

## Dynamical and geometrical effects on the physisorption of atoms

Thomas L. Ferrell\* and R. H. Ritchie†

Health and Safety Research Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

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The physisorption of atoms moving uniformly parallel to a plane surface and of atoms situated near a metal sphere is analyzed. A local dielectric function is used to calculate the energy of interaction in each case. The dynamical case is shown to give significant effects for atomic energies well beyond the thermal domain. The energy for both instances is calculated using a frequency- and space-dependent quantum-mechanical self-energy function.

### I. INTRODUCTION

The analysis of the physical interaction of an atom with a surface has a history which demonstrates its fundamentally interesting character. A pioneering work based on the image potential was presented in 1932 by Lennard-Jones, who remarked, even then, at the extensive literature on the subject.<sup>1</sup> His calculation was substantially improved during the ensuing decade by several investigators who, while maintaining the inverse-cube nature of the energy, modified the coefficient to include the electronic response characteristics of the surface.<sup>2,3</sup> The spatial dependence (for distances which are large compared to the wavelength of the ground-state-to-excited-state transitions) was modified in 1948 by Casimir and Polder by including retardation.<sup>4</sup> They found an inverse-fourth-power dependence using quantum electrodynamic calculations, although the same result was found within ordinary quantum theory by McLachlan fifteen years later.<sup>5</sup>

Intensive investigations of van der Waals energies with modern quantum field theory were carried out by Power and Zienau<sup>6</sup>; Aub, Power, and Zienau<sup>7</sup>; Dzialoshinskii<sup>8</sup>; and Dzialoshinskii, Lifshitz, and Pitaevskii<sup>9</sup> resulting in inclusion of many-body forces and the contributions of all the interaction frequencies. Parsegian has utilized the Lifshitz dispersion theory for macroscopic bodies in biological applications.<sup>10</sup>

Mavroyannis considered the problem of physisorption with the radiative correction in 1963, obtaining the results of the Lifshitz theory in this case.<sup>11</sup> For reference purposes, the leading term in the asymptotic series in inverse powers of distance from the surface in the "close-distance" limit (distance much less than the smallest wavelength of the atom's spectrum) of the result of Mavroyannis [Eq. (21)] is given here as

$$\langle V \rangle = \frac{1}{6\pi z_0^3} \sum_n' |\langle q \rangle_{1n}|^2 \int_0^\infty d\omega \frac{\omega_{n1}}{\omega_{n1}^2 + \omega^2} \left( \frac{1 - \epsilon(i\omega)}{1 + \epsilon(i\omega)} \right), \quad (1)$$

where  $\langle V \rangle$  is the energy of interaction of the atom with a plane surface a distance  $z_0$  away;  $\frac{1}{3} |\langle q \rangle_{1n}|^2 = |\langle 1|z|n \rangle|^2 = |\langle 1|x|n \rangle|^2 = |\langle 1|y|n \rangle|^2$ , with each matrix element taken using the ground state and the  $n$ th excited state with appropriate angular-momentum quantum numbers (left understood) to satisfy the selection rules;  $\omega_{n1}$  is the angular frequency associated with the energy of the ground-state-to- $n$ th-state transition; and  $\epsilon(i\omega)$  is the frequency-dependent dielectric constant of the surface bulk material evaluated at an imaginary frequency  $i\omega$ . In hartree atomic units ( $e = \hbar = m = 1$ ), Eq. (1) reduces for a perfect conductor to the Lennard-Jones energy  $-\langle r^2 \rangle / 12z_0^3$ , with  $\langle r^2 \rangle$  the ground-state expectation value of the square of the radius vector. For hydrogen  $\langle r^2 \rangle = 3$  hartree a.u.

