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Effective polarizability of polarizable atoms near metal surfaces*

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The density-functional formalism of an inhomogeneous electron gas is applied to compute the effective polarizability of polarizable atoms and molecules adsorbed on metal surfaces. The metal is treated in the "jellium" approximation and the adatom is approximated by a point dipole. The effects of screening of a small uniform external field are also considered. This approach is found to yield effective polarizabilities compatible with experiment and is expected to provide a useful qualitative description of the effective polarizability of atoms and molecules adsorbed on metal surfaces.

I. INTRODUCTION

A new piece of information in surface physics, the effective polarizability, has become available experimentally within the last few years.[1,2] The effective polarizability is the apparent polarizability of an atom or molecule in the vicinity of a surface. Its knowledge would help in the untangling of the behavior of atoms and molecules on surfaces. The effective polarizability is important in theories of physical adsorption, chemisorption, field emission, field ionization, and field desorption. Large enhancements of the effective polarizability over the free atomic or molecular polarizability have been observed for both xenon[1] and nitrogen[2] adsorbed on metals.

Representing the adsorbed atom by a point dipole near a perfect metal, one can compute the effective polarizability from classical image theory.[3] However, this model fails to account for the observed enhancements of the effective polarizability over the free atomic polarizability.[1] Attempts to include finite screening effects in the metal within the framework of the Thomas-Fermi approximation by Antoniewicz[4] and by Heinrichs[5] indicate that the effective image plane of the metal is recessed below the surface, reducing the image field at the dipole position, and consequently predicts less of an enhancement in the effective polarizability than does classical image theory. It was felt, therefore, that additional theoretical work was needed in this area.

In a real metal, the surface is not sharply defined, but is diffuse over a width of about 2 Å. For an adsorbed atom lying within 5 Å of the surface, one would expect to see effects in the effective polarizability owing to the finite screening length of the metal and to the diffuseness of the surface. At closer distances where the metallic and atomic-charge densities begin to overlap considerably, the structure of the adsorbate would become important. In this paper we study the effects of the diffuseness of the metal surface on the effective polarizability, assuming the atom is located sufficiently far from the surface to be approximated by a point dipole. For the metal we use a planar-uniform-background model in which the electrons have been allowed to relax into the vacuum. A linear-response formalism is used to compute the response of the metal surface to the perturbing point dipole. To illustrate our results, we present the effective polarizabilities of the noble-gas atoms adsorbed on metals over the range of metallic electron densities. Also, we compare our results with the available experimental evidence and find qualitative agreement.

II. THEORY

A. Formulation of the problem

We shall restrict ourselves to considering the effective polarizability of a nonpolar atom or molecule physically adsorbed on a metallic surface. The adatom-metal distance is assumed to be sufficiently large that a linear-response solution is appropriate. The atom, lying a distance, d, outside the metal, is approximated by a point atom with polarizability α_0. The metal is treated in the planar-uniform-background model, with the metal occupying the negative z half space.

The presence of a small external electric field $\vec{E}_0$ in the vicinity of the adatom will induce a small atomic dipole moment $\vec{p}=\alpha_0\vec{E}_0$. It is well known from classical image theory that a point dipole located a distance d from a metal surface will induce a screening charge on the surface. This screening charge will give rise to an additional electric field $\vec{E}_d$ at the position of the point dipole, an additional field equivalent to the field produced by an image dipole located at $z=-d$. If the point dipole is oriented normal to the surface, E_d is, in the classical case, given simply by $E_d=2p/(2d)^3$ where $p=|\vec{p}|$. Thus, the actual induced atomic dipole moment of an atom near a metallic surface is enhanced, since the effective field at the atom is given by E_0+E_d, i.e.,

$$p=\alpha_0(E_0+E_d)\ . \tag{2.1}$$

The "effective polarizability," α is defined as the induced atomic dipole moment divided by the external electric field at the atom. This definition and equation (2.1) can be combined to eliminate the external field to give,

$$\alpha = \frac{p}{E_0} = \frac{\alpha_0}{1 - \alpha_0 E_d / p} \; . \tag{2.2}$$

In a linear-response formalism, E_d will depend linearly on the atomic dipole moment p. Consequently, E_d/p is independent of both the external field E_0, and the induced atomic dipole moment p. The quantity of interest in determining the effective polarizability will be the electric field induced by a unit point dipole at the position of the dipole.

