Bound electronic states in a statically screened electric-dipole potential

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The problem of the minimum value of the dipole moment needed to assure the existence of a bound electronic state has been addressed for the electrostatically screened Coulomb interaction of the Yukawa type. Our variational calculation demonstrates that the value of the minimum dipole moment increases as the screening parameter increases. More interestingly, we have found that the dipole's length has a remarkable effect on the minimum dipole moment; a feature not found for the unscreened case. This effect yields a rapid increase of the value of the minimum dipole moment, particularly for large values of the screening parameter, with the increasing dipole moment's length. [S1050-2947(96)10610-7]

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I. INTRODUCTION

The existence of bound states for an electron moving in the field of a dipole has importance in solid state physics and in the theory of electron scattering from polar molecules [1–4], and has recently generated renewed interest, due to its use in a technique that permits nondestructive selection of mass and geometrical configurations of both neutral and charged polar weakly bound complexes [5]. It has been shown, following various methods [6–12], that the minimum value of the dipole moment, $D_{\min}$, required for electronic binding is $D_{\min}=0.6393$ a.u.$=1.625D$. It has also been deduced [7,10,11] that the value of $D_{\min}$ is independent of whether the dipole is a finite or a point dipole, that is, it is independent of the dipole size. Fox and Turner [13], using a variational treatment, obtain an upper bound, namely, $3\sqrt{3}/8$ a.u., to the $D_{\min}$ value. In this work we investigate how this minimum value of the dipole moment, required for the existence of bound electronic states, is affected by the electrostatical screening of the Coulomb potential. The weakly screened Coulomb interaction of the Yukawa type is considered, and the existence of a bound electronic state as a function of the screening intensity studied.

II. METHOD

A. Screened electric-dipole potential

We consider two point charges q and $-q$ located at $\mathbf{r}_+$ and $\mathbf{r}_-$, respectively, from the origin. The Poisson equation for the unscreened dipole potential $\Phi_0(\mathbf{r})$ is [14]

$$\nabla^2\Phi_0(\mathbf{r})=-4\pi q[\delta(\mathbf{r}-\mathbf{r}_+)-\delta(\mathbf{r}-\mathbf{r}_+)], \tag{1}$$

which, using the Fourier representation to express $\Phi_0(\mathbf{r})$, $\delta(\mathbf{r}-\mathbf{r}_+)$, and $\delta(\mathbf{r}-\mathbf{r}_+)$, can be written as

$$\frac{1}{(2\pi)^3}\int d\mathbf{k}\nabla^2\Phi_0(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}} =\frac{-4\pi q}{(2\pi)^3}\int d\mathbf{k}[e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_+)}-e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_-)}] \tag{2}$$

The Fourier components of the screened and the unscreened potentials satisfy [15]

$$\Phi(\mathbf{k})=\frac{\Phi_0(\mathbf{k})}{\epsilon(k)}, \tag{3}$$

where $\epsilon(k)$ is the momentum-dependent dielectric constant, which within the Thomas-Fermi approximation can be expressed as

$$\epsilon(k)=1+\frac{\lambda^2}{k^2}, \tag{4}$$

where λ is the screening parameter and is related to $D(\epsilon_F)$, the density of states for a free electron gas,

$$\lambda^2=4\pi e^2D(\epsilon_F). \tag{5}$$

Using Eqs. (2)–(4) we get for the screened dipole potential the expression

$$\Phi(\mathbf{k})=\frac{4\pi q}{k^2+\lambda^2}[e^{-i\mathbf{k}\cdot\mathbf{r}_+}-e^{-i\mathbf{k}\cdot\mathbf{r}_-}]. \tag{6}$$

Then in the position space

$$\Phi(\mathbf{r})=\frac{4\pi q}{(2\pi)^3}\int d\mathbf{k}\frac{1}{k^2+\lambda^2}[e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_+)}-e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_-)}], \tag{7}$$

which as a result

$$\Phi(\mathbf{r})=q\left[\frac{e^{-\lambda|\mathbf{r}-\mathbf{r}_+|}}{|\mathbf{r}-\mathbf{r}_+|}-\frac{e^{-\lambda|\mathbf{r}-\mathbf{r}_-|}}{|\mathbf{r}-\mathbf{r}_-|}\right]. \tag{8}$$