Many of the developments pertaining to physisorption are discussed in the text by Margenau and Kestner.<sup>12</sup> The discussion of the dielectric constant and polarizability which is germane to the present work is given by Landau and Lifshitz.<sup>13,14</sup>

New investigations of physisorption have been stimulated by the great scope and variety of experimental techniques in surface physics which have evolved in recent years.<sup>15,16</sup> Effects due to surface diffuseness were analyzed in 1976 by Zaremba and Kohn.<sup>17</sup> More recently, Mehl and Schaich<sup>18</sup> have verified a significant difference between theory and experiment found by Raskin, Kusch, Shih, and others<sup>19-23</sup> and conclude that the theory overestimates the interaction. This apparent overestimation has been a recurring problem in the field, and the issue remains unresolved. Of course, the problem may lie in the host of difficulties well known to occur in this type of experimental work, and only further detailed work can isolate the discrepancies.

Motivated then in part by the necessity of providing a theoretical framework for new experiments, we have analyzed two modifications of the static, planar, quantum image energy. [We use the terminology "quantum image" to distinguish  $\langle V \rangle$  of Eq. (1) from the classical image energy.]

Both modifications are obtained with an efficient scheme involving the frequency- and space-dependent self-energy, which is illustrated in Sec. II by rederiving Eq. (1). The first modification considered is a dynamical one due to motion of the atom near the surface at energies extending well beyond the thermal domain. This is also accomplished in Sec. II. The second modification is a geometrical one and is analyzed in Sec. III where we consider an atom in the vicinity of a spherical surface.

Since the experiments cited above as analyzed by Mehl and Schaich involve the scattering of moving atoms from a cylinder, one really should consider quantitatively both dynamical and geometrical effects in the analysis. While both effects are undoubtedly small, since the atoms have only thermal energies and scatter within a few hundred Å of a one-inch cylinder, Mehl and Schaich did uncover some peculiarities in the trajectory analysis. They found that an added attractive interaction which varies as the inverse sixth power could affect the data in such a way as to make it appear as if an added repulsive force were acting. Indeed, by calculating the effect of surface roughness, they found just such an inverse-sixth-power energy. Unfortunately, its strength was too weak to affect the discrepancy between the data and the Lifshitz dispersion theory. It is interesting that the spherical geometry examined in Sec. III below also contains a small corrective term in the energy with an inverse-sixth-power dependence. (It also contains other dependences and actually is cast as a series.) Yet it is certainly true that one would have to conjure up much more to explain satisfactorily the currently available data, and we hope for additional experiments, both on atoms and on ions near surfaces. (Some experiments involving aloof scattering of charged particles near surfaces are currently under way.<sup>24</sup>) Data obtained under circumstances governed by the applicability of the formulas developed below would be very useful in deciding the adequacy of dispersion theory in general. It would be particularly valuable to contrast ion and atomic scattering near surfaces, especially in light of the wealth of theoretical analyses of dynamical effects for the former.<sup>25-32</sup> One might then discern whether inconsistencies, if they arise, are due to inadequate description of the surface or of the projectiles.

## II. THE SELF-ENERGY OF A MOVING ATOM NEAR A SURFACE

We first examine the case of an atom at a distance  $z_0$  from a planar surface with condensed matter filling the space  $z < 0$ . Subsequently, we

allow the surface to move in order to describe the equivalent situation of a static surface and a moving atom in the simplest fashion. We wish ultimately to calculate the effect upon the energy of interaction of the motion for the case of an atom moving parallel to the surface with the uniform velocity  $\vec{v} = v\hat{i}$ . The surface is taken to lie in the  $xy$  plane; and except for the atom, we assume vacuum everywhere for  $z > 0$ .

As a first requirement one needs the electrostatic potential for  $z > 0$  if a unit charge appears with charge density

$$\rho = \delta(x - x')\delta(y - y')\delta(z - z')\delta(t - t'). \quad (2)$$

The solution of this boundary-value problem is obtained here with the surface characterized by a local, frequency-dependent, dielectric function  $\epsilon(\omega)$ .