For some applications, however, the external field at the position of the atom is unknown. For example, in a capacitance measurement, only the electric field far from the metal surface E_∞ may be known. We define the "apparent polarizability" as the induced atomic dipole moment divided by the applied external electric field E_∞, i.e.,

$$\alpha_{\text{app}} = p/E_\infty \; . \tag{2.3}$$

For atoms lying close to the metal surface, the applied external field may be partially screened by the metal. Let $E_0(z)$ be the actual applied field at z. We can represent $E_0(z)$ by $E_\infty s(z)$, where $s(z)$ is a continuous function of z, varying from a value of 1 at $z = +\infty$ to 0 at $z = -\infty$. With this expression for $E_0(z)$, the apparent polarizability is found to be

$$\alpha_{\text{app}} = \alpha s(d) = \frac{\alpha_0 s(d)}{1 - \alpha_0 E_d / p} \; . \tag{2.4}$$

Thus, the apparent polarizability will be reduced by a factor of $s(d)$ from the effective polarizability α.

To compute the effective and apparent polarizabilities of atoms adsorbed on metallic surfaces, we need to know the electronic response of the metal surface to a perturbing point dipole and to a uniform external field. To accomplish this, we employ a linear-response function similar to that used by Ying, Smith, and Kohn[6] in their theory of hydrogen chemisorption.

B. Linear-response formalism

The theory used is based on the Hoenberg and Kohn[7] theorems, which demonstrate the existence of a universal functional of the electron density $G[n]$, such that for any static external potential $V_0^{\text{ex}}(\vec{r})$, the correct electron charge density $n_0(\vec{r})$ can be found by minimizing the energy functional,

$$E[n] = -\int V_0^{\text{ex}}(\vec{r})\, n_0(\vec{r})\, d\vec{r} + \frac{1}{2}\int \frac{n_0(\vec{r})\, n_0(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} \times d\vec{r}\, d\vec{r} + G[n] \tag{2.5}$$

subject to the condition that the total number of electrons remain constant. Introducing this condition through a Lagrange multiplier μ_0 gives

$$-V_0^{\text{tot}}(\vec{r}) + \frac{\delta G[n]}{\delta n} = \mu_0 \, , \tag{2.6}$$

where $V_0^{\text{tot}}(\vec{r})$ is the total electronic potential,

$$V_0^{\text{tot}}(\vec{r}) = V_0^{\text{ex}}(\vec{r}) - \int \frac{n_0(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}\, d\vec{r}\,' \tag{2.7}$$

and μ_0 is the chemical potential. We use atomic units throughout.

Let us assume that $n_0(\vec{r})$ corresponding to $V_0^{\text{ex}}(\vec{r})$ is known for some system, and introduce a small additional charge density $\rho_1^{\text{ex}}(\vec{r})$ giving rise to a small perturbing potential,

$$V_1^{\text{ex}}(\vec{r}) = -\int \frac{\rho_1^{\text{ex}}(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}\, d\vec{r}\,' \; . \tag{2.8}$$

$V_1^{\text{ex}}(\vec{r})$ will induce a small screening charge $n_1(\vec{r})$ in the system. The energy functional in Eq. (2.5) can then be rewritten

$$\begin{aligned} E[n_0 + n_1] = &-\int [V_0^{\text{ex}}(\vec{r}) + V_1^{\text{ex}}(\vec{r})][n_0(\vec{r}) + n_1(\vec{r})]\, d\vec{r} \\ &+ \frac{1}{2}\int \frac{[n_0(\vec{r}) + n_1(\vec{r})][n_0(\vec{r}\,') + n_1(\vec{r}\,')]}{|\vec{r} - \vec{r}\,'|}\, d\vec{r}\, d\vec{r}\,' \\ &+ G[n_0] + \Delta G[n_1] \, , \end{aligned} \tag{2.9}$$

where $\Delta G[n_1]$ is defined by

$$\Delta G[n_1] = G[n_0 + n_1] - G[n_0] \; . \tag{2.10}$$

Minimizing the energy with respect to variations in the charge density, subject to the condition that the total number of electrons remain constant, and linearizing with respect to n_1, one obtains the following linearized Euler's equation for n_1:

$$-[V_1^{\text{ex}}(\vec{r}) + V_1(\vec{r})] + \int \left. \frac{\delta^2 G[n]}{\delta n(\vec{r})\, \delta n(\vec{r}\,')} \right|_{n_0} n_1(\vec{r}\,')\, d\vec{r}\,' = \mu_1 \, , \tag{2.11}$$

where μ_1 is the change in the chemical potential and

$$V_1(\vec{r}) = \int \frac{-n_1(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}\, d\vec{r}\,' \tag{2.12}$$

is the electrostatic potential of the induced screening charge. Equation (2.11) must be solved self-consistently with Poisson's equation,

$$\nabla^2 V_1(\vec{r}) = 4\pi n_1(\vec{r}) \, , \tag{2.13}$$

to obtain $n_1(\vec{r})$ and $V_1(\vec{r})$.

