Interaction of Helium with a Metal Surface: Determination of Corrugation Profile of Cu(110)

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Starting from a microscopic description of the interaction of a helium atom with a metal surface, a simple approximate result is derived which shows that the lateral corrugation of the repulsive potential decreases exponentially with distance z from the surface. For Cu(110) this theory leads to an interaction potential that reproduces all the observed bound states and gives a quantitative fit of recent helium diffraction data taken at various incident energies and angles.

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Helium scattering from surfaces is currently a field of some interest because of its potential as a probe of the atomic geometry of surfaces.[1] In order to extract such information from measured diffraction data, a relationship must be found which expresses the helium potential in terms of the electronic properties of the surface. In a recent paper[2] we showed that the repulsive part of the interaction may approximately be written in a simple form

$$V_R(\vec{r}) = \int_{-\infty}^{\epsilon_F} d\epsilon\, g(\epsilon)\rho(\epsilon, \vec{r}), \tag{1}$$

where ϵ_F is the Fermi energy, $g(\epsilon)$ is a smooth function of energy depending only on the properties of the helium 1s function, and $\rho(\epsilon, \vec{r})$ is the local density of states of the bare metal surface. The purpose of the present paper is to derive from the above expression the general behavior of V_R at large distances z from the surface and to demonstrate that the uncorrugated part of the repulsive helium potential as well as the corrugation height decrease exponentially with z. This is a direct consequence of the spatial variation of the local density of states outside the surface.

The asymptotic form of V_R involves parameters which could be calculated if the weights of the Bloch functions in the selvedge were accurately known. An alternative is to determine these parameters experimentally. We illustrate how this can be done with the aid of data recently reported for helium diffraction from Cu(110).[3] Using the simple two-parameter expression for V_R which is obtained for this surface, we show that a quantitative and consistent fit of all diffraction intensities and bound-state energies can be achieved.

This represents the first successful application of a microscopically derived interaction in helium scattering from metal surfaces. Model potentials using constant (z-independent) corrugation amplitudes can give a good fit to data,[3] but only if the amplitude is adjusted for each incident energy. Part of our aim in this paper is to emphasize that "energy-dependent" corrugations obtained in this way do not give the true corrugation at the classical turning point, but a systematic underestimate.

In Ref. 2, expression (1) was shown to be valid once the variation of the Bloch tails over the helium atom is exponential. The local density of states may then be written

$$\rho(\epsilon, \vec{r}) = 2\sum_{\vec{k}}\sum_{\vec{g}\vec{g}'} C_{\vec{g}} C_{\vec{g}'}^{*} \exp[i(\vec{g}-\vec{g}')\cdot\vec{r}]\exp[-(\kappa_{\vec{g}}+\kappa_{\vec{g}'})z]\,\delta(\epsilon-\epsilon_{\vec{k}}), \tag{2}$$

where $\kappa_{\vec{g}}^2 = (\vec{k}_{\parallel}+\vec{g})^2 - 2\epsilon$ and $\vec{g}$ are the surface reciprocal lattice vectors. For simplicity, band indices and the $\vec{k}_{\parallel}$ dependence of the coefficients $C_{\vec{g}}$ are suppressed. (Energies are measured relative to vacuum and Hartree atomic units are used throughout unless stated otherwise.)

At large values of z, it is sufficient to retain in (2) only those terms that give rise to the leading exponents. In the case of (110) faces of fcc transition metals which show an essentially one-dimensional corrugation, this gives

$$V_R(x, z) \approx 2\sum_{\vec{k}}{}' |C_0|^2 \exp(-2\kappa_0 z)[1 + 4\{\mathrm{Re}(C_0 C_1^{*})/|C_0|^2\}\exp\{-(\kappa_1-\kappa_0)z\}\cos(2\pi x/a)]\,g(\epsilon_{\vec{k}}), \tag{3}$$

