van der Waals interaction between an atom and a surface at finite separations

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A general expression for the van der Waals energy of an atom near a planar surface is derived in terms of the imaginary part of the retarded surface response function $\mathrm{Im}[g(q,\omega)]$. This expression allows a direct calculation of the asymptotic coefficient C_3 of the van der Waals energy using response functions determined from optical data. For simple metal surfaces we introduce a dispersed surface plasmon-pole approximation to the response function. The van der Waals energy calculated with this response function reproduces the asymptotic coefficient C_3 and effective image-plane position Z_{vdW} calculated by Zaremba and Kohn, and is also finite at all atom-surface separations unlike the usual asymptotic series approach. Using this van der Waals energy we calculate the binding energies of helium on simple metal surfaces. We also take into account the velocity of the atom parallel to the surface, giving a velocity-dependent contribution to the van der Waals and, at high velocities, an imaginary part due to real excitations.

I. INTRODUCTION

The van der Waals interaction between an atom and a surface has been a subject of theoretical interest for many years. Recently, interest has been stimulated by the development of helium atom diffraction as an experimental probe of surface structure.[1] Observations of selective adsorption resonances[2,3] in helium diffraction allow direct measurements of the quantum states of the helium atom bound to the surface, thus providing detailed information about the strength of the van der Waals potential. Another very recent development has been the construction of an atomic force microscope[4] capable of directly measuring van der Waals forces.

The van der Waals interaction arises because of correlation between the adatom electrons and those of the substrate.[5] In semiclassical terms this corresponds to the formation of an image dipole in the substrate in response to the instantaneous dipole moment of the adatom.[6] At large separations between the atom and the surface the van der Waals energy can be written as an asymptotic expansion,[5]

$$U_{\mathrm{vdW}}(z) = -\frac{C_3}{(z-z_{\mathrm{vdW}})^3} + O(z^{-5}), \tag{1}$$

defining the asymptotic coefficient C_3 and an effective image-plane position z_{vdW}. Clearly this expression will only be correct at large separations, for example, the asymptotic form diverges at the image plane z_{vdW} while the true van der Waals potential will always be finite. In this paper we shall calculate the van der Waals energy at finite separations between the atom and the surface. We shall thus investigate the differences that arise between the asymptotic form of the potential given in Eq. (1) and a more realistic van der Waals potential. This is of particular interest for the binding energies of inert gasses on metal surfaces since the majority of calculations to date have assumed that the van der Waals can be accurately approximated with the asymptotic expansion in the region of the potential minimum.[7]

The outline of this paper is as follows: In Sec. II we shall derive a general expression for the van der Waals energy in terms of the imaginary part of the retarded surface response function $\mathrm{Im}[g(q,\omega)]$. The asymptotic expansion of the van der Waals energy can then be derived from the Taylor expansion of $\mathrm{Im}[g(q,\omega)]$ in powers of q. In Sec. III we introduce a surface plasmon-pole approximation to the response function. With this response function the van der Waals reproduces the C_3 and z_{vdW} coefficients of the asymptotic expansion calculated by Zaremba and Kohn,[5] but also remains finite at all atom-surface separations. We find that our calculated van der Waals energy differs significantly from the asymptotic form at typical physisorption distances. In Sec. IV we calculate the binding energies of helium on simple metal surfaces using these results for the van der Waals potential. Finally, in Sec. V we generalize our formalism to take into account the velocity of the atom parallel to the surface. This results in a small velocity-dependent contribution to the van der Waals energy and, at very high atom velocities, loss processes due to real excitations.

II. GENERAL FORMULATION

In this section we shall derive a general expression for the van der Waals energy which is valid for all atom-surface separations. To do this we formulate the problem in terms of the imaginary part of the retarded surface response function $\mathrm{Im}[g(q,\omega)]$.

