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van der Waals interaction in atom-surface scattering

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Corrections to the conventional dipole expression for the attractive interaction between an atom and a metal surface are calculated and discussed in several models: (i) the electrostatic image model, primarily used to define the multipole corrections and to give a simple, although accurate, estimate thereof; (ii) a model that includes both s and d electrons in the metallic dielectric response together with an atomic polarizability accounting for multipole contributions; and (iii) a model with a realistic treatment of the coupling between density fluctuations in the metal and on the atom (the conventional methods overestimate it). The models show what factors are needed to avoid a singular interaction at the dynamical image plane. While the point dipole of model (ii) allows polarization response at all wavelengths, and leads to singular behavior, model (iii) shows how the finite extent of the atom limits the ability of the system to respond to polarizing fields of short wavelengths. The latter "saturation" of the response competes with the multipole contributions and reduces their influence on the interaction potential over the whole range of distances, and leads to a finite potential also for shorter distances, where the saturation is particularly important. The models are illustrated with numerical calculations for helium on noble metals. With a proper description of the repulsive interaction the resulting physisorption potential is in agreement with experimental findings. We also apply our results for helium to give some brief comments for another interesting atom/substrate system: H_2 on noble metals.

I. INTRODUCTION

In recent years, atom-scattering experiments have become increasingly important tools to investigate the characteristics of metal surfaces.[1] By an interplay between experimental and theoretical studies,[2-5] one tries to find the interaction potential between the incoming atom and the surface. Formally, this interaction potential is obtained by solving the Schrödinger equation for the many-electron system of the combined atom-metal system in a self-consistent way,[3] varying the atomic configuration, particularly the atom-metal distance d. This gives the total interaction potential. For the inert-gas atoms, commonly used in atom-surface–scattering experiments, a simpler description of the potential as a sum of a (corrugated) repulsive part[2] and an (uncorrugated) attractive part[3] is often used. The attractive part, the van der Waals interaction, is usually described by the first term ($\sim d^{-3}$) in an asymptotic power-law expansion with respect to the separation d.[3] This is an acceptable representation at large distances. For smaller separations, however, it diverges as $\sim d^{-3}$. A divergence like this is not physically correct, since the correlation effects embodied in the van der Waals interaction should give a finite potential everywhere in the bulk. Instead, the attractive interaction is expected to be a smooth function of the distance, with a d^{-3} dependence far away from the surface and a finite value for shorter distances. The purpose of this work is to give a more accurate description of the attractive part of the potential, which eliminates this misleading divergence and has a realistic behavior over the entire range of atom-metal separations.

There is a large number of relevant and important contributions to the theory of the van der Waals interaction between bodies of various shapes and dimensions. We will indicate here some of the relevant theoretical papers for this work.[6] Calculations of the interaction between neutral species were first done for molecules,[7,8] leading to the well-known d^{-6} form of London.[9] The first person to consider the interactions between an atom and a substrate ($\sim d^{-3}$) was Lennard-Jones[10] in a model with a perfectly reflecting metal. Lennard-Jones's treatment was later found[11-14] to overestimate the strength of the interaction—it does not take into account the limited ability of the substrate electrons to follow the instantaneous polarization of the atom.

Casimir and Polder[15] have subsequently introduced retardation effects and the idea of the van der Waals interaction being a change in the electromagnetic field energy brought about by the interaction. This was then, independently, developed into a general form for the van der Waals interaction, which we currently recognize as the Lifshitz formula.[16] In Lifshitz's treatment, fluctuating electric and magnetic currents have been introduced into the Maxwell equations. In a similar spirit the van der Waals interaction was later identified as a change in surface normal-mode frequencies.[17] In the early 1970s, calculations of the attractive interaction which a neutral body feels outside a polarizable medium have focused on a better treatment of the medium.[3,18-23] This has been done by taking into account the spatial dispersion in the dielectric response of the metal, i.e., the response of the metal to fields varying in space, within a linear-response formalism.[22]

With the advent of more realistic electronic wave functions for the substrate, the calculations along these lines by Zaremba and Kohn[3] currently serve as the "standard" reference for atom-surface interactions. It is only quite recently that there have been any serious attempts to also treat the spatial response of the atom in a better way, mainly triggered by the improved experimental accuracy. This has been made by studying multipole moments higher[24–27] than the dipolar one.

In this paper we will first review two simple multipole models before performing a calculation of the atomic response to all multipole orders, together with a realistic treatment of the metal surface. The calculations have the same starting point as the approach of Zaremba and Kohn[3] and are very similar in outcome for the metal response, although using a much simpler procedure. The description of the atomic polarizability in this work is far more realistic than the point-dipole approximation. It leads to a finite potential close to the surface, but to similar results for intermediate and large separations. The latter is shown to be due to compensation of two different types of corrections to the Zaremba-Kohn treatment.

In terms of the response functions χ_a for the atom and χ_m for the metal, the van der Waals (vdW) interaction can be "quite generally" expressed as[3]

$$E_{\mathrm{vdW}}=-\int d\vec{r}\int d\vec{r}\,'\int d\vec{x}\int d\vec{x}\,'v(\vec{R}+\vec{x}-\vec{r})v(\vec{R}+\vec{x}\,'-\vec{r}\,')\int_{-\infty}^{\infty}du(2\pi)^{-1}\chi_a(\vec{x},\vec{x}\,',iu)\chi_m(\vec{r},\vec{r}\,',iu)\,, \tag{1.1}$$

where $v(\vec{R}+\vec{x}-\vec{r})$ is the Coulomb potential between the electrons on the atom and the metal, respectively, when they are separated by the vector $\vec{R}$. We represent v in terms of its two-dimensional Fourier transform[3]

$$v(\vec{r}-\vec{r}\,')=\frac{1}{L^2}\sum_{\vec{k}_{\|}}\left[\frac{2\pi}{k_{\|}}\right]e^{i\vec{k}_{\|}\cdot(\vec{r}_{\|}-\vec{r}\,'_{\|})}e^{-k_{\|}|z-z'|}\,,$$

where L^2 is the surface area of the solid, and $\vec{r}=(\vec{r}_{\|},z)$. This implies that

$$v(\vec{R}+\vec{x}-\vec{r})\propto\sum_{\vec{k}_{\|}}e^{i\vec{k}_{\|}\cdot(\vec{R}+\vec{x}_{\|}-\vec{r}_{\|})}e^{-k_{\|}|d+z_a-z_m|}$$

for an atom at a distance d from the surface (Fig. 1). If the overlap between the atom and the metal electron wave functions were exactly zero, then $|d+z_a-z_m|=d+z_a-z_m$. Equation (1.1) then separates into two uncoupled integrals over the atomic and the metallic coordinates, respectively,

$$\begin{aligned}E_{\mathrm{vdW}}=-\int_0^{\infty}du\frac{1}{2\pi L^4}\sum_{\vec{k}_{\|},\vec{k}\,'_{\|}}\left[\frac{2\pi}{k_{\|}'}\right]\left[\frac{2\pi}{k_{\|}}\right]&e^{-d(k_{\|}+k'_{\|})}e^{i\vec{R}\cdot(\vec{k}_{\|}-\vec{k}\,'_{\|})}\\ &\times\int d\vec{x}\int d\vec{x}\,'e^{i\vec{k}\cdot\vec{x}}e^{-i\vec{k}^{*\prime}\cdot\vec{x}\,'}\chi_a(\vec{x},\vec{x}\,',iu)\\ &\times\int d\vec{r}\int d\vec{r}\,'e^{-i\vec{k}\cdot\vec{r}}e^{i\vec{k}^{*\prime}\cdot\vec{r}\,'}\chi_m(\vec{r},\vec{r}\,',iu),\quad\vec{k}=(\vec{k}_{\|},ik_{\|})\end{aligned} \tag{1.2}$$

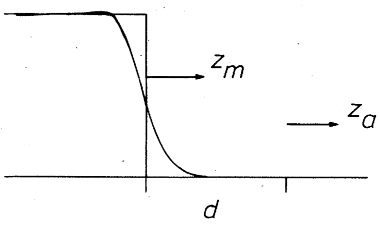

FIG. 1. Parameters of the physisorption geometry. The metal coordinate z_m is defined from the jellium edge, negative in the bulk, z_a is the atomic coordinate, and d is the distance from the nuclei to the jellium edge.

where $\vec{k}\,'_{\|}=\vec{k}_{\|}+\vec{G}$, $\vec{G}$ being a reciprocal-lattice vector in the plane of the surface. Only the $\vec{G}=\vec{0}$ term gives a power-law-dependent interaction energy, which corresponds to the conventional van der Waals energy. All the other terms decay exponentially. Limiting ourselves to the power-law terms, we thus obtain

$$E_{\mathrm{vdW}}=-\frac{\hbar}{4\pi}\int_0^{\infty}dk_{\|}\int_{-\infty}^{\infty}du\,e^{-2k_{\|}d}\alpha(k_{\|},iu)\rho(k_{\|},iu)\,, \tag{1.3}$$

where

$$\alpha(k_{\|},iu)=\int d\vec{x}\int d\vec{x}\,'e^{i\vec{k}\cdot\vec{x}}e^{-i\vec{k}^{*}\cdot\vec{x}\,'}\chi_a(\vec{x},\vec{x}\,',iu)\,,\qquad \vec{x}=(\vec{x}_{\|},z_a) \tag{1.4}$$

is the atomic polarizability, and

$$\rho(k_{\parallel},iu)=\frac{2\pi}{k_{\parallel}}\int dz_m\int dz_m' e^{-k_{\parallel}(z_m+z_m')}\chi_m(k_{\parallel},z_m,z_m',iu) \tag{1.5}$$

is the reflection coefficient of the metal.[28]

From a physical point of view it is not a bad approximation to neglect the overlap when the atom is located at distances typical for physisorption. Furthermore, the large metallic screening limits the penetration of the mutual polarizing field. This is not contained in Eq. (1.3), however. The result of using this form is that the integrand for E_{vdW} in Eq. (1.3) diverges when $k_{\parallel}\to 0$ due to the growth of $\exp(-k_{\parallel}z_a)$ in the polarizability for large, negative z_a values. It is then incorrect to neglect the overlap and afterwards integrate over all space. The latter leads to an infinite value for the overlap. Zaremba and Kohn[3] avoid this problem by restricting the treatment to the asymptotic region, retaining only the dipole contribution to the polarizability.

