

Minimum dipole moment required to bind an electron to a screened dipole field

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The critical dipole moment required to bind an electron is known since Fermi and Teller published its exact value in a historical contribution [E. Fermi and E. Teller, *Phys. Rev.* **72**, 399 (1947)]. We revisit the problem and calculate self-consistently the critical dipole moment for a dipole field embedded in a homogeneous polarizable medium. We show that, although the capability of polar systems to capture electrons in the dipole field is much reduced by the screening, a screened dipole field is still attractive enough to bind one electron for a wide range of embedding media.

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The appearance of bound states for an electron in a dipole field is a problem of central importance in molecular and condensed-matter physics. The history of the research on the subject is appealing as well. In 1947, Fermi and Teller were the first to publish the value of the minimum dipole moment required to bind an electron (also known in the literature as the critical dipole moment), namely $D_{\min}^0 = 0.639$ a.u.¹ This value was given in their paper in passing, without further mention of it. The actual method that they used to obtain it still remains unclear, and was the subject of an interesting search by Turner.² Later works rediscovered the dipole critical value using several methods³⁻⁵ in the context of low-energy electron scattering in polar molecules.

After these pioneering studies, and for more than two decades, literature on the problem was scarce. In the past few years, however, the concept of the minimum dipole required to bind an electron has been recovered and widely used in the study of dipole-bound anions, to which much theoretical and experimental work has been dedicated.⁶⁻⁹ Dipole-bound anions are negatively charged molecular compounds in which the binding of the outer electron can be basically interpreted in terms of the dipole field of the neutral molecule. The concept of the critical dipole moment is used in this context to predict the existence of such molecular anions. Higher multipole-bound anions have been studied as well.¹⁰ The problem of the critical dipole also reappeared in a quite different context recently: Camblong *et al.* showed that the binding of an electron to a polar molecule is the realization of a quantum anomaly.¹¹

Less attention has been paid, however, to the binding of electrons to dipolar fields *screened* by an external electronic density, which is the relevant situation in condensed matter. Screened dipole fields appear, for example, in metal-semiconductor junctions,¹² liquid-solid interfaces between polar solvents and metals,¹³ and heterogeneous interfaces in which nanoparticles are formed.¹⁴ Polar defects stabilized by electron capture were also proposed as responsible for polarization fatigue in ferroelectric materials.¹⁵ In surface chemistry, the screening of polar structures appears in problems such as the adsorption of small polar molecules on metal surfaces.¹⁶ The electronic properties of such systems would be very much affected by the binding of electrons in the

dipole field. Our purpose in this paper is to determine the appropriate conditions under which this binding can take place.

The screening effect of an external electronic charge into a dipole field implies that higher dipole moments are required to bind one electron. In this paper, we focus our attention on such a problem by calculating the critical dipole moment required to bind one electron when a finite dipole is embedded in a jellium. This model is useful to understand the complex mechanisms of electron binding by screened dipole fields and provides an estimate of the actual dipole fields required to bind electrons in real systems.

The binding of electrons by a screened dipole was preliminarily studied using linear theory of screening (Thomas-Fermi potentials) and a variational approach for the electron wave function.^{17,18} It is well known, however, that linear theory underestimates the rearrangement of electronic charge induced by a charged particle in a homogeneous medium.¹⁹ Hence, we calculate the embedding of a dipole in a jellium using density-functional theory (DFT). The screening of the dipole by the external electronic density and the critical dipole moment are thus obtained in a self-consistent way and beyond linear theory. For the sake of comparison, we will also show the results obtained in linear theory of screening. The inclusion of nonlinearity in the description of the screening has important consequences, with two effects of opposite sign competing.

The system on which we focus our attention is a finite dipole defined by two point charges $\pm q$ separated by a distance d (atomic units are used throughout). The dipole is embedded in a jellium (a constant background of positive charge in which the electrons move), whose mean electronic density is n_0 . The electron-density parameter r_s is usually defined by the relation $1/n_0 = 4\pi r_s^3/3$. D is the dipole moment $D = qd$.