Following Ferrell and Ritchie[8] we use a self-energy formalism to derive the van der Waals energy. This formalism provides a natural description of the effective potential for charged and neutral particles interacting with surfaces.[8-11] For completeness we shall summarize the important formulas of Ferrell and Ritchie, which we generalize to include the q dependence of the surface response function. The self-energy is defined by

$$\Sigma(\mathbf{r},\mathbf{r}',\omega) = i \int \frac{d\omega'}{2\pi} W(\mathbf{r},\mathbf{r}',\omega') G(\mathbf{r},\mathbf{r}',\omega+\omega') e^{i\delta\omega'}, \tag{2}$$

where G is the atomic Green function and W is the

screened interaction. δ is a positive infinitesimal. In terms of this self-energy the expression for the van der Waals energy is

$$U_{vdW}(z_0) = \int \int u_0(\mathbf{r})\Sigma(\mathbf{r},\mathbf{r}',\omega_0)u_0(\mathbf{r}')d^3r\,d^3r' , \quad (3)$$

where u_0 is the atomic ground-state wave function, with energy ω_0. The atomic nucleus is located at z_0. An implicit summation over spin degeneracy is included in (3). The atomic Green function is given by

$$G(\mathbf{r},\mathbf{r}',\omega) = \sum_n \frac{u_n(\mathbf{r})u_n^*(\mathbf{r}')}{\omega - \omega_n} , \quad (4)$$

where u_n is the nth excited-state wave function with energy ω_n.

In order to find the self-energy we need the screened interaction W. To define W we must introduce the surface response function $g(q,\omega)$. Consider the surface to occupy $z < 0$, and to be subjected to an external potential of the form

$$\phi_{ext} = e^{qz}e^{i(\mathbf{q}\cdot\mathbf{R}-\omega t)} , \quad (5)$$

where $\mathbf{q}$ is a wave vector parallel to the surface and $\mathbf{r} = (\mathbf{R},z)$. The linear response to this external potential must be of the form

$$\phi_{ind} = -g(q,\omega)e^{-qz}e^{i(\mathbf{q}\cdot\mathbf{R}-\omega t)} , \quad (6)$$

for $z > 0$, thus defining the response function $g(q,\omega)$.[12,13] Since any external potential may be decomposed into Fourier components as in Eq. (5) the function $g(q,\omega)$ completely determines the response of the surface. Note that $g(q,\omega)$ is a retarded response function and therefore satisfies the Kramers-Kronig relations. Using this response function the screened interaction may be written as follows:

$$W(\mathbf{r},\mathbf{r}',\omega) = -\int \frac{d^2q}{2\pi q}g_t(q,\omega)$$
$$\times \exp[i\mathbf{q}\cdot(\mathbf{R}-\mathbf{R}')-q(z+z')]$$
$$\times \exp(-2qz_0) \quad (7)$$

(we shall use atomic units throughout), where we have taken the atomic nucleus as the origin of the coordinates. The function $g_t(q,\omega)$ is the time-ordered response function corresponding to $g(q,\omega)$, which is given by $g_t(q,\omega) = g(q,\omega)$ if $\omega > 0$ and $g_t(q,\omega) = g(q,\omega)^*$ if $\omega < 0$.

We can now combine these equations to give an expression for the van der Waals energy. Substituting the screened interaction and the atomic Green function into the expression for the self-energy we find

$$U_{vdW}(z_0) = i\sum_n \frac{f_{n0}}{\omega_{n0}}\int \frac{d\omega}{2\pi}\int \frac{d^2q}{2\pi q}q^2e^{(-2qz_0)}\frac{g_t(q,\omega)}{\omega - \omega_{n0}} . \quad (8)$$

In deriving (8) we have made a dipole approximation for the atomic matrix elements. f_{n0} is the oscillator strength for the atomic dipole transition from state 0 to state n; here $\omega_{n0} = \omega_n - \omega_0$.

Finally, we can use the known analytic properties of the response function $g(q,\omega)$ to write the van der Waals energy in terms of $\text{Im}[g(q,\omega)]$. This results in

$$U_{vdW}(z_0) = -\sum_n \frac{f_{n0}}{\omega_{n0}}\int_0^\infty \frac{d\omega}{\pi}\int_0^\infty dq\,q^2e^{(-2qz_0)}$$
$$\times \frac{\text{Im}[g(q,\omega)]}{\omega + \omega_{n0}} \quad (9)$$

after integrating over the directions of q. Equation (9) represents our general expression for the van der Waals energy.