C. Application to metal surfaces

To apply this formalism to the screening of external charges by metallic surfaces, we treat the metal in the jellium approximation, with the metal occupying the negative z half space. For $n_0(z)$, we use the self-consistent solution found by Lang and Kohn,[8] and concentrate our efforts on determining the first-order screening charge density and potential, $n_1(\vec{r})$ and $V_1(\vec{r})$. For $G[n]$, we use the first two terms of a more general gradient expansion,[6,7]

$$\begin{aligned} G[n] &= \int g_0(\vec{r})\,d\vec{r} + \int g_2(\vec{r})\,|\nabla n(\vec{r})|^2\,d\vec{r} + \cdots \\ &= \tfrac{3}{10}(2\pi^2)^{2/3} \int n^{5/3}(\vec{r})\,d\vec{r} - \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} \\ &\quad \times \int n^{4/3}(\vec{r})\,d\vec{r} + \frac{\lambda}{8} \int \frac{|\nabla n(\vec{r})|^2}{n(\vec{r})}\,d\vec{r}\,, \end{aligned} \tag{2.14}$$

where $\lambda = \frac{1}{9}$. Here, the correlation contribution to $g_0(\vec{r})$ and the exchange and correlation contributions to $g_2(\vec{r})$ have been omitted. The local correlation contribution to g_0 is small and its inclusion in Eq. (2.14) is found to have little effect on the results. This form for $G[n]$ is known to work well for bare surface properties, such as work function and charge density variation,[9] and it also gives reasonable results for hydrogen chemisorption.[6,10] The validity of this approximation is discussed in more detail in Ref. 6. To gain insight into how well approximation (2.14) works for the physisorption problem, it is of interest to compare results obtained with Eq. (2.14) for hydrogen chemisorption with a self-consistent calculation of the same problem by Lang and Williams,[11] who treated the kinetic energy functional exactly. Lang and Williams[11] noted that (a) the response of the metal to a proton in the surface region is nonlinear; and (b), the response found with approximation (2.14) grossly underestimates the screening charge near the proton. We believe that neither of these objections is serious in the physisorption problem being considered here. A point dipole perturbation is a much weaker perturbation than that of a point charge. Also, physisorption occurs at distances which are much larger than hydrogen chemisorption. The induced charge in the vicinity of the physisorbed atom is expected to be small, in contrast to hydrogen chemisorption.

A problem which will concern us is the proper choice for the coefficient λ of the gradient term in Eq. (2.14). This term represents the first quantum correction to the Thomas-Fermi kinetic energy [given by the first term in Eq. (2.14)]. It has the functional form originally proposed by von Weizsacker with $\lambda = 1$, and has been analyzed extensively by several authors.[12] Jones and Young[12] have compared the response function obtained from the truncated gradient expansion with variable coefficient λ to the Lindhard response function. They found that choosing $\lambda = 1$ yields the correct response for perturbations whose wavelength of importance is small with respect to the Fermi wavelength, while $\lambda = \frac{1}{9}$ is appropriate for perturbations whose wavelength is large with respect to the Fermi wavelength. Thus, choosing $\lambda = \frac{1}{9}$, we would expect the induced screening charge to be relatively accurate at distances far from the point dipole, and relatively inaccurate at distances near to the dipole. Since the dipole is located outside the metal where an induced charge is expected to be small, we expect a choice of $\lambda = \frac{1}{9}$ to be appropriate for this problem. The choice of λ is discussed further in the Appendix.

It is convenient to Fourier transform all variables in the plane parallel to the surface, i.e., let

$$\begin{aligned} n_1(\vec{r}) &= \int \frac{d^2Q}{(2\pi)^2}\, e^{i\vec{Q}\cdot\vec{\rho}}\, n_1(\vec{Q}, z)\,, \\ V_1(\vec{r}) &= \int \frac{d^2Q}{(2\pi)^2}\, e^{i\vec{Q}\cdot\vec{\rho}}\, V_1(\vec{Q}, z)\,, \end{aligned} \tag{2.15}$$

etc., where $\vec{r} = (\vec{\rho}, z)$, $\vec{\rho} = (x, y, 0)$, $\vec{Q} = (Q_x, Q_y, 0)$, and $Q = |\vec{Q}|$. Substitution of Eq. (2.14) for $G[n]$ into Eq. (2.11), and Fourier transforming everything using Eq. (2.15), we obtain the following equation for $n_1(Q, z)$:

$$\begin{aligned} &\left[\frac{d^2}{dz^2} - \frac{n_0'(z)}{n_0(z)}\frac{d}{dz} - \frac{4}{3\lambda}(2\pi^2)^{2/3} n_0^{2/3}(z) + \frac{4}{3\lambda}\left(\frac{3}{\pi}\right)^{1/3} n_0^{1/3}(z) + \left(\frac{n_0'(z)}{n_0(z)}\right)^2 - \frac{n_0''(z)}{n_0(z)} - Q^2\right] n_1(Q, z) + \frac{4n_0(z)}{\lambda} V_1(Q, z) \\ &\qquad = -\frac{4n_0(z)}{\lambda}\left[V_1^{\text{ex}}(Q, z) - \mu_1\delta(Q)\right], \end{aligned} \tag{2.16}$$

where the primes refer to differentiation by z. The above must be solved self-consistently with Poisson's equation,

$$\left(\frac{d^2}{dz^2} - Q^2\right) V_1(Q, z) - 4\pi n_1(Q, z) = 0 \tag{2.17}$$

subject to the boundary conditions

$$\begin{aligned} &n_1(Q, z) \to 0 \quad \text{as } z \to \pm\infty \\ &V_1^{\text{tot}}(Q, z) = V_1^{\text{ex}}(Q, z) + V_1(Q, z) \to 0 \quad \text{as } z \to \pm\infty \\ &\text{for } Q \neq 0\,. \end{aligned} \tag{2.18}$$

Equations (2.16) and (2.17) constitute a set of two coupled second-order differential equations which can be solved numerically for $n_1(Q, z)$ and $V_1(Q, z)$ by a method proposed by Wachspress.[13]

To apply this formalism to the computation of the effective polarizability of an adatom near a metal surface, we take $n_0(z)$ from the calculation of Lang and Kohn.[14] The external perturbing potential is that of a point dipole located at $z' = d$, with p oriented normal to the surface. Thus,

$$V_1^{\text{ex}}(Q, z) = \int \frac{d^2Q}{(2\pi)^2}\, e^{i\vec{Q}\cdot\vec{\rho}}\, \frac{p(z-z')}{[\rho^2 + (z-z')^2]^{3/2}}$$
$$= 2\pi p \,\text{sgn}(z-z')\, e^{-Q|z-z'|} \, . \qquad (2.19)$$

Substituting Eq. (2.19) into Eq. (2.17), and solving equations (2.16)–(2.18) for $V_1(Q, z)$, the quantity E_d/p may be obtained from

$$\frac{E_d}{p} = \int -\frac{\partial}{\partial z}\left(\frac{V_1(Q, z)}{p}\right) e^{i\vec{Q}\cdot\vec{\rho}}\, \frac{d^2Q}{(2\pi)^2}\bigg|_{\rho=0,\, z=d}$$
$$= \int_0^\infty \frac{QdQ}{2\pi} J_0(Q\rho)\left(-\frac{\partial}{\partial z}\;\frac{V_1(Q, z)}{p}\right)\bigg|_{\rho=0,\, z=d} \, , \qquad (2.20)$$

where J_0 is Bessel function of zero order. Substitution of E_d/p into Eq. (2.2) will give the effective polarizability, α, for an atom with free atomic polarizability α_0.

The above formalism can also be used to compute the response of a metal to a uniform field. We assume, for convenience, that the metal is grounded, fixing the chemical potential at μ_0 ($\mu_1 = 0$). A uniform field E_∞ applied normal to the surface, induces a surface charge, $n_1(Q=0, z)$. The external perturbing charge is taken to be a uniform sheet of charge lying in the plane $z = z'$, which is located far out into the vacuum, well outside the region of interest. Equations (2.16) to (2.18) then are modified to read:

$$\left[\frac{d^2}{dz} - \frac{n_0'(z)}{n_0(z)}\,\frac{d}{dz} + \frac{4}{3\lambda}\,(2\pi^2)n_0^{2/3}(z) - \frac{4}{3\lambda}\left(\frac{3}{\pi}\right)^{1/3} n_0^{1/3}(z)\right.$$
$$\left. + \left(\frac{n_0'(z)}{n_0(z)}\right)^2 - \frac{n_0''(z)}{n_0(z)}\right] n_1(Q=0, z)$$
$$+ \frac{4n_0^{(z)}}{\lambda}\, V_1^{\text{tot}}(Q=0, z) = 0 \, , \qquad (2.21)$$