The potential due to the surface charge and engendered by the unit instantaneous charge is the homogeneous portion of the total potential for  $z > 0$  and is used in forming the potential energy. The homogeneous potential is here calculated to be

$$\int \frac{d\vec{K}}{K} \int_{-\infty}^{\infty} \frac{d\omega}{(2\pi)^2} \left( \frac{1 - \epsilon(\omega)}{1 + \epsilon(\omega)} \right) \times \exp\{i[\vec{K} \cdot (\vec{R} - \vec{R}') - \omega(t - t')] - K(z + z')\}, \quad (3)$$

where  $\vec{K}$  is  $k_x\hat{i} + k_y\hat{j}$  and  $\vec{R}$  is  $x\hat{i} + y\hat{j}$ .

For the present purposes we require the frequency component of the expression in Eq. (3) for the case of an atom with its nucleus located at  $z_0$ . That is, we take

$$V_\omega(r, r') = \frac{1}{2\pi} \int \frac{d\vec{K}}{K} \left( \frac{1 - \epsilon(\omega)}{1 + \epsilon(\omega)} \right) \times \exp[i\vec{K} \cdot (\vec{R} - \vec{R}') - K(z + z' + 2z_0)], \quad (4)$$

where  $z \rightarrow z + z_0$  and  $z' \rightarrow z' + z_0$ . The frequency component of the self-energy function is then obtained from  $V_\omega(\vec{r}, \vec{r}')$  and the Green's function of the Schrödinger equation for the atom.

Incorporating all the atomic quantum numbers into the single index  $n$  and writing a general wave function as  $u_n(\vec{r})$ , the self-energy function is<sup>33</sup>

$$\Sigma_{\omega_1}(\vec{r}, \vec{r}') = i \int \frac{d\omega}{2\pi} \sum_n' V_\omega(\vec{r}, \vec{r}') \frac{u_n(\vec{r})u_n^*(\vec{r}')}{\omega + \omega_1 - \omega_n}, \quad (5)$$

where  $\hbar\omega_n$  is the energy eigenvalue belonging to  $u_n$  and the prime on the summation indicates one must take proper account of the angular-momentum states.

From the Schrödinger equation of the system, the effective potential energy operator  $\hat{V}_{\text{eff}}(\vec{r})$  satisfies

$$\hat{V}_{\text{eff}}(\vec{r})u_1(r) = \int d\vec{r}' \sum_{\omega_1}(\vec{r}, \vec{r}')u_1(r'), \quad (6)$$

where  $u_1$  is the ground-state wave function.

The ground-state expectation value,

$$\langle V \rangle = \int u_1(r) \hat{V}_{\text{eff}}(\vec{r}) u_1(r) d\vec{r}, \quad (7)$$

is the interaction energy essentially equivalent to that obtained in second-order perturbation theory by a more standard approach. (Note that  $u_1$  is real.)

In the dipole approximation, one finds

$$\langle V \rangle = \frac{i}{2} \sum_n' \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \left( \frac{1 - \epsilon(\omega)}{1 + \epsilon(\omega)} \right) \int_0^{\infty} dK K^2 e^{-2Kz_0} \times \frac{4|\langle q \rangle_{1n}|^2}{3(\omega - \omega_{n1})}, \quad (8)$$

where the square of the magnitude of the electron's dipole matrix element  $|\langle q \rangle_{1n}|^2$  enters for  $(x, y, z)$  as

$$|\langle 1|x|n \rangle|^2 + |\langle 1|y|n \rangle|^2 + 2|\langle 1|z|n \rangle|^2 = \frac{4}{3} |\langle q \rangle_{1n}|^2, \quad (9)$$

the spatial average being taken, and  $\omega_{n1} \equiv \omega_n - \omega_1$ .

For comparison with standard results, one utilizes the known behavior of  $\epsilon(\omega)$  in the complex plane to convert to imaginary frequency, as shown by Landau and Lifshitz.<sup>13</sup> One obtains

$$\langle V \rangle = \frac{4}{3\pi(2z_0)^3} \sum_n' |\langle q \rangle_{1n}|^2 \int_0^{\infty} d\omega \frac{\omega_{n1}}{\omega^2 + \omega_{n1}^2} \times \left( \frac{1 - \epsilon(i\omega)}{1 + \epsilon(i\omega)} \right), \quad (10)$$

which is the same as Eq. (1).