For physical reasons one expects that only the lowest terms in a Taylor expansion of $\exp(-i\vec{k}\cdot\vec{x})$ contribute to the interaction, when the distance is large (the metal only "sees" a point dipole when the atom is very far away). Inclusion of only these terms means that Eq. (1.3) describes the situation in an asymptotically exact way.

In Sec. II we derive the relevant terms (dipole, quadrupoles, and octupoles) in a multipole expansion using simple perturbation theory[27] in the spirit of Lennard-Jones[10] for the case of perfect metallic screening. We also discuss the modifications due to a limited screening ability. This gives an upper bound for the corrections from multipoles to the dominating dipole contribution.

In Sec. III we improve this expansion[26] by using Eq. (1.3) with a more realistic surface response, including a smooth variation in the dielectric properties at the interface, as well as the d-electron contribution to the screening. The polarizability of the atom is calculated with rather simple, though properly orthogonalized, wave functions, yielding a good value for the static polarizability. The resulting van der Waals potential combined with a proper repulsive interaction gives a slightly deeper physisorption well than a standard treatment.[3] For He on noble metals the correction is less than 10% at relevant physisorption distances. Inclusion of all higher-order terms in the Taylor expansion leads to a divergence of Eq. (1.3) for all distances. This is a situation analogous to the Stark effect,[29] where the perturbation series diverges but the predictions from the leading terms are borne out very well by experiment. The mathematical series contains the possibility that the electron can be in a region where the field is stronger than the Coulomb potential. Equation (1.1) does not contain this divergence since $\exp(-k_{\parallel}\,|\,d+z_a-z_m\,|\,)\leq 1$ over all space. This means that E_{vdW} is finite even when $d\to 0$.

To avoid cutting off the exponential tails of the wave functions, it is necessary to integrate over all space, but then one is faced with the effects of overlap. The factor $\exp(-k_{\parallel}\,|\,d+z_a-z_m\,|\,)$ contains a coupling between the coordinates of the atom and the metal, which makes it impossible to separate the integrals and then calculate the atomic polarizability and the metallic response function according to Eqs. (1.4) and (1.5), respectively. Zaremba and Kohn[3] circumvent this difficulty by letting $|\,d+z_a-z_m\,|=d+z_a-z_m$ (the zero-overlap approximation). As mentioned earlier, this implies a divergent van der Waals interaction as $d\to 0$. By using the triangle inequality, $|\,d+z_a-z_m\,|<|\,d+z_a\,|+|\,z_m\,|$, however, one can decouple the coordinate systems. Then the polarizability and the reflection coefficient can be calculated separately, yielding a finite E_{vdW} interaction as $d\to 0$ since we retain the important property of the full expression, namely that $\exp(-k_{\parallel}\,|\,d+z_a-z_m\,|\,)<1$. In Sec. IV we show that this is a better model than neglecting the overlap completely, and that it leads to a smooth, nonsingular behavior of the van der Waals interaction at all distances, even when the atom nears the surface.

II. ELECTROSTATIC IMAGE MODEL

In this section we calculate the multipole corrections to the standard dipole interaction potential using an extension of the electrostatic image model studied by Lennard-Jones.[10] The quadrupoles and octupoles are found to give at most a 15% deeper potential at relevant physisorption distances.

Within the Born-Oppenheimer approximation, the electronic problem can be solved in a model with a proton at a fixed distance d outside a perfectly reflecting metal substrate, the sharp boundary of which is at $z=-d$. The electron thus moves in the attractive potential from the proton, as shown in Fig. 2. The system is then described by the following total Hamiltonian:

$$H=H_0+V(\vec{r})\ ,$$

where

$$H_0\psi_0=E_0\psi_0$$

is the Schrödinger equation for the free atom, and where the perturbation

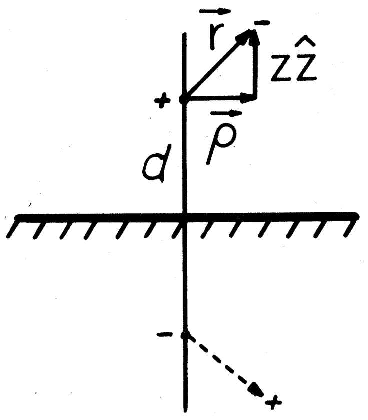

FIG. 2. Adsorption coordinates for a polarizable atom, in the form of a proton, a distance d outside the substrate, and an electron with coordinates $\vec{r}=(\vec{\rho},z)$.

$$V(\vec{r})=-\frac{e^2}{4d}-\frac{e^2}{4(d+z)}+\frac{e^2}{[(2d+z)^2+\rho^2]^{1/2}} \tag{2.1}$$

contains the interactions of the proton and electron with their image charges. Recently,[27] we calculated the energy shift due to the image interaction for an atom, which is not allowed to deform in the presence of the substrate, and showed that to $O(d^{-8})$ it is sufficient to use first-order perturbation theory. In principle, there are both deformations due to overlap with the metal wave functions and due to the image potential itself. Far away from the surface ($d \gg z$), V is expanded in terms of z/d:

$$V(\vec{r})=-\frac{e^2}{4d}-\frac{e^2}{4d}\sum_{n=0}^{\infty}(-z/d)^n + \frac{e^2}{2d}\sum_{n=0}^{\infty}P_n(-\cos\theta)(r/2d)^n \,. \tag{2.2}$$

Both the $n=0$ and $n=1$ terms in Eq. (2.2) vanish, leaving the leading term proportional to d^{-3}, which is the standard dipole contribution. Inserting V between the unperturbed states $|0\rangle=\psi_0$, assumed spherically symmetric, we find

$$\Delta E=\langle 0|V|0\rangle=-\sum_{l=1}^{\infty}\frac{C_{2l+1}}{d^{2l+1}} \,, \tag{2.3}$$

where the coefficient for the lth multipole moment is

$$C_{2l+1}=\frac{e^2\langle r^{2l}\rangle}{4(2l+1)} \,. \tag{2.4}$$

The terms relevant for physisorption,

$$\Delta E=-\frac{e^2\langle r^2\rangle}{12d^3}-\frac{e^2\langle r^4\rangle}{20d^5}-\frac{e^2\langle r^6\rangle}{28d^7}-\cdots \,, \tag{2.5}$$

are successively decreasing. The dipole term is the Lennard-Jones result.[10] To assess the importance of the quadrupole and octupole contributions it is convenient to normalize ΔE to the standard $-C_3/d^3$ dipole term,

$$\Delta E/(-C_3/d^3)=1+d_q^2/d^2+d_o^4/d^4+O(1/d^6) \,. \tag{2.6}$$

Using hydrogenlike wave functions, $|0\rangle=(\lambda^3/\pi)^{1/2}e^{-\lambda r}$ with $\lambda=a_0^{-1}$ for H and $1.453a_0^{-1}$ for He, the characteristic quadrupole (length)^2 and the octupole (length)^4 are

$$d_q^2=C_5/C_3=9/2\lambda^2 \tag{2.7}$$

and

$$d_o^4=C_7/C_3=45/\lambda^4 \,, \tag{2.8}$$

respectively. For He, $d_q^2=0.60$ Å^2 and $d_o^4=0.79$ Å^4. These quadrupole and octupole contributions are plotted in Fig. 3. They give at most a 15% more attractive potential in the range $d=4$–8 a.u. For H, the corresponding corrections are twice as large since H is larger than He and then less pointlike.