Our goal is to calculate the critical dipole D_{\min} , defined as the minimum dipole moment required to bind an electron, as a function of the external electronic density n_0 . We use the Kohn-Sham (KS) equations to solve the problem:²⁰

$$\left\{ -\frac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r}) \right\} \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \quad (1)$$

where $\psi_i(\mathbf{r})$ are the one-electron orbitals of a system of non-interacting particles, $V_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_{\text{es}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r})$ is the one-electron effective potential, and ϵ_i are the eigenenergies of the KS states. The external potential $V_{\text{ext}}(\mathbf{r})$ is the bare Coulomb potential of the two charges $\pm q$, $V_{\text{es}}(\mathbf{r})$ is the electrostatic potential of the total electronic density, and the exchange-correlation potential $V_{\text{xc}}(\mathbf{r})$ is calculated in the local-density approximation (LDA), using Gunnarson and Lundqvist parametrization.²¹

Equation (1) requires to solve self-consistently the KS equations for a nonspherical potential. The numerical procedure that we use is the same that was thoroughly explained in Ref. 22. The axial symmetry of the system allows us to simplify the calculation by taking the dipole axis (the line that links the positions of the charges) as the OZ axis. Expanding the KS orbitals in the spherical-harmonic basis set $Y_l^m(\Omega)$, and the effective potential $V_{\text{eff}}(\mathbf{r})$ and the electronic density in terms of Legendre polynomials $P_l(\cos \theta)$, Eq. (1) is transformed into a system of coupled equations. The axial symmetry of the problem keeps ϵ_i and m as good quantum numbers, but not the angular momentum l . For every fixed value of ϵ_i and m we have

$$\left[\frac{1}{2} \frac{\partial^2}{\partial r^2} - \frac{l(l+1)}{2r^2} + \epsilon_i \right] u_{l,\epsilon_i}^m(r) = \sum_{l'}^{l_{\text{max}}} U_{ll'}^m(r) u_{l',\epsilon_i}^m(r), \quad (2)$$

where $u_{l,\epsilon_i}^m(r)$ are the radial components of the KS orbitals, and the coupling terms $U_{ll'}^m(r)$ between the different l -partial waves are

$$U_{ll'}^m(r) = \int d\Omega V_{\text{eff}}(\mathbf{r}) Y_l^m(\Omega) [Y_{l'}^m(\Omega)]^*. \quad (3)$$

In practice, only a finite number of terms ν_{max} in the expansion of the external potential $V_{\text{eff}}(\mathbf{r})$, and a finite number of terms l_{max} in the expansion of the KS orbitals are included. We check the accuracy of the results by assuring the convergence of the studied magnitudes with the number of components in the expansions. Typical values used in this work are $\nu_{\text{max}}=8$ and $l_{\text{max}}=10$.

The DFT is rigorously founded only for the description of the system ground state. Usual prescription in the KS scheme is that the lower-energy KS states up to the Fermi level should be filled to properly describe the ground state. This is not what we have done in this work. We are interested in dipole binding just one electron. Hence, we populate just one of the two KS orbitals with negative ϵ_i (there is one for each spin component). All the continuum KS states, from zero energy to the Fermi level, are filled as well. Occupancy of the two bound orbitals would bring them to merge into the continuum for the typical values of the dipole parameters D and d considered in this work. Furthermore, we consider that the presence of an electron bound to the dipole is indicated by the existence of a negative KS eigenvalue.

Let us start by showing the rearrangement of electronic charge induced by the dipole in the medium. We plot in Fig. 1 the DFT calculation of the electronic density induced by the dipole in a jellium $\Delta n(\mathbf{r}) = n(\mathbf{r}) - n_0$, in units of n_0 . The dipole parameters are $q = \pm 1$ and $d=4$ a.u. The electronic-