For the point-dipole case, where the distance between the two charges $|\mathbf{r}_+-\mathbf{r}_-|=2a$ is very small with respect to $r=|\mathbf{r}|$, we can approximate

$$|\mathbf{r}-\mathbf{r}_+|=r-a\cos\theta \tag{9}$$

$$|\mathbf{r}-\mathbf{r}_-|=r+a\cos\theta, \tag{10}$$

where θ is the angle between the dipole direction and $\mathbf{r}$, and then

$$\Phi(\mathbf{r})=q\frac{e^{-\lambda r}}{r}\left[\frac{e^{\lambda a\cos\theta}}{1-\frac{a}{r}\cos\theta}-\frac{e^{-\lambda a\cos\theta}}{1+\frac{a}{r}\cos\theta}\right]. \tag{11}$$

If we now expand the exponentials inside the brackets to first order in a, we get

$$\Phi(\mathbf{r})=q\frac{e^{-\lambda r}}{r}\left[\frac{2\frac{a}{r}\cos\theta+2\lambda a\cos\theta}{1-\left(\frac{a}{r}\right)^2\cos^2\theta}\right]$$

$$\approx\frac{D\cos\theta}{r^2}e^{-\lambda r}(1+\lambda r), \tag{12}$$

where $D=2qa$ is the dipole moment. The effect of the screening on the point-dipole potential is therefore to introduce a multiplicative factor of $e^{-\lambda r}(1+\lambda r)$ in its potential.

B. Variational calculation for bound states in the screened dipole

To investigate the effect that the screening of the dipole potential has on the minimun dipole moment necessary to assure the existence of a bound state, we carry out a variational calculation using the Fox and Turner [13] trail wavefunction,

$$\Psi(r,\theta,\phi)=g(r)Y(\theta,\phi), \tag{13}$$

with

$$g(r)=ne^{-\alpha r^t} \tag{14}$$

and

$$Y(\theta,\phi)=C_0Y_{00}(\theta,\phi)+C_1Y_{10}(\theta,\phi) \tag{15}$$

being the normalized radial and angular functions, respectively; therefore,

$$n=\left[\frac{t(2\alpha)^{3/t}}{\Gamma(3/t)}\right]^{1/2} \tag{16}$$

and

$$|C_0|^2+|C_1|^2=1. \tag{17}$$

The functions $Y_{lm}(\theta,\phi)$ are the orthogonal spherical harmonics and α, t, C_0, and C_1 are parameters. A sufficient condition [13] for the existence of a bound state of the electron is that $\langle H\rangle_{\min}$ be negative or equivalently

$$\nu>2\mu[(t+1)(t+9)]^{1/2}, \tag{18}$$

where

$$\nu=\frac{-\langle V\rangle}{C_1(1-C_1^2)^{1/2}} \tag{19}$$

and

$$\mu=\frac{\langle T\rangle}{(t+1+8C_1^2)} \tag{20}$$

with $\langle V\rangle$ and $\langle T\rangle$ being the mean values of the potential and kinetic energies, respectively, of the Hamiltonian operator $\hat{H}=\hat{T}+\hat{V}$. The functional form of $\langle T\rangle$ is the same as the one given by Fox and Turner [13], as the mean value of the kinetic energy is only wave function dependent, namely,

$$\mu=\frac{1}{8}(2\alpha)^{2/t}\frac{\Gamma(1/t)}{\Gamma(3/t)}, \tag{21}$$

where $\Gamma(n/t)$ is the gamma function. So, we have to calculate the mean value of the potential energy $V(\mathbf{r})$ of the electron in the field of the screened electric-dipole $\Phi(\mathbf{r})$ (all quantities are given in atomic units unless the contrary is said)

$$V(\mathbf{r})=-\Phi(\mathbf{r})=q\left[\frac{e^{-\lambda|\mathbf{r}-\mathbf{r}_-|}}{|\mathbf{r}-\mathbf{r}_-|}-\frac{e^{-\lambda|\mathbf{r}-\mathbf{r}_+|}}{|\mathbf{r}-\mathbf{r}_+|}\right]. \tag{22}$$

