Dependence of the He-Scattering Potential at Surfaces on the Surface-Electron-Density Profile

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It is shown that the repulsive part of the He-surface interaction is given by an almost linear, surface-independent function of the surface electron density at the He site. This gives a very simple connection between the measured low-energy He-beam scattering potentials and the substrate electron densities. The scheme is applied to an analysis of the He-scattering potential outside Al.

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Scattering of low-energy He atoms has become an increasingly popular method in the structural analysis of both clean and adsorbate-covered surfaces.[1-7] Bragg diffraction has now been observed for a number of systems and information about the periodicity and lattice constants along the surface can readily be extracted. The main advantages of the experiment are that it is extremely surface sensitive and that it is nondestructive. Furthermore, the experimental data do, in principle, contain information about the whole He-scattering potential $E_{\mathrm{He}}(\vec{r})$. A more detailed understanding of the He-surface interaction is thus needed if all the information available in the experimental data is to be extracted.

In the present paper we address this problem. We show that the He-surface interaction energy $E_{\mathrm{He}}(\vec{r})$ is basically proportional to the substrate electron density at the He site. This result, which is is expected to hold with a great deal of accuracy for any surface, allows first of all a determination of $E_{\mathrm{He}}(\vec{r})$ once the electron-density profile of the substrate is known. Moreover, it suggests that a measurement of the He-scattering potential actually determines the electron-density profile of the surface in question. This makes He-scattering measurements a potentially very powerful technique. In the paper we apply the method to an analysis of the scattering potential of Al. A number of experimentally observed trends in the variation of the scattering potential with surface structure, beam direction, and energy are explained.

The interaction between a He atom and a surface has traditionally been divided into an attractive part due to polarization or van der Waals forces, and a repulsive one due to the direct overlap between the He atom and the surface electrons.[8] The attractive interaction is typically a few millielectronvolts for He.[8] Since typical He kinetic energies in a scattering experiment are larger than 20 meV, we will neglect this part in the following.[9] We thus concentrate on the interaction energy due to the embedding of the He atom in the electron profile of the host. A few calculations of the repulsive He-surface interaction exist. Kleinmann and Landman,[8] Zaremba and Kohn,[10] and van Himbergen and Silbey[11] have attacked the problem using a jellium model[12] for the surface, and Freeman[13] has considered He outside graphite. The method presented in the present paper is much simpler than the two first approaches and is not limited to jellium surfaces. It is even simpler than the Kim–Gordon[14] approach used in Refs. **11** and **13**, and it does not assume that the He density profile is unchanged at the surface. The basic idea is to replace the inhomogeneous host electron system by an effective homogeneous medium with an electron density equal to the average host electron density $\bar{\rho}_0$ seen by the He atom. That is, we make the approximation

$$E_{\mathrm{He}}(\vec{r}) \cong E_{\mathrm{He}}{}^{\mathrm{hom}}(\bar{\rho}_0(\vec{r})), \tag{1}$$

where $E_{\mathrm{He}}{}^{\mathrm{hom}}(\rho_0)$ is the energy change on embedding a free He atom in a homogeneous electron gas of density ρ_0.

The simple approximation in Eq. (1) can be regarded as the zeroth-order contribution to the energy in a systematic expansion of $E_{\mathrm{He}}(\vec{r})$ in the deviations of the host from the effective medium. The details of this are presented elsewhere.[15] If we choose $\bar{\rho}_0$ in Eq. (1) as the average of $\rho_0(\vec{r})$ over the electrostatic potential $\Delta\varphi(\vec{r})$ introduced by the He atom in the homogeneous medium, with

$$\bar{\rho}_0 \int \Delta\varphi(\vec{r})\, d^3r = \int \rho_0(\vec{r})\, \Delta\varphi(\vec{r})\, d^3r,$$
$$\Delta\varphi(\vec{r}) = \int \frac{\Delta\rho(\vec{r}\,') - 2\delta(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}\, d^3r', \tag{2}$$

[$\Delta\rho(\vec{r})$ being the He-induced charged density and the term involving the δ function stems from the nucleus], then simple perturbation theory[12] gives the first-order correction to Eq. (1) as[15]

$$E_{\mathrm{He}}^{(1)}(\vec{r})=\int[\Delta\rho(\vec{r})-2\delta(\vec{r})]\varphi_0(\vec{r})d^3r, \qquad (3)$$

where $\varphi_0(\vec{r})$ is the host electrostatic potential.