Further insight into the question of the contributions from the higher poles can be obtained in the case of limited screening. Using a model with one dominant transition for each metal and atom, respectively, we have shown[27] that the strength of the different poles are reduced according to

$$C_{2l+1}\rightarrow\frac{\omega_s}{\omega_s+\omega_0}C_{2l+1} \,,$$

where ω_s is the surface-plasmon frequency and ω_0 is the frequency of the atomic transition. For He on a metal surface, ω_0 is of the order of several ω_s, which means a significant reduction of the attractive potential. This is reasonable since the atom cannot interact any longer with a perfect image of itself. However, the ratios d_q^2 and d_o^4 remain unchanged, which is what one would expect since they are basically atomic measures. Including more transitions in the system, as is done in the next section, will change them slightly, but the values calculated above are indeed upper bounds for the multipole corrections also for a calculation with a metal substrate having a finite plasma frequency. We conclude that this model, though admittedly crude, can be expected to yield reasonable *estimates* for corrections in other atom-surface systems of interest.

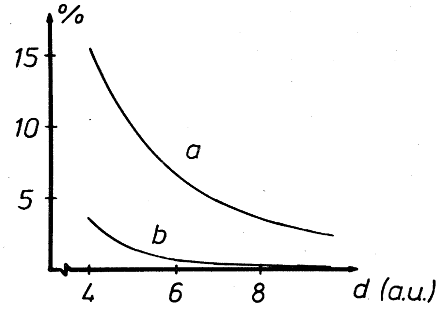

FIG. 3. Percentage corrections to the standard dipole van der Waals interaction from (a) quadrupole and octupole contributions, and (b) from octupole contributions alone, calculated with parameters for helium a distance d outside a perfectly reflecting metal (d in a.u.).

III. IMPROVED DESCRIPTION OF THE MULTIPOLE CONTRIBUTIONS

The expression for the van der Waals interaction in Eq. (1.3) is based on the neglect of the overlap between the atomic and metallic electron wave functions. As we have argued in Sec. I the multipole contributions to the interaction have a meaning only when the atom is located away from the surface, e.g., at the physisorption equilibrium distance. The model breaks down completely close to the surface since all terms in the series diverge.

In this section we improve the description by accounting for both the metal reflection coefficient and the atomic polarizability in an optimal way. By this we mean that these quantities are described by the simplest possible mathematical expressions which include the relevant physics. For the metal we use a model dielectric function, which for noble-metal substrates includes s- and d-electron contributions in such a way that the main peaks in an electron-energy-loss spectrum[30] are reproduced. The influence of d electrons on the effective surface position (image plane) is described according to self-consistent local-density calculations.[31]

The atomic polarizability of the He atom is described by two types of transitions, a discrete one, from primarily $|0\rangle$ to $|2p\rangle$, and one from $|0\rangle$ to continuum states $|Q\rangle$, where the latter state is orthogonalized to the other ones (compare the orthogonalized-plane-wave method[32]). The method is described in further details in Secs. III A and III B. The resulting multipole corrections contribute less than 5% to the interaction at relevant physisorption distances. This is in accordance with experimental findings that for the scattering of a helium atom against a noble metal, the dipole term together with a repulsive potential seem to give a reasonable description of the interaction potential.[1]

A. Metal response

The response of the metal to external electromagnetic fields can be expressed in one quantity, the surface response function[28]

$$\rho(k_{\|},iu)=\frac{[\epsilon(iu)-1](1-k_{\|}d_{\perp})}{\epsilon(iu)+1+[\epsilon(iu)-1]k_{\|}d_{\perp}}\ , \tag{3.1}$$

which is another way of expressing Eq. (1.5). Here, $\epsilon(iu)$ is the bulk dielectric function at infinite wavelength, and $d_{\perp}$ is the center of gravity of the density δn, induced in the metal by the atom,

$$d_{\perp}=\int dz\, z\,\delta n\Big/\int dz\,\delta n\ . \tag{3.2}$$

For the calculation of multipole contributions in the physisorption range, we are interested only in the small wave-vector limit. Thus, expanding Eq. (3.1) to lowest order in $k_{\|}d_{\perp}$ gives

$$\rho=\frac{\epsilon-1}{\epsilon+1}\left[1-2k_{\|}d_{\mathrm{IP}}+\frac{\epsilon-1}{\epsilon+1}\left[1+\frac{\epsilon-1}{\epsilon+1}\right]d_{\perp}^2k_{\|}^2+\cdots\right]\ , \tag{3.3}$$

where $d_{\mathrm{IP}}\equiv[\epsilon/(1+\epsilon)]d_{\perp}$ defines the so-called dynamical image plane.

In a classical treatment, $d_{\perp}\equiv 0$, since the center of gravity then is located exactly at $z=0$, and ρ takes the classical form

$$\rho_0=\frac{\epsilon-1}{\epsilon+1}\ . \tag{3.4}$$

Using ρ_0 together with a point-dipole form of $\alpha(k_{\|},iu)$ in Eq. (1.3) gives the well-known result for the van der Waals interaction.[16]

In our improved description it is not sufficient to use the free-electron form for the dielectric function ϵ, $\epsilon_s=1-\omega_p^2/\omega^2$, with ω_p being the free-electron plasma frequency. For noble metals it is important to incorporate the d electrons, which can be made by adding a d-electron contribution to ϵ_s. For our purpose a physically well-motivated two-parameter expression for this quantity is

$$\epsilon=\epsilon_s+N\omega_p^2/(\omega_0^2-\omega^2)\ . \tag{3.5}$$

N is the effective number of d electrons responding in the frequency range of interest $[N(\omega=\infty)=10]$. The two parameters N and ω_0 are chosen such that two of the main peaks in a bulk or surface electron-energy-loss spectrum[30] of the pertinent metal are reproduced ($\mathrm{Im}(-1/\epsilon)$ or $\mathrm{Im}[-1/(1+\epsilon)]\to\infty$, respectively). Equation (1.1) contains an integration over an imaginary frequency argument $\omega=iu$. In Appendix A, we show that

$$\rho_0(iu)=\frac{E^2u^2+F^4}{(u^2+B^2)(u^2+C^2)}\ , \tag{3.6}$$

where

$$E^2=(N+1)\omega_s^2\ ,$$

$$F^2=\omega_s\omega_0(\omega_s=\omega_p/\sqrt{2})\ ,$$

and

$$B(C)=\tfrac{1}{2}[(E^2+\omega_0^2+2F^2)^{1/2}\pm(E^2+\omega_0^2-2F^2)^{1/2}]$$

are the surface-plasmon poles.

We must also include the d-electron contribution to $d_{\perp}$, which we write as

$$d_{\perp}=d_{\perp}^s f\ , \tag{3.7}$$

where

$$d_{\perp}^s=\int dz\, z\,\delta n^s\Big/\int dz\,\delta n^s$$

and

$$f=\int dz\,\delta n^s\Big/\int dz\,\delta n\ .$$

We then used the fact that $\int dz\, z\,\delta n^d\simeq 0$ when the jellium edge is at $z=0$. The function f measures the extent to which the d electrons participate in the response of the metal to the electromagnetic field. We can relate δn to the polarizing field and can, therefore, relate ϵ with Poisson's equation. This gives[3]

$$f=\frac{\epsilon_s-1}{\epsilon-1}\ . \tag{3.8}$$

Defining

$$d_{\mathrm{IP}}^s=\frac{\epsilon}{\epsilon+1}d_{\perp}^s \tag{3.9}$$

and

$$\rho_s\equiv\frac{\epsilon_s-1}{\epsilon+1}=\frac{\omega_s^2u^2+F^4}{(u^2+B^2)(u^2+C^2)}\ , \tag{3.10}$$

and keeping only the first terms in Eq. (3.3) (since the third term is negligible, which will be demonstrated in Sec. III C), we thus obtain the final form for the reflection coefficient used in our calculation,

$$\rho=\rho_0-2k_{\|}\rho_s d_{\mathrm{IP}}^s\ . \tag{3.11}$$

For d_{IP}^s we use the following form:

$$d_{\mathrm{IP}}^s=\frac{D^2d_{\perp}^s(0)}{D^2+u^2}\ , \tag{3.12}$$

where the parameters D and $d_{\perp}(0)$ are taken from a density-functional calculation for the metal[33] and are tab-

TABLE I. Parameters characterizing the noble metals in calculating E_{vdW}.