If one takes the simple form

$$\epsilon(\omega) = 1 - \omega_p^2/\omega^2, \quad (11)$$

there results the quantum image energy,

$$U_{\text{QI}} = -\frac{\omega_{\text{sp}}}{12z_0^3} \sum_n' \frac{|\langle q \rangle_{1n}|^2}{\omega_{\text{sp}} + \omega_{n1}}, \quad (12)$$

where  $\omega_{\text{sp}} \equiv \omega_p/\sqrt{2}$  is the surface-plasmon frequency.

It is now an uncomplicated step to take if one seeks to describe the situation in which the atom moves parallel to the surface with uniform speed  $v$ . By examining the Fourier components of the potential, charge density, and dielectric function, one finds the energy of the dynamical case to be

$$\langle V \rangle = \frac{2i}{3} \int_{-\infty}^{\infty} \frac{d\omega}{(2\pi)^2} \left( \frac{1 - \epsilon(\omega)}{1 + \epsilon(\omega)} \right) \times \int_0^{\infty} K^2 e^{-2Kz_0} dK \times \int_0^{2\pi} d\theta \sum_n' \frac{|\langle q \rangle_{1n}|^2}{\omega - vK \cos \theta - \omega_{n1}}, \quad (13)$$

where we have replaced  $\omega$  in Eq. (8) by  $\omega - vK \cos \theta$  and have an integral over  $\theta$  to perform.

Again converting to imaginary frequency, Eq. (13) becomes

$$\langle V \rangle = \frac{2}{3} \sum_n' |\langle q \rangle_{1n}|^2 \int_0^{\infty} \frac{d\omega}{(2\pi)^2} \left( \frac{1 - \epsilon(i\omega)}{1 + \epsilon(i\omega)} \right) \times \int_0^{\infty} K^2 e^{-2Kz_0} I(\omega, K) dK, \quad (14)$$

where

$$I(\omega, K) = \int_0^{2\pi} d\theta \left( \frac{1}{\omega_{n1} + i\omega - vK \cos \theta} + \frac{1}{\omega_{n1} - i\omega - vK \cos \theta} \right). \quad (15)$$

If one uses here Eq. (11), the result is that

$$\langle V \rangle = -\frac{\pi\omega_{\text{sp}}}{6v} \sum_n' |\langle q \rangle_{1n}|^2 \frac{d^2}{d(2z_0)^2} \times [I_0(u) - L_0(u)], \quad (16)$$

where  $u$  is  $2z_0(\omega_{n1})/v$ ,  $I_0(u)$  is a zero-order Bessel function, and  $L_0(u)$  is a zero-order Struve function.<sup>34</sup>

If  $v \ll 2z_0(\omega_{\text{sp}} + \omega_{n1})$ , one may use the asymptotic form

$$\langle V \rangle \sim -\frac{\omega_{\text{sp}}}{12z_0^3} \sum_n' \frac{|\langle q \rangle_{1n}|^2}{\omega_{\text{sp}} + \omega_{n1}} \times \left[ 1 + \frac{3v^2}{2z_0^2} \left( \frac{1}{\omega_{\text{sp}} + \omega_{n1}} \right)^2 \right]. \quad (17)$$

This approximation has been numerically evaluated for atomic hydrogen as a function of  $r_s$  the "one-electron radius." In hartree atomic units,

$$\omega_{\text{sp}}^2 = 3/2r_s^3, \quad (18)$$

and the graphical results are shown in Fig. 1. For simplicity, we have divided  $\langle V \rangle$  by the Lennard-Jones classical image energy  $[-(1/4z_0^3)$  hartree a.u.] in obtaining the curves shown. Several different values of  $v/z_0$  are shown in the figure. We have displayed only the velocity-dependent portion of  $\langle V \rangle$  for each given  $v/z_0$ . The static portion is also shown. At  $v=0.1 z_0$  the velocity-dependent portion is about 4% of the static portion and at  $z_0=1$  Bohr radius this corresponds to an energy of 250 eV for the kinetic energy of the hydrogen atom.