For simplicity we take the dipole centered at the origin and along the z axis and take $\mathbf{r}_+=\mathbf{a}$ and $\mathbf{r}_-=-\mathbf{a}$; then

$$V(\mathbf{r})=q\left[\frac{e^{-\lambda|\mathbf{r}+\mathbf{a}|}}{|\mathbf{r}+\mathbf{a}|}-\frac{e^{-\lambda|\mathbf{r}-\mathbf{a}|}}{|\mathbf{r}-\mathbf{a}|}\right]. \tag{23}$$

We expand $e^{-\lambda|\mathbf{r}+\mathbf{a}|}/|\mathbf{r}+\mathbf{a}|$ and $e^{-\lambda|\mathbf{r}-\mathbf{a}|}/|\mathbf{r}-\mathbf{a}|$ in terms of the spherical Bessel functions [16]

$$\frac{e^{-\lambda|\mathbf{r}+\mathbf{a}|}}{|\mathbf{r}+\mathbf{a}|}=-\lambda\sum_{l=0}^{\infty}(2l+1)j_l(i\lambda r_<)h_l^1(i\lambda r_>)P_l(-\cos\theta), \tag{24}$$

$$\frac{e^{-\lambda|\mathbf{r}-\mathbf{a}|}}{|\mathbf{r}-\mathbf{a}|}=-\lambda\sum_{l=0}^{\infty}(2l+1)j_l(i\lambda r_<)h_l^1(i\lambda r_>)P_l(\cos\theta), \tag{25}$$

where $j_l(x)$ are the spherical Bessel functions of first kind, $h_l^1(x)$ are the spherical Bessel functions of third kind, $P_l(x)$ are the Legendre polynomials, and $r_<$ $(r_>)$ designates the smaller (larger) of the two moduli of $\mathbf{r}$ and $\mathbf{a}$.

Taking into account the symmetry properties of the Legendre polynomials, the potential energy is written as

$$V(r,\theta,a,\lambda)=2q\lambda\sum_{l=\mathrm{odd}}(2l+1)j_l(i\lambda r_<)h_l^1(i\lambda r_>)P_l(\cos\theta) \tag{26}$$

and then the mean value of the potential energy is

$$\begin{aligned}\langle V\rangle=|n|^2\int d\mathbf{r}\,e^{-2\alpha r^t}[&|C_0|^2P_0^2(\cos\theta)+3|C_1|^2P_1^2(\cos\theta)\\&+2\sqrt{3}\,\mathrm{Re}(C_0C_1^*)P_0(\cos\theta)P_1(\cos\theta)]\\&\times\left[2q\lambda\sum_{l=\mathrm{odd}}(2l+1)j_l(i\lambda r_<)h_l^1(i\lambda r_>)P_l(\cos\theta)\right],\end{aligned} \tag{27}$$