We can see from Eq. (9) that if $\text{Im}[g(q,\omega)]$ were independent of q we would find an inverse cube z dependence in the potential. Similarly the part of $\text{Im}[g(q,\omega)]$ linear in q gives a z^{-4} term in the potential, thus defining the effective image-plane position z_{vdW}. The usual treatments of the van der Waals potential[5] only include these leading powers of q in the surface response and therefore give the asymptotic expansion of the van der Waals as in Eq. (1). In Sec. III we shall introduce a model response function which reproduces the correct asymptotic limit for the van der Waals but which also remains finite at all z_0. With this response function we can therefore test the validity of the asymptotic expansion at finite atom-surface separations.

The importance of writing the van der Waals in terms of the imaginary part of the response function $\text{Im}[g(q,\omega)]$, as in Eq. (9), is that the response function can in principle be determined experimentally. For example, $\text{Im}[g(q,\omega)]$ is proportional to the electron energy loss probability in EELS experiments.[12,13] In addition, at $q = 0$ the response function can be related to optical data. This is because at $q = 0$ the surface response function can be found by elementary electrostatics and is given by

$$g(0,\omega) = \frac{\epsilon(\omega)-1}{\epsilon(\omega)+1} , \quad (10)$$

where $\epsilon(\omega)$ is the dielectric function of the solid. Equation (9) shows that the response function at $q = 0$ gives the asymptotic coefficient of the van der Waals energy, C_3, therefore C_3 can be found directly from optical data. Using the experimental frequency-dependent dielectric function of silver[14] we have calculated C_3 helium on silver; we find the value of $C_3 = 0.0618$ a.u. in excellent agreement with the work of Zaremba and Kohn.[5]

We can also rewrite Eq. (9) in terms of a frequency-dependent atomic polarizability $\alpha(\omega)$. This gives

$$U_{vdW}(z) = -\int_0^\infty dq\,q^2e^{-2qz}\int_0^\infty \frac{d\omega}{\pi}\int_0^\infty \frac{d\omega'}{\pi}\frac{\text{Im}[g(q,\omega)]\text{Im}[\alpha(\omega')]}{\omega + \omega'} . \quad (11)$$

It is of course possible to show that this is equivalent to the usual expressions for the van der Waals energy involving analytic continuation of the response function and polarizability to the imaginary frequency axis.[5,15] By using Eq. (9) for the van der Waals energy we avoid any need for analytic continuation.

van der WAALS INTERACTION BETWEEN AN ATOM AND A . . .

III. DISPERSED SURFACE-PLASMON—POLE APPROXIMATION

In this section we shall introduce a plasmon-pole approximation for the surface response function $\text{Im}[g(q,\omega)]$. Using this response function the calculated van der Waals energy has the correct asymptotic coefficients C_3 and z_{vdW} but also remains finite for all distances.

For simple metal surfaces the response function $\text{Im}[g(q,\omega)]$ is dominated by a single peak at the surface-plasmon frequency. Furthermore the van der Waals energy calculated using Eq. (9) will be relatively insensitive to the detailed shape of the peak. We shall therefore approximate the response function by a single plasmon pole,[16] giving

$$\text{Im}[g(q,\omega)] = \frac{\pi}{2} \frac{\omega_s^2}{\omega_s(q)} \delta(\omega - \omega_s(q)) \tag{12}$$

for $\omega > 0$. Here ω_s is the surface-plasmon frequency at $q = 0$ and $\omega_s(q)$ is the surface-plasmon dispersion relation. It is clear that this approximation for the response function satisfies the following sum rule:

$$\frac{2}{\pi} \int_0^\infty \omega \, \text{Im}[g(q,\omega)] d\omega = \omega_s^2 , \tag{13}$$

which is the surface generalization of the well-known f sum rule in the bulk. The surface sum rule can be derived from the bulk one using the specular reflection model[16] which gives the surface response in terms of the bulk dielectric function $\epsilon(q,\omega)$. Following Echenique et al.[16] we take the surface-plasmon dispersion relation to have the following form:

$$\omega_s(q)^2 = \omega_s^2 + \alpha q + \beta q^2 + \tfrac{1}{4} q^4 . \tag{14}$$

The αq term gives the linear surface-plasmon dispersion at small q. The $q^4/4$ term is included to represent the continuum of single-particle excitations at large q. The βq^2 term is included to interpolate between these two regimes. Following Echenique et al.[16] we choose the value of β by requiring that the surface-plasmon line $\omega_s(q)$ joins the single-particle continuum at the same point as the bulk-plasmon line does, as prescribed by Wikborg and Inglesfield.[17]