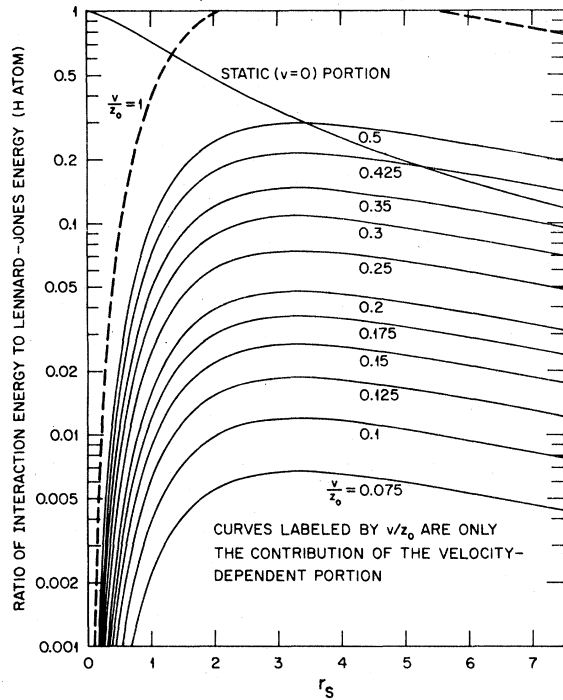


FIG. 1. Ratio of the energy of interaction of atomic hydrogen with a conducting wall to the Lennard-Jones energy as a function of  $r_s$  in Bohr radii (Eq. 17). The static and dynamic contributions are shown separately.

The summation in Eq. (17) was accomplished using the general formulas for the oscillator strengths first found by Sugiura.<sup>35</sup> That is, one introduces the oscillator strength  $f_{n1}$  by (in hartree a.u.)

$$|\langle q \rangle_{1n}|^2 = 3f_{n1}/2\omega_{n1}$$

with  $\omega_{n1} = (n^2 - 1)/2n^2$ , and for the discrete states of the sum for hydrogen one uses

$$f_{n1} = \frac{2^8}{3} \frac{n^5(n-1)^{2n-4}}{(n+1)^{2n+4}},$$

while for the continuum, one uses (in hartree a.u.)

$$\frac{df}{dE} = \frac{2^4 \exp[-4(2E)^{-1/2} \tan^{-1}(2E)^{1/2}]}{3(E+1/2)^4 [1 - \exp[2\pi/(2E)^{1/2}]}.$$

The usual sum rule for the oscillator strengths is then

$$1 = \frac{2^8}{3} \sum_n \frac{n^5(n-1)^{2n-4}}{(n+1)^{2n+4}} + \frac{2^4}{3} \int_0^\infty \frac{df}{dE} dE.$$

We have also tested the much simpler forms for the oscillator strengths given by Dalgarno and Victor<sup>36</sup> for our calculations. Their variational results are accurate to a few tenths of a percent. In

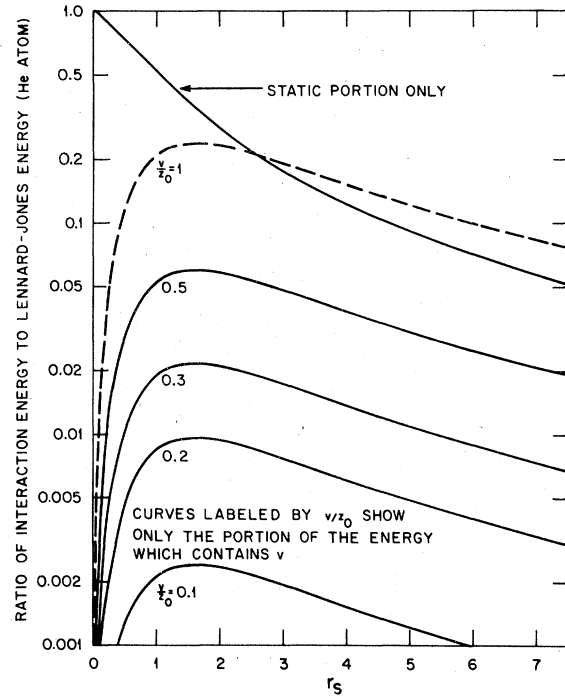


FIG. 2. Ratio of the energy of interaction of atomic helium with a conducting wall to the Lennard-Jones energy as a function of  $r_s$  in Bohr radii (Eq. 17). The static and dynamic contributions are shown separately.

