

Corrugating and Anticorrugating Static Interactions in Helium-Atom Scattering from Metal Surfaces

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We perform a density-functional-theory calculation of the static repulsive potential of He scattering off a noble and a simple metal surface. The classical turning point of He on Cu(111) is found to be closer to the metal when the adatom is at top than at bridge site (anticorrugating effect). The potential of He on Al(111) is instead corrugated. By comparing the results of the two systems, we conclude that the He-metal anticorrugating effect occurs when the kinetic energy difference for He at top and bridge sites is larger than the electrostatic one, and an induced localized dipole on He is formed.

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Elastic and inelastic scattering of He atoms from surfaces has proven a very powerful surface physics technique. Elastic scattering is a leading tool to determine the morphology of a surface both clean or covered with adsorbates, since it can resolve a corrugation as small as 0.01 Å [1]. Inelastic scattering offers impressively high resolution down to 90 μeV . This allows one to study the dispersion relation and the line shape of surface phonons, and the low frequency vibrations and diffusion of weakly bonded adsorbates [2]. However, the interpretation of the measured spectra is a difficult task because their features are complicated functions of both the static and dynamic potential, which describes the interaction of the projectile with the target, as well as the properties of the investigated surfaces. The He-surface interaction potential is characterized by a strongly repulsive part closer to the physical surface and a long range attractive dispersive contribution, which produces a shallow physisorption well. An appealing description of the repulsive interaction is based on an effective medium approach, which assumes that the He-surface potential is proportional to the unperturbed electron charge density protruding from the surface at the position of the adatom [3,4]. However, comparison with experimental elastic scattering spectra suggested early that He probes a surface corrugation that is weaker than the corresponding surface electron charge density [5,6].

More recently, elastic scattering measurements of He performed by Rieder *et al.* [7] on Rh(110) and Ni(110) showed unexpected features in full disagreement with the effective medium theory. In order to explain their data, these authors assumed that the corrugation profile seen by He is off phase with respect to the surface lattice atom positions, and that the classical turning point of the interaction potential is farther away at the short bridge position than at the top one, for a fixed kinetic energy of the impinging He atoms. This behavior is called the anticorrugating effect. A firm basis for these results

was provided by the *ab initio* density-functional-theory (DFT) calculations of Petersen *et al.* [8]. Very recent DFT investigations of Xe on metals showed that the low-coordination top sites are the preferred ones for adsorption [9].

On the other hand, the interaction of He with noble metals has been described only by phenomenological models thus far. Among such atom-metal systems, He on copper is particularly interesting because of the observed anomalies in the intensity of the inelastic scattering spectra [10], which challenge also recent *ab initio* computations of surface phonons [11]. To interpret such spectra for He-Cu(111), Benedek and co-workers [12,13] introduced pseudocharges at midpoints between nearest neighbor surface ions. More recently, following a previous work of He on Rh(111) [14], Bortolani and co-workers proposed an anticorrugated He-surface potential, which explains very satisfactorily the observed anomalies in the inelastic scattering spectra of He with the Cu(111) [15]. Therefore one wonders whether such an anticorrugated feature is only a dynamical one or is already set up in the static gas-surface interaction of He-Cu(111). This would be a surprising effect, since the explanation by Petersen *et al.* [8] is specific to a transition metal, i.e., Rh, and cannot be paralleled to Cu whose *d* band spectral weight is located below the Fermi level.

For all the above-mentioned reasons, it is essential first to determine the static interaction of He with Cu(111) in an *ab initio* framework. To accomplish this goal, we perform DFT calculations of such He-metal potential and confront them with those of a He-metal system whose dynamical properties can be accounted for by a corrugated potential, i.e., He-Al(111) [16]. We find that the interaction energy of He-Cu(111) is indeed, though weakly, anticorrugated, differently from that of He-Al(111) which is instead corrugated. We discuss both how the partitioning of the atom-metal energy into its kinetic, classical Coulomb and exchange-correlation

terms and the rearrangement of the electronic charge result in the anticorrugating behavior of He on Cu(111).

In the DFT calculations, we treat exchange and correlation in the Perdew-Burke-Ernzenhof generalized gradient approximation (GGA) [17]. The nonrelativistic Kohn-Sham wave functions and potentials are evaluated self-consistently within the all electron potential and the linearized augmented plane wave (LAPW) basis set framework using the full-potential LAPW (FLAPW) code [18]. The (111) surface of the metal is described by a five layer slab to which we add a (1×1) monolayer of He atoms on both sides. We have verified that the total energy is unaffected at very large atom-surface distances, if one shifts the He monolayer parallel to the surface. By moving this layer in plane and normal to the surface, we can evaluate the potential energy of one He atom coupled to the substrate. The LAPW wave function energy cutoff is $E_{\text{cutoff}} = 12.96$ Ry, and their maximum angular momentum in the muffin tin sphere is $l_{\text{max}} = 8$. The \mathbf{K}_{\parallel} integration is performed on an equally spaced mesh of 66 points in the whole surface Brillouin zone. The calculation is carried out with the metal ions clamped in their clean surface optimal configuration.