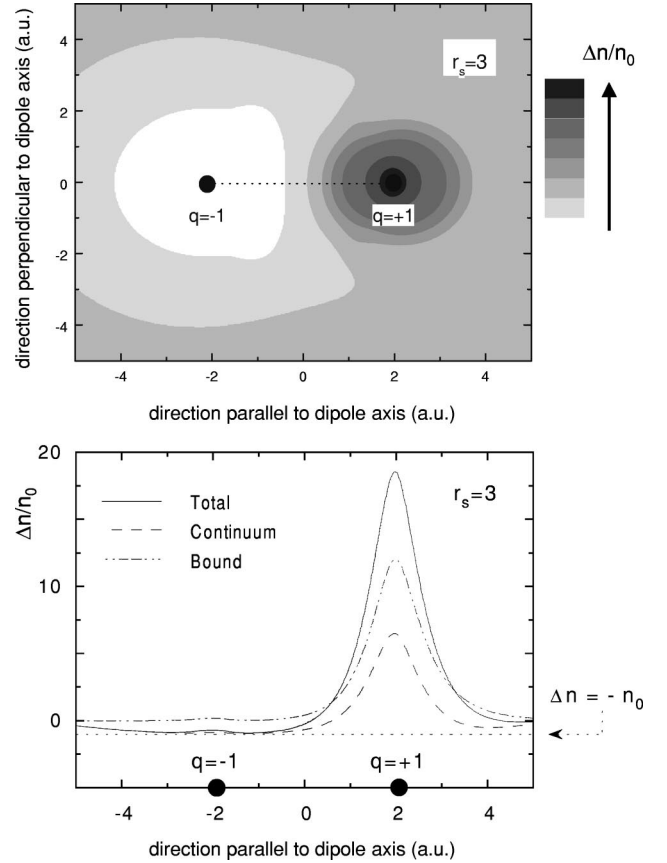


FIG. 1. DFT calculation of the electronic density $\Delta n(\mathbf{r})$ induced by a dipole in a jellium of $r_s=3.0$. The charges of the dipole are $q = \pm 1$ and the distance between them is $d=4.0$ a.u. $\Delta n(\mathbf{r})$ is plotted in units of the background density n_0 . The upper panel shows a contour plot of $\Delta n(\mathbf{r})$ in a plane in which the dipole axis is contained. Darker zones correspond to higher values of $\Delta n(\mathbf{r})$. Abscissas represent distances in the direction parallel to the dipole axis, and ordinates represent distances in the direction perpendicular to it. All distances are in atomic units. The lower panel shows the same calculation making a cut along the dipole axis. The bound (dash-dotted line) and continuum (dashed line) contributions to the total induced density (solid line) are shown as well.

density parameter of the unperturbed jellium in which the dipole is embedded is $r_s=3.0$. The upper panel of Fig. 1 shows a contour plot of the total electronic density induced by the dipole, in a plane defined by the dipole axis and any direction perpendicular to it. The lower panel of Fig. 1 shows the induced electronic density along the dipole axis. The bound and continuum contributions to the total induced electronic density are plotted in the lower panel of Fig. 1 as well. The sum of both contributions leads to a piling up of electronic charge (a screening cloud) about the positive charge q . Furthermore, electrons are repelled from the neighborhood of the dipole negative charge $-q$. $\Delta n(\mathbf{r})$ is negative and roughly compensates the background electronic density n_0 in this region. Only the continuum density contributes to the depletion of charge about $-q$. The small bump in the density close to $-q$ is unphysical. It is a consequence of the finite number of density and potential components ($\nu_{\text{max}}=8$) used in our calculation.

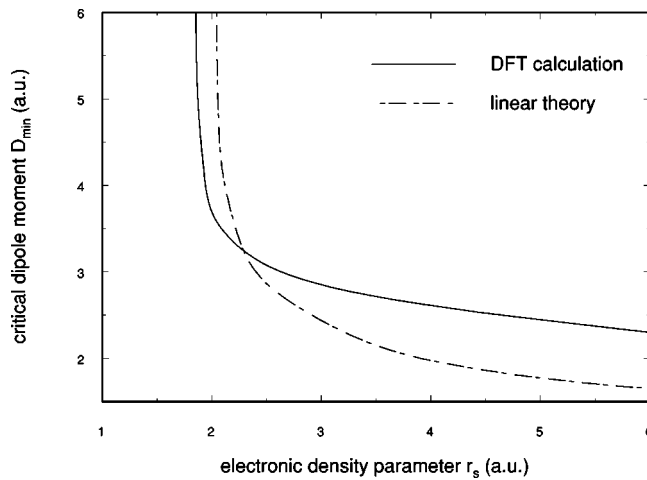


FIG. 2. Critical dipole moment D_{\min} (in atomic units) to bind an electron as a function of the external electronic-density parameter r_s (in atomic units as well). The solid line is the DFT calculation. The dash-dotted line is the result in linear theory of screening. Charges of the dipole are fixed to $q = \pm 1$.