	ω_p	ω_0^2/ω_p^2	N	B/ω_s	C/ω_s	E^2/ω_s^2	F^4/ω_s^4	$d_\perp(0)$	D^2/ω_s^2
Ag	8.98	1.37	5.44	2.98	0.56	6.44	2.74	1.42	0.380
Au	9.03	0.62	5.94	2.83	0.39	6.94	1.24	1.42	0.380
Cu	10.80	0.25	2.59	1.99	0.36	3.59	0.50	1.48	0.345

ulated in Table I. This form was recently suggested by Persson and Apell,[31] and has the virtue of fulfilling important sum rules for the surface response.[31,34]

B. Atomic polarizability

In order to calculate the polarizability, i.e., the response of the atom to the polarization from the metal, we need to calculate the density-density response function

$$\chi_a(\vec{x},\vec{x}\,',iu)=\sum_i \left[\frac{\langle 0 \,|\, \hat{n}(\vec{x}) \,|\, i \rangle\langle i \,|\, \hat{n}(\vec{x}\,') \,|\, 0 \rangle}{\epsilon_i-\epsilon_0-iu} + \text{c.c.} \right] , \tag{3.13}$$

where the sum goes over all intermediate states. In this calculation we will only consider excited states which give the major contribution to the polarizability. Thus we only take into account transitions from $|\,1s\,\rangle$ to $|\,2p\,\rangle$ using Slater orbitals,

$$|\,s\,\rangle=(\lambda^3/\pi)^{1/2}e^{-\lambda r}$$

and

$$|\,2p,m\,\rangle=(4\mu^5/3)^{1/2}r\,e^{-\mu r}Y_{1m}(\hat{\Omega}_r), \quad m=0,\pm 1 \, ,$$

where $\lambda=1.453$ and $\mu=0.525$ a.u., and transitions from $|\,1s\,\rangle$ to continuum states,

$$|\,Q\,\rangle=|\,\tilde{q}\,\rangle-\langle\,\tilde{q}\,|\,s\,\rangle\,|\,s\,\rangle-\sum_m\langle\,\tilde{q}\,|\,m\,\rangle\,|\,m\,\rangle \, ,$$

($|\,\tilde{q}\,\rangle=e^{i\vec{q}\cdot\vec{r}}$, and $|\,m\,\rangle$ is short for $|\,2p,m\,\rangle$). The coefficients $\langle\,\tilde{q}\,|\,s\,\rangle$ and $\langle\,\tilde{q}\,|\,m\,\rangle$ make the continuum states orthogonalized to the other states. This gives a static polarizability $\alpha(0)=1.43$ a.u., very close to the exact value, 1.38 a.u.[35]

Rewriting the matrix elements in Eq. (3.13), α needed in Eq. (1.4) can be expressed in the familiar form

$$\alpha(k_{\parallel},iu)=\sum_i \frac{2A_i}{A_i^2+u^2}\,|\,f_i(\vec{k})\,|^2 \, , \tag{3.14}$$

where $A_i=\epsilon_i-\epsilon_0$ is the excitation energy, and

$$f_i(\vec{k})=\langle 0 \,|\, e^{i\vec{k}\cdot\vec{x}} \,|\, i \rangle$$

is a generalized oscillator-strength amplitude. In the calculation of α the full Taylor expansion of $f_i(\vec{k})$ can be used. As we are only interested in the first three terms, these can be taken into account afterwards. Using the transitions mentioned above gives two contributions to the polarizability,

$$\alpha_B(k_{\parallel},iu)=2\sum_m \frac{2A_1}{A_1^2+u^2}\,|\,f_{pm}\,|^2 \tag{3.15}$$

and

$$\alpha_{\mathrm{sc}}(k_{\parallel},iu)=\sum_q \frac{2A_2}{A_2^2+u^2}\,|\,f_q\,|^2 \tag{3.16}$$

(B denotes bound, and sc denotes scattering), where $A_1=\epsilon_p-\epsilon_s$ and $A_2=\epsilon_q-\epsilon_s$. The factor 2 in Eq. (3.15) comes from summing over spin, and

$$f_{pm}=\langle s \,|\, \tilde{k} \,|\, m \,\rangle, \quad \tilde{k}=e^{i\vec{k}\cdot\vec{x}} \, . \tag{3.17}$$

This kind of matrix element is conveniently calculated, expanding $e^{i\vec{k}\cdot\vec{x}}$ in spherical harmonics. Since $\vec{k}\cdot\vec{k}=0$, one has to be careful, however. We have found that

$$e^{i\vec{k}\cdot\vec{x}}=\sum_{l,m}(-k_{\parallel}r)^l A_{lm}Y_{lm}(\hat{\Omega}_r) \tag{3.18}$$

is a useful expansion.[36] In this expression,

$$A_{lm}=(-i\,)^m e^{im\phi_k}\left[\frac{4\pi}{(2l+1)(l+m)!(l-m)!}\right]^{1/2} , \tag{3.19}$$

and ϕ_k is the azimuthal angle of $k_{\parallel}$. Using this expansion in Eq. (3.17), and the fact that spherical harmonics are orthogonal, immediately leads to

$$f_{pm}=-(\lambda^3/\pi)^{1/2}(4\mu^5/3)^{1/2}\frac{24k_{\parallel}}{(\mu+\lambda)^5}A_{1m} \, .$$

Thus the bound contribution to α is given by

$$\alpha_B(k_{\parallel},iu)=2k_{\parallel}^2\frac{2^{11}\lambda^3\mu^5}{(\mu+\lambda)^{10}}\frac{2A_1}{A_1^2+u^2}=2k_{\parallel}^2\tilde{\alpha}_B\frac{2A_1}{A_1^2+u^2} \, . \tag{3.20}$$

For continuum states,

$$f_q=\langle s \,|\, \tilde{k} \,|\, Q\,\rangle=\langle s \,|\, \tilde{k} \,|\, \tilde{q}\,\rangle-\langle\,\tilde{q}\,|\,s\,\rangle\langle s \,|\, \tilde{k} \,|\, s\,\rangle-\sum_m\langle\tilde{q}\,|\,m\,\rangle\langle s \,|\, \tilde{k} \,|\, m\,\rangle \, , \tag{3.21}$$

with the same expansion as before for $\tilde{k}$, and the conventional expansion for $|\,\tilde{q}\,\rangle$,

$$|\,\tilde{q}\,\rangle=4\pi\sum_{l=0}^{\infty}i^l j_l(qr)\sum_{m=-l}^{l}Y_{lm}^*(\hat{\Omega}_r)Y_{lm}(\hat{\Omega}_q) \, . \tag{3.22}$$

In Eq. (3.21),

$$\langle\,\tilde{q}\,|\,s\,\rangle=(\lambda^3/\pi)^{1/2}\frac{8\pi\lambda}{(q^2+\lambda^2)^2}$$

and

$$\langle\,\tilde{q}\,|\,m\,\rangle=32i\pi(4\mu^5/3)^{1/2}\frac{q\mu}{(q^2+\mu^2)^3}Y_{1m}(\hat{\Omega}_q) \, ,$$

and the first term of f_q can easily be evaluated,

$$\langle s\,|\,\tilde{k}\,|\,\tilde{q}\,\rangle=\sum_{l=0}^{\infty}k_{\parallel}^{l}F_l\sum_{m=-l}^{l}A_{lm}Y_{lm}(\hat{\Omega}_q)\ , \tag{3.23}$$

where

$$F_l=4\pi(\lambda^3/\pi)^{1/2}i^l(-1)^l\int_0^{\infty}dr\,r^{2+l}e^{-\lambda r}j_l(qr)\ . \tag{3.24}$$

Representing $j_l(qr)$ as $(-q/r)^l(d/q\,dq)^l j_0(qr)$,[37] we can perform the radial integration and obtain

$$F_l=4\pi(\lambda^3/\pi)^{1/2}i^l(-1)^l 2\lambda\frac{(2q)^l[(l+1)!]}{(q^2+\lambda^2)^{l+2}}\ . \tag{3.25}$$

The $l=0$ term is immediately seen to cancel the second term in the expression for the generalized oscillator strength f_q. The third term in Eq. (3.21) is evaluated in analogy to Eq. (3.17). The contributions from transitions to continuum states can be written as

$$\begin{aligned}\alpha_{\mathrm{sc}}(k_{\parallel},iu)&=\sum_{l=1}^{\infty}2^l k_{\parallel}^{2l}\int_0^{\infty}dq\,q^2\frac{2A_2}{A_2^2+u^2}\tilde{\alpha}_l(q)\\&=\sum_{l=1}^{\infty}2^l k_{\parallel}^{2l}\alpha_l\ .\end{aligned} \tag{3.26}$$

The $l=1$ term of this expression, and α_B, form the ordinary dipole contribution

$$\tilde{\alpha}_1=\frac{2^{10}\lambda^5q^2}{3\pi}\left[\frac{1}{(q^2+\lambda^2)^3}-\frac{32\mu^6}{\lambda(\lambda+\mu)^5(q^2+\mu^2)^3}\right]^2\ . \tag{3.27}$$

For $l\geq 2$,

$$\tilde{\alpha}_l=\frac{1}{4\pi^3}\frac{F_l^2}{2^l}\sum_{m=-l}^{l}|A_{lm}|^2\ . \tag{3.28}$$

Only $\tilde{\alpha}_2$ and $\tilde{\alpha}_3$ are interesting. The higher-order terms represent multipole contributions, which, in practice, affect the atom-metal interaction only when the atom is so close to the surface that there is strong overlap. In summary, Eqs. (3.20) and (3.26) give all the important contributions to the atomic polarizability. This representation of α together with Eq. (3.11) for ρ allows the calculation of the van der Waals interaction according to Eq. (1.3).

C. Evaluation of the potential

The simplest step in the evaluation of Eq. (1.3) is the $k_{\parallel}$ integration with

$$\alpha(k_{\parallel},iu)=\alpha_1(iu)2k_{\parallel}^2+\sum_{l}\alpha_l(iu)2^lk_{\parallel}^{2l}+\cdots\ , \tag{3.29}$$

where

$$\begin{aligned}\alpha_1(iu)&=\tilde{\alpha}_B\frac{2A_1}{A_1^2+u^2}+\int_0^{\infty}dq\,q^2\frac{2A_2}{A_2^2+u^2}\tilde{\alpha}_1(q)\\&=\hat{c}_1\frac{2A_1}{A_1^2+u^2}+\hat{c}_2\frac{2A_2}{A_2^2+u^2}=\sum_{i=1}^{2}\hat{c}_i\frac{2A_i}{A_i^2+u^2}\end{aligned} \tag{3.30}$$

and

$$\alpha_l(iu)=\int_0^{\infty}dq\,q^2\frac{2A_2}{A_2^2+u^2}\tilde{\alpha}_l(q)\ . \tag{3.31}$$

Using Eq. (3.11) for ρ, the $k_{\parallel}$ integration gives

$$\begin{aligned}E_{\mathrm{vdW}}(d)=-\frac{C_{\mathrm{vdW}}}{(d-d_{\mathrm{vdW}})^3}\Bigg[1&+\frac{d_q^2}{(d-d_{\mathrm{vdW}})^2}\\&+\frac{d_o^4}{(d-d_{\mathrm{vdW}})^4}+\cdots\Bigg]\ .\end{aligned} \tag{3.32}$$

In this expression the constant of the dipole term is

$$C_{\mathrm{vdW}}=\tfrac{1}{8}\hbar\int_{-\infty}^{\infty}du\,\pi^{-1}\rho_0(iu)\alpha_1(iu)\ , \tag{3.33}$$

and

$$d_{\mathrm{vdW}}=-\tfrac{1}{8}\hbar\int_{-\infty}^{\infty}du\,\pi^{-1}\rho_s(iu)\alpha_1(iu)d_{\mathrm{IP}}^{s}(iu)/C_{\mathrm{vdW}} \tag{3.34}$$

is the effective surface position for the van der Waals interaction. Equation (3.34) thus represents a correction to Eq. (2.6), where a model with a sharp boundary at $z=-d$ is used. As we will show, the corrections are small, however. Finally,

$$d_q^2=\tfrac{3}{4}\hbar\int_{-\infty}^{\infty}du\,\pi^{-1}\rho_0(iu)\alpha_2(iu)/C_{\mathrm{vdW}}+O(d_{\mathrm{vdW}}^2) \tag{3.35}$$

is a measure of the quadrupole contribution. Here, we have neglected the $k_{\parallel}^2d_{\perp}^2$ contribution to d_q^2 from (i) the second-order term in ρ, as mentioned in Sec. III A, and (ii) the expansion of $(d-d_{\mathrm{vdW}})^{-3}$, since they are both proportional to $d_{\mathrm{vdW}}^2\ll d^2$ ($d\simeq$4–8 a.u.), and thus only make a very small correction to d_q^2. Replacing α_2 in Eq. (3.36) by $15\alpha_3$ gives the octupole contribution, d_o^4.

Expressions (3.30) and (3.31) for α, and Eqs. (3.6) and (3.10) for ρ_0 and ρ_s, respectively, are then substituted into Eqs. (3.33)–(3.35). The identities

$$I(A,B)+\int_{-\infty}^{\infty}du\frac{1}{\pi}\frac{1}{u^2+A^2}\frac{1}{u^2+B^2}=\frac{1}{AB(A+B)}\ , \tag{3.36a}$$

$$I(A,B,C)=\frac{A+B+C}{ABC(A+B)(A+C)(B+C)}\ , \tag{3.36b}$$

and

$$I(A,B,C,D)=\frac{A^2(B+C+D)+A(B+C+D)^2+(B+C)(B+D)(C+D)}{ABCD(A+B)(A+C)(A+D)(B+C)(B+D)(C+D)} \tag{3.36c}$$

TABLE II. Results for C_{vdW}, d_{vdW}, d_q^2, and d_o^4 for He interacting with Ag, Au, and Cu. Perfect-image—model results are within parentheses.

	C_{vdW} (eV Å^3)	d_{vdW} (Å)	d_q^2 (Å^2)	d_o^4 (Å^4)
Ag	0.250	0.154	0.504 (0.60)	0.661 (0.79)
Au	0.274	0.126	0.505 (0.60)	0.659 (0.79)
Cu	0.253	0.168	0.499 (0.60)	0.650 (0.79)

are used. Then we finally end up with the following expression for the van der Waals coefficient (in a.u.),

$$C_{\mathrm{vdW}}=\tfrac{1}{4}\sum_{i=1}^{2}\hat{c}_i[(E^2I(A_i,C)-(E^2B^2-F^4)I(A_i,B,C)]A_i\ , \tag{3.37}$$

the van der Waals surface position

$$d_{\mathrm{vdW}}=\frac{-d_\perp^s(0)D^2}{4C_{\mathrm{vdW}}}\sum_{i=1}^{2}\hat{c}_i[\omega_s^2I(A_i,C,D) -(\omega_s^2B^2-F^4)I(A_i,B,C,D)]A_i\ , \tag{3.38}$$

and the quadrupole-correction coefficient

$$d_q^2=\frac{1}{C_{\mathrm{vdW}}}\int_0^\infty dq\, q^2A_2(q)\frac{q^4}{(q^2+\lambda^2)^8}\frac{2^{10}9\lambda^5}{5\pi} \times[E^2I(A_2,C)-(E^2B^2-F^4)I(A_2,B,C)]\ . \tag{3.39}$$

Since D^2 is a small factor, d_{vdW} characterizes a plane close to the jellium edge. This also means that to a high degree of accuracy d_q^2 is given by the first term in Eq. (3.35). Table II summarizes the results for C_{vdW}, d_{vdW}, d_q^2, and d_o^4 for a helium atom interacting with the noble metals Ag, Au, and Cu. Whereas the values for the ordinary van der Waals coefficient C_{vdW} agree well with the results of Zaremba and Kohn,[3] except for a somewhat larger value for Cu, d_{vdW} does not. This is because of our different choice of D in Eq. (3.38), connected with the requirement of fulfilling sum rules for the surface response.[31,34] Finally, the quadrupole and octupole contributions are only slightly reduced from those in the very simple model in Sec. II, and d_q^2 gives a 5% correction to the d^{-3} term at 6 a.u., whereas d_o^4 only contributes 0.5% at the same distance.

IV. van der WAALS POTENTIAL CLOSE TO THE SURFACE

We now turn to the question of the divergence of the potential (3.32) when the atom approaches the surface. It is obvious that this divergence cannot be a real physical feature. Since the singularity lies in the region of strong overlap, which means that the repulsive part of the potential dominates the attractive one, this problem is usually neglected. The bulk value of the van der Waals interaction, $E_{\mathrm{vdW}}^{\mathrm{bulk}}$, is finite, however. Thus E_{vdW} is expected to be a smooth function of d, as it varies between the asymptotic $1/d^3$ behavior far outside, and $E_{\mathrm{vdW}}^{\mathrm{bulk}}$. The possibility of significant corrections to the common dipole term at relevant physisorption distances cannot be excluded.

In this section E_{vdW} is calculated from Eq. (1.1) in yet another approximation. Equation (1.2) neglects the overlap between metal and atom wave functions completely. As we have argued in Sec. I, this is incorrect when integrating (1.1) over all space. Here, we use instead the fact that

$$e^{-k_{\parallel}(|d+z_a|+|z_m|)}<e^{-k_{\parallel}|d+z_a-z_m|}<e^{-k_{\parallel}(d+z_a-z_m)}\ ,$$

for z_m inside the metal, to separate the atom and metal coordinate systems in Eq. (1.1). The right-hand side of the inequality is the Zaremba-Kohn[3] ansatz, which gives an upper bound to the strength of the attractive potential, i.e., $|E_{\mathrm{vdW}}|$. The left-hand side, which is the approximation to be used in this section, clearly gives a lower bound. However, it also fulfills the important criterion that it always vanishes for large values of d, z_a, or z_m. Thus it does not only give a lower bound, but a value, which is much closer to the exact one using $e^{-k_{\parallel}|d+z_a-z_m|}$, than the upper bound. For large separations the difference is negligible.

Modifying Eq. (1.3), which corresponds to the upper bound, gives

$$E_{\mathrm{vdW}}(d)=-\frac{\hbar}{4\pi}\int_0^\infty dk_{\parallel}\int_{-\infty}^{\infty}du\,\gamma(k_{\parallel},iu)\rho(k_{\parallel},iu)\ , \tag{4.1}$$

where we use the same approach as in Sec. III for ρ, and where

$$\gamma(k_{\parallel},iu)=\sum_i\frac{2A_i}{A_i^2+u^2}|\tilde{f}_i(\vec{\mathrm{k}})|^2\ , \tag{4.2}$$

with

$$\tilde{f}_i(\vec{\mathrm{k}})=\langle 0|\tilde{\kappa}|i\rangle \text{ and } \tilde{\kappa}=e^{i\vec{\mathrm{k}}_{\parallel}\cdot\vec{\mathrm{x}}}e^{-k_{\parallel}|z+d|}\ .$$

Representing the factor $e^{-k_{\parallel}|z+d|}$ by its Fourier transform, we find

$$\tilde{f}_i(\vec{\mathrm{k}})=\int_{-\infty}^{\infty}dp\frac{1}{2\pi}\frac{2k_{\parallel}}{p^2+k_{\parallel}^2}e^{ipd}\langle 0|\tilde{v}|i\rangle\ , \tag{4.3}$$

where $\tilde{v}=e^{i\vec{\mathrm{v}}\cdot\vec{\mathrm{x}}}$ and $\vec{\mathrm{v}}=(\vec{\mathrm{k}}_{\parallel},p)$. Now, $\vec{\mathrm{v}}\cdot\vec{\mathrm{v}}\neq 0$, which allows the use of the conventional expansion of $\tilde{v}$ in spherical harmonics. Using the same transitions as in Sec. III, we again find two types of contributions, i.e., from transitions to bound and continuum states, respectively.