The plasmon dispersion parameter α can be directly related to the static image-plane position of the surface. This follows from the low-q expansion of the response function $g(q,\omega)$. The small wave-vector limit of the surface response function can be written in the following form:[18]

$$g(q,\omega) = \frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 1} [1 + 2d_{\text{IP}}(\omega)q] + O(q^2) , \tag{15}$$

where the quantity $d_{\text{IP}}(\omega)$ can be interpreted as a dynamical image-plane position. As $\omega \to 0$, $d_{\text{IP}}(\omega)$ becomes the static image-plane position of the surface $d_{\text{IP}}(0)$. We can relate this image-plane position to our model response function as follows: Using the Kramers-Kronig relations we obtain

$$g(q,0) = \frac{\omega_s^2}{\omega_s(q)^2} = 1 - \frac{\alpha q}{\omega_s^2} + O(q^2) . \tag{16}$$

TABLE I. Dispersion coefficients for surface-plasmon—pole approximation.

r_s (a_0)	α (a.u.)	β (a.u.)
2	-0.6000	2.0660
3	-0.1589	0.8603
4	-0.0609	0.4684
5	-0.0295	0.2960
6	-0.0167	0.2058

We thus find that the value of α is determined by the static image-plane position of the surface

$$\alpha = -2\omega_s^2 d_{\text{IP}}(0) . \tag{17}$$

There are accurate calculations available for the static image-plane position of simple metal surfaces in the jellium approximation and the values of ω_s are determined by the jellium Wigner-Seitz radius according to $\omega_s^2 = 3/2r_s^3$. For $r_s = 3$ jellium using Lang and Kohn's calculation of the image plane[19] gives $d_{\text{IP}}(0) = 1.43$ from the jellium edge, and thus we find $\alpha = -0.1598$. Once α is known we can determine the value of β as described above, for $r_s = 3$ this gives $\beta = 0.8603$. In Table I we give a summary of our calculated values of α and β for various substrates.

Note that our values of α (and hence also of β) differ from those of Echenique et al. This is because they used positive values of the plasmon dispersion coefficient α which were consistent with the work of Ritchie and Marusak,[20] Inkson,[21] and Inglesfield and Wikborg,[22] on the other hand, the calculations of Feibelman[23] give a negative value for the dispersion coefficient α. A positive value of α would correspond to a static image plane located behind the jellium edge, while it is well established that for realistic treatments of the surface barrier the image plane is located outside the jellium edge.

IV. RESULTS AND DISCUSSION

We can now calculate the van der Waals energy using the surface response function discussed above. Substituting the plasmon-pole response function into the general formula of Eq. (9), we obtain

$$U_{\text{vdW}}(z) = -\tfrac{1}{2} \sum_n \frac{f_{n0}}{\omega_{n0}} \int_0^\infty dq \, q^2 e^{-2qz}$$
$$\times \frac{\omega_s^2}{\omega_s(q)[\omega_s(q) + \omega_{n0}]} . \tag{18}$$

This integral will remain finite for all $z \geq 0$ and so the calculated van der Waals energy will not suffer from divergences. It is straightforward to evaluate the integral numerically to give the van der Waals energy as a function of z. We can find the behavior at large z by making the asymptotic expansion

$$U_{\text{vdW}}(z) = -\frac{1}{8z^3} \sum_n \frac{f_{n0}}{\omega_{n0}} \frac{\omega_s}{(\omega_s + \omega_{n0})}$$
$$+ \frac{3}{16z^4} \sum_n \frac{f_{n0}}{\omega_{n0}} \frac{(2\omega_s + \omega_{n0})\omega_s}{(\omega_s + \omega_{n0})^2} \frac{\alpha}{2\omega_s^2} + O(z^{-5}) . \tag{19}$$

Comparison with Ref. 5 shows that the asymptotic coefficient C_3 and the effective image-plane position z_{vdW} that we calculate agree exactly with the calculations of Zaremba and Kohn. Recent detailed calculations of the electron-hole pair contribution to the surface response[24,25] give a van der Waals reference plane position which is somewhat smaller (by about 20%) than given by Zaremba and Kohn. Instead of determining the dispersion coefficient α from the static image-plane position we could choose α so as to reproduce these more exact calculations of the van der Waals reference plane. We would not expect such a 20% change in α to significantly alter our conclusions. To summarize, Eq. (18) gives a van der Waals potential which remains finite at all atom-surface separations; furthermore, using the dispersion parameters α and β given in Table I the van der Waals potential has an asymptotic expansion identical to that calculated by Zaremba and Kohn.

