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Minimum dipole moment required to bind an electron in a polarizable medium

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Assuming a Yukawa potential, the minimum value of the dipole moment required to bind an electron in a medium is studied. The value of the minimum dipole moment is found to depend only on a dimensionless parameter. A variational procedure with simple wave functions depending on only one parameter is used. For realistic screening, the results improve significantly the previously calculated values.

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INTRODUCTION

Understanding the nature and behavior of the bound states of an electron in the field of an electric dipole is crucial for many areas of physics, including electron scattering[1] and capture phenomena of Rydberg electrons by polar molecules,[2] and recent experimental results concerning the electron affinity of neutral molecules possessing a dipole moment large enough to bind an electron outside its valence shell.[3]

In a seminal paper,[4] Fermi and Teller demonstrated that a point dipole larger than $\rho_c = 1.625$ D, can bind an electron. Since then, many others have considered the case of real molecular systems and reached the conclusion that Fermi and Teller's critical dipole must be increased by 10–20 % for the dipolar molecule to support at least one bound state for the electron.[5] Nevertheless, having an accurate theoretical estimation of the minimum dipole required to bind an electron has been proven to be crucial for the assessment of *ab initio* calculations on the electron affinity of the resulting dipolar closed-shell molecules. Indeed, it has been recently shown[6] that both very large and flexible basis sets sophisticated treatment of the electron correlation problem are mandatory in order to reach agreement with both the above mentioned theoretical prediction and experiment.

Less studied but equally important is the behavior of an electron bind to a screened dipole. In particular, the nature of emerging dipolar structures around very electronegative defects in solids,[7] so that the defect atom is able to withdraw an electron from a crystal atom, can be modeled by a screened dipolar model system. Namely, when the defect atom occupies a substitutional site nearby the positively charged crystal site, a screened dipolar structure emerges, with the valence electrons of the crystal setting up the screening environment. Then, the question arises whether this structure can trap either a conduction electron or a hole. Another crystalline system that can be related to the model system considered in this paper is a positive vacancy brought near an *F* center in alkali halide crystals.[8]

Recently, Ugalde and Sarasola[9] have studied the minimum dipole moment required to bind one electron in the field of a screened electric dipole. Their work, based on the Yukawa potential to account for the screening effects, reveals some very interesting and unexpected features of the dipole-bound state of the electron. However, their variational wave function is appropriate only for weak screening while for larger screening, wave functions with exactly the same symmetry as the Hamiltonian are presumably needed. Thus, the aim of this paper is to give accurate values of the energy of the bound state of a screened dipole-bound electron, for a wider range of screening. These should be used to build a solid ground for validation of required *ab initio* levels of theory that should be used in following up calculations of the electron affinities of screened dipole-bound anions. We establish that the problem features a scaling propriety, which allows to evaluate the minimum dipole moment as a function of an unique parameter. then we use a very simple, but still appropriate variational wave function. The validity of this approach is established by investigating both the weak and strong screened limits.

VARIATIONAL CALCULATION

We consider two point charges $-Q$ and Q located at $(0,0,-a)$ and $(0,0,a)$ along the z axis in an electron gas described by a Thomas Fermi dielectric function, thus leading to an exponential Yukawa like screened interaction, characterized by the screening parameter λ_0. In prolate spheroidal coordinates,[10] the Schrödinger equation corresponding to the ground state of a particle of mass M in the vicinity of the dipole writes as

$$H\psi(\xi,\eta) = \varepsilon\psi(\xi,\eta), \tag{1}$$

where the Hamiltonian H is given by

$$H = \frac{1}{\xi^2-\eta^2}\left\{ -\frac{\partial}{\partial\xi}\left[(\xi^2-1)\frac{\partial}{\partial\xi}\right] - \frac{\partial}{\partial\eta}\left[(1-\eta^2)\frac{\partial}{\partial\eta}\right] + \rho e^{-\lambda\xi}\left[(\xi+\eta)e^{\lambda\eta} - (\xi-\eta)e^{-\lambda\eta}\right]\right\}, \tag{2}$$

where we have introduced a reduced screening parameter $\lambda = \lambda_0 a$ and the dimensionless parameters:

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$$\varepsilon=\frac{2Ma^2}{\hbar^2}E;\qquad \rho=\frac{2MeQa}{\hbar^2}=\frac{eM}{\hbar^2}D, \tag{3}$$

where $D=2aQ$ is the dipole moment of the two-charge system.

A scaling property of the dipole Hamiltonian arises from Eq. (1); for a given value of the parameter ρ, i.e., the dipole moment, the Hamiltonian depends only on the reduced parameter λ. Therefore, for zero-energy states, one can calculate the minimum value of the parameter ρ as a function of one unique parameter λ.

To find, for a given λ, the minimum dipole moment necessary to bind an electron we suggest the following variational wave functions

$$\Psi(\xi,\eta)=\sum_{q=0}^{j_{\max}} C_q\phi_q(\xi,\eta)\qquad \phi_q(\xi,\eta)=\frac{1}{\sqrt{2\pi a^3}}\xi^{-p}\eta^{q} \tag{4}$$

where q is always a positive integer and p is a variational real parameter. We add the condition $p\leqslant 0.5$, which guarantees that the average value of the kinetic energy remains positive.