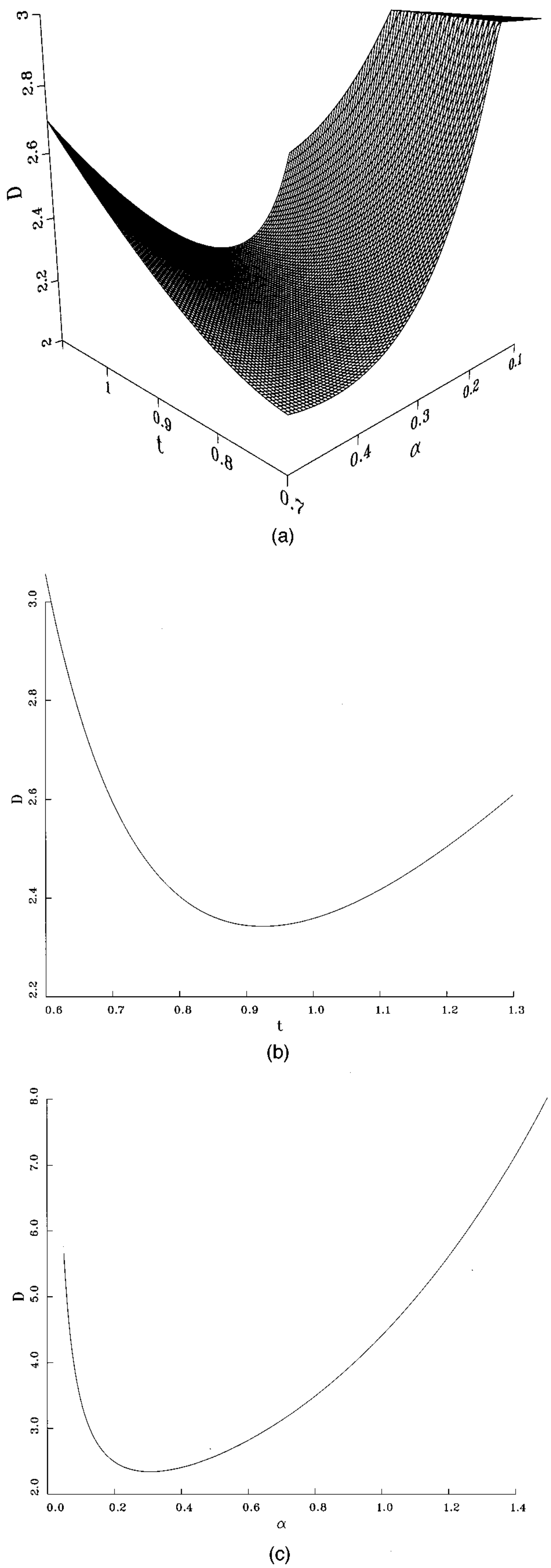

FIG. 1. $D_0^\lambda(t,\alpha)$ surface, in a.u., for values $\lambda = 0.6$ a.u.$^{-1}$ and $a = 1$ a.u. of the screening parameter and dipole length, respectively. (b) and (c) show cuts to the surface passing through the minimum, for values $t = 0.93$ and $\alpha = 0.31$, respectively.

where the orthonormal spherical harmonics in the wave function have been expressed in terms of the Legendre polynomials. The orthonormal properties of the Legendre polynomials make zero the contribution of all the terms in the summation over l except the one for $l = 1$. Therefore, after angular integration, the mean value of V reduces to

$$\langle V\rangle = 4\sqrt{3}q\lambda|n|^2\mathrm{Re}(C_0C_1^*)\int_0^\infty r^2e^{-2\alpha r^t} \times j_1(i\lambda r_<)h_1^1(i\lambda r_>)dr. \tag{28}$$

Both C_0 and C_1 can be taken as real without loss of generality; then using the normalization condition of the angular part of the wave function, that is, $C_0^2 + C_1^2 = 1$, and using Eq. (16) for the value of the normalization of the radial part, we get

$$\langle V\rangle = 4\sqrt{3}q\lambda\frac{t(2\alpha)^{3/t}}{\Gamma(3/t)}C_1(1-C_1^2)^{1/2}\int_0^\infty r^2e^{-2\alpha r^t} \times j_1(i\lambda r_<)h_1^1(i\lambda r_>)dr; \tag{29}$$

hence, from Eq. (19)

$$\nu = \frac{-\langle V\rangle}{C_1(1-C_1^2)^{1/2}} = -4\sqrt{3}q\lambda\frac{t(2\alpha)^{3/t}}{\Gamma(3/t)}\int_0^\infty r^2e^{-2\alpha r^t}j_1(i\lambda r_<)h_1^1(i\lambda r_>)dr. \tag{30}$$

Taking into account the definition of the spherical Bessel functions, the product

$$j_1(i\lambda r_<)h_1^1(i\lambda r_>) \tag{31}$$

can be written as

$$j_1(i\lambda r_<)h_1^1(i\lambda r_>) = \frac{-1}{2}\left(\frac{e^{-\lambda r_<}-e^{\lambda r_<}}{(\lambda r_<)^2} + \frac{e^{-\lambda r_<}+e^{\lambda r_<}}{\lambda r_<}\right) \times e^{-\lambda r_>}\left(\frac{1}{(\lambda r_>)^2} + \frac{1}{\lambda r_>}\right) \tag{32}$$

and the integral in Eq. (30) becomes

$$\begin{aligned}\int_0^\infty r^2e^{-2\alpha r^t}j_1(i\lambda r_<)h_1^1(i\lambda r_>)dr &= \frac{-1}{2\lambda^2}e^{-\lambda a}\left(\frac{1}{(\lambda a)^2}+\frac{1}{\lambda a}\right) \\ &\quad \times\int_0^a dre^{-2\alpha r^t}[e^{-\lambda r}-e^{\lambda r}+(e^{-\lambda r}+e^{\lambda r})] \\ &\quad +\left(\frac{e^{-\lambda a}-e^{\lambda a}}{(\lambda a)^2}+\frac{e^{-\lambda a}+e^{\lambda a}}{\lambda a}\right) \\ &\quad \times\int_a^\infty dre^{-2\alpha r^t}e^{-\lambda r}(1+\lambda r).\end{aligned} \tag{33}$$