The region over which we are sampling the host is given through Eq. (2) as the screening length of $\Delta\varphi$. This is typically 0.15 Å for He, indicating that a local description with only the zeroth and perhaps first-order terms [Eqs. (1) and (3)] should be sufficient. This is so even for H and O outside surfaces although these atoms are not as localized as He.[15]

To test the method quantitatively in connection with He-scattering potentials, we have used the method to calculate the He-scattering potential outside another He atom. For this system both detailed experiments and very involved configuration interaction calculations exist for comparison. This is shown in Fig. 1. First of all the evaluation showed that the first-order term (3) is always at least one order of magnitude smaller than the zeroth-order term (1) with the average density defined by Eq. (2). The simplest zeroth-order theory thus suffices in this case. Furthermore, the figure shows clearly that the accuracy of the method is as good as for the more elaborate calculations. The great advantage of the present method is then, that it is readily applied to the much more complicated case of the surface. Also the accuracy and the conclusion that the zeroth-order theory suffices are expected to be the same, since the density variations at a surface are of the same order of magnitude as at a He atom.

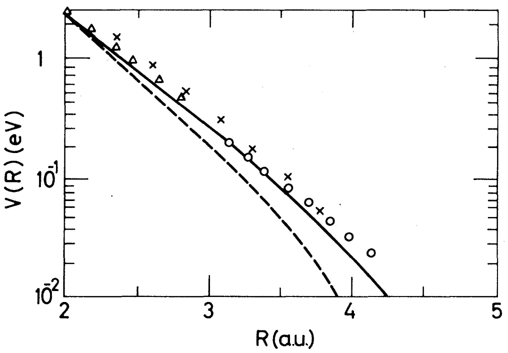

FIG. 1. The He-He scattering potential $V(R)$ as a function of the He-He distance R, based on Eq. (1) (full curve). The "substrate" electron-density profile is taken to be $\rho_0(\vec{r})=(2\alpha^3/\pi)e^{-2\alpha|\vec{r}-\vec{R}|}$, $\alpha=1.68$ in Eq. (2). The simple calculation is compared to (crosses) Phillipson (Ref. 20) (configuration interaction calculations), (open circles) Blais and Mann (Ref. 21) (experiment), and (Δ) Amdur *et al.* (Ref. 22) (experiment). The approximate theory of Gordon and Kim (Ref. 14) is also shown (dashed curve).

From this we conclude that the simple local approximation (1) should be sufficient for a quantitative determination of the scattering potential for a low-energy He beam. This means that once the electron-density profile is known (calculated) for a given surface, the He-scattering potential can readily be obtained from the known embedding energy $E_{\mathrm{He}}^{\mathrm{hom}}(\rho_0)$ of He in a homogeneous electron gas as a function of electron gas density ρ_0.

The function $E_{\mathrm{He}}^{\mathrm{hom}}(\rho_0)$ can be calculated once and for all. The result (within the local-density approximation[16]) is shown in Fig. 2.[17] It is seen that $E_{\mathrm{He}}^{\mathrm{hom}}(\rho_0)$ is an essentially linear, increasing function of ρ_0. The increasing repulsion between the atom and the electron gas is primarily connected with the increase in kinetic energy introduced by the exclusion of the electron gas from the volume occupied by the He 1s electrons.