The main result of this Letter is shown in Fig. 1 which displays the He-metal potential $V(\mathbf{R}_{\parallel}, Z)$ as a function of the normal atom-surface coordinate Z , starting from the Cu(111) outermost layer, for the configuration with \mathbf{R}_{\parallel} at bridge (B) and top (T) sites. Especially from the magnified portion of this figure, we observe that the He-Cu(111) energy shows an anticorrugating behavior; i.e., at a fixed incoming atom kinetic energy, E_{kin} , He gets closer to the surface at T than at B positions. We note that the inclusion of some correlation in the GGA functional determines a

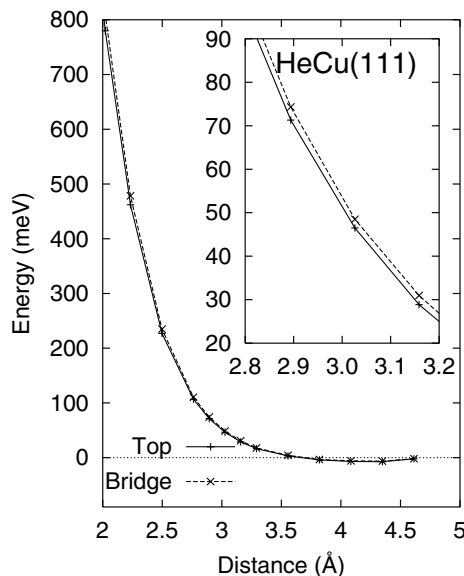


FIG. 1. Interaction potential energy for He approaching Cu(111) on-top (solid line) and bridge (dashed line) positions as a function of the distance from the surface layer. The inset shows a magnified portion for He energies used in experiments.

minimum of reasonable depth of the physisorption well of about 6–7 meV. Since the van der Waals interaction is not accounted correctly by the GGA, the region around the minimum is described only approximately, while the long range tail is incorrect. However, we are interested in the He-surface repulsive potential, where the GGA is expected to work well [9]. For an incoming He atom with a kinetic energy of experimental interest, $E_{\text{kin}} = 50$ meV, the results in Fig. 1 indicate that the corrugation of the atom-surface potential is very small indeed, about 0.01 \AA , in agreement with the assumption in Ref. [15]. In this case, the classical turning point occurs around $Z = 3.02 \text{ \AA}$ from the surface, and we note that the potential energy difference Δ_{BT} between B and T positions is about 1.7 meV. Such a weak effect is not influenced by the He-He lateral interaction. In fact, FLAPW calculations for an unsupported He monolayer show that the lateral interaction is 1 meV [19]. In any case, such an energy contribution should not change by varying the adatom position from top to bridge in the He-metal slab. We also observe that Δ_{BT} lies at the limit of precision of current DFT calculations. To show that our results are reliable, we recall first that all our calculations are fully convergent and optimized in the parameter choice with an energy accuracy of the order of the hundredth of meV. Second, since we are interested in an energy difference, computational inaccuracies, if any, should compensate. Consequently, the possible source of inexactness is to be attributed to the approximated GGA potential in the KS equation, which describes exchange-correlation effects plus a kinetic correction. However, the detailed analysis of the total energy, reported later, suggests that, in the delicate energy balance leading to the energy difference Δ_{BT} , exchange-correlation does not contribute in a relevant way.

We examine now the potential energy of He-Al(111), a system in which the dynamical gas-surface interaction is known to show no peculiar features and, hence, is assumed to be of corrugating nature. Indeed, the two curves in Fig. 2 with He at T and B positions display such a property. To be more accurate, at $Z = 3.02 \text{ \AA}$, we find that the corrugation of the potential is about 5 times larger than for He-Cu(111). The He energy at $Z = 3.02 \text{ \AA}$ is 76 meV at the T site, and that at the B site smaller by about 10 meV.