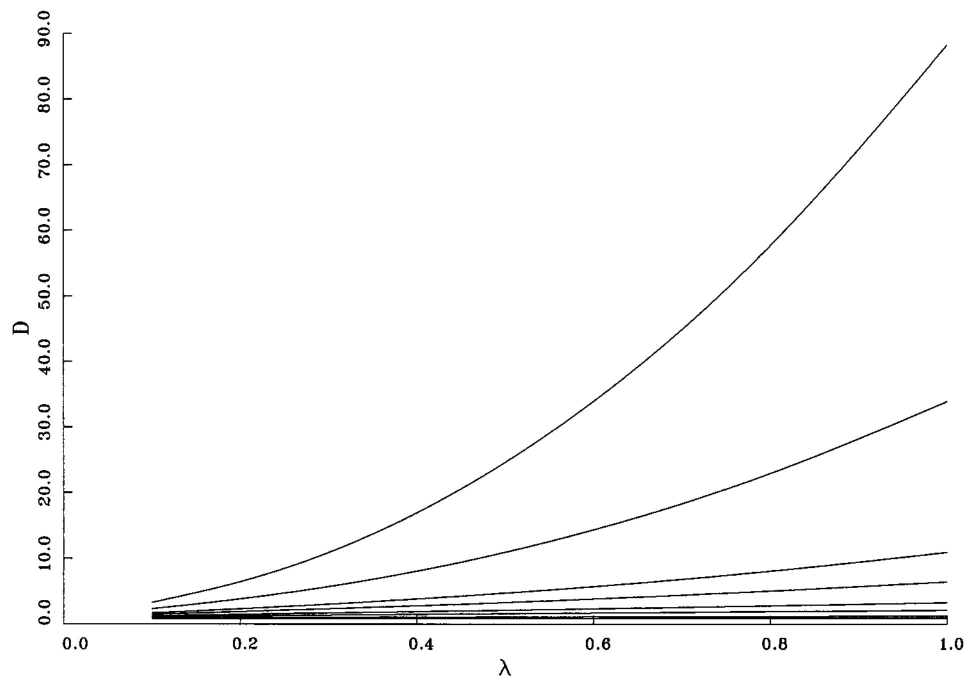

FIG. 2. Minimum of $D_0^\lambda(t,\alpha)$, in a.u., as a function of the screening parameter λ, in a.u.$^{-1}$, for the selected dipole length shown in Table I. Each curve corresponds to a different a value, starting at $a=0.01$ a.u., from the bottom, and increasing steadily until $a=10.0$ a.u., at the top of the graph.

Making use of expressions (21), (30), and (33), the condition for the existence of a bound electronic state in the screened dipole field [Eq. (18)] can be written as

$$\frac{\sqrt{3}qt(2\alpha)^{3/t}}{\lambda\Gamma(3/t)}\left\{e^{-\lambda a}\left(\frac{1}{(\lambda a)^2}+\frac{1}{\lambda a}\right)\times\int_0^a dr\, e^{-2\alpha r^t}[e^{-\lambda r}-e^{\lambda r}+\lambda r(e^{-\lambda r}+e^{\lambda r})]+\left(\frac{e^{-\lambda a}-e^{\lambda a}}{(\lambda a)^2}+\frac{e^{-\lambda a}+e^{\lambda a}}{\lambda a}\right)\times\int_a^\infty dr\, e^{-2\alpha r^t}e^{-\lambda r}(1+\lambda r)\right\}$$

$$>\frac{1}{8}(2\alpha)^{2/t}\frac{\Gamma(1/t)}{\Gamma(3/t)}[(t+1)(t+9)]^{1/2}. \tag{34}$$