For densities ρ_0 less than around 0.0002 a.u. (energies less than 0.1 eV), the linear dependence in Fig. 2 can be written $E_{\mathrm{He}}^{\mathrm{hom}}(\rho_0)=\alpha\rho_0$, with $\alpha=750$ eV/a.u. This gives a He-scattering potential $E_{\mathrm{He}}(\vec{r})$ for He outside a surface with a

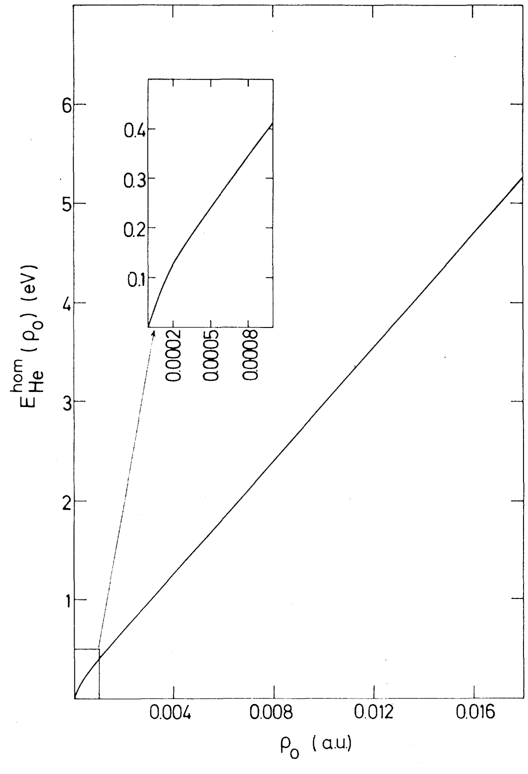

FIG. 2. Energy of a He atom in an infinite electron gas minus that of the bare electron gas and a free atom as a function of electron-gas density ρ_0 (Ref. 17).

density profile $\rho_0(\vec{r})$ (in a.u.) as

$$E_{\rm He}(\vec{r}) = 750\bar{\rho}_0 \text{ eV}; \; E_{\rm He} \lesssim 0.1 \text{ eV}. \tag{4a}$$

For higher densities (energies) another linear dependence takes over:

$$E_{\rm He}(\vec{r}) = 375\bar{\rho}_0 + 0.065 \text{ eV}; \; E_{\rm He} \gtrsim 0.1 \text{ eV}. \tag{4b}$$

The He-scattering potential is thus a direct measure of the surface electron density. This makes the scattering experiment unique. If the analysis of the experimental data is good enough for a detailed mapping of the scattering potential, the experiment does not only give information about the geometrical arrangement of the surface atoms but also about the electron structure by a complete mapping of the electron density. At surfaces, the averaging of $\rho_0(\vec{r})$ [Eq. (2)] is usually not even necessary because of the smoothness of $\rho_0(\vec{r})$ parallel to the surface.

As mentioned above, the only input in a calculation of the scattering potential is the surface density $\rho_0(\vec{r})$. At present the only surface-density profiles available to us are those of jellium surfaces.[12] In the jellium model of a metal the ion cores are substituted by a uniform, positive background. The surface is modeled by taking away the background in one half-space. The model gives a good description of many properties of free-electron-like metal surfaces, especially if the pseudopotentials from the ion cores are reintroduced in first-order perturbation theory.[12] In order to study the qualitative aspects of a typical He-scattering potential outside a metal surface, we have applied the simple scheme above to the He outside Al. The effect of the conduction electrons is included through Eq. (1), where $\rho_0(\vec{r})$ is taken from the jellium-surface calculations corresponding to Al.[12] The effects of the pseudopotentials are then included through a first-order correction

$$\Delta E_{\rm ps}(\vec{r}) = \int \Delta V_{\rm ps}(\vec{r}\,')[\Delta\rho(\vec{r}\,') - 2\delta(\vec{r}\,' - \vec{r})]\, d^3r', \tag{5}$$

where $\Delta V_{\rm ps}$ is the difference between the actual pseudopotential of the substrate and the potential from the positive background used in the jellium calculation,[13] $\Delta\rho(\vec{r})$ is the He-induced electron density in a homogeneous electron gas of density $\rho_0(\vec{r})$, and the last term involving the δ function is due to the He nucleus of charge 2. Such an approach has been used before in, e.g., calculating chemisorption energies of hydrogen outside these surfaces.[18,19] It must be pointed out that if the true density profile of the Al surface had been available, it would not have been necessary to include a term like (5), and the whole procedure would have been even simpler.