To get insight into the surprising results of He-Cu(111) in Fig. 1, we have examined the various contributions to the atom-surface potential. We have verified that the difference of the kinetic terms, with the He nucleus at B and T positions at the same distance from the ion surface plane, $\Delta K = K(B) - K(T)$, is positive. This suggests that the Pauli repulsion is weaker at the T site in agreement with the results in Ref. [9]. In other words, the kinetic energy displays an anticorrugating behavior. The Coulomb term, U , which includes the classical electron-electron, the electron-ion, and the ion-ion electrostatic interactions, is corrugated. We note that $|\Delta K| > |\Delta U|$.

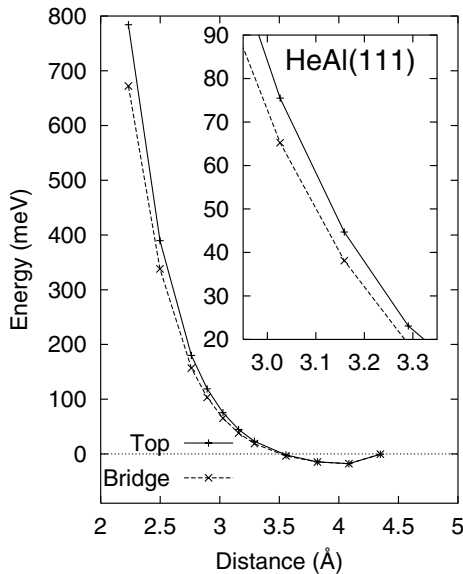


FIG. 2. The same as Fig. 1 for He-Al(111).

The smaller exchange-correlation term difference with He at *B* and *T* positions ΔE_{xc} , though of corrugating character, cannot correct the overall anticorrugating behavior in Fig. 1. We have also separated the corrugated potential of He-Al(111) in the same way. We have verified that $|\Delta K| < |\Delta U|$, opposite to that for He-Cu(111). Since also for this system ΔE_{xc} does not affect the qualitative trend of the atom-surface potential curve, we obtain the expected corrugated potential.

It is also interesting to analyze the charge displacements (total electronic charge of the interacting system minus that of the adatom layer and of the clean metal), say $\Delta\rho(\mathbf{r})$. For He far away from the metal $\Delta\rho$ shows a weak induced dipole localized on the adatom for both systems, with its negative lobe pointing towards the metal. We investigate $\Delta\rho$ at $Z = 3.02 \text{ \AA}$, which corresponds to a turning point of experimental interest, in more detail in Fig. 3. We observe that an induced dipole is still present on He interacting with Cu(111). For He-Al(111), $\Delta\rho$ around He looks more spherical, and a net dipole on the adatom is much less evident. At closer distances, the mixing between atom and metal charge is much larger for both systems, and we have verified that a net induced dipole on the adatom cannot be identified for He-Cu(111) also. Note that, while the upper panels of Fig. 3 resemble those of He-Rh(110), the lower ones do not show an appreciable induced dipole on He similarly to those of Ne-Rh(110) in Ref. [8]. On this transition metal, the gas-surface interaction was proven to be anticorrugated for He and corrugated for Ne. From our qualitative analysis of Fig. 3, we can add that the anticorrugating behavior is related to the existence of an induced dipole localized on the adatom, as for He-Cu(111).

To account for the results in Figs. 1 and 2, we have also studied the local density of states of the systems integrated in the metal muffin tins. Since the electronic states

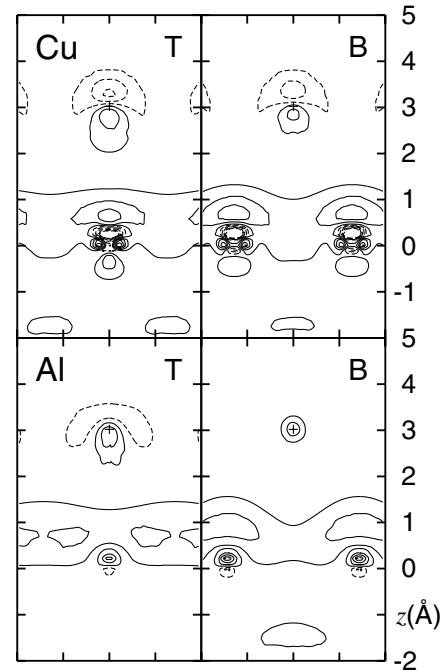


FIG. 3. Contour plots of charge displacements (see text) for He on Cu(111) (upper panels) and He on Al(111) (lower panels) for top (left panels) and bridge (right panels) positions at atom-surface distance $Z = 3.02 \text{ \AA}$. Full lines denote an increase and dashed lines denote a decrease in electron charge; the values are equidistant separated by $\pm 2 \times 10^{-4}$ a.u.

of the metal about the Fermi energy ε_F interact more strongly with the He orbital, we focus on their behavior. For He-Cu(111), we have checked that at ε_F the density of *d* and of *s* - *p* states are comparable at 5% [20]. This indicates that there is a noticeable hybridization between them. So, differently from He-Rh(110) in which a large part of the *d* band lies at the Fermi level, the anticorrugating behavior of He-Cu(111) cannot be mainly explained by the *d* metal orbital properties [8].