Consequently, from this expression one can easily obtain

$$2qa=D^\lambda>\frac{\frac{\sqrt{3}}{8}\Gamma\left(\frac{1}{t}\right)[(t+1)(t+9)]^{1/2}}{\frac{3t(2\alpha)^{1/t}}{2\lambda a}W}, \tag{35}$$

where

$$W=\frac{e^{-\lambda a}}{\lambda a}\left(\frac{1}{\lambda a}+1\right)\times\int_0^a dr\, e^{-2\alpha r^t}[e^{-\lambda r}-e^{\lambda r}+\lambda r(e^{-\lambda r}+e^{\lambda r})]+\left(\frac{e^{-\lambda a}-e^{\lambda a}}{(\lambda a)^2}+\frac{e^{-\lambda a}+e^{\lambda a}}{\lambda a}\right)\int_a^\infty dr\, e^{-2\alpha r^t}e^{-\lambda r}(1+\lambda r). \tag{36}$$

For $\lambda\to 0$ Eq. (35) reduces to

$$2qa=D>\frac{\frac{\sqrt{3}}{8}\Gamma\left(\frac{1}{t}\right)[(t+1)(t+9)]^{1/2}}{t(2\alpha)^{1/t}\left(\frac{1}{a^3}\int_0^a dr\, e^{-2\alpha r^t}r^3+\int_a^\infty dr\, e^{-2\alpha r^t}\right)}. \tag{37}$$

This expression is in agreement with the result obtained by Fox and Turner [13] for the unscreened potential case.

For the point dipole case, that is, in the limit $a\to 0$, the condition for the existence of a bound electron state for the screened potential is

$$2qa=D^\lambda>\frac{\frac{\sqrt{3}}{8}\Gamma\left(\frac{1}{t}\right)[(t+1)(t+9)]^{1/2}}{t(2\alpha)^{1/t}\int_0^\infty dr\, e^{-2\alpha r^t}e^{-\lambda r}(1+\lambda r)} \tag{38}$$

TABLE I. Values of $D_0^\lambda(t,\alpha)_{\min}$ (a.u.), t, and α for different values of the screening parameter λ (a.u.$^{-1}$) and the dipole length a (a.u).

$D_0^\lambda(t,\alpha)_{\min}$	t	α	λ	$D_0^\lambda(t,\alpha)_{\min}$	t	α	λ
	$a=0.01$				$a=2.0$		
0.91	0.39	2.68	1.0	6.43	1.19	0.15	1.0
0.90	0.37	2.59	0.8	5.03	1.14	0.15	0.8
0.88	0.35	2.50	0.6	3.83	1.07	0.15	0.6
0.86	0.33	2.39	0.4	2.80	0.99	0.16	0.4
0.83	0.29	2.29	0.2	1.91	0.85	0.17	0.2
0.80	0.26	2.24	0.1	1.48	0.72	0.19	0.1
	$a=0.1$				$a=3.0$		
1.24	0.62	1.35	1.0	10.91	1.29	0.08	1.0
1.19	0.59	1.29	0.8	8.05	1.24	0.09	0.8
1.13	0.56	1.23	0.6	5.70	1.17	0.09	0.6
1.06	0.51	1.17	0.4	3.83	1.09	0.10	0.4
0.97	0.44	1.11	0.2	2.34	0.93	0.11	0.2
0.91	0.39	1.09	0.1	1.70	0.79	0.13	0.1
	$a=0.5$				$a=6.0$		
2.12	0.89	0.57	1.0	33.91	1.45	0.02	1.0
1.91	0.85	0.55	0.8	22.91	1.40	0.03	0.8
1.70	0.79	0.53	0.6	14.33	1.33	0.03	0.6
1.48	0.72	0.51	0.4	8.05	1.24	0.04	0.4
1.24	0.62	0.50	0.2	3.83	1.08	0.05	0.2
1.09	0.54	0.51	0.1	2.34	0.93	0.06	0.1
	$a=1.0$				$a=10.0$		
3.29	1.04	0.32	1.0	88.28	1.54	0.009	1.0
2.80	0.99	0.31	0.8	57.68	1.50	0.010	0.8
2.34	0.93	0.31	0.6	33.91	1.45	0.012	0.6
1.91	0.85	0.30	0.4	16.92	1.36	0.015	0.4
1.48	0.72	0.31	0.2	6.43	1.20	0.021	0.2
1.24	0.62	0.32	0.1	3.29	1.04	0.029	0.1

III. DISCUSSION

For the unscreened case, letting the parameter α approach zero, the smallest value for the right-hand side of Eq. (37) is obtained for $t=0$ and is $\frac{3}{8}\sqrt{3}$ a.u., which allows Fox and Turner [13] to conclude that a dipole moment as small as $1.65D$ gives a bound electronic state for the unscreened dipole. For the screened case, however, the parameter α can no longer tend to zero because, in this case, the right-hand side of Eq. (35) goes to infinity as the two integrals in the denominator converge to finite numbers and are both multiplied by $\alpha^{1/t}$.