$$\frac{d^2}{dz^2} V_1^{\text{tot}}(Q=0, z) - 4\pi n_1(Q=0, z) = 0 \qquad (2.22)$$

subject to the boundary conditions

$$\begin{aligned} &n_1(Q=0, z) \to 0 && \text{as } z \to 0 \, , \\ &V_1^{\text{tot}}(Q=0, z) \to 0 && \text{as } z \to 0 \, , \\ &n_1(Q=0, z) = 0 && \text{at } z = z_1 \, , \\ &\frac{\partial}{\partial z} V_1^{\text{tot}}(Q=0, z) = -E_\infty && \text{at } z = z_1 \, , \end{aligned} \qquad (2.23)$$

where z_1 is a point well outside the surface region. The screening of the external field is then computed from

$$s(z) = \frac{E_0(z)}{E_\infty} = \left(-\frac{\partial}{\partial z}\, V_1^{\text{tot}}(Q=0, z)\right)\bigg/ E_\infty \, . \qquad (2.24)$$

III. RESULTS

A. Induced field and effective polarizability

We have computed the response of a metal surface to a perturbing point dipole over the range of metallic densities from $r_s = 2$ to 6. r_s is the Wigner-Seitz radius defined by $r_s = (\frac{3}{4}\pi\bar{n})^{1/3}$ where $\bar{n}$ is the mean electron density in the interior of the metal. Unfortunately, our results for E_d, and hence for the effective polarizability α are sensitive to the choice for the coefficient λ of the gradient term in the kinetic energy [see Eq. (2.14)]. Smith, Ying, and Kohn[6] have noted that the position of the image plane of the metal is also sensitive to the choice for λ. These problems are related. Smith[9] has shown that inclusion of the gradient term in Eq. (2.14) is necessary to obtain reasonable work functions for metals. The gradient term essentially confines the screening charge to the surface region of the metal. If electrons were to flow out into the tail of the electron distribution, large gradients in the charge density would be created in a region where the charge density was small, giving a large positive contribution to the energy. Thus, a larger coefficient, λ, on this term would carry a larger energy penalty for a given charge distribution. This would prevent the induced charge from relaxing as far out into the tail of the electron charge distribution as well as smoothing out the induced charge. The image plane, which is tied to the center of mass of the induced charge,[15] should then move in closer to the metal substrate for larger λ values.

It is possible to determine an appropriate "range" of λ's which would indicate the uncertainties in this problem. See the Appendix for details. We found that for metallic densities, the range of λ from $\frac{1}{9}$ to 0.22 is adequate for the entire range of metallic densities. We used these values for λ in computing the response of the metal surface to a uniform external field.

In Fig. 1 we show the induced field at the dipole position E_d/p as a function of the point-dipole-metal separation distance d, for (a) $r_s = 2$, (b) $r_s = 4$, and (c) $r_s = 6$. The upper (lower) bound on each curve corresponds to $\lambda = \frac{1}{9}$ (= 0.22), respectively. The classical result, $E_d = p/4d^3$ is also shown (dashed line) for comparison. Note that the induced field E_d is greater than the classical result for distances greater than 2 or 3 a.u. Thus, it is possible for effective polarizabilities to be greater than the classical predictions. At smaller distances, the divergence in E_d as d goes to zero has been removed.[16] Finally the response of high-

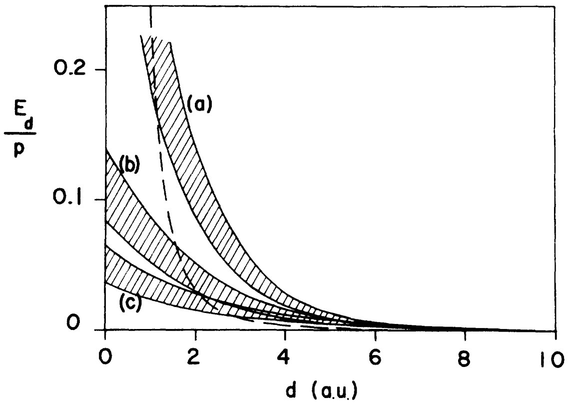

FIG. 1. Electric field induced by a point dipole at the dipole position vs the point-dipole–metal separation distance d is shown for metallic densities with (a) $r_s = 2$, (b) $r_s = 4$, and (c) $r_s = 6$. Classical result is indicated by the dashed curve. Jellium boundary is at $d = 0$. Width of the curves is obtained from calculations with $\lambda = \frac{1}{9}$ (upper bound) and $\lambda = 0.22$ (lower bound).

density metals (small r_s) is much greater than that of low-density metals. The width of the curves corresponds in a rough way to the uncertainty in the choice of λ.