We note that a qualitatively different behavior when He is at the *T* or at the *B* site is shown by the charge displacement, $\Delta\rho_F$, around the Fermi level, namely, calculated in an energy window large about 30 meV up to ε_F . This difference is particularly evident in a 3D plot. So in Fig. 4 we present the isosurface of $\Delta\rho_F = \pm 10^{-4}$ a.u. for He located at *T* (upper panel) and *B* (lower panel) sites at $Z = 3.02 \text{ \AA}$ from Cu(111). When the adatom lies at the *T* position, there is memory of the metal *d* states. On the other hand, for He at the *B* site, some electronic charge only piles between the metal ions while that around the Cu ions is depleted. This suggests an overall more repulsive behavior of the He-metal coupling at the *B* site, in agreement with the anticorrugated potential in Fig. 1. If we widen the energy window, the neat difference between $\Delta\rho_F$ in Fig. 4 vanishes rapidly. For He on Al(111) in the same energy range, we have checked that $\Delta\rho_F$ is qualitatively the same for the adatom at *T* and *B* sites. We summarize this discussion by saying that the features in

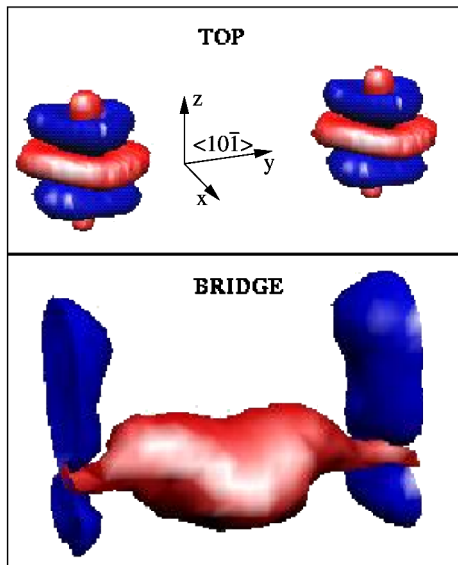


FIG. 4 (color online). 3D plot of the charge displacement of the first ion layer at the Fermi level (see text) for He on Cu(111) at top (upper panel) and bridge (lower panel) positions at atom-surface distance $Z = 3.02 \text{ \AA}$. Light (red) denotes an increase and dark (blue) a decrease in electron densities. The values of the isosurface charge are $\pm 10^{-4}$ a.u.

Fig. 4 are a signature of the anticorrugating behavior of He-Cu(111).

On the basis of the results of Ref. [9], which mainly concentrate on the attractive potential, and of our work, which instead is focused on the repulsive He-surface potential in the region of experimental interest, the following picture emerges for a noble atom-surface interaction. At large atom-surface distances down to the equilibrium adsorption minimum, the interaction, mainly of van der Waals type, is attractive, and the potential displays an anticorrugating behavior. Consequently, binding occurs at a T site. For He-metal distances much closer to the surface than those experienced in atom-surface scattering, Pauli repulsion dominates the atom-metal interaction, which has to be of corrugating character. This implies that the atom-surface potential transforms from an anticorrugated to a corrugated one. From our results in Fig. 2, we infer that such a potential crossing lies near zero energy for He-Al(111), a region in which the van der Waals interaction, not treated correctly in GGA, may be important. On the other hand, for He-Cu(111) such crossing happens for adatom kinetic energy larger than those of experimental interest. In this case, we have calculated that the atom-metal potential becomes corrugated for He kinetic energy about 1.7 eV at 1.71 \AA from the Cu surface layer.

In conclusion, in this Letter we have shown by DFT calculations that the repulsive potential of the static interaction of the He with Cu(111) is weakly anticorrugated. There is no simple way to account for such an effect. In

fact s , p , and d hybridization of the Cu electrons at the Fermi level prevents an explanation solely based on a clear assignment of orbital modifications due to the gas-surface interaction. However, following the analysis in this Letter, we can conclude that the anticorrugating behavior is a subtle one occurring within a specific range of the repulsive atom-surface potential probed experimentally by He-metal scattering, when (i) the kinetic energy term difference between He at top and bridge positions is larger than the electrostatic one, and (ii) an induced localized dipole on He is formed. We have verified that both effects are present for He-Cu(111).

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