Any external distribution of charge that is embedded in a polarizable medium is screened so that the total net charge seen at long distances is zero, i.e., the potential is not Coulombic anymore.²³ Let us remark at this point that the dipolar component of the potential is screened at long distances as well. We have numerically checked that the dipole moment of the induced electronic density $\Delta n(\mathbf{r})$ exactly compensates the external dipole moment embedded in the medium. This is just a consequence of the perfect screening made by the medium.

We have checked that the results for the total electronic charge induced by the dipole are qualitatively similar for other values of the dipole parameters and/or the background electronic density. A lower binding energy for the bound state (a weaker dipole moment) introduces a bound contribution more extended in space. However, the continuum contribution adds up to compensate, gathering most of the total induced density in a relatively small region of space. The bound contribution will eventually disappear for the dipole parameters that correspond to those of the critical dipole moment.

The DFT calculation of the critical dipole D_{\min} required to bind an electron is shown in Fig. 2, as a function of the electronic-density parameter r_s . The values of r_s used in Fig. 2 cover the whole range of metallic densities.²³ The charges of the dipole are fixed to $q = \pm 1$ and the distance between them is varied. In general terms, the values of the critical dipole moment for a screened dipole are much higher than the nonscreened critical dipole $D_{\min}^0 = 0.639$ calculated by Fermi and Teller.¹ This is true even for values of the electronic density relatively low, such as $r_s = 6$. Notice, however, that our calculation would not provide the exact value $D_{\min}^0 = 0.639$ in the limit of $r_s \rightarrow \infty$ due to the well-known deficiencies of LDA to treat self-interaction terms.²⁴ For high values of the electronic densities of the medium ($r_s < 1.85$), there is no dipole moment capable of binding an electron. $r_s \approx 1.85$ is the lowest value of r_s for which the

bound state of a neutral hydrogen atom (H^0) embedded in a jellium does exist. Hence no dipole with $q = \pm 1$ would be able to support a bound state for $r_s < 1.85$, even in the limit $d \rightarrow \infty$.

The results for the critical dipole moment using linear theory of screening are shown in Fig. 2 as well. In linear theory, the screened dipole potential is represented by two Thomas-Fermi potentials separated by a distance d . The charges of the dipole are $q = \pm 1$. We calculate the bound-state wave function by numerical integration of Schrödinger equation, avoiding any possible inaccuracies that might arise from the choice of a given basis set. In linear theory, the results can be scaled to any other parameters of the system.¹⁸ However, this is not true for the DFT calculation: any other values of the charges $\pm q$ would require a separate calculation.

The DFT calculation predicts a higher value of D_{\min} for low electronic densities of the jellium and a lower value of D_{\min} for high electronic densities. To understand this, a dipole with a bound electron could be viewed as a positive charge q binding one electron, perturbed by the screened Coulomb interaction of the negative charge $-q$. For a neutral hydrogen atom H^0 embedded in a jellium, the linear theory underestimates the strength of the electron binding.²⁵ In other words, the electronic density at the positive-charge position is smaller in linear theory of screening. For a dipole, however, an additional effect comes into play: the repulsive screened Coulomb interaction between the negative charge $-q$ of the dipole and the bound electron, which is also underestimated in linear theory. Hence, there are two effects of opposite sign that are introduced with nonlinearity. In the limit of small r_s and large distances d , the two point charges $\pm q$ do not see each other, and the situation is closer to the H^0 case (linear theory underestimates the electron binding). The opposite is true for small d and high r_s .

In summary, we have performed a nonlinear calculation of the critical dipole moment required to bind an electron to a screened dipole field. We have shown that, although the capability of polar systems (molecules, clusters, polar defects in solids) to support bound states is much reduced when the dipole field is embedded in a polarizable medium, a screened dipole field is still able to bind an electron for a wide range of electronic densities $r_s > 1.85$. The electronic properties of these polar systems at surfaces or in solids would be very much affected by the capture of electrons in their dipole field. The results presented in this paper provide the critical values of the dipole moment for such capture process to take place.

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