Equation (3.17) will be changed to

$$\tilde{f}_{pm}=\int_{-\infty}^{\infty} dp\frac{1}{2\pi}\frac{2k_{\parallel}}{p^2+k_{\parallel}^2}e^{ipd}\langle s\,|\,\tilde{v}\,|\,m\,\rangle\ , \tag{4.4}$$

which is evaluated in Appendix B. Defining

$$b_1^2=k_{\parallel}^2+q^2+\lambda^2,\ \ b_2^2=k_{\parallel}^2+(\mu+\lambda)^2,\ \ b_3^2=k_{\parallel}^2+4\lambda^2\ , \tag{4.5}$$

the contribution from transitions to bound states can be expressed as

$$\begin{aligned}\gamma_B(k_{\parallel},iu)&=\tfrac{1}{2}e^{-2k_{\parallel}d}\alpha_B(k_{\parallel},iu)[I_0^2(b_2)+I_1^2(b_2)]\\&=\tilde{\gamma}_B\frac{2A_1}{A_1^2+u^2}\ ,\end{aligned} \tag{4.6}$$

where the functions

$$\begin{aligned}I_0(b)=\Bigg[1-e^{(k_{\parallel}-b)d}\bigg[1+\frac{d}{2b}(b^2-k_{\parallel}^2)\\+\frac{d}{8b^3}(1+bd)(b^2-k_{\parallel}^2)^2\bigg]\Bigg]\end{aligned} \tag{4.7}$$

and

$$\begin{aligned}I_1(b)=\Bigg[1-\frac{k_{\parallel}}{b}e^{(k_{\parallel}-b)d}\bigg[1+\frac{1}{2b^2}(1+db)(b^2-k_{\parallel}^2)\\+\frac{1}{8b^4}[3(1+db)+d^2b^2]\\\times(b^2-k_{\parallel}^2)^2\bigg]\Bigg]\end{aligned} \tag{4.8}$$

contain the entire difference between this approach and the earlier one in Sec. III. These functions will cut off the atomic response close to the surface. This cutoff can be understood in terms of the smaller ability of the adatom to respond to polarization fields of shorter wavelengths ($\sim d$). Such fields become increasingly important when the atom approaches the surface. When $d\to\infty$, both I_0 and I_1 approach unity in such a way that their influence is already negligible at physisorption distances. Equation (3.21) changes also:

$$\tilde{f}_q=\int_{-\infty}^{\infty} dp\frac{1}{2\pi}\frac{2k_{\parallel}}{p^2+k_{\parallel}^2}e^{ipd}\left[\langle s\,|\,\tilde{v}\,|\,\tilde{q},0\rangle-\langle\tilde{q}\,|\,s\,\rangle\langle s\,|\,\tilde{v}\,|\,s\,\rangle-\sum_m(\langle\tilde{q}\,|\,m\,\rangle\langle s\,|\,\tilde{v}\,|\,m\,\rangle-\langle s\,|\,\tilde{v}\,|\,\tilde{q},m\,\rangle)\right]\ . \tag{4.9}$$

In Appendix C we show how to obtain

$$\langle s\,|\,\tilde{v}\,|\,\tilde{q}\,\rangle=\langle s\,|\,\tilde{v}\,|\,\tilde{q},0\rangle+\sum_m\langle s\,|\,\tilde{v}\,|\,\tilde{q},m\,\rangle\ , \tag{4.10}$$

where

$$\langle s\,|\,\tilde{v}\,|\,\tilde{q},0\rangle=(\lambda^3/\pi)^{1/2}\frac{8\pi\lambda}{(v^2+q^2+\lambda^2)^2}$$

and

$$\begin{aligned}&\langle s\,|\,\tilde{v}\,|\,\tilde{q},m\,\rangle\\&\quad=-\tfrac{1}{3}(\lambda^3/\pi)^{1/2}\frac{2^7\pi^2\lambda qv}{(v^2+q^2+\lambda^2)^3}Y_{1m}(\hat{\Omega}_v)Y_{1m}^*(\hat{\Omega}_q)\end{aligned}$$

from an expansion to first order in $\hat{v}\cdot\hat{q}\,vq/(v^2+q^2+\lambda^2)$. This approximation works well, except in a negligible small interval where $|\,\hat{v}\cdot\hat{q}\,|\sim1$ and $v,q\sim\lambda$. Since the two first terms in Eq. (4.9) are proportional to $Y_{00}(\hat{\Omega}_v)\cdot Y_{00}^*(\hat{\Omega}_q)$, $|\,\tilde{f}_q\,|^2$ does not give any cross terms.

$$\begin{aligned}\gamma_{\rm sc}(k_{\parallel},iu)&=\int_0^{\infty}dq\,q^2\left[\alpha_s^2+\sum_{m=0}^{1}\alpha_p^2\right]\frac{2A_2}{A_2^2+u^2}\\&=\int_0^{\infty}dq\,q^2\tilde{\gamma}_{\rm sc}\frac{2A_2}{A_2^2+u^2}\ ,\end{aligned} \tag{4.11}$$

where the first two terms in Eq. (4.9) for $\tilde{f}_q$ build up α_s, and α_p is built up by the third and the fourth term. We find

$$\alpha_s=(\lambda^3/\pi)^{1/2}\frac{8\lambda k_{\parallel}}{(q^2+\lambda^2)^2}[\xi(b_1)-\xi(b_3)]\ , \tag{4.12}$$

where

$$\xi(b)=\frac{1}{b}e^{-bd}\left[1+\frac{1}{2b^2}(b^2-k_{\parallel}^2)(1+bd)\right]\ . \tag{4.13}$$

This contribution was cancelled completely in Sec. III [the first term in Eq. (4.9) corresponds to the zeroth-order term in Eq. (3.23)]. Within the present model it gives a small contribution which decays exponentially fast for large distances. In an analogous way as the contribution from the $s\to p$ transition (see Appendix B), the following equation for α_p is obtained:

$$\begin{aligned}\alpha_p=\frac{2^5(\lambda^5)^{1/2}}{(3\pi)^{1/2}}e^{-k_{\parallel}d}qk_{\parallel}\Bigg[\frac{I_m(b_1)}{(q^2+\lambda^2)^3}\\-\frac{32\mu^6I_m(b_2)}{\lambda(\mu+\lambda)^5(q^2+\mu^2)^3}\Bigg]\ .\end{aligned} \tag{4.14}$$

This expression corresponds to Eq. (3.27) and differs only from that expression through the factors I_m, which are plotted in Fig. 4. The figure shows that their influence is to cut off the integrand for small atom-surface distances. These factors give rise to only a 1% correction at $d=5$–6 a.u., since in the total van der Waals interaction they are weighted with $k_{\parallel}e^{-k_{\parallel}d}$, which has maximum when $k_{\parallel}=1/d$. Nordlander and Harris[38] have derived a cutoff function with a similar behavior by imposing a cutoff on the $k_{\parallel}$ integration in Eq. (1.3). They have determined this by matching $E_{\rm vdW}$ to its value inside the bulk metal.

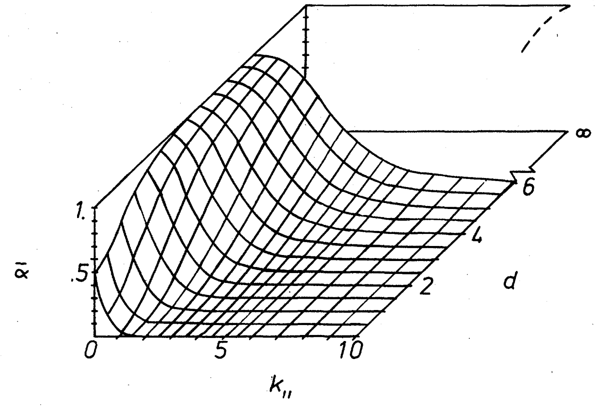

FIG. 4. Saturation effects on the atomic polarizability $\alpha(k_{\parallel},d)$. The influence of the cutoff functions $I_m(b)$ are illustrated by normalizing the contribution to α from transitions to bound states, to the "bound" polarizability of the free atom (Sec. III). We have then defined

$$\tilde{\alpha}=\alpha_B(k_{\parallel},d)/\alpha_B(k_{\parallel},\infty)\equiv\tfrac{1}{2}\,|I_0^2(b_2)+I_1^2(b_2)|\ .$$

Since the most important contributions to E_{vdW} come from $k_{\parallel}\leq 1/d$, the saturation effects are limited to $d\sim$0–6 a.u.