We have calculated the van der Waals energy given by Eq. (18) for helium on a variety of simple metal substrates. The oscillator strengths and frequencies were taken from Dalgrano and Victor,[26] and the values of α and β were as given in Table I. Our results for helium on $r_s = 3$ jellium are shown in Fig. 1 (solid line). For comparison we also show the potential calculated using the asymptotic form of Eq. (1). Figure 1 shows that at typical atom-surface separations the calculated van der Waals potential is significantly weaker than that given by the asymptotic form. For example, at $z = 7$ our calculation gives only about 60% of the asymptotic result. This difference has important consequences for calculations of the binding energies of helium on simple metal surfaces, which we discuss below.

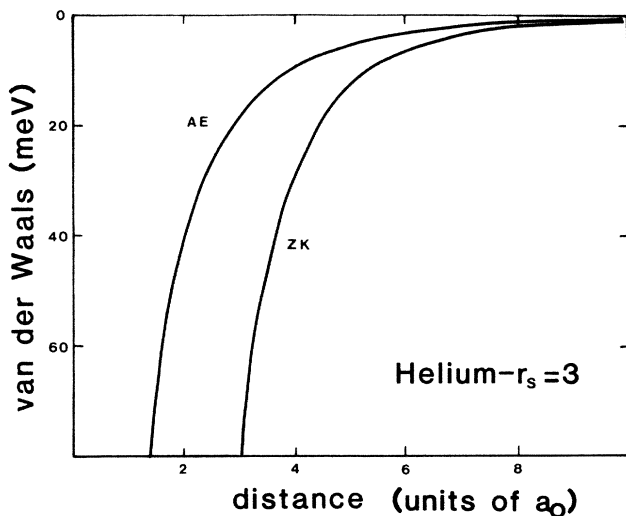A number of other approaches have been suggested for suppressing the divergence at the image plane of the asymptotic van der Waals potential. We compare these calculations with ours in Fig. 2. What is plotted is the ratio of the calculated van der Waals energy to the asymptotic approximation, thus giving a measure of how quickly the potential achieves its limiting form. Our calculation is given by the solid line in Fig. 2. The dashed lines in Fig. 2 were calculated following the prescription of Nordlander and Harris.[27] These authors simulated the falloff of the response function $g(q,\omega)$ at high q by simply introducing a cutoff k_c in the integrals over q. Before introducing the cutoff they also translated the origin to the van der Waals reference plane z_{vdW}, and so they obtained the following result:

$$U_{vdW}(z) = -\frac{C_3}{(z - z_{vdW})^3} f(k_c(z - z_{vdW})) , \tag{20}$$

where

$$f(x) = 1 - (2x^2 + 2x + 1)e^{-2x} .$$

Nordlander and Harris estimated the value of the cutoff k_c by requiring that the van der Waals energy approach its "bulk" value (estimated as about 1 eV) at the reference plane z_{vdW}, this procedure gave $k_c \cong 1$. In our calculations for helium on $r_s = 3$ jellium the van der Waals energy was found to be about 0.16 eV at z_{vdW}, this is substantially less than the values of about 1 eV assumed by Nordlander and Harris, suggesting that a more appropriate value of k_c would be 0.5. In Fig. 2 we show the potential calculated from Eq. (20) using either $k_c = 1$ or $k_c = 0.5$ for comparison with our results. It is clear from the figure that the Nordlander-Harris potential approaches its asymptotic limit much sooner than ours. This is because the cutoff procedure forces the potential to approach the asymptotic limit exponentially rather than as a power law in z as in our calculation. We can therefore conclude that the differences between the van der Waals energy at finite distances and the asymptotic expansion of Zaremba and Kohn are much larger than Nordlander and Harris es-
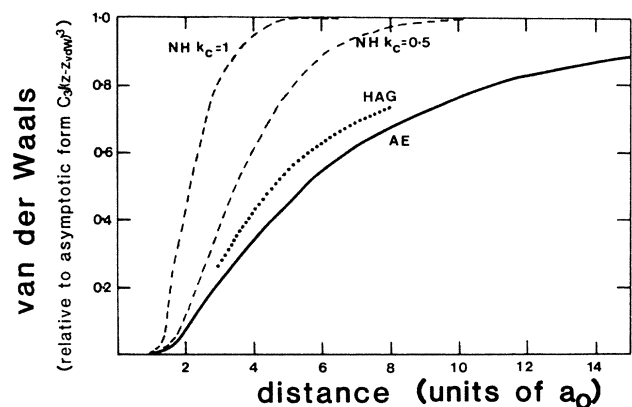

FIG. 1. van der Waals energies for helium on $r_s = 3$ jellium calculated using the dispersed surface-plasmon—pole approximation of this work (labeled AE) and using the asymptotic approximation of Zaremba and Kohn (Ref. 5), $-C_3/(z - z_{vdW})^3$ (labeled ZK). The jellium edge is located at $z = 0$.

FIG. 2. Comparison of different calculations of the van der Waals energy. We plot the ratio of the energy to its asymptotic limit $-C_3/(z - z_{vdW})^3$. The calculations shown are the dispersed surface-plasmon—pole approximation (solid line), the Nordlander-Harris wave-vector cutoff method (dashed lines) for $k_c = 1$ or $k_c = 0.5$, and the calculations of Holmberg, Apell, and Giraldo (dotted line).

timated. This implies that the binding energies of helium on simple metals would be smaller than obtained by either Zaremba and Kohn[7] or Nordlander and Harris.

Very recently Holmberg, Apell, and Giraldo[28] have also calculated the saturation of the van der Waals potential at small separations. We show their results in the dotted line in Fig. 2. These authors used a model surface response function similar to ours, although they explicitly separated the terms linear in q (giving the reference plane position z_{vdW}) from the behavior at large q (giving the "cut-off"). Despite the differences between their response function and ours, Fig. 2 shows that their results are very similar to our calculations. We would expect their calculated van der Waals to be slightly larger than ours (as Fig. 2 shows) since they include the quadrupolar polarizability of the atom, which we have neglected.

V. HELIUM BINDING ENERGY

The calculations discussed above show that the van der Waals energy is significantly weaker at typical atom-surface separations than other authors had supposed. This implies that the binding energies of helium on simple metal substrates would be less than had been previously supposed. At present there seem to be no experimental observations of selective adsorption resonances of helium on simple metal substrates that could test this hypothesis.

We can write the energy of the helium atom near a metal surface as a sum of three terms,

$$U(z) = U_R(z) + U_{hyb}(z) + U_{vdW}(z) . \tag{21}$$

These terms are, respectively, the repulsion energy due to overlap of the occupied metal electronic wave function with the helium $1s$ orbital,[29] the hybridization due to coupling of the occupied helium $1s$ into unoccupied metal states,[30,31] and finally the van der Waals interaction discussed above.

We calculate the overlap repulsion energy U_R using the approach of Harris and Liebsch.[29] This gives the repulsion energy as an integral over the occupied local density of states of the metal at the helium atom position. Since the local density of states outside the metal is sharply peaked at the Fermi level, a good approximation to this integral should be given by

$$U_R(z) = 0.8g(\Phi + \Delta)\rho(z) , \tag{22}$$

where the function $g(E)$ is the function given by Harris and Liebsch for the scattering of electrons of energy E below vacuum. Φ is the work function of the metal and Δ is an energy shift representing the mean of the metal local density of states relative to the Fermi level; we took Δ as 1.5 eV. $\rho(z)$ is the charge density of the jellium surface, which we take from the self-consistent calculation of Lang and Kohn.[32] The factor of 0.8 is included to approximately take into account the second and higher-order scatterings of the metal electrons by the helium $1s$ core, as suggested by Nordlander.[33]

The hybridization energy U_{hyb} takes into account the relaxation of the helium core due to overlap with unoccupied states in the metal. We take the magnitude of the hybridization energy $U_{hyb}(z)$ from the calculations of An-

nett and Haydock.[31] The calculations of Annett and Haydock made use of the image potential of the surface, in a more exact treatment the nonlocal self-energy defined in Eq. (2) should be used instead. Note that the hybridization is a second-order effect of the self-energy, while the van der Waals defined in Eq. (3) is a first-order process.

