Scattering of Rare-Gas Atoms at a Metal Surface: Evidence of Anticorrugation of the Helium-Atom Potential Energy Surface and the Surface Electron Density

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Recent measurements of the scattering of He and Ne atoms at Rh(110) suggest that these two rare-gas atoms measure a *qualitatively* different surface corrugation: While Ne atom scattering seemingly reflects the electron-density undulation of the substrate surface, the scattering potential of He atoms appears to be anticorrugated. An understanding of this perplexing result is lacking. We present density functional theory calculations of the interaction potentials of He and Ne with Rh(110). We find and explain why the nature of the interaction of the two probe particles is qualitatively different, which implies that the topographies of their scattering potentials are indeed anticorrugated.

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The presumed simplicity of the interaction of low energy rare-gas atoms with surfaces has strongly promoted the use of He atoms as *ideal probe particles* in scattering experiments in order to determine the surface atomic geometry and the corrugation of the surface electron density [1–3]. Reconstructed surfaces have been successfully investigated and even light adsorbates like hydrogen, which are scarcely seen with other techniques, can be located. As a consequence, helium-atom scattering (HAS) is one of the leading tools for the analysis of structural and vibrational properties of surfaces. A widely used form for the interaction potential has been derived by Esbjerg and Nørskov [4] who argue that the interaction energy of a He atom and a surface is simply proportional to the unperturbed electron density of the substrate at the position of the He atom. Although widely accepted, the credibility of this approach has been questioned: For Ni(110) Rieder and Garcia [5] reported a serious discrepancy in the corrugation amplitude when comparing their measurements with the results of the Esbjerg-Nørskov approach taken together with good quality calculations of the surface electron density. Annett and Haydock [6] tried to reconcile the disagreement by introducing an additional term in the interaction potential. This addition, named the *anticorrugating term*, arises from the hybridization between the occupied 1s orbital of the He atoms and the unoccupied states of the metal surface and results in an attractive contribution to the potential which should be stronger at on-top positions than at bridge sites. Harris and Zaremba [7] criticized the estimates by Annett and Haydock and argued that the *anticorrugating term* should be, by more than an order of magnitude, smaller than what Annett and Haydock had evaluated. Harris and Zaremba [7] claimed that the discrepancy between theory and experiment lies in an improper description of the van der Waals contribution and a tendency to overcorrugate the He-surface interaction potential within the framework of the local-density approximation (LDA) of the exchange-correlation interaction. A general consensus on the origin of the effect noted by Rieder and Garcia [5] has not been reached.

Recent elegant measurements [8] enforced the interest in this important question and, in fact, raised significant doubts about the meaning and interpretation of the important HAS method. Rieder and co-workers found unexpected differences in the interaction potentials and measured corrugations when comparing the scattering of He and Ne atoms at surfaces. For Rh(110) and Ni(110) and using the Esbjerg-Nørskov approach they concluded that the Ne diffraction data reflect the corrugation of the surface atomic structure and the unperturbed electron density. In the case of He-atom scattering, however, the same type of analysis gave an electron corrugation shifted away from the atomic positions: The electron density at the short-bridge position appeared in HAS to be higher above the surface than the on-top site. Rieder's explanation, following the arguments of Annett and Haydock [6], is that, especially at the on-top position, the He 1s orbitals, as well as the Ne 2s orbitals, and the empty metal s states hybridize, giving rise to an anticorrugating contribution. For Ne, however, this contribution is overcompensated by the repulsive interaction between the Ne $2p_{x,y}$ orbitals and the metal s states. Severe doubts about this explanation are in place because it assumes that the additional term introduced by Annett and Haydock is now even dominating the interaction potential.

Obviously, there is profound need for a direct calculation of the interaction of a rare-gas atom with a metal surface. For this it is important that practically no serious constraints on the electronic response of the surface and the inertness and polarizability of the rare-gas atoms are introduced. A related important aspect of such a theoretical study is that the interaction of a He or Ne atom with a metal surface is an example of weak physisorption, and such a calculation represents a critical test of the exchange-correlation functional used in *ab initio* calculations.