The effective polarizability can be reduced considerably if the applied external field is screened out by the metal surface. Results for E_0/E_∞ for $\lambda = \frac{1}{9}$ are shown in Fig. 2. Increasing λ to 0.22 mainly shifts the curves toward the metal substrate by about one atomic unit. Note that the external field is partially screened even at distances as large as 6 or 7 a.u. from the surface. The effect of this screening on the effective polarizabilities is most easily seen on atoms with small free atomic polarizabilities, as shown in Fig. 3. Here, the effective polarizabilities for the noble gases are shown for several metal substrates. Atoms with large free atomic polarizabilities, like xenon, show enhancements in the effective polarizabilities while atoms with small polarizabilities show little or no enhancement. Also enhancements in the effective polarizabilities are larger for atoms adsorbed on higher-density metals.

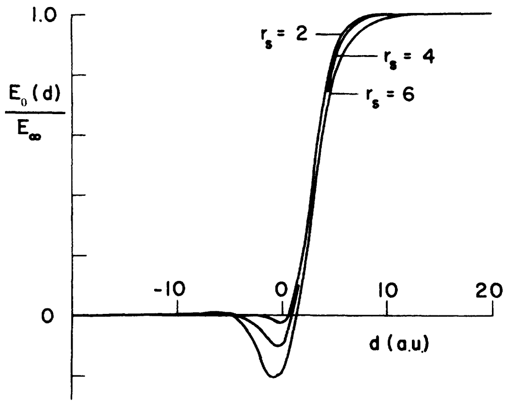

FIG. 2. Screening of a uniform external field at a metal surface. Results using $\lambda = \frac{1}{9}$ are shown.

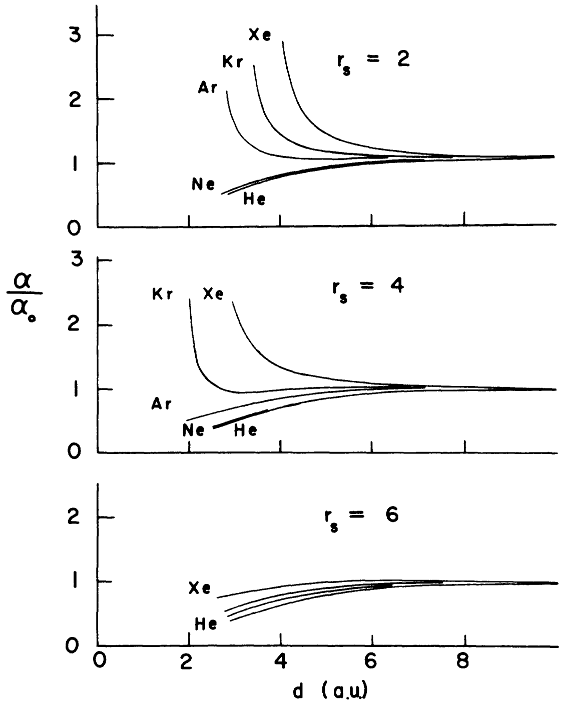

FIG. 3. Apparent effective polarizabilities computed from Eq. (2.4) for the noble gases. The free atomic polarizabilities for the noble gases are: α_0 (He) = 0.21 Å^3, α_0(Ne) = 0.39 Å^3, α_0(Ar) = 1.63 Å^3, α_0(Kr) = 2.48 Å^3, and α_0(Xe) = 4.01 Å^3. Results shown for $\lambda = \frac{1}{9}$. Increasing λ will shift the curves toward the metal surface as indicated in the text.

B. Application to xenon on palladium

Palmberg[1] has determined from work function vs coverage measurements that the effective polarizability of xenon atoms adsorbed on palladium (100) is approximately twice the free-atom polarizability of xenon ($\alpha_0^{Xe} = 4.01$ Å^3, $\alpha_{expt}^{Xe} = 8.2$ Å^3).[17] To apply our theory to this problem, we approximate palladium with an $r_s = 2.5$ metal.[18] We assume that the xenon adatom will lie at a distance from the surface determined by its atomic radius, 3.9 a.u. This assumption is supported by work of Webb and co-workers,[19] who have determined the spacing between a xenon monolayer and Ag(111) substrate to be given accurately by the sum of the atomic radii of xenon and silver atoms. Since the position of the metal surface is not well defined here, we take the minimum value of d to be about 4 a.u. From Fig. 4, the enhancement at this distance is 1.3 to 2. However, this minimum dis-