Fig. 2 we have used their results for helium. In the case of atomic helium, the Lennard-Jones image energy is roughly  $-3/(16z_0^3)$ , but rather than dividing by this, we have simply normalized the static portion of  $\langle V \rangle$  for helium at  $r_s = 0$ . This makes the normalizing factor the correct result for a conductor with zero response time, as in the Lennard-Jones limiting case. We then used the same value of the normalizing energy to divide the dynamical portion of  $\langle V \rangle$ . Calling the normalizing energy  $V_{\text{He}}$ , Fig. 2 shows the static and dynamical portions of  $\langle V \rangle/V_{\text{He}}$  as a function of  $r_s$  just as in Fig. 1. At  $r_s = 2$ , the velocity-dependent portion is roughly 21% of the static contribution for  $v = 0.5z_0$  and is about 8% of the static contribution for  $v = 0.3z_0$ .

It is evident from the above results that the dynamical contribution to the interaction, as given by Eq. (17), is negligible for thermal atoms. Experimentally one might consider passing keV protons through water vapor, electrostatically deflecting away from the beam those protons which do not capture an electron and subsequently scattering the remaining H atoms near a surface. In this instance the dynamical contribution would be highly significant.

## III. INTERACTION WITH A SPHERE

The electrostatic Green's function for an instantaneous charge with spherical coordinates  $(r', \theta', \phi')$  outside a sphere of radius  $a$  has a frequency component which we have calculated to be

$$G_\omega(\vec{r}, \vec{r}') = 4\pi \sum_{l=0}^{\infty} \sum_{m=0}^l \sum_{p=-1,1} \left( \frac{1 - \epsilon(\omega)}{\epsilon(\omega)l + l + 1} \right) \frac{l a^{2l+1}}{(2l+1)(r'r)^{l+1}} Y_{lm}^p(\theta, \phi) Y_{lm}^p(\theta', \phi'), \quad (19)$$

where if  $P_l^m(\cos\theta)$  is the associated Legendre function, the real spherical harmonic is

$$Y_{lm}^p(\theta, \phi) = \left( \frac{(2 - \delta_m^0)(2l+1)(l-m)!}{4\pi(l+m)!} \right) P_l^m(\cos\theta) \begin{cases} \cos m\phi, & p=1 \\ \sin m\phi, & p=-1 \end{cases}. \quad (20)$$

One may transform  $G_\omega$  to an origin at  $z_0 > a$ , with  $r \rightarrow r_0$ ,  $r' \rightarrow r'_0$  as illustrated in Fig. 3 using<sup>37</sup>

$$r^{-(l+1)} P_l^m(\cos\theta) = \sum_{n=m}^{\infty} \frac{(l+n)!}{(l-m)!(n+m)!} \times \frac{r_0^n}{z_0^{n+l+1}} P_n^m(\cos\gamma). \quad (21)$$

The angle  $\gamma$  is shown in Fig. 3.

After this transformation, which yields  $V_\omega$  for the present case, one follows the same procedure as in Sec. II and obtains the dipole approximation to the energy of the interaction to be

$$\langle V \rangle = \sum_n \sum_{l=0}^{\infty} \frac{|\langle q \rangle_{ln}|^2}{6\pi r^3} \left( \frac{a}{r} \right)^{2l+1} \times l(l+1)(2l+1) \int_0^\infty d\omega A_{nl}(\omega), \quad (22)$$

where

$$A_{nl}(\omega) = \frac{\omega_{nl}}{\omega_{nl}^2 + \omega^2} \left( \frac{1 - \epsilon(i\omega)}{\epsilon(i\omega)l + l + 1} \right), \quad (23)$$

and where  $r$  is now the distance of the atom from the center of the sphere.

