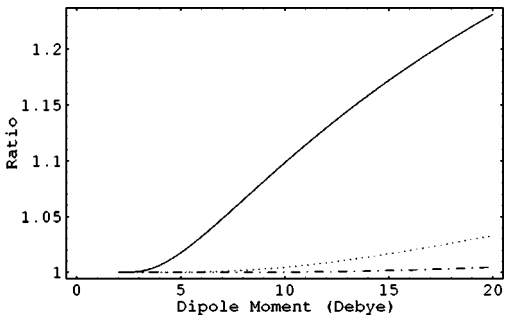


FIG. 2. Shown is the ratio of the exact first three critical cage sizes, from Fig. 1, to the approximate expression Eq. (12) in the text. The top line, for $n=1$, shows the largest deviation. Very good approximation is achieved already for $n=3$ (bottom line).

Finally, we may repeat the comparison made in Ref. [8] between the results for the two confined dipole-bound models and the confined hydrogen problem. The critical cage radii for the hydrogen states $(n,l)$ are given [10,11,20] in terms of roots of the Bessel function of the first kind:

$$J_{2l+1}(2\sqrt{2R_{nl}}) = 0. \tag{14}$$

It is seen that for the hydrogen problem $R_n \propto n^2$ for large $n$, while for the dipole-bound case we have $R_n \propto \exp(n)$.


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