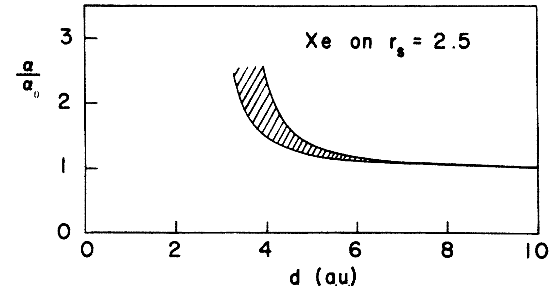

FIG. 4. Apparent effective polarizability for xenon adsorbed on $r_5 = 2.5$ metal. Upper bound computed with $\lambda = \frac{1}{9}$, lower bound with $\lambda = 0.22$. At $d = 4$ a.u., the atomic radius, the enhancement of the polarizability is 30% or more.

tance is very close to the distance where $\alpha_0 E_d / p$ approaches one, where the effective polarizability becomes infinite. Because of this and uncertainties in the xenon-metal distance, a quantitative value for α cannot be obtained. Qualitatively, however, one can see the large experimentally observed enhancement.

C. Application to nitrogen adsorbed on gold

Lin and McCormick[2] have determined the polarizability of nitrogen gas adsorbed on smooth polycrystalline gold surfaces at 77 °K using a capacitance measurement. They find $\alpha_{\text{expt}}^{N_2} = 2.43$ Å^3. Nitrogen, being a diatomic molecule, has a polarizability tensor with the values of polarizability along the principal axes of $\alpha_{\parallel}^{N_2} = 2.38$ Å^3 and $\alpha_{\perp}^{N_2} = 1.45$ Å^3,[17] for the longitudinal and transverse axes, respectively. It can be adsorbed on the surface in either of two extreme positions: (a) "lying end on" the surface, with the interatomic axis perpendicular to the surface, or (b) "lying flat" on the surface, with the interatomic axis parallel to the surface. The observed effective polarizability would require an enhancement of either $\alpha/\alpha_{\perp} = 1.68$ if the molecule were adsorbed "lying flat," or $\alpha/\alpha_{\parallel} = 1.02$ if the molecule were adsorbed "lying end on."

In this experiment, the polarizing field arises from the electric field applied across the capacitor plates. Thus, we should compare the experimental result with the apparent polarizability of Eq. (2.4) which includes effects owing to the screening of the external field by the surface electrons.

The free-electron density of gold, $n_+ = 5.9 \times 10^{22}$ cm^{-1}, gives an r_s value of 3.01.[20] We set $r_s = 3.0$ to approximate the gold surface. Major and minor radii of the nitrogen molecule are roughly 1.56 and 1.18 Å, respectively.[2] Thus we choose the minimum value of d to be about 3.0 a.u. for the molecule adsorbed "end on" and 2.2 a.u. for the molecule adsorbed "lying flat." The results for the effective polarizabilities for both orientations are shown in Fig. 5. The theory indicates that a molecule adsorbed "lying flat" should see no enhancement in its effective polarizability, while a molecule adsorbed "on end" might see as much as 20% enhancement. In order to agree with the experimental result, our results would indicate that the adsorbed molecules are adsorbed predominantely "standing on end." This is contrary to what one would expect from considerations of the adsorption energy. If, however, the nitrogen intramolecular distance becomes larger than in the free molecule, then our results would tend to agree with the observed effective polarizability and the expected molecular position on the metal surface.

IV. CONCLUSION

We have calculated the response of a realistic charge distribution at a metal surface to an external point dipole. From this we are able to calculate the effective polarizability of an atom or molecule in the vicinity of this surface. We find that the effective polarizability depends strongly on the location of the image plane of the surface and on the free-electron density of the metal. For comparison, taking the positive background boundary of the metal as a classical surface and calculating the classical effective polarizability, we find that the results at intermediate distances obtained in this paper are consistently larger than