One may compare the form of the terms in the large parentheses on the right-hand side of Eq. (23) with similar terms in the classical expression for a dipole interacting with a dielectric sphere. The classical energy in the latter case is found by us for a dipole of moment  $p$  to be

$$V_\epsilon = \frac{-p^2(\bar{\epsilon} - 1)}{6r^3} \sum_{l=0}^{\infty} \frac{l(l+1)(2l+1)}{\bar{\epsilon}l + l + 1} \left( \frac{a}{r} \right)^{2l+1}, \quad (24)$$

where  $\bar{\epsilon}$  is the static dielectric constant for an insulator. For  $\bar{\epsilon} \rightarrow \infty$ , Eq. (24) becomes (note that the  $l=0$  term contributes in this limit but does not contribute for finite  $\bar{\epsilon}$ )

$$V_\infty = \frac{-ap^2}{6(r^2 - a^2)^2} - \frac{2a^3 p^2}{3(r^2 - a^2)^3}, \quad (25)$$

which is the classical image result for a conducting sphere.

For  $\epsilon$  given by Eq. (11), the integration in Eq. (22) can be performed, and one finds in this case

the energy  $\langle V_s \rangle \rightarrow \langle V_{s0} \rangle$ , where

$$\langle V_{s0} \rangle = \frac{\omega_p^2}{6r^3} \sum_{n=2}^{\infty} \sum_{l=0}^{\infty} \frac{|\langle q \rangle_{ln}|^2 l(l+1)}{\omega_l(\omega_l + \omega_{nl})} \left( \frac{a}{r} \right)^{2l+1}, \quad (26)$$

where the angular frequency of the surface-plasmon resonance is given for the  $l$ th mode of the sphere by

$$\omega_l^2 = \frac{l\omega_p^2}{2l+1}. \quad (27)$$

If one takes  $\omega_p \rightarrow \infty$  so that  $\epsilon(\omega)$  in Eq. (11) goes to  $-\infty$ , the instantaneous-response, perfectly conducting limit, then Eq. (26) reduces to Eq. (25) with  $p^2$  equal to 3 hartree a.u. for hydrogen; i.e., the sum over  $n$  of  $|\langle q \rangle_{ln}|^2$  is  $p^2$ . Just as in the reduction of Eq. (24) in the limit  $\bar{\epsilon} \rightarrow \infty$ , the monopole term  $l=0$  contributes only in the limiting case. Thus, Eq. (26) does not uniformly converge to Eq. (25) as  $\omega_p$  is increased, since for any finite value of  $\omega_p$  the monopole term in Eq. (26) is zero. There would be a discontinuous difference in the binding of either a neutral atom or an ion in orbit

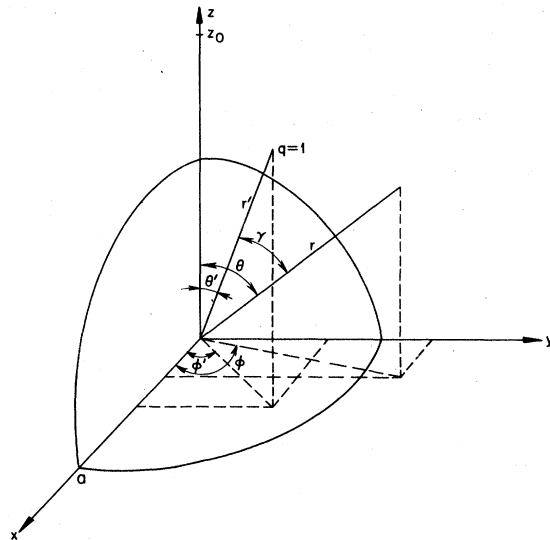


FIG. 3. Geometry used in reference to Eq. (21).