The analytical calculation of the values of the parameters α and t that minimize the right-hand side of Eq. (35), that we will call for simplicity $D_0^\lambda(t,\alpha,a,\lambda)$, is complicated and we have proceeded to do it numerically. For fixed values of a and λ we look for the minimum of the surface $D_0^\lambda(t,\alpha)$ that we denote as $D_0^\lambda(t,\alpha)_{\min}$.

Figure 1 shows the $D_0^\lambda(t,\alpha)$ surface for values $\lambda=0.6$ a.u.$^{-1}$ and $a=1$a.u. of the screening parameter and dipole length, respectively. For small and large values of both t and α, D_0^λ increases and the minimum is obtained for $t=0.93$ and $\alpha=0.31$, as it can be seen better in Figs. 1(b) and 1(c). The value of the minimum is $D_{0\,\min}^\lambda=2.34$ a.u.

In Fig. 2 we show the minimum of the surfaces $D_0^\lambda(t,\alpha)$ for various selected choices of λ, and a. These values $D_0^\lambda(t,\alpha)_{\min}$, t, α, λ, and a are shown in Table I. As it can be seen, when λ approaches zero, the value of $D_{0\,\min}^\lambda$ decreases and tends to a constant independent of the distance between charges a, and that is close to the value $3\sqrt{3}/8$ a.u. obtained by Fox and Turner [13] for the unscreened dipole. It is also seen that for small values of the dipole length a, $D_{0\,\min}^\lambda$ is less sensitive to the screening parameter λ than for larger dipole lengths.

Notice that for the unscreened case, the minimum value of the dipole moment needed to assure the existence of a bounded electronic state is the same for both the finite dipole and the point dipole. In other words, it is independent of the dipole length. However, for the screened case, the behavior of the dipole is strongly dependent on the dipole's length. According to our results, and for the variational wave function used, for the point dipole the value of the dipole moment needed to assure the existence of a bound electronic state is only weakly dependent on the screening parameter λ. However, for the finite dipole, this minimun value of the dipole moment becomes more sensitive to the screening as the dipole length increases. This different behavior between the point dipole and the finite dipole where the screening is present can be explained taking into account that the effect of the screening is as less important as smaller is the a/r relation. Note that when a/r is small the electron ''sees'' the two charges of the dipole mutually neutralized, and the screening does not have much effect, while for large values of a/r the electron ''sees'' the two charges clearly differentiated, and in this latter case the effect of the screening is felt by the electron. In other words, it is the intercharge region of the dipole that is mainly responsible for the sensitivity to the screening which increases with the length of the dipole. In the case of the point dipole, for which the intercharge region is negleted, the screening effect is much smaller.

IV. SUMMARY

Our calculation has demostrated that the value of the minimum dipole moment to assure the existence of at least one bound electronic state increases as the screaning parameter increases. More interestingly, our calculations predict a different behavior of the point dipole or the finite dipole models. This feature is not encountered for the unscreened Coulomb potential case, for which both the point dipole and the finite dipole models lead to a minimum dipole moment of 1.625D to obtain at least one bound electronic state. However, we have predicted that for a given dipole moment $2da$, the existence of at least one bound electronic state, for the screened Coulomb potential, depends on both the screening parameter and the dipole length. For a given value of the screening parameter, it is observed that the minimum value of the dipole increases as its length increases.

This behavior of the dipolar molecules, with respect to their binding capability to external electrons, could be used to further separate different geometrical isomers of weakly bound intermolecular complexes [5] which have the same dipole moments and different dipole lengths, by carrying out the experiment in a screening medium, instead of in a vacuum. Weakly coupled plasma enviroments provide the most obvious examples for such media, since their effects on molecules can be adequately represented by a Yukawa-type screened Coulomb potential [17].

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