where a denotes the lattice constant in the direction x of the corrugation and the sum over $\vec{k}$ is only over occupied states. For other crystal faces it would be necessary to retain also the smallest $\vec{g}$ vector in the y direction. The coefficients C_0 and C_1 in (3) can be generated from a self-consistent film program,[4] so that V_R can be determined from first principles. However, because the exponent $2\kappa_0$ increases steadily away from the Fermi surface, the z dependence of the integrals is rather simple. We have evaluated the first term for jellium using a variety of values of work function, φ, and band width and find the z dependence to be remarkably well approximated by a single exponential. Whereas the factor multiplying the exponential depends sensitively on the procedure used in constructing the surface potential, the exponent is very well represented by $2[2(\varphi+\Delta)]^{1/2}$, where Δ is an energy shift of $\sim 1-2$ eV that depends primarily on the band width. This shift appears in the exponent because there is zero phase space for states with $\vec{k}_\parallel = 0$ and $k_\perp = k_F$. This means that the dominant contribution to the integral comes from states with κ_0 somewhat larger than the minimum value of $2(2\varphi)^{1/2}$.[5]

These arguments indicate that, provided the C_0 and C_1 do not show sharp structure near the Fermi energy, (3) is well approximated by[6]

$$V_R(x,z) = V_0 e^{-\alpha z}\{1 + \tfrac{1}{2}\alpha h_0 \exp[-\beta(z-z_0)]\cos(g_1 x)\}, \tag{4}$$

where $g_1 = 2\pi/a$, $\alpha = 2[2(\varphi+\Delta)]^{1/2}$, and $\beta = [2(\varphi+\Delta) + g_1{}^2]^{1/2} - \frac{1}{2}\alpha$. The amplitude of the cosine term has been written so as to facilitate contact with conventional model potentials. In principle the values of Δ in the definitions of α and β could differ slightly. However, since $2\varphi + g_1{}^2 \gg 2\Delta$, this will have negligible influence on the value of β. The exponents α and β can therefore be regarded as known, so that Eq. (4) contains only two parameters, the overall strength of the repulsive potential, V_0, and the corrugation amplitude, h_0. (The arbitrary distance z_0, with respect to which h_0 is defined, will later be chosen as the location of the minimum of the total uncorrugated helium potential.) If we define the corrugation functions

$$\begin{aligned} h(z) &= h_0 \exp[-\beta(z-z_0)], \\ h(x,z) &= \tfrac{1}{2}\cos(2\pi x/a)h(z), \end{aligned} \tag{5}$$

and take advantage of the fact that the second term in the brackets of (4) is small compared to unity at large z, V_R may be rewritten as

$$V_R(x,z) = V_0 \exp\{-\alpha[z - h(x,z)]\}. \tag{6}$$

This form is similar to that used in earlier work with the important difference that $h(z)$ is exponentially decreasing. Thus, the corrugated part of V_R decays more rapidly than the uncorrugated part.

We now apply Eq. (4) to the case of Cu(110) for which $g_1 = 0.92$ and $\varphi = 4.48$ eV.[7] The attractive part of the helium interaction is taken to be given by the van der Waals expression $-c_{\mathrm{VW}}(z - z_{\mathrm{VW}})^{-3}$ with $c_{\mathrm{VW}} = 1.52$ eV $a_0{}^3$, and $z_{\mathrm{VW}} = 0.461 a_0$.[8] The origin of z lies one half a layer spacing outside the topmost plane of nuclei. From a jellium calculation, we obtain $\Delta = 2.1$ eV so that $\alpha = 1.39$ and $\beta = 0.46$ a.u.[9] He-Cu(110) is a good test system because Perreau and Lapujoulade[3] have recently reported accurate $T=0$ diffraction data for two well-separated helium energies and a wide range of incident angles. Furthermore, on the basis of selective adsorption features observed for the Cu(113) and Cu(115) faces, these authors were able to give figures for the energies of the bound levels of He in the well. This is important information because the bound levels are only weakly influenced by the corrugation and can be calculated with the laterally averaged potential to give a unique value for V_0. For $V_0 = 12$ eV, giving a well with minimum -6.2 meV, at $z_0 = 5.7 a_0$, we find the sequence -4.52, -2.15, -0.86, -0.27 meV, which agrees with the observed spectrum within the quoted accuracy (~ 0.2 meV). This well is ~ 1 meV deeper than that calculated for Cu (jellium) by Zaremba and Kohn[8] whose potential is accurately reproduced if we take $V_0 \simeq 16$ eV. This difference would result if the wave-function tail coefficients given by the jellium surface potential were in error by as little as 15%.