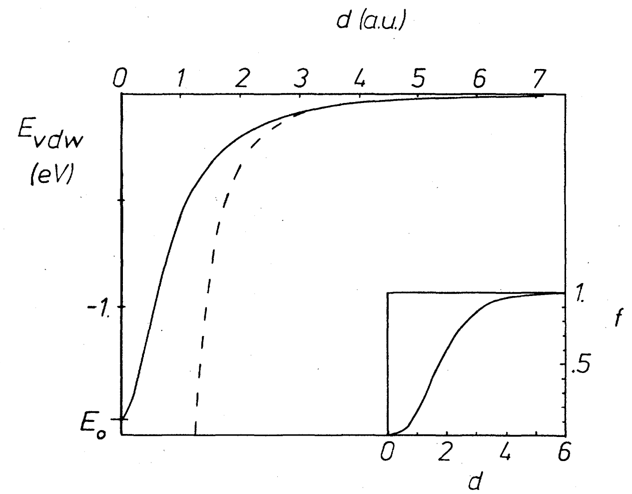

FIG. 5. Calculated van der Waals interaction for a He atom outside a noble metal. The solid curve is the full saturated van der Waals potential, and the dashed curve is the conventional dipole contribution. The latter is formally applicable only asymptotically for $d\rightarrow\infty$. The combined effects from saturation and multipole corrections make the difference between the two curves negligible at the relevant physisorption distances, however. The inserted curve gives the ratio f between the two potentials which rapidly approaches 1 with increasing d. $E_0\equiv E_{\mathrm{vdW}}(d=0)=-1.51$ eV (Ag), -1.55 eV (Au), and -1.59 eV (Cu).

With the same treatment of the metal as in the preceding section and with Eqs. (4.6) and (4.11) for the contributions to $\gamma(k_{\parallel},iu)$ from the different kinds of transitions, we can perform the u integration in Eq. (4.1) and obtain

$$E_{\mathrm{vdW}}(d)=E_{\mathrm{vdW}}^{(1)}+E_{\mathrm{vdW}}^{(2)}\ , \tag{4.15}$$

where

$$E_{\mathrm{vdW}}^{(1)}=-\tfrac{1}{2}\hbar\int_0^{\infty}dk_{\parallel}\sum_{i=1}^{2}\hat{\gamma}_i\,A_i[E^2I(A_i,C)-(E^2B^2-F^4)I(A_i,B,C)] \tag{4.16a}$$

and

$$E_{\mathrm{vdW}}^{(2)}=-\hbar\int_0^{\infty}dk_{\parallel}k_{\parallel}D^2d_{\perp}^{s}(0)\times\sum_{i=1}^{2}\hat{\gamma}_i\,A_i[\omega_s^2I(A_i,C,D)-(\omega_s^2B^2-F^4)I(A_i,B,C,D)]\ , \tag{4.16b}$$

where we have introduced the operator $\hat{\gamma}_i$ for the "bound" and "scattering" contributions to the polarizability; $\hat{\gamma}_1=\hat{\gamma}_B$ [Eq. (4.6)] and the integral operator $\hat{\gamma}_2=\int_0^{\infty}dq\,q^2\hat{\gamma}_{\mathrm{sc}}$ [Eq. (4.11)], respectively. In Fig. 5 we have plotted E_{vdW} according to Eq. (4.15) together with the dipole contribution, i.e., the one obtained with $I_m(b)=1$ and $\alpha_s=0$. The figure shows that the full van der Waals interaction is finite even for $d=0$, and that the influence of the cutoff functions $I_m(b)$ is negligible when the atom-metal distance is around 5–6 a.u. (physisorption distance).

In the scheme of Nordlander and Harris,[38] this saturation corresponds to a cutoff $k_c=0.87a_0^{-1}$ which is roughly 20% larger than the one estimated from the size of the atom ($k_c^{\mathrm{atom}}\simeq\lambda/2$, where λ is the decay parameter of the ground-state wave function). Using the same argument, one can estimate k_c^{atom} for H_2 to be approximately $0.32a_0^{-1}$ (with $\lambda\simeq 1.189a_0^{-1}$ and an internuclear separation of $1.4a_0$), and with the same scaling as for He this leads to a value of $0.39a_0^{-1}$ for k_c as a zeroth-order estimate. Together with a proper repulsive potential, the van der Waals interaction potential, which is then found for H_2, seems to give a reasonable total potential.[39]

V. SUMMARY

We have calculated the attractive interaction between an atom and a metal, successively improving the description. Starting from the perfect-image model in Sec. II, the improvements concern the inclusion of imperfect screening and a better treatment of the Coulomb coupling between the atom and the metal. The perfect-image model is shown to give a good account for the relative size of the multipole contributions. Doing poorer for the leading dipole term, however, the model has to be improved with respect to the metal response and the atomic polarizability.

Treating the metal, not as a perfect mirror, but as a medium with a dielectric response, where both free and bound electrons take part in the screening, and using several atomic transitions instead of only one characteristic frequency for the atomic response, we find a dipole coefficient which agrees well with other more elaborate calculations. The effective surface position, the image plane, is found to be somewhat closer to the positive background of the metal than in earlier theoretical studies. This is caused by the inclusion of the d electrons in the metallic response in a way that fulfills recently found sum rules for the surface response.[31,34] A very small change in the relative multipole contributions compared with the result in the perfect-image model was found. We thus conclude that for a zeroth-order estimate of the quadrupole and octupole coefficients d_q^2 and d_o^4, the simple model is sufficient, while the dipole term and the image-plane position need to be evaluated in the improved model. The multipole contribution is about 5% at relevant physisorption distances for He on noble metals. This means that, when combining the multipole terms with the dipole term and a proper repulsive part, we find a slightly deeper potential well than in the standard treatment, which only retains the dipole term. This result seems in accordance with most experimental results and with the analysis of Ref. 38. Such a judgement must be made carefully, however. What can be stated with certainty is that in the region where the overlap between the atom and the metal wave functions is negligible, the metal feels a pointlike atom, i.e., a dipole plus a small contribution from higher multipoles. The latter decays faster than the dipole term for large distances. There is no doubt that in this region the multipole approach is the correct and most physically appealing one. For shorter distances this picture breaks down completely, however.

From a physical point of view we expect a limited possibility of the system to respond to polarizing fields, which have a small wavelength compared with the dimension of the system. Such wavelengths become more and more important as the atom approaches the surface. The wavelength spectrum extends typically up to $k_{\parallel}\sim d^{-1}$, which means that there should be a cutoff value for $k_{\parallel}$ corresponding to the minimal wavelength, which can be "felt" by the system, i.e., typically the size of the atom. This will lead to a saturation of the van der Waals interaction, which is strongest close to the surface.

Going beyond the approximation requiring zero overlap (Sec. IV), we find that the saturation effect cancels the multipole corrections over the entire range of distances where the latter make a substantial contribution to the interaction. The resulting attractive potential is finite close to the surface, and is, further out, reasonably well described by a term of dipolar character.

It is customary when interpreting atom-surface—scattering experiments to combine an attractive $1/d^3$ dipole term from the Zaremba-Kohn calculation[3] with a repulsive potential, yielding a satisfactory description of the experimental outcome. Evidently, this cannot be taken as any evidence for that the $1/d^3$ term has any *a priori* justification as such. In fact, as we have shown in this paper and a point which is also clearly realized by Zaremba and Kohn,[3] there are the additional contributions to the simple *asymptotic* $1/d^3$ term coming from the detailed atomic response. These multipole and saturation effects have compensating effects, as can be expected on general grounds. The degree of compensation depends on the system under study, and it so turns out, in our example of He on noble metals, that they in fact are almost equal in magnitude at the atom physisorption position, making the apparent potential well described by a $1/d^3$ term. However, this does not have to be the case for other atom/metal or molecule/metal systems, and we hope that our study can stimulate further efforts in this area in order to use and investigate the deviations from the simple dipole term to learn more about the nature of the atom-substrate interaction. A study of the H_2-metal interaction is in progress.[39]

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APPENDIX A

Starting from

$$\rho_0=\frac{\epsilon-1}{\epsilon+1}\,, \tag{A1}$$

where for $\omega=iu$ and $\omega_s^2=2\omega_p^2$,

$$\epsilon=1+\frac{2\omega_s^2}{u^2}+\frac{2N\omega^2}{\omega_0^2+u^2}\,. \tag{A2}$$

We first have to calculate N and ω_0 from the poles ω_1 and ω_2 of $I_m(-1/\epsilon)$, which we take from an electron-energy-loss spectrum,

$$\frac{1}{\epsilon}=\frac{u^2(\omega_0^2+u^2)}{(u^2+2\omega_s^2)(\omega_0^2+u^2)+2N\omega_s^2u^2}\,. \tag{A3}$$