We performed density-functional-theory (DFT) calculations exploiting two different functionals for the

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exchange-correlation interaction, namely the LDA [9] and the generalized gradient approximation (GGA) [10]. If not stated explicitly, the below reported results refer to a DFT-GGA calculation. The nonrelativistic Kohn-Sham equations and energy functionals are evaluated self-consistently using the full-potential linear augmented plane wave (LAPW) method [1112]. The Rh(110) surface is treated by a supercell approach, using five layer thick slabs, which are separated by a vacuum region of 18 Å. The slab thickness is rather small for a fcc (110) surface, but because of the weakness and localization of the interaction it is sufficiently large for the present study. The energy cutoff for the LAPW wave functions is chosen to be $E_{\text{cut}} = 15.5$ Ry, the muffin tin radius R_{MT} is 1.24 Å, the angular momenta of wave functions inside of the muffin tin spheres are taken up to $l_{\text{max}} = 10$. The muffin tin radius for the He and Ne atoms is $R_{\text{MT}} = 0.9$ Å. For the potential expansion we use a plane-wave cutoff of 70 Ry and a (l, m) representation (inside the muffin tin spheres) with $l_{\text{max}} = 4$. The $\mathbf{k}$ integration is performed on an equally spaced mesh of 88 points in the whole two-dimensional surface Brillouin zone of a (1×1) surface cell. For the evaluation of the potential energies of impinging He and Ne atoms we use a (1×2) surface cell.

As a first test of the accuracy of the calculations we studied the equilibrium structure of Rh bulk and the clean Rh(110) surface. The theoretical lattice constant ($a_0^{\text{th}} =$ 3.89 Å, without accounting for zero point vibrations) agrees well with that measured at room temperature ($a_0^{\text{exp}} = 3.80$ Å [13]). We find the first layer relaxes inwards by $\Delta d_{12}/d_0 = -4.9\%$, and the second layer relaxes outwards by $\Delta d_{23}/d_0 = +2.3\%$, with d_0 being the interlayer distance in the bulk. These results are in good agreement with the values obtained by a LEED analysis ($\Delta d_{12}/d_0 = -6.8\%$, $\Delta d_{23}/d_0 = +1.9\%$ [14]).

The interaction potential energy was calculated for many positions of the He and Ne atoms (see Fig. 1). At a distance of 6.0 Å above the surface we find that the atom-substrate interaction is negligible and hence use this geometry to define the energy zero of our calculations. The theoretical results for He (Fig. 1, left) show clearly that the potential energy is anticorrugated with respect to the unperturbed substrate electron density and atomic structure: At the repulsive part and same distance from the surface the energies for the short-bridge geometries are higher than those of the on-top geometries. Thus, for the whole range of particle energies typically used in HAS experiments (~20–100 meV) the turning point above the on-top position is closer to the surface than that above the short-bridge position. The behavior of Ne nearing the Rh(110) surface is qualitatively different. The potential energy curves for Ne atoms above the short-bridge and on-top sites almost coincide, but in the repulsive regime there is a clear difference and at the same distances

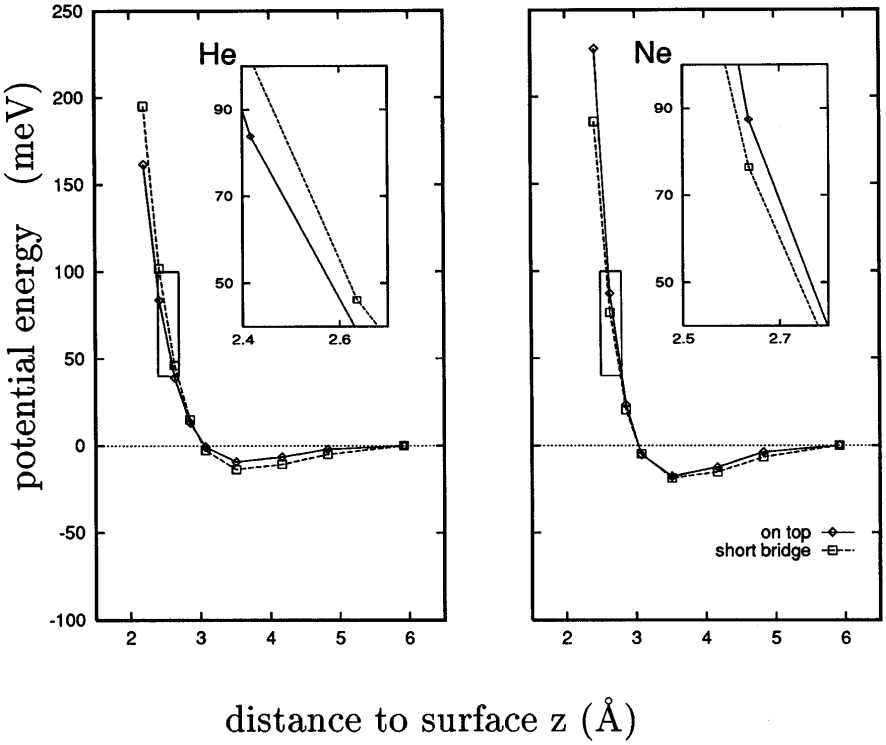

FIG. 1. Calculated potential energy using DFT-GGA (see text) for a He (left) and Ne (right) approaching the on-top and short-bridge positions of Rh(110) as a function of the distance z from the center of the first surface layer. The insets show a magnification of the repulsive part of the potential for particle energies used in experiment. Solid lines are guides to the eye.