With V_0 determined by the selective adsorption spectra, we have only one free parameter, the corrugation height, h_0, with which to fit the entire set of diffraction data. Figure 1 shows a comparison of measured and calculated intensities for incident energies 21 and 63 meV. The experimental values were obtained from low-temperature extrapolations. Except for the smallest angles, the diffraction intensities in the plane of incidence add up to unity within experimental accuracy. To facilitate the comparison, the measured intensities have been renormalized to exact in-plane unitarity. The theoretical diffraction intensities are for $h_0 = 0.048 a_0$ and are obtained by use of an exact coupled-channels method.[10] The fit is seen to be excellent for both energies and all angles. The weaker $+1$ and $+2$ beams, which are not shown for the sake of clarity, are reproduced with the same accuracy. Furthermore, a

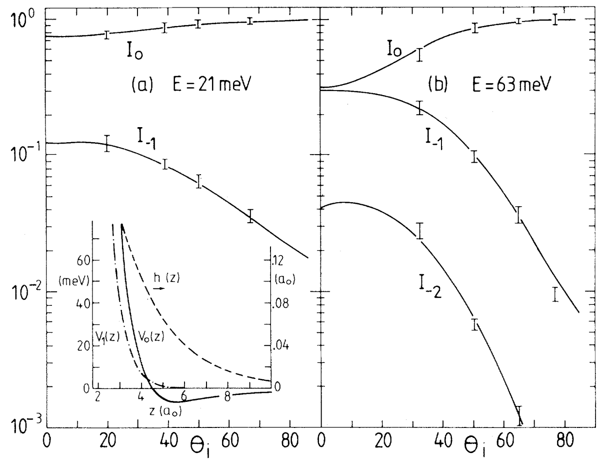

FIG. 1. Comparison of calculated (solid lines) and measured (vertical bars) helium diffraction intensities for Cu(110). Inset: uncorrugated and corrugated parts of the helium interaction, as well as the corrugation function $h(z)$.

comparison with preliminary data taken at higher energies[11] gave equally good agreement, indicating that for Cu(110) the asymptotic form (4) for V_R remains a good approximation up to $z \sim 3$ a.u. For illustrative purposes we show in the inset in Fig. 1 the corrugation function $h(z)$ and the final potentials:

$$\begin{aligned} V_0(z) &= V_0 e^{-\alpha z} - c_{\mathrm{VW}}/(z - z_{\mathrm{VW}})^3, \\ V_1(z) &= \alpha h(z) V_0 e^{-\alpha z}. \end{aligned} \tag{7}$$

Here $V_0(z)$ is the lateral average and $V_1(z)$ the amplitude of the cosine term. It would naturally be of great interest to compare this with a complete calculation using (1) and (2) with the local density of states determined by a film program.[4]

In order to make contact with previous intensity calculations using empirical potentials, we have compared the theoretical results shown in Fig. 1 with those obtained on replacing $h(z)$ by constants $h_1 = 0.114$ and $h_2 = 0.147 a_0$. These values correspond to the corrugation at the classical turning points for helium particles of 21 and 63 meV incident energy, respectively (see inset). At 21 meV, both values give too-strong diffraction whereas, at 63 meV, the nonspecular intensities for h_1 are too small while those for h_2 are too large. Obviously, no single constant value of h is able to reproduce the measured intensities consistently at both energies. On the other hand, the angular dependence of the intensities at a particular incident energy is remarkably insensitive to the form of $h(z)$. As noted in Ref. 3, this dependence can be reproduced quite well with h_E an energy-dependent constant. However, our calculations show that this "apparent" constant corrugation amplitude h_E does *not* correspond to the true corrugation at the classical turning point. The reason is that a constant h_E represents some spatial average of the actual exponentially decreasing $h(z)$. Thus, h_E must be systematically smaller than $h(z)$ at the turning point in order to compensate for the too-large corrugation at large z. At 21 and 63 meV, we have found that the apparent corrugations h_E underestimate the true turning-point values h_1 and h_2 by about 16%.