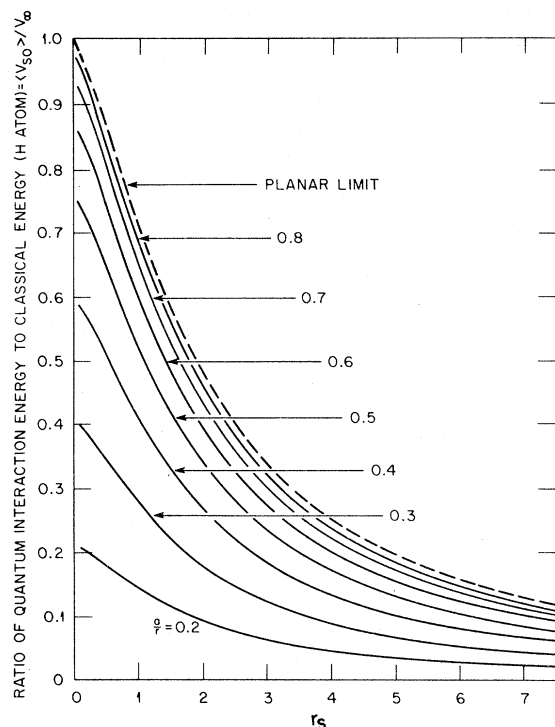


FIG. 4. Energy of atomic hydrogen near a metal sphere as a function of  $r_s$ . The energy is divided by the image energy, and curves for various values of  $a/r$  in Eq. (26) are shown.

about a sphere between the case of a good conductor and the case of a perfect conductor having an instantaneous response (a fictitious case).

Schmeits and Lucas<sup>38</sup> have considered geometrical effects on physisorption. A later paper by Cole and Schmeits<sup>39</sup> also treats several geometries. The present results differ from these authors in the fact that we have done the sum over atomic transitions in Eq. (26), while they approximated the sum by a single term. There is an alteration in the spatial dependence of  $\langle V_{s0} \rangle$  when the sum on  $n$  is done as Eq. (26) shows.

It should also be noted that the  $r$  dependence of  $\langle V_{s0} \rangle$ , as well as the coefficient of the interaction, is different from the  $r$  dependence of  $V_\infty$ . In the planar limit the quantum and classical energies differ only in the coefficient. The variation in  $r$  dependence between  $\langle V_{s0} \rangle$  and  $V_\infty$  is due in part to the variation in  $r$  dependence between  $V_e$  and  $V_\infty$  and in part to the sum over  $n$  in Eq. (26). For the latter variation, the fluctuating dipole moment causes therefore an alteration in the  $r$  dependence not found in the planar limit ( $a \rightarrow \infty$ ). These features are potentially encouraging for experimental prospects. Including retardation effects would further add to the variation in the  $r$  dependence, although we reserve this for future work.

One may use Eq. (26) to plot  $\langle V_{s0} \rangle / V_\infty$  for atomic hydrogen as a function of  $r_s$ . The results are shown in Fig. 4 for several values of  $a/r$ . The curves for larger  $a/r$  approach the planar limit, which is shown as the dashed line and which is taken from Fig. 1. One discerns from Fig. 4 that, as the planar limit is approached, the slope for small  $r_s$  increases. Since the finite  $r_s$  results converge continuously to the  $r_s = 0$  limit for a plane, one expects the behavior shown for  $a/r$  near unity and  $r_s$  small. The missing  $l = 0$  term in the sum in Eq. (26) for finite  $r_s$  is less significant for  $a/r$  near unity, the higher values of  $l$  being then the more important. [Notice  $\omega_l$  from Eq. (27) becomes  $\omega_{sp} = \omega_p / \sqrt{2}$  as  $l \rightarrow \infty$ .]

In conclusion, while curvature effects are not significant for experiments done to date, the use of small target spheres (and cylinders) would provide substantial information on the adequacy of dispersion theory.

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\*Also, Department of Physics, Appalachian State University, Boone, N.C. 28608.

†Also, Department of Physics, University of Tennessee, Knoxville, Tenn. 37916.

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