from the surface the short-bridge position is energetically favored over the on-top position (see Fig. 1, right). Thus, according to the calculations the corrugation experienced by the Ne atom corresponds qualitatively to that of the clean surface electron density. This anticorrugation for HAS and "normal" corrugation for Ne atom scattering agrees with the experimental analysis of Rieder, Parschau, and Burg [8]. Using the data of Fig. 1 we estimate the corrugation amplitude along the [110] direction $\zeta_{10}^{\text{scatt}}$ at the particle energies used by Rieder, Parschau, and Burg [8] as the difference in the classical turning point over the on-top and the short-bridge positions. We obtain $\zeta_{10}^{\text{scatt}} \sim -0.06$ Å for He and $\zeta_{10}^{\text{scatt}} \sim +0.04$ Å for Ne. The comparison of these results with those derived in Ref. [8], $\zeta_{10}^{\text{scatt}} \sim -0.04$ Å for He and $\zeta_{10}^{\text{scatt}} = +0.089$ Å for Ne, shows that our results agree qualitatively, and even somehow quantitatively, with those of the experimental analysis. The quantitative disagreement may be due to the GGA but it may also be due to the fact that the measurements were not performed for a clean Rh(110) but a H-covered surface, since the adsorbates enabled the identification of the on-top and short-bridge positions. Thus, the experimental corrugation amplitude for the clean surface was extrapolated from the measured data by assuming that the H atoms give rise to a Gaussian contribution to the clean surface electron density [8].

Our DFT-GGA results reproduce not only the experimental corrugation but are also consistent with other features of the probe atoms potential energy. For example, the calculated potential well for a He atom is 13 meV (8 meV, if we include the zero-point vibration), which compares nicely with the value derived from selective adsorption measurements, 8.2 meV [15]. For Ne we find 18 meV (11 meV with the zero-point vibration). On the other hand, with the LDA exchange-correlation functional these quantities are in poor accordance with the experimental data: The turning points for He and Ne are systematically closer to the surface and the potential wells are too deep (27 meV for He and 61 meV for Ne). This is consistent with the well-known behavior that the LDA systematically gives rise to an overbinding in polyatomic systems.

In order to analyze the differences of He and Ne atom scattering we discuss the changes in the electron density of the surface and of the rare-gas atoms induced by the interaction. Figure 2 displays the difference between the self-consistent electron density of the interacting systems and the superposition of the densities of the clean Rh(110) surface and a He (Ne) atom. Three positions of the probe atoms are selected which correspond to a slightly attractive interaction (left panel), to the minimum of the interaction energy (middle panel), and to a position in the repulsive part close to the turning point assuming a kinetic energy of 150 meV (right panel). The figure shows clearly that both rare-gas atoms change the substrate surface electron density noticeably and that they are also significantly polarized themselves. Thus, it is obvious that it is not the unperturbed surface electron density which is probed by the scattering. Figure 2 shows that for the surface the main changes occur in the d shell. The leading effects for both probe atoms are a depletion of the $d_{3z^2-r^2}$ states and an increase of d_{xz} and d_{yz} occupation at the on-top position, and a depletion of the d_{xy} states and an increase of d_{xz} and d_{yz} at the short-bridge site (the x axis lies along the short-bridge and the y direction along the long-bridge direction). The largest effect happens for the d_{xz} electrons: Compared to the unperturbed surface the d_{xz} contribution is increased at the turning point by about 1%. This increase is partially due to the fact that the Pauli repulsion of the rare-gas atoms with the spilling out substrate s electrons is reduced by transferring s electron density into the d_{xz} band, which for Rh has a particularly high density of filled and empty states right at the Fermi level. We come back to the important role of the d_{xz} band below.