The poles are solutions to the equation

$$(u^2+2\omega_s^2)(\omega_0^2+u^2)+2N\omega_s^2u^2=0\,, \tag{A4}$$

which is equivalent to

$$(u^2+\omega_1^2)(u^2+\omega_2^2)=0\,. \tag{A5}$$

Identifying

$$\omega_1^2\omega_2^2=2\omega_s^2\omega_0^2$$

and

$$\omega_1^2+\omega_2^2=2(N+1)\omega_s^2+\omega_0^2\,,$$

it is trivial to obtain

$$\omega_0^2=\omega_1^2\omega_2^2/2\omega_s^2 \tag{A6}$$

and

$$N=\tfrac{1}{2}(\omega_1^2+\omega_2^2-\omega_0^2-2\omega_s^2)\,. \tag{A7}$$

From Eqs. (A1) and (A2) we obtain

$$\rho_0=\frac{2\omega_s^2(\omega_0^2+u^2)+2N\omega_s^2u^2}{2(\omega_0^2+u^2)u^2+2\omega_s^2(\omega_0^2+u^2)+2N\omega_s^2u^2}$$

$$=\frac{\omega_s^2\omega_0^2+(N+1)\omega_s^2u^2}{u^4+[(N+1)\omega_s^2+\omega_0^2]u^2+\omega_s^2\omega_0^2}$$

$$=\frac{E^2u^2+F^4}{u^4+(E^2+\omega_0^2)u^2+F^4}\ , \tag{A8}$$

with $E^2=(N+1)\omega_s^2$ and $F^2=\omega_s\omega_0$. Now, B and C in Eq. (3.6) can easily be identified as the imaginary roots of the equation

$$u^4+(E^2+\omega_0^2)u^2+F^4=0\ .$$

APPENDIX B

We shall evaluate the generalized oscillator-strength amplitude $\tilde{f}_{pm}$ in order to prove Eq. (4.6). First, consider the matrix element

$$\langle s\,|\,\tilde{v}\,|\,m\,\rangle=(\lambda^3/\pi)^{1/2}(4\mu^5/3)^{1/2}\times\langle e^{-\lambda r}\,|\,e^{i\vec{v}\cdot\vec{x}}\,|\,r\,e^{-\mu r}Y_{1m}(\hat{\Omega}_r)\rangle\ . \tag{B1}$$

Using the expansion

$$e^{i\vec{v}\cdot\vec{x}}=4\pi\sum_l i^l j_l(vr)\sum_{m=-l}^{l}Y_{lm}(\hat{\Omega}_v)Y^*_{lm}(\hat{\Omega}_r)\ , \tag{B2}$$

and the fact that

$$\int d\Omega\, Y^*_{lm'}(\hat{\Omega}_r)Y_{1m}(\hat{\Omega}_r)=\delta_{l1}\delta_{mm'}\ ,$$

we easily evaluate Eq. (B1). We thus obtain

$$\tilde{f}_{pm}=\int_{-\infty}^{\infty}dp\frac{1}{2\pi}\frac{2k_{\|}}{p^2+k_{\|}^2}e^{ipd}\left[32i\pi(\lambda^3/\pi)^{1/2}(4\mu^5/3)^{1/2}\frac{v(\mu+\lambda)}{[v^2+(\mu+\lambda)^2]^3}Y^*_{1m}(\hat{\Omega}_v)\right]\ .$$

With $b_2^2=k_{\|}^2+(\mu+\lambda)^2$,

$$Y^*_{1m}(\hat{\Omega}_v)=(3/4\pi)^{1/2}\frac{1}{v}\begin{cases}\mp\frac{1}{\sqrt{2}}k_{\|}e^{\mp i\phi_k} & \text{if } m=\pm1,\\ p & \text{if } m=0,\end{cases}$$

and

$$\frac{1}{(p^2+b_2^2)^3}=\frac{1}{8}\left[\frac{\partial}{b_2\partial b_2}\right]^2\frac{1}{p^2+b_2^2}\ ,$$

we obtain

$$\tilde{f}_{pm}=-32(\lambda^3\mu^5)^{1/2}\frac{k_{\|}}{(\mu+\lambda)^5}I_m(b_2)\ . \tag{B3}$$

Here we have defined

$$I_m(b_2)=\frac{(\mu+\lambda)^6}{8}\left[\frac{\partial}{b_2\partial b_2}\right]^2\times\int_{-\infty}^{\infty}dp\frac{1}{2\pi i}\frac{2e^{ipd}(\Phi_m k_{\|},p)}{(p^2+k_{\|}^2)(p^2+b_2^2)}\ , \tag{B4}$$

where $\Phi_m=\mp e^{\mp i\phi_k}/\sqrt{2}$. However, since I_m will only enter the different contributions of $\alpha(k_{\|},iu)$ as $\Phi_m\Phi^*_m$, we can set $\Phi_m=1$ and only sum over $m=0$ and $m=1$. After evaluating the integral in Eq. (B4), we find

$$I_m(b)=\frac{(\mu+\lambda)^6}{8}\left[\frac{\partial}{b\partial b}\right]^2\times\frac{1}{k_{\|}^2-b^2}\left[e^{-k_{\|}d}(i,1)-e^{-bd}\left[\frac{ik_{\|}}{b},1\right]\right]\ ,$$

where the first term in the vector represents the $m=1$ term, and the second term is the $m=0$ term. After the derivation step we finally obtain

$$I_0=1-e^{(k_{\|}-b)d}\left[1+\frac{d}{2b}(b^2-k_{\|}^2)+\frac{d}{8b^3}[(1+bd)(b^2-k_{\|}^2)^2]\right]\ , \tag{B5}$$

$$I_1=1-\frac{k_{\|}}{b}e^{(k_{\|}-b)d}\left[1+\frac{1}{2b^2}(1+bd)(b^2-k_{\|}^2)+\frac{1}{8b^4}[3(1+db)+d^2b^2](b^2-k_{\|}^2)^2\right]\ . \tag{B6}$$

Equations (B5) and (B6) are divided by $e^{-k_{\|}d}$ identical to Eqs. (4.7) and (4.8).

APPENDIX C

When evaluating matrix elements of the following type,

$$\langle s\,|\,\tilde{v}\,|\,\tilde{q}\,\rangle=\int d\vec{x}\,\psi_s e^{i(\vec{v}+\vec{q})\cdot\vec{x}}\ , \tag{C1}$$

it is not necessary to expand the exponential factors at all since we have a spherically symmetric problem. Then we immediately find

$$\langle s\,|\,\tilde{v}\,|\,\tilde{q}\rangle=(\lambda^3/\pi)^{1/2}\frac{8\pi\lambda}{[(\vec{v}+\vec{q})^2+\lambda^2]^2}=(\lambda^3/\pi)^{1/2}\frac{8\pi\lambda}{(v^2+q^2+\lambda^2+2vq\cos\phi)^2}\ , \tag{C2}$$

where ϕ is the angle between $\vec{v}$ and $\vec{q}$. It is not an easy task to evaluate the p integral $[v=(k_{\|}^2+p^2)^{1/2}]$ with this ϕ dependence, and it will give rise to unnecessary complications when taking $|\tilde{f}_q|^2$ and integrate over all $\vec{q}$ space.

Rewriting expression (C2), which is maximum when $(\vec{v}+\vec{q})^2=0$, as

$$\langle s\,|\,\tilde{v}\,|\,\tilde{q}\rangle=(\lambda^3/\pi)^{1/2}\frac{8\pi\lambda}{(v^2+q^2+\lambda^2)^2}\times\left[\frac{1}{1+2vq\cos\phi/(v^2+q^2+\lambda^2)}\right]^2 , \tag{C3}$$

the ϕ-dependent term is small everywhere except when $|\cos\phi|\sim 1$ and $v\sim q$ dominates over λ. However, for large v and q the entire matrix element is small and everything else in $\gamma_{\rm sc}$ which should be multiplied with $\langle s\,|\,\tilde{v}\,|\,\tilde{q}\rangle$ is also small. Thus we expand Eq. (C3) to first order:

$$\langle s\,|\,\tilde{v}\,|\,\tilde{q}\rangle\simeq(\lambda^3/\pi)^{1/2}\frac{8\lambda\pi}{(v^2+q^2+\lambda^2)^2}\times\left[1-\frac{4vq\cos\phi}{v^2+q^2+\lambda^2}+\cdots\right] . \tag{C4}$$

This approximation works well, except in a negligible, small interval where $|\cos\phi|\sim 1$ and $v,q\sim\lambda$ (the important contributions to $\gamma_{\rm sc}$ occur when v and q are small), and has the advantage of making the calculation feasible. We now expand $\cos\phi$ in spherical harmonics:

$$\cos\phi=P_1(\cos\phi)=\frac{4\pi}{3}\sum_{m=-1}^{l}Y_{1m}(\hat{\Omega}_v)Y^{*}_{1m}(\hat{\Omega}_q) . \tag{C5}$$

Setting

$$\langle s\,|\,\tilde{v}\,|\,\tilde{q},0\rangle=(\lambda^3/\pi)^{1/2}\frac{8\pi\lambda}{(v^2+q^2+\lambda^2)^2} \tag{C6}$$

and

$$\langle s\,|\,\tilde{v}\,|\,\tilde{q},m\rangle=-(\lambda^3/\pi)^{1/2}\frac{2^7\pi^2\lambda qv}{3(v^2+q^2+\lambda^2)^3}\times Y_{1m}(\hat{\Omega}_v)Y^{*}_{1m}(\hat{\Omega}_q) , \tag{C7}$$

we find Eq. (4.10).

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