In summary, we have shown that, because of the general asymptotic behavior of the electronic density of states outside metal surfaces, both the uncorrugated part of the repulsive helium interaction and the corrugation height fall off exponentially at large distances. For surfaces displaying an essentially one-dimensional corrugation, the repulsive part of the helium potential, V_R, can be reduced to a simple two-parameter expression. Determining one of these parameters from experimental selective adsorption spectra, we have achieved, using the one remaining free parameter, a quantitative fit of diffraction data for He-Cu(110) for a wide range of incident angles and energies. The extension of our procedure to surfaces where two reciprocal lattice vectors must be retained in (2) is essentially trivial. Adsorbate-covered surfaces present a problem, however, in that the local density of states will show structure within the band. For example, if g_1 in (3) represented a vector of the adsorbate lattice, the corresponding coefficient C_1 may be small at the Fermi energy and large deeper in the band, in which case the simple parametrization (4) would be inaccurate.

We thank J. Lapujoulade for communicating results prior to publication, and, in particular, for supplying preliminary data that enabled us to check our potential at energies higher than those quoted in this Letter.

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[5] An exact asymptotic expansion for jellium gives a variation of $V_R \sim \exp[-2(2\varphi)^{1/2} z][1 + o(1/z)]/z^2$, with

the factor z^{-2} a direct consequence of the vanishing of the phase space at $\vec{k}_{\parallel} = 0$, $k_{\perp} = k_F$. In practice, for the values of z relevant in helium scattering, the first term in this series gives a substantially worse representation of the correct result than a single exponential with exponent $2[2(\varphi+\Delta)]^{1/2}$.

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[9] Note that these exponents, particularly β, do not depend strongly on the value of Δ. For $\Delta = 1$ eV, for example, we get $\alpha = 1.28$, $\beta = 0.48$.

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[11] We thank J. Lapujoulade for making these data available.

Correlated-Wave-Function Calculation of the Chemisorption of CO on Ti(0001)

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The chemisorption of CO on Ti(0001) is treated with a many-electron configuration-interaction theory for adsorbate-surface interactions. When perpendicular, threefold, atop-atom and bridge adsorption sites are compared with CO adsorption parallel to the surface, CO parallel with C and O stretched toward adjacent threefold sites is the more stable (60 kcal/mole exothermic). A distinctive upward shift of CO energy levels occurs for stretched and dissociated CO adsorption as a result of increased electron transfer from the lattice. Binding-energy contributions are discussed.

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The chemisorption of CO on transition-metal surfaces has been the subject of numerous photoemission and low-energy electron diffraction (LEED) studies.[1-4] However, on surfaces where dissociation is a possibility, major unanswered questions remain. For example, for CO chemisorbed on Ti(0001) only fair agreement between calculated and observed LEED intensities has been obtained for various models involving dissociated CO; molecular CO perpendicular to the surface yielded definitively negative results.[3] On Ti($10\bar{1}1$), dissociative chemisorption of CO resulting in carbide and oxide type structures is suggested by ultraviolet photoelectron spectroscopy and other studies by Fukuda *et al.*[4]

This Letter describes an accurate theoretical treatment of the chemisorption of CO at certain sites on Ti(0001) using correlated configuration-interaction (CI) wave functions for the adsorbate-surface interactions. The lattice is modeled as an atomic cluster treated initially at the self-consistent-field (SCF) level, followed by a localization transformation to define an adsorbate-surface region which is treated more accurately by improving the basis and using CI theory. All electrostatic interactions are evaluated accurately. A full account of the theory is published elsewhere.[5]

To approximate the unreconstructed, close-packed titanium surface a 28-atom, two-layer model of the hcp lattice was chosen with 16 atoms in the surface layer and 12 in the second layer. This cluster is part of the 54-atom lattice treated in Ref. 5 with internuclear distances the same as in bulk Ti. A five-atom surface region including both hcp and fcc bonding sites was chosen for the CO adsorption studies. The orbital basis for these atoms was augmented by an additional 4s, 4p, and 3d basis function. A double zeta basis was used for CO.[6] Core potentials and Ti basis functions are given in Ref. 5. The unitary localization transformation was carried out using carbon and oxygen orbitals and the neighboring Ti atoms on the surface to define the localization site. This procedure limits the CI to a tractable subspace of localized electrons and at the same