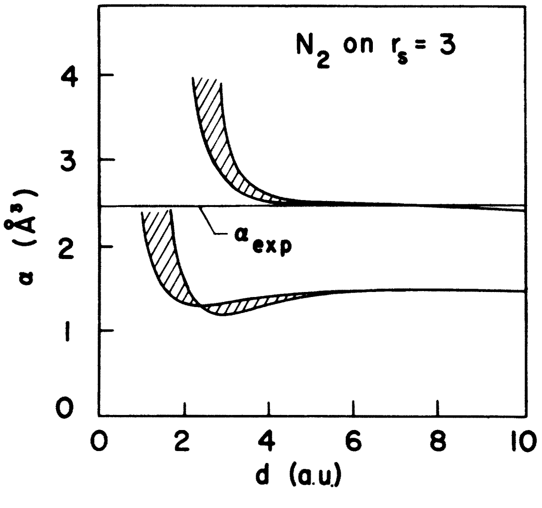

FIG. 5. Apparent effective polarizability for nitrogen adsorbed on gold. Experimental result ($\alpha_{\text{expt}} = 2.43$ Å^3) is taken from Ref. 2. Effective polarizabilities for the two possible orientations are shown, the upper curve representing the molecular axis oriented perpendicular to the surface ($\alpha_{0\parallel} = 2.38$ Å^3), and the lower curve with molecular axis oriented parallel to the surface ($\alpha_{0\perp} = 1.45$ Å^3).

the classical results. The two results merge at large distances. The result that the effective polarizability is larger at intermediate distances than one would obtain classically appears to be borne out by experiment. However, we are unable to obtain quantitative prediction for the effective polarizability.

We have also considered the effect of screening of an external field by the metal surface. This tends to reduce the apparent effective polarizability of the adatom-metal complex. This reduction can be great enough to prevent any enhancement of the polarizability, and even cause it to decrease.

Several areas of improvements are indicated for future work: the formalism itself with the uncertainty in λ and the treatment of the finite size of the atom or molecule. We believe, however, that the qualitative behavior will not be affected.

APPENDIX

The major uncertainty in the present theory lies in the use of the gradient expansion for the kinetic energy,

$$T=\tfrac{3}{10}(3\pi^2)^{2/3}\int n^{5/3}d^3r+\frac{\lambda}{8}\int\frac{|\nabla n|^2}{n}\,d^3r\ . \quad \text{(A1)}$$

The first term in Eq. (A1) is the Thomas-Fermi energy of a uniform electron gas with density n, and the second term, known as the von Weizsäcker term, is valid for slowly varying densities. There has been some uncertainty in the size of the coefficient of the gradient term above. The original choice, and the only choice for λ consistent with the variational principle is $\lambda=1$.[12] However, gradient expansion methods have been developed which indicate that $\lambda=\frac{1}{9}$ is a more appropriate choice.[12] Jones and Young[12] have examined a case where analytical expressions for the response function could be determined for both the von Weizsäcker approximation and the random-phase approximation. They showed that if F is the response function of an extended system of noninteracting fermions in a small static potential,

$$\delta n=F\,\delta V\ , \quad \text{(A2)}$$

where δn is the change in the density corresponding to the small perturbation δV, then the Fourier transform

$$F(q)=-\frac{k_F}{\pi^2}\,\frac{1}{1+3\lambda\eta^2}\ ,\qquad \eta=\frac{q}{2k_F} \quad \text{(A3)}$$

in the von Weizsäcker approximation, and

$$F(q)=-\frac{k_f}{\pi^2}\,\frac{1}{2}\left(1+\frac{1-\eta^2}{2\eta}\ln\left|\frac{1+\eta}{1-\eta}\right|\right) \quad \text{(A4)}$$

in the random-phase approximation. Thus, while $\lambda=1$ is the only choice consistent with the variational principle and is asymtopically correct for large q ($q\gg 2k_F$ or short-wavelength perturbations), the choice of $\lambda=\frac{1}{9}$ is asymtopically correct for small q ($q\ll 2k_F$ or long-wavelength perturbations).

Since we are interested in quantities which depend on integrations of the density functional over all configuration space, it has suggested[6] that the accuracy of the calculation would depend on the average η of the response. This is a linear-response theory, and a point dipole can be constructed from two point charges, separated by a small distance. We should be able to construct an average η based on the response of a metal to a point-charge perturbation. We have evaluated an average η based on the average q of the response and the average Fermi wave vector of the substrate in the region of the response as discussed in Appendix A of Ref. 6. An effective λ, λ_{eff}, is then computed from comparison of Fqs. (A3) and (A4). From a calculation on an $r_s=2$ metal surface, we found an initial $\lambda=\frac{1}{9}$ yielded a $\lambda_{\text{eff}}=0.18$, which is closer to $\frac{1}{9}$ than it is to 1. Increasing λ to 0.16 is sufficient to obtain a $\lambda_{\text{eff}}\approx 0.16$. For metallic densities ranging from $r_s=2$ to 6, we found that an initial λ less than or equal to 0.22 is sufficient to yield a λ_{eff} approximately equal to the initial λ. This provided us with a "range" of λ's which would indicate the uncertainties in this calculation.

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