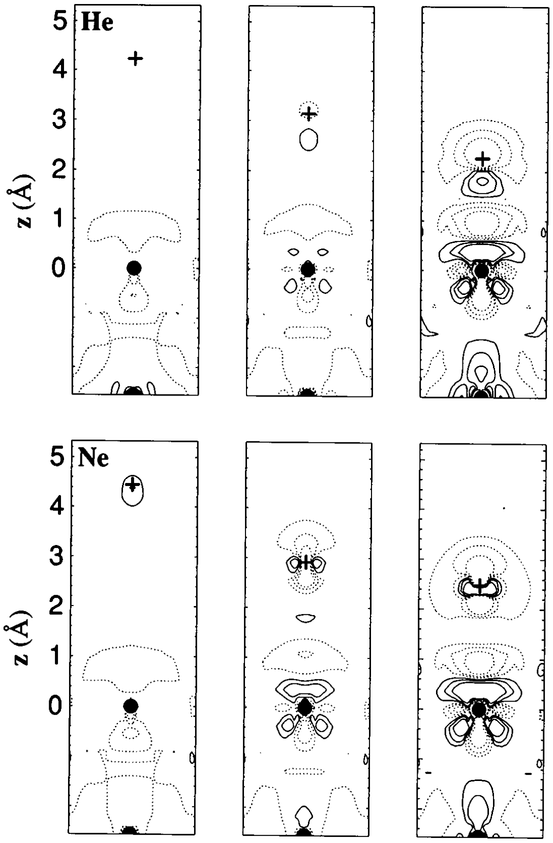

FIG. 2. Density difference plots (see text) for a He (top panels) and Ne (bottom panels) atom over the on-top position at three different distances from the topmost surface layer. The crosses indicate the positions of He (Ne) above the surface. The distances are from left to right: 4.2, 3.7, and 2.2 Å for He, and 4.4, 3.7, and 2.4 Å for Ne. Full lines note an increase and dashed lines a decrease in electron density; the values are ±0.5, ±1.0, ±2.0, and 10^{-3} bohr^{-3}.

While the reaction of the substrate is similar for both probe atoms, the polarization densities of the He and Ne atoms are clearly different as is the nature of their interaction with the surface. For He the interaction is mediated by the He $1s$ electrons and a polarization of the He atom away from spherical symmetry which implies a hybridization of $1s$ and $2p_z$ orbitals, clearly visible in Fig. 2 (top right panel). On the other hand, the interaction of Ne is dominated by the $2p$ electrons and the easier polarization of the Ne atom which requires a $2p \rightarrow 3s$ virtual transition. This contradicts the interpretation of Rieder [3] which was based on a strong involvement of the Ne $2s$ orbitals. As our calculations show (see also Fig. 2) at the on-top position He exhibits a reduction of the $1s$ density and an increase of the $2p$ density (mainly $2p_z$), a result similar to that found in studies of He physisorption at a jellium surface [16]. On the other hand, for Ne we find a reduction of the $2p_z$ occupation and a slightly stronger localization of the p_x, p_y states. At the short-bridge site the polarization of the He atom is similar to that at the on-top geometry, although weaker, but that of Ne is different; i.e., here the occupancy of all three $2p$ states is reduced.

The results are understood as follows. The reflection of He and Ne atoms happens rather close to the surface, at a distance slightly less than 3 Å, i.e., closer than the position of the physisorption well. Here the DFT-GGA approach describes the interaction with sufficient accuracy. The nature of the interaction is determined by electron polarizations and hybridizations. Thus, it is not the *total* electron density of the substrate surface which determines the interaction, but the electronic wave functions which lie close to the Fermi level. The He $1s$ orbital and the Ne $2p$ orbitals interact with these substrate states in a qualitatively different manner. For Rh(110) the states which are most important at the distance of reflection have d_{xz} character, because these substrate states give rise to a very flat band (thus high density) which crosses the Fermi level close to the Brillouin zone boundary. In other words, these orbitals change phase when going from one Rh atom to the next one along the short-bridge direction. Thus, the Bloch state is bonding in character, although, due to the weak overlap (reflected by the band's flatness) one may call it nonbonding.

At the short-bridge position these d_{xz} substrate states are thus symmetric with respect to mirror planes along xz and yz, and their electron density is low. A He atom, with its $1s$ state, feels a Pauli repulsion with these states and is efficiently reflected. On the other hand, for Ne the $2p_x$ and $2p_y$ states are antisymmetric. Thus, at the short-bridge position they will not interact with the d_{xz} band. Only the Ne $2p_z$ orbital has the same symmetry, but due to its narrow lobe and the low density of the substrate states at the short-bridge position, it can still approach the surface rather close before the Pauli repulsion becomes important.

The opposite situation occurs for the on-top geometry where the He $1s$ state is orthogonal to the substrate d_{xz} wave functions and can thus approach the surface quite close up to the point were the repulsion with the energetically lower lying $d_{3z^2-r^2}$ states dominates. Some of this repulsion is removed by transferring $d_{3z^2-r^2}$ electrons into the d_{xz} and d_{yz} bands. For Ne the repulsion at the on-top site is much stronger: The $2p_z$ electrons interact repulsively with the substrate $d_{3z^2-r^2}$ electrons, and the Ne $2p_x$ interact repulsively with the d_{xz} electrons. The Ne $2p_y$ orbital is found to be affected only slightly.

These results imply that the interaction between rare-gas atoms and a surface is significantly more complicated that hitherto assumed: It is not the total *electron density* of the surface which is probed, but the interaction is determined by the substrate surface *wave functions* at the Fermi level. Our explanation of the interaction mechanism has interesting consequences. For example, we expect similar "anticorrugation" effects for the d metals which belong to the same or a direct neighbor column of the periodic table, but for systems with a different band structure we expect different effects.

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