

Interaction of helium with a metal surface

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It is shown that the binding of a helium atom to a metal surface is well described using the local-density approximation to treat exchange and correlation effects. The self-consistent solution is in turn well approximated by the effective-medium theory. In this theory the interaction is dominated by a repulsive term proportional to the surface electron density.

In the present paper we consider the interaction of a helium atom with a metal surface. We show that a fully self-consistent calculation of the helium-surface interaction energy within the local-density approximation¹ gives a physisorption well depth comparable to usual experimentally determined values. We further show that the self-consistent solution is well approximated using the much simpler effective-medium theory, which gives the helium-surface interaction from a knowