

Electron structure of a dipole-bound anion confined in a spherical box

S. Ronen*

School of Chemistry, Tel Aviv University, Tel Aviv 69978, Israel

(Received 3 April 2003; published 22 July 2003)

We propose a model describing the interaction of an electron confined in a spherical box with a polar molecule in the center of the box, including an inner repulsive potential. As a preparation to its investigation, we calculate the average radius of a dipole-bound nonconfined electron, for which a closed form expression is found. The angular dependence of the wave function is also discussed, with implications for the choice of basis functions for *ab initio* calculations. The Schrödinger equation in the spherical box is then solved. The negative energy eigenstates of the system and the dependence of the ground-state energy on the radius of the confining sphere are obtained. Interestingly, a very simple expression is found for the total number of negative energy levels for a given dipole strength and confining sphere radius.

DOI: 10.1103/PhysRevA.68.012106

PACS number(s): 03.65.Ge, 31.10.+z, 31.70.-f, 31.70.Dk

I. INTRODUCTION

Presently, there is a considerable experimental and theoretical interest in the formation and structure of dipole-bound anions, i.e., the binding of electrons to highly polar molecules [1–5]. The wave functions describing these anions are much more diffuse than those of more tightly bound conventional “valence” anion. Consequently, such states have small electron affinities, typically below 300 meV. In 1947, 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. This is in contrast to the binding of an electron to a charge, which occurs for any charge greater than zero. This phenomenon was discovered and clarified in molecular physics twenty years later [7–10]. It was shown that the critical dipole does not depend on the details of the short-range interaction. Early *ab initio* calculations of dipole-bound states were carried out, e.g., in Refs. [11–13]. Considering rotational degrees of freedom [14–16], it was found that the critical dipole moment is about 2.5 D (depending on the moment of inertia, and also somewhat on the short distance repulsive potential). However, non-BO effects are relatively unimportant for dipole-bound states with electron binding energies much larger than the molecular rotational constants. In agreement with the theory, only molecules with a dipole moment greater than 2.5 D have been found experimentally to possess a dipole-bound electron. In some cases, this provides the only route to bind excess electrons to molecules or clusters. Higher dipole moments are required for the existence of two or more dipole-bound states with binding energy above a practical value of 1 meV. Such higher excited states were observed experimentally [2]. Recently, it has been suggested that the critical dipole required for electron binding provides a physical realization of the phenomenon of quantum anomaly, known from the quantum-field theory [3].

In the view of very diffuse nature of dipole-bound states, it is evident that such an anion will be particularly sensitive to environmental effects, i.e., if put in an external field, near a

wall, or embedded as an impurity in a quantum dot (for a finite dipole embedded inside a polarizable medium, the critical dipole moment to bind an electron was recently calculated in Ref. [17]). It may thus serve as a useful environmental probe. Here, we wish to consider the problem of confinement by a spherical box. The model of an atom or a molecule confined in a box has proved to be a useful model for simulating the effect of neighboring atoms in many physical situations. Such a model was first proposed by Michels, de Boer, and Bijl [18], who considered the hydrogen atom enclosed in a sphere of a finite radius. A detailed investigation of it was carried by Sommerfeld and Welker [19], and more recently by Refs. [20,21]. In Ref. [22], the model is applied for a hydrogenic impurity inside a quantum dot. The electron structure of endohedrally confined hydrogen was studied in Ref. [23]. Investigations have also been carried out for the hydrogen molecular anion inside hard and soft spherical and prolate spheroidal boxes [24–26].

The problem of confinement of a dipole-bound electron has another practical aspect. Algorithms for *ab initio* calculations of molecular states employ a finite basis set, usually of Gaussian functions. Normally, these Gaussian functions are localized around the nuclei. But for the description of dipole-bound states, there is a need to include very diffuse Gaussians. One wishes to add as little diffuse functions as possible, while still obtaining a quantitatively satisfying approximation for the binding energy. The problem was addressed in Ref. [27], based on the examination of a few molecular systems employing full *ab initio* calculation. It should be useful to look for the general trend of the error introduced by the spatial localization of the basis set in a simple model. In the context of the present work, we assume that the effect of truncation of the diffuse functions series should be roughly equivalent to that of a confining box with a radius of the order of the spatial extent of the most diffuse function. That is, assuming that the basis set is made good enough to describe wave functions localized within this volume.

II. A SIMPLE MODEL AND SOME PROPERTIES

For a diffuse dipole-bound electron, the long-range interaction is given by that of an ideal dipole. As argued in Ref.

*Electronic address: sronen@post.tau.ac.il

[28], the effect of a short-range repulsive interaction may be modeled by requiring the electron function to be zero inside a sphere of radius a of the order of the molecular core dimension. For our problem, we also add the requirement that the wave-function be zero outside an external confining sphere of radius $b > a$. We neglect the effects of the dipole rotation.

The Schrödinger equation is

$$\left(-\frac{\hbar^2}{2m_e} \nabla^2 - e \frac{\mathbf{D} \cdot \mathbf{r}}{r^2} - E \right) \Psi = 0, \quad (1)$$

and the boundary conditions are

$$\Psi(a, \theta, \phi) = \Psi(b, \theta, \phi) = 0. \quad (2)$$

Dimensional analysis shows that only two independent dimensionless quantities can be constructed, which may be chosen as

$$\alpha = \frac{2MeD}{\hbar^2} = 2 \frac{D}{ea_0} \quad \text{or} \quad D = \alpha \times 1.271 \text{ D}, \quad (3)$$

where a_0 is the Bohr radius and

$$R = \frac{b}{a}. \quad (4)$$

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 repulsive core potential which brings a typical length scale into the problem.

From now on, we shall use atomic units, i.e., $\hbar = e = m_e = 1$. We put $a = 1$ and $b = R$. Equation (1) is separable in spherical coordinates. Choosing the z axis along the dipole moment, and putting

$$\Psi(r, \theta, \phi) = F(r)\Theta(\theta)e^{im\phi}, \quad (5)$$

we obtain the following equations:

$$\left[-\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) - \frac{C}{r^2} + 2E \right] F = 0 \quad (6)$$

and

$$\left[-\frac{1}{\sin^2 \theta} \frac{d}{d\theta} \left(\sin^2 \theta \frac{d}{d\theta} \right) + \frac{m^2}{\sin^2 \theta} - \alpha \cos \theta - C \right] \Theta = 0, \quad (7)$$

where C is the separation constant, and m is an integer.

With no confining sphere, i.e., $R = \infty$, the radial equation is known¹ to have no bound states at all if $C > -\frac{1}{4}$, and an infinite number of bound states, converging toward zero

binding energy, if $C < -\frac{1}{4}$. Therefore, the critical dipole α is that minimal value for which $C = -\frac{1}{4}$ is an eigenvalue of the angular equation.

We follow Ref. [7] in the analysis of the angular equation, which remains unchanged for radially confined problem. We restrict ourselves to the case $m = 0$. We look for a solution as a sum of Legendre polynomials:

$$\Theta(\theta) = \sum_{l=0}^{\infty} d_l P_l(\cos \theta). \quad (8)$$

Equation (7) is equivalent to the following three-term recursion relation to be obeyed by the coefficients d_l 's:

$$\alpha \frac{l}{2l-1} d_{l-1} + [l(l+1) - C] d_l + \alpha \frac{l+1}{2l+3} d_{l+1} = 0. \quad (9)$$

According to a standard method [21], the set of all these recursion relations can be transformed into a continued fraction expansion for the eigenvalue C in terms of itself and the parameter α . In the present case, we obtain

$$C = - \frac{\alpha^2}{3(1 \times 2 - C) - \frac{(2\alpha)^2}{5(2 \times 3 - C) - \frac{(3\alpha)^2}{7(3 \times 4 - C) - \dots}}}. \quad (10)$$

This is an implicit equation determining C as a function of α . It has a discrete infinity of solutions, corresponding to the number of nodes of the angular wave function, the ground state being without any nodes. For $\alpha = 0$, we already know that

$$C_l(\alpha = 0) = l(l+1), \quad l = 0, 1, 2, \dots \quad (11)$$

Here, we shall limit ourselves to the discussion of the lowest eigenvalue C of the angular equation. In Ref. [7], C was expressed as a power series in α , which with the requirement $C = -\frac{1}{4}$, leads to the determination of the critical dipole moment: $\alpha = 1.27863$, i.e., $D = 1.6250 \text{ D}$.

The series is converging fast for small dipole moments. For the range of dipole moments we wish to consider here, we take another approach. We terminate the continued fraction at the 15th depth level and solve the equation by numerical root finding. In this and in the following computations, we have made use of the symbolic and numerical software package MATHEMATICA.² In this way, the lowest eigenvalue C was found for dipole moments in the range 0–20 D, as depicted in Fig. 1.

We now wish to make an observation, which although not directly related to the confinement problem, is of importance for the choice of the angular range of basis functions in realistic *ab initio* calculations. Knowing C for each given α , we can now use the recursion relation of Eq. (9) to find the coefficients d_l of the Legendre polynomials. We determine

¹See, for instance, Ref. [33], Sec. 35.

²MATHEMATICA 4, version 4.2.0.0, Wolfram Research, Inc.

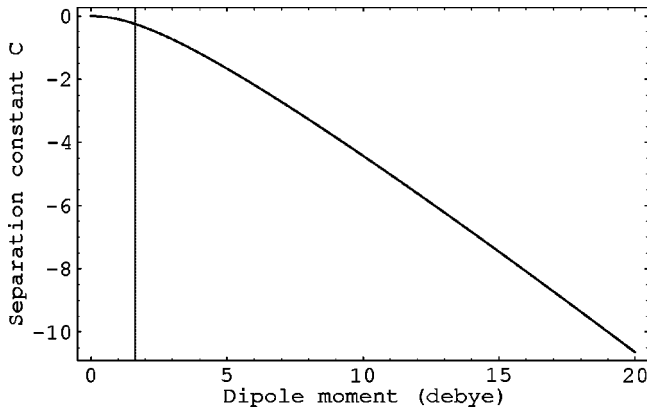


FIG. 1. The separation constant C for eigenstates with no nodes in the angular coordinates, as a function of dipole moment strength. The vertical grid line marks the critical dipole for the existence of a bound state, at 1.6250 D.

d_0 by requiring normalization of the wave function. For this aim, we computed d_l for $l=1-8$ with a good convergence for the higher dipole moments. Defining

$$d'_l = \frac{1}{\sqrt{2l+1}} d_l, \quad (12)$$

the new scaled coefficients d'_l correspond to normalized Legendre polynomials. In Fig. 2, we plot d'_l for $l=1-4$. As usual, the wave functions with $l=0,1,2,3 \dots$ are denoted by $s, p, d, f \dots$. We note, first, that the p -type contribution rises initially linearly with the dipole moment, the d -type quadratically, etc. This is as should be expected from considering the ideal dipole interaction as a perturbation to free spherical harmonics, since only levels differing by $\Delta l=1$ are coupled. However, for the bigger dipole moments, there is a significant contribution even from d functions.

In Ref. [5], adding d diffuse functions (on top of sp) to describe the dipole-bound state of the LiH^- anion, with a dipole moment of 5.88 D, was shown to increase the binding energy by 13%. On the other hand, in Ref. [27], an energy

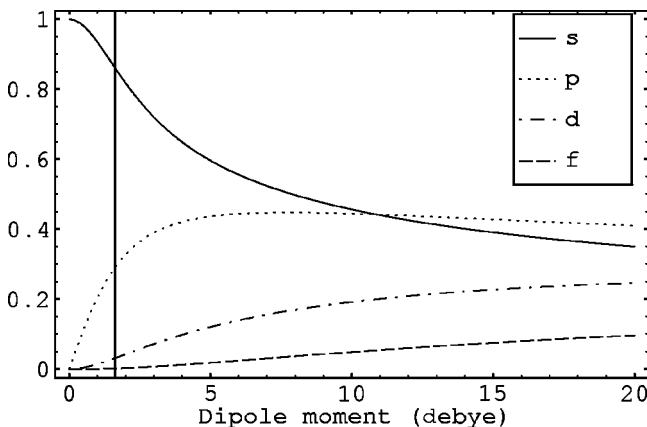


FIG. 2. The coefficients of functions of type s , p , d , and f for the angular wave function with no nodes. The vertical grid line marks the critical dipole.

change of only 1.6% for a linear water trimer with a dipole moment of 7 D was found, while a change of 14% was found for a cyclic water trimer with a smaller dipole moment of 3.4 D. How could these contradicting trends be understood?

As shown below, the lowest dipole-bound state of a system with big dipole moment is considerably more localized than that of a small dipole, and its spatial extent becomes more comparable with the size of the molecule. This is also evident from Fig. 1 of [27]. In such a case, the approximation made in our model of an ideal dipole interaction ceases to be valid. But if so, then for higher (excited) dipole-bound states, which are much more diffuse, the model should again apply. It seems therefore, that for molecules with a large dipole moment, the importance of including d functions should be greater for higher excited dipole-bound states.

For the two water trimer configurations, it was also found [25] that electronic correlation effects beyond second-order perturbation theory (which make significant contribution to the total binding energy) are quite insensitive to the addition of the d functions. The simple model considered here obviously cannot address this phenomenon. It might be addressed with the recently proposed pseudopotential methods including dispersion interactions [29,30].

Next, consider the radial equation, Eq. (6), first for the nonconfined problem. In this case, its solution is given by³

$$F(r) = A \frac{K_\nu(kr)}{\sqrt{r}}, \quad (13)$$

where

$$\nu = \sqrt{C + \frac{1}{4}} \quad (14)$$

and

$$k^2 = -2E, \quad (15)$$

with the boundary condition, at $r=a=1$, of

$$K_\nu(k) = 0. \quad (16)$$

Here, $K_\nu(x)$ is the modified Bessel function of the second kind, and A is a normalization constant. For dipole moments above the critical value, $C < -\frac{1}{4}$ so that we encounter a pure imaginary order $\nu = is$, with

$$s = \sqrt{-\left(C + \frac{1}{4}\right)}. \quad (17)$$

The function $K_\nu(r)$ of pure imaginary order and real r is real. Its behavior as $x \rightarrow 0$ is given by

$$K_{is}(r) = -\sqrt{\frac{\pi}{s \sinh(\pi s)}} \sin \left[s \ln \left(\frac{z}{2} \right) - \sigma(s) \right] [1 + O(r^2)], \quad (18)$$

³See Ref. [34], p. 1665.

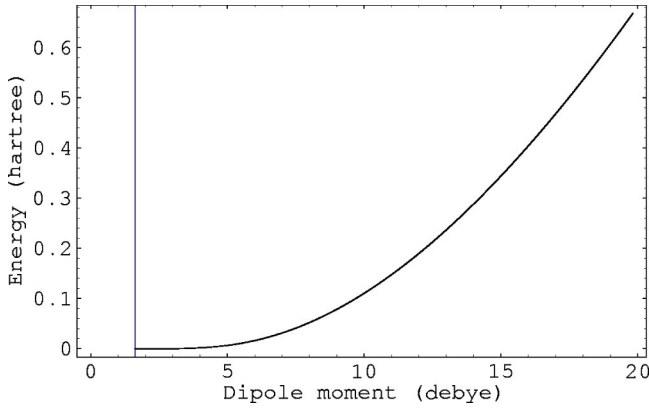


FIG. 3. The ground-state binding energy of the dipole-bound electron. Note that the energy should be scaled according to the repulsive potential length scale by $(a_0/a)^2$. The vertical grid line marks the critical dipole.

where

$$\sigma(s) = \arg[\Gamma(1 + is)]. \quad (19)$$

It is seen that for $k \rightarrow 0$, this function crosses zero an infinite number of times, thus satisfying the boundary condition, Eq. (16), for an infinite number of eigenstates with exponentially decreasing binding energy. We denote the n th root of Eq. (16) for a given value of s as k_{sn} . From Eq. (18), we obtain the asymptotic ratio between successive energy eigenvalues E_{sn} for a large n :

$$\frac{E_{s(n+1)}}{E_{sn}} \rightarrow \exp\left(-\frac{2\pi}{s}\right). \quad (20)$$

This ratio holds for an attractive long-range $1/r^2$ potential with any short-range repulsive potential, though the absolute position of the energy levels is dependent on the later. The form of this dependence was established in Ref. [31].

For each value of the dipole moment, using the results for the lowest eigenvalue C , the largest root k_{s1} , corresponding to the ground state, was calculated. The dependence of the ground-state energy on the dipole moment is presented in Fig. 3.

For the n th level, the normalization constant A in Eq. (13) is given by

$$A = \frac{\sqrt{2}}{K_{is+1}(k_{sn})}. \quad (21)$$

It may be expected that a given eigenvalue of the nonconfined system will be significantly perturbed by the confinement only when the radius of the sphere is not much larger than the spatial extent of the corresponding eigenstate. It is therefore of interest to calculate the mean radial distance of the wave function. This is given by

$$\bar{r} = \int_1^\infty r^3 [F(r)]^2 dr = A^2 \int_1^\infty r^2 [K_{is}(k_{sn}r)]^2 dr. \quad (22)$$

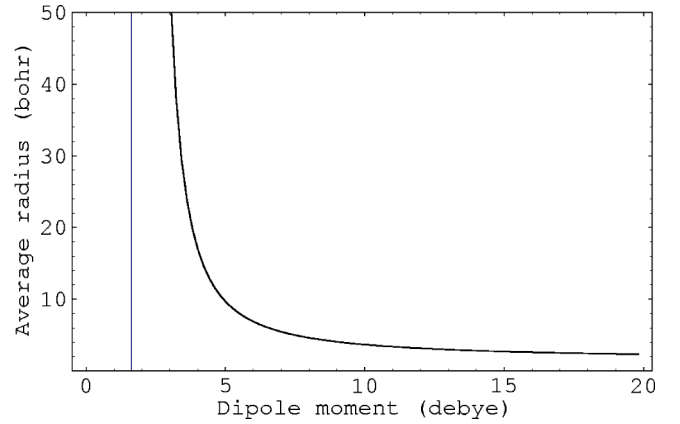


FIG. 4. The average electron radius at the ground state as a function of the dipole moment strength. This should be scaled according to the repulsive potential length scale by (a_0/a) .

Using the symbolic capability of MATHEMATICA, an analytic expression for this integral involving hypergeometric functions ${}_2F_3$ was found, which holds for an arbitrary value of k_{ns} , not necessarily a root of Eq. (16). This expression is quite complicated and is given in the Appendix, but evaluating it within MATHEMATICA is much faster than performing numerical integration to the same degree of accuracy. The result is presented in Fig. 4. It can be seen that for dipole moments smaller than 4 D, there is a very rapid rise in the distance of the electron from the center, while for dipole moments larger than 6 D, there is a gradual decrease, and the average distance of the electron is of the order of the molecular core size.

III. THE NEGATIVE ENERGY SPECTRUM OF THE CONFINED ELECTRON

We shall now determine the negative energy spectrum of the confined electron. Strictly speaking, the level $E=0$ does not have any special physical meaning for a confinement with an infinite potential. However, this is an approximation to a more realistic model in which the potential barrier shall be large and finite. Then, energy levels above zero will describe nonbound states, so that $-E$ again corresponds to the binding energy.

The general solution of Eq. (6) can be written as

$$F(r) = \frac{AI_\nu(kr) + BK_\nu(kr)}{\sqrt{r}}, \quad (23)$$

with the boundary conditions

$$F(1) = F(R) = 0, \quad (24)$$

where $I_\nu(r)$ is the modified Bessel function of the first kind, and ν and k are the same as in Eqs. (14) and (15).

For an imaginary order $\nu = is$, $I_{is}(r)$ is a complex-valued function. Negative values of the energy correspond to real k , while positive ones to imaginary k . For a real r , we have $I_\nu(r) = I_{-\nu}^*(r)$. It is convenient to work with real functions. We define

$$P_{is}(r) = \text{Re}[I_{is}(r)], \quad (25)$$

and

$$Q_{is}(r) = \text{Im}[I_{is}(r)] = -\frac{\sinh(s\pi)}{\pi} K_{is}(r), \quad (26)$$

and we rewrite Eq. (23) as

$$F(r) = \frac{AP_{is}(kr) + BQ_{is}(kr)}{\sqrt{r}}, \quad (27)$$

with A and B real.

The small- r behavior of $P_{is}(kr)$ and $Q_{is}(kr)$ is given by

$$P_{is}(r) = \sqrt{\frac{\sinh(\pi s)}{\pi s}} \cos\left[s \ln\left(\frac{r}{2}\right) - \sigma(s)\right] [1 + O(r^2)], \quad (28)$$

and

$$Q_{is}(r) = \sqrt{\frac{\sinh(\pi s)}{\pi s}} \sin\left[s \ln\left(\frac{r}{2}\right) - \sigma(s)\right] [1 + O(r^2)], \quad (29)$$

with $\sigma(s)$ as in Eq. (19).

For a large r , their asymptotic behavior is given by

$$P_{is}(r) \sim \frac{e^r}{\sqrt{2\pi r}}, \quad (30)$$

and

$$Q_{is}(r) \sim -\frac{\sinh(s\pi)}{\sqrt{2\pi r}} e^{-r}. \quad (31)$$

Equations (27) and (24) lead to the following equation for the eigenvalues k :

$$W_{is}(k) \equiv P_{is}(k)Q_{is}(kR) - P_{is}(kR)Q_{is}(k) = 0. \quad (32)$$

This implicitly determines the dependence of the energy levels on R and the dipole moment.

Let us first examine the condition for a given energy eigenvalue to become zero as a result of changing the confining sphere radius R . For $k \rightarrow 0$, we may replace the functions $P_{is}(k)$ and $Q_{is}(kR)$ with their small argument behaviors, Eqs. (28) and (29). We then obtain

$$W_{is}(k \rightarrow 0) \sim \sin[s \ln(R)] = 0. \quad (33)$$

Its solutions are

$$R_n = \exp\left(\frac{n\pi}{s}\right), \quad n = 1, 2, 3, \dots \quad (34)$$

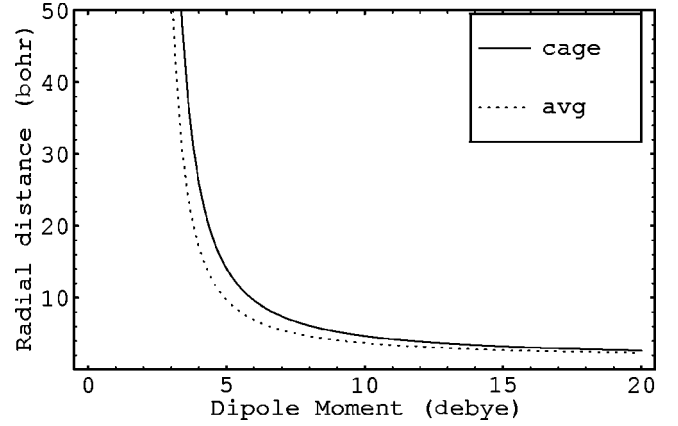


FIG. 5. Upper curve: the ground-state critical cage radius as a function of the dipole moment strength. For a comparison, the lower curve shows the average radius of the unconfined electron, from Fig. 4. Both scale as a/a_0 with the repulsive potential length scale a .

This equation describes the successive external radii R_n at which the n th dipole-bound state is ionized. We call them “critical cage radii,” after Ref. [20]. At the smallest critical cage radius,

$$R_1 = \exp\left(\frac{\pi}{s}\right), \quad (35)$$

the ground state is ionized. For smaller radii, there are no negative energy eigenvalues. Another way to derive this result is to put $E=0$ directly in Eq. (6). The general solution is given by

$$F(r) = \frac{A \cos[s \ln(r)] + B \sin[s \ln(r)]}{\sqrt{r}}. \quad (36)$$

Requiring this solution to satisfy the boundary conditions leads again to Eq. (33).

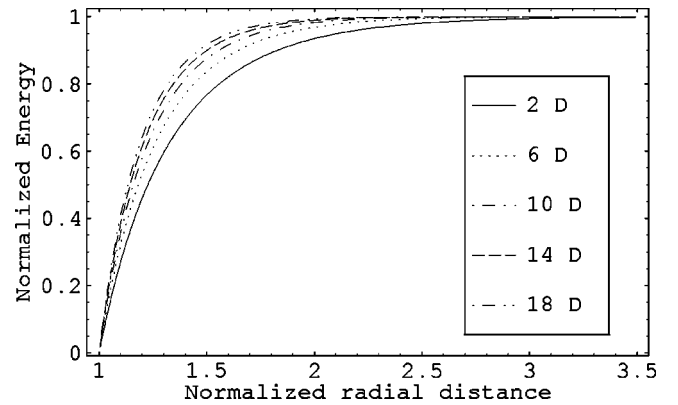


FIG. 6. Plots of the ground-state energy of the confined electron as a function of the radius of the spherical box. The energy is normalized by the energy of the unconfined case, and the radius by the critical cage radius. Each curve corresponds to a given dipole moment.

The dependence of the ground-state critical cage radius on the dipole moment strength is depicted in Fig. 5. For a comparison, the average radius of the unconfined electron is also shown on the same plot. The critical cage radius is bigger, with the ratio between them varying from 1.14 at 20 D to 1.76 at 2 D. So far, we have discussed the case for which the eigenstates have no nodes in the orbital coordinates θ, ϕ . In general, the same relation holds, with the parameter s being dependent not only on the dipole moment but also on the number of orbital nodes.

It is interesting to compare this result with that for the confined hydrogen problem, for which the critical cage radii for the hydrogen states (n, l) are given [19,20,32] in terms of roots of the Bessel function of the first kind:

$$J_{2l+1}(2\sqrt{2R_{nl}}) = 0. \quad (37)$$

An immediate consequence of Eq. (34) is that for a given radius R , the number $N(s)$ of bound states is given by

$$N(s) = \left\lfloor \frac{s \ln R}{\pi} \right\rfloor, \quad (38)$$

where $\lfloor x \rfloor$ is the biggest integer, not bigger than x .

We have calculated numerically the biggest root, corresponding to the ground state, for various values of the dipole moment and R . We normalize the energy of the confined electron by that of the unconfined case, from Fig. 3. Also, because the relevant range of R depends on the dipole moment strength, it is convenient to normalize it by the ground-state cage radius, Eq. (35) and Fig. 5. The results are depicted in Fig. 6. When interpreting this figure, it is important to bear in mind the huge variability of the actual (non-normalized) radii and energies between large and small dipole moments. The figure shows that the scaled quantities exhibit a similar, though not identical, functional dependence. The larger the dipole moment, the less sensitive is the normalized energy to the confinement and it begins to drop toward zero at smaller normalized confinement radius.

ACKNOWLEDGMENTS

I thank Professor O. Cheshnovsky and Professor P. Jungwirth for introducing me to the subject of dipole-bound states, and for their encouragement.

APPENDIX

Using MATHEMATICA, it is found that

$$\begin{aligned} \int_1^\infty r^2 [K_\nu(kr)]^2 dr = & \frac{4^{\nu-1} \Gamma(\nu)^2 {}_2F_3\left(\frac{1}{2} - \nu, \frac{3}{2} - \nu; 1 - \nu, \frac{5}{2} - \nu, 1 - 2\nu; k^2\right) (k^2)^{-\nu}}{2\nu - 3} \\ & - \frac{4^{-\nu-1} \Gamma(-\nu)^2 {}_2F_3\left(\frac{1}{2} + \nu, \frac{3}{2} + \nu; 1 + \nu, \frac{5}{2} + \nu, 1 + 2\nu; k^2\right) (k^2)^\nu}{2\nu + 3} \\ & - \frac{\pi \csc(\pi\nu) {}_2F_3\left(\frac{1}{2}, \frac{3}{2}, \frac{5}{2}; 1 - \nu, 1 + \nu; k^2\right)}{6\nu} + \frac{\pi^2 (4\nu^2 - 1) \sec(\pi\nu)}{32(k^2)^{3/2}}. \end{aligned} \quad (A1)$$

The generalized hypergeometric function ${}_2F_3(a, b; c, d, e; x)$ is defined by the power series:

$${}_2F_3(a, b; c, d, e; x) = \sum_{n=0}^{\infty} \frac{(a)_n (b)_n}{(c)_n (d)_n (e)_n} \frac{x^n}{n!}, \quad (A2)$$

where the Pochhammer symbol $(a)_n$ is given by

$$(a)_n = \frac{\Gamma(a+n)}{\Gamma(a)}. \quad (A3)$$

The integral was verified with numerical integration of test cases.⁴ We note that in this formula, the parameter k does not have to be a root of $K_\nu(k)$. The formula is valid for any k with $\text{Re}(k) > 0$. It seems plausible that the additional condition $K_\nu(k) = 0$ which corresponds to the boundary condition discussed in the text, may lead to further simplification of the formula.

⁴MATHEMATICA is not free of bugs. In fact, in version 4.2.0.0, we caution against a bug in the evaluation of a similar Bessel integral with r instead of r^2 .

- [1] R.N. Compton, H.S. Carman, Jr., C. Desfrancois, H. Abdoul-Carime, J.P. Schermann, J.H. Hendricks, S.A. Lyapustina, and K.H. Bowen, *J. Chem. Phys.* **105**, 3472 (1996).
- [2] F.K. Fatemi, A.J. Dally, and L.A. Bloomfield, *Phys. Rev. Lett.* **84**, 51 (2000).
- [3] H.E. Camblong, L.N. Epele, H. Fanchiotti, and C.A.G. Canal, *Phys. Rev. Lett.* **87**, 220402 (2001).
- [4] J. Kalcher and A.F. Sax, *Chem. Phys. Lett.* **326**, 80 (2000).
- [5] G.L. Gustev, M. Nooijen, and R.J. Bartlett, *Phys. Rev. A* **57**, 1646 (1998).
- [6] E. Fermi and E. Teller, *Phys. Rev.* **72**, 406 (1947).
- [7] J.-M. Lévy-Leblond, *Phys. Rev.* **153**, 1 (1967).
- [8] W.B. Brown and R. Roberts, *J. Chem. Phys.* **46**, 2006 (1967).
- [9] O.H. Crawford, *Proc. Phys. Soc. London* **91**, 279 (1967).
- [10] J.E. Turner, *Am. J. Phys.* **45**, 758 (1977).
- [11] K.M. Griffing, J. Kenney, J. Simons, and K.D. Jordan, *J. Chem. Phys.* **63**, 4073 (1975).
- [12] K.D. Jordan, K.M. Griffing, J. Kenney, E.L. Andersen, and J. Simons, *J. Chem. Phys.* **64**, 4730 (1976).
- [13] J. Simons and K.D. Jordan, *Chem. Rev. (Washington, D.C.)* **87**, 535 (1987).
- [14] W.R. Garrett, *Phys. Rev. A* **3**, 961 (1971).
- [15] W.R. Garrett, *J. Chem. Phys.* **73**, 5721 (1980).
- [16] W.R. Garrett, *J. Chem. Phys.* **77**, 3666 (1982).
- [17] R.D. Muiño, M. Alducin, and P.M. Echenique, *Phys. Rev. B* **67**, 121101(R) (2003).
- [18] A. Michels, J. de Boer, and A. Bijl, *Physica (Amsterdam)* **4**, 981 (1937).
- [19] A. Sommerfeld and H. Welker, *Ann. Phys. (N.Y.)* **32**, 56 (1938).
- [20] Y.P. Varshni, *J. Phys. B* **31**, 2849 (1998).
- [21] Y.P. Varshni, *Z. Naturforsch., A: Phys. Sci.* **57**, 915 (2002).
- [22] D.S. Chuu, C.M. Hsiao, and W.N. Mei, *Phys. Rev. B* **46**, 3898 (1992).
- [23] J.P. Connerade, V.K. Dolmatov, P.A. Lakshmi, and S.T. Manson, *J. Phys. B* **32**, 239 (1999).
- [24] E. Ley-Ko and S.A. Cruz, *J. Chem. Phys.* **74**, 4603 (1981).
- [25] J. Gorecki and W.B. Brown, *J. Chem. Phys.* **89**, 2138 (1988).
- [26] S. Mateos-Cortés, E. Ley-Koo, and S.A. Cruz, *Int. J. Quantum Chem.* **86**, 376 (2002).
- [27] P. Skurski, M. Gutowski, and J. Simons, *Int. J. Quantum Chem.* **80**, 1024 (2000).
- [28] M.R.H. Rudge, S. Trajmar, and W. Williams, *Phys. Rev. A* **13**, 2074 (1976).
- [29] M. Sindelka, V. Spirko, and P. Jungwirth, *J. Chem. Phys.* **117**, 5113 (2002).
- [30] F. Wang and K.D. Jordan, *J. Chem. Phys.* **114**, 10717 (2001).
- [31] M.J. Moritz, C. Eltschka, and H. Friedrich, *Phys. Rev. A* **63**, 042102 (2001).
- [32] R.B. Dingle, *Proc. Cambridge Philos. Soc.* **49**, 103 (1953).
- [33] L.D. Landau and E.M. Lifshitz, *Quantum Mechanics*, 3rd ed. (Butterworth-Heinemann, Oxford, 1991).
- [34] M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953).