The results for the Al(110) surface are shown in Fig. 3. Here, equipotential curves are drawn in the [10] direction perpendicular to the close-packed rows of the fcc (110) surface. The variations in the [01] direction parallel to the rows are very small. This means that if the equipotential-energy surface $\xi_E(\vec{r})$ of energy E is Fourier expanded in the two-dimensional reciprocal lattice:

$$\xi_E(\vec{r}) = \sum_{\vec{g}} \xi_E(\vec{g}) e^{-i\vec{g}\cdot\vec{r}}, \tag{6}$$

only the $\vec{g} = \pm 1, 0$ components will be significant for this surface. Since $\xi_E(\vec{r})$ describes the classical turning point of a He atom of energy E (in the normal direction) scattering off the surface, the corrugation parameters $\xi_E(\vec{g})$ are similar to those often used in presenting experimental data on He-scattering potentials.[1-7] For the Al(110) surface only one parameter $\xi_E(\pm 1, 0) \sim 0.03$ Å (E = 40–100 Mev) is significant. We note that this value for the Al(110) surface is of the same order of magnitude for the similar Ni(110) surface (0.013 Å).[2] All other $\xi_E(\vec{g})$ values for the Al(110) surface and for the more close-packed Al(100) and Al(111) surfaces are smaller than ~0.01 Å. This is also in agreement with the corrugation parameters measured for close-packed metal

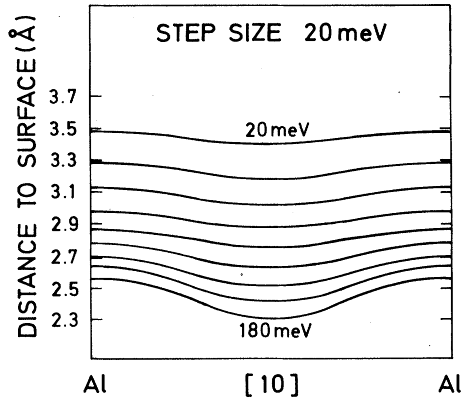

FIG. 3. Equipotential energy curves for He outside an Al(110) surface. The curves are shown for a cut between two Al atoms in the [10] direction perpendicular to the close-packed Al rows. The variations parallel to the rows are insignificant on this scale. The distance perpendicular to the surface is measured from the first Al layer. The corrugation amplitude $\xi(\pm 1.0)$ of Eq. (6) is $\frac{1}{4}$ times the total amplitude of the curves in the figure.

surfaces like the Ag(111) (<0.01 Å).[3] All the calculated values are smaller than the one measured on the very open W(112) surface (0.04 Å)[6] and much smaller than on an ionic crystal like LiF(100) (0.08 Å).[7] On the basis of Eq. (1) or (4), the generally small corrugation parameters for metals and the extraordinarily small values for the close-packed structures must be attributed to the fact that the scattering potential is a measure of the electron density profile. This is much smoother on metals than on, e.g., ionic crystals, and on close-packed metal surfaces it is smeared out almost uniformly along the surface.

The results in Fig. 3 also show a dependence on energy. The general trend is that the corrugation increases with increasing kinetic energy. This simply reflects the fact that the high-energy atoms penetrate deeper into the electron-density profile, where the density inhomogeneities parallel to the surface are larger. The results do show that for energies around 100 MeV there is a small local minimum in the energy dependence of the corrugation parameter. In the simple picture developed here, this can be ascribed to the fact that the corrugation parameter roughly measures the amplitude perpendicular to the surface of the variations in electron density, and not the size of the variations themselves. If the density varies rapidly perpendicular to the surface, this may result in a decrease in amplitude of the constant density profile with increasing energy (deeper penetration) even though the absolute density variations become larger. The existence of such a local minimum for He scattering on Ag(111) can be inferred from Ref. 4.

The theory thus provides a conceptually and calculationally simple way of relating the He-scattering potential to the surface electron density. Application to the Al surfaces reproduces and explains a number of experimentally observed trends, and the absolute values calculated seem to be of the right size.

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