Figure 3 shows our results for the potential energy of a helium atom near an $r_s = 3$ jellium surface. To illustrate the relative importance of the different terms the curve is broken down into its constituent contributions. We can see from the figure that in the well region potential is entirely dominated by the van der Waals and the repulsion since the hybridization falls off quickly with distance. In the repulsive region the (appropriate for helium diffraction experiments) the U_R term dominates while the hybridization is the second largest term. At a typical helium atom classical turning point of $z = 3U_{hyb}$ is about 25% of U_R, consistent with the arguments of Annett and Haydock.[30]

We find that the well depth of the helium $r_s = 3$ potential is 1.25 meV and that the minimum is located at around $z = 8$. This binding energy is substantially less than that found by either Zaremba and Kohn[5] or by Nordlander and Harris.[27] The difference arises because our calculated van der Waals energy is significantly less than that calculated by these authors (see, for example, Fig. 2). For example, had we used the Nordlander-Harris
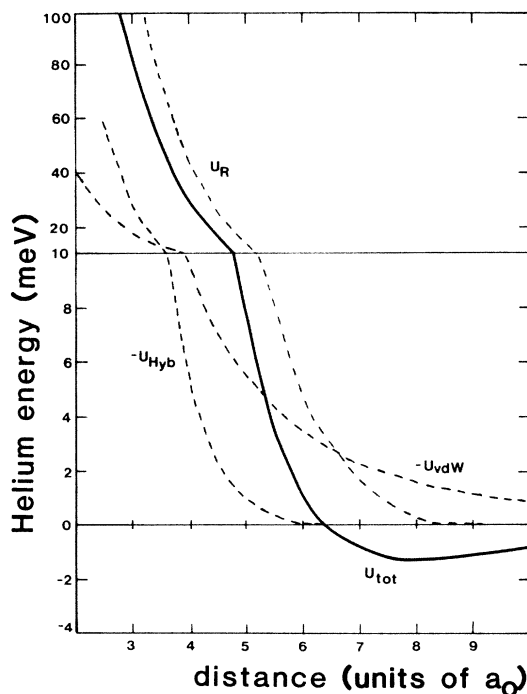

FIG. 3. Calculated potential energy of a helium atom near $r_s = 3$ jellium (solid curve). The dashed curves show the three contributions to the energy: the orthogonalization repulsion energy due to overlap of the helium $1s$ with occupied metal states (U_R), the hybridization energy due to mixing of the helium $1s$ with unoccupied metal states (U_{hyb}), and the van der Waals energy (U_{vdW}).

TABLE II. Potential minimum energies and separations for helium on jellium.

r_s (a_0)	U_m (meV)	z_m (a_0)
2	2.63	7.5
3	1.26	8.0
4	0.71	8.0
5	0.32	8.5
6	0.26	9.0

approach to U_{vdW} with $k_c = 1$ our potential would have had a depth of 2.5 meV occurring at $z = 7$, in agreement with the results of Nordlander and Harris. Such a large difference between theories could certainly be tested by helium diffraction experiments. At present there appear to be no selective adsorption resonance data for helium on simple metal surfaces, although there seems no reason in principle why these experiments could not be carried out in the near future.

We have also calculated the binding energies and equilibrium separations of helium on a number of substrates; these results are summarized in Table II.

VI. PARALLEL VELOCITY DEPENDENCE

In the self-energy approach to the van der Waals energy it is straightforward to include the velocity of the atom parallel to the surface. Following Ferrell and Ritchie[8] this leads to the following generalization of Eq. (9):

$$U_{vdW}(z) = -\sum_n \frac{f_{n0}}{\omega_{n0}}$$

$$\times \int_0^\infty \frac{d\omega}{\pi} \int d^2q \frac{q^2 e^{-2qz}}{2\pi q}$$

$$\times \frac{\text{Im}[g(q,\omega)]}{\omega + \omega_{n0} - \mathbf{v} \cdot \mathbf{q} + q^2/2M} .$$

(23)

Here $\mathbf{v}$ is the velocity vector parallel to the surface and M is the mass of the atom. The extra terms in the denominator $-\mathbf{v} \cdot \mathbf{q} + q^2/2M$ are the change in the kinetic energy of the atom due to interaction with the virtual quantum of wave vector q. In the static case $\mathbf{v} = 0$ and Eq. (23) reduces to Eq. (9), since the recoil term $q^2/2M$ is negligible.