We now evaluate the matrix element $H(p,q,j)=\langle\phi_q|H|\phi_j\rangle$

$$\begin{aligned} H(p,q,j)&=\frac{4}{[4p^2-1][(q+j)^2-1]}\\ &\quad\times[p^2(q+j-1)+qj(2p+1)],\qquad q+j\ \text{even}\\ &=4\rho[A_{q+j}R_{2p}+B_{q+j}R_{2p\text{-}1}],\qquad q+j\ \text{odd}, \end{aligned} \tag{5}$$

where

$$A_{2n+1}=\frac{1}{2}\int_{-1}^{1}d\eta e^{\lambda\eta}\eta^{2n+2}=\sum_{k=0}^{\infty}\frac{\lambda^{2k}}{(2k)!(2n+3+2k)} \tag{6a}$$

$$B_{2n+1}=\frac{1}{2}\int_{-1}^{1}d\eta e^{\lambda\eta}\eta^{2n+1}=\sum_{k=0}^{\infty}\frac{\lambda^{2k+1}}{(2k+1)!(2n+3+2k)} \tag{6b}$$

$$R_s=\int_{1}^{\infty}d\xi\xi^{-s}e^{-\lambda\xi}. \tag{6c}$$

Due to the symmetry of the integrals in the η coordinate, the contribution of the kinetic energy in Eq. (5) arises from even values of $q+j$, while that of the potential energy corresponds to odd values of $q+j$.

First, we revise the well-known limit case $\lambda=0$. We consider the variational exponent $p=0.5+\varepsilon$, where $\varepsilon\to 0$, and calculate the minimum value of the dipole ρ, which satisfies the equation $\det|\langle\phi_q|H|\phi_j\rangle|=0$. The result converges very fast with the number of η-components considered in the wave function to the value $\rho=0.6393148772$; the same value obtained previously by Turner and Fox using a different two-parameter dependent variational wave function.[11,12]

For a given $\lambda\neq 0$, we consider p as a variational parameter and then we find the value that makes minimum the dipole moment ρ required to satisfy the equation $\det|\langle\phi_q|H|\phi_j\rangle|=0$. The dependence of this result on $j_{\max}$, i.e., the number of η components considered, has been studied: we achieve good convergence very quickly as we increase the number of η components. The results for both parameters p and ρ corresponding to $j_{\max}=9$ and $j_{\max}=19$ differ less than 10^{-5} for all values of λ considered.

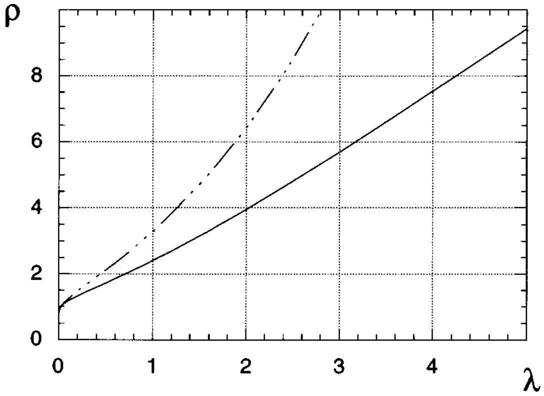

FIG. 1. Minimum dipole moment required to bind an electron in a polarizable medium as a function of the reduced screening parameter (solid line). The broken line corresponds to the results from the work of Ugalde and Sarasola (Ref. 9).

In Fig. 1 we plot the minimum dipole ρ, as a function of λ. Around $\lambda=0$, this plot shows a fast increasing; this fact is due to the long range of the dipole interaction that, for zero energy states, leads to highly nonlocalized electron state, while in the screened case the finite range of the interaction forces the electron to be more localized around the dipole, thus increasing the kinetic energy and consequently requiring a larger dipole to balance the total energy. In this figure we have represented the results of a previous work by Ugalde *et al.* for comparison. For very weak screening both approaches lead to similar results. The large difference between both plots for $\lambda>0.2$ is due to the fact that in the polar expansion of the dipole potential used in that work the dipole term is no longer the main one at large distances; and given that the variational wave function used only couples to this term, the potential energy is there underestimated, and then the required dipole moment is larger.

A check to this result is derived from the well-known fact that for any positive charge Q there exists a critical value of the screening parameter λ_{0c}, above which the positive charge cannot bind an electron. In our problem, for values of the screening parameter λ_0 near the critical value λ_{0c} the minimum value of the dipole moment to bind an electron increases rapidly; it goes to infinity when $\lambda_0\to\lambda_{0c}$. An estimation of such critical value λ_{0c} can be obtained the variation of the minimum dipole $\rho=2Qa$ as a function of $\lambda=\lambda_0 a$, since ρ and λ are almost proportional in this region. If s is the slope of the plot $\rho(\lambda)$, then the critical value λ_{0c} is given as $\lambda_{0c}=2Q/s$. From Fig. 1 we obtain the value $\lambda_{0c}=1.06$ a.u.$^{-1}$, for $Q=1$. This value is to be compared with the exact one[13] of 1.1906 a.u.$^{-1}$. Considering both requirements on the function $\rho(\lambda)$: the above discussed increasing near the origin and this asymptotic behavior, one can claim that the plot of Fig. 1 is very close to the exact solution of the problem.

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