For small velocities we may expand the van der Waals potential in a power series in v. The leading velocity-dependent term is found to be

$$-\sum_n \frac{f_{n0}}{\omega_{n0}} \int_0^\infty \frac{d\omega}{\pi} \int_0^\infty dq \, q^2 e^{-2qz} \frac{\text{Im}[g(q,\omega)]}{(\omega + \omega_{n0})^3} \frac{1}{2} q^2 v^2 .$$

(24)

We have again neglected the $q^2/2M$ recoil term since it is negligible whenever $q^2 \ll 2M\omega_{n0}$ or $z \gg (2M\omega_{n0})^{-1/2}$. If we substitute our dispersed surface-plasmon—pole approximation for the response function $\text{Im}[g(q,\omega)]$ we find the velocity-dependent part of the potential to be

$$-\sum_n \frac{f_{n0}}{\omega_{n0}} \int_0^\infty dq \, q^4 e^{-2qz} \frac{\omega_s^2}{4[\omega_s(q) + \omega_{n0}]^3 \omega_s(q)} v^2 .$$

(25)

This has the asymptotic limit of

$$-\frac{v^2}{z^5} \sum_n \frac{f_{n0}}{\omega_{n0}} \frac{3\omega_s}{16(\omega_s + \omega_{n0})^3} ,$$

(26)

in agreement with the work of Ferrell and Ritchie.

In order to investigate the importance of dispersion on the velocity-dependent part of the potential we have calculated the potential of Eq. (25) for helium on $r_s = 3$ jellium. The results of this calculation are shown in Fig. 4, where we plot the ratio of the calculated potential to the asymptotic form given by Eq. (26). We see that the velocity-dependent part of the potential is only about 50% of its asymptotic value at a typical atom-surface separation. The approach to the asymptotic limit appears to occur more slowly than for the static potential shown in Fig. 2. For helium on $r_s = 3$ jellium the magnitude of the asymptotic form given in Eq. (26) was calculated to be $0.0334 v^2/z^5$. For typical helium atom scattering velocities and distances this gives only a minute change in the van der Waals energy due to the atom velocity. However these velocity-dependent effects may well become significant for atoms which are more polarizable than helium, or at higher beam energies than for low-energy atom scattering.

It is interesting to note that for very high atom velocities the van der Waals energy given in Eq. (23) has an imaginary part. This is a result of loss processes that can occur due to real excitations of the atom and the solid. The condition for these processes to occur is the vanishing of the denominator of Eq. (22), which occurs when

$$\frac{1}{2} M v^2 > \omega_{n0} + \omega .$$

(27)

This implies that these loss processes will not occur except for high atom energies (for helium ω_{n0} is of order 20 eV),
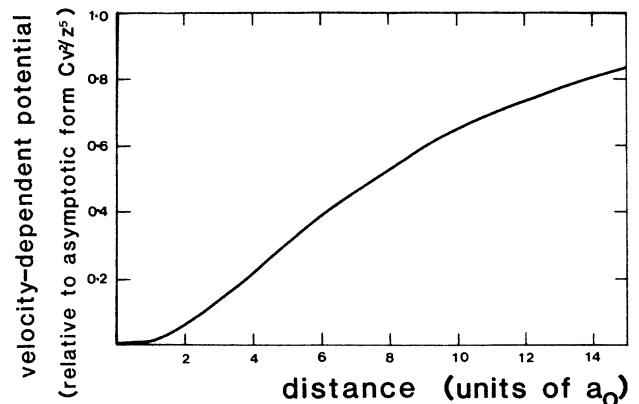

FIG. 4. Velocity-dependent part of the van der Waals potential. We plot the contribution to the potential proportional to v^2, where v is the atom velocity parallel to the surface. The calculations are for helium on $r_s = 3$ jellium. The curve plotted is the ratio of the velocity-dependent potential to its asymptotic form of Cv^2/z^5, thus giving an indication of the effects due to the finite separation between the atom and the surface.

and furthermore that the low-energy excitations of the solid (i.e., electron-hole pairs) will be the most significant. Work is under progress to calculate the total loss probability for an atom impinging on a surface. Sols, Flores, and Garcia have calculated loss processes that occur at lower atom velocities due to second-order terms in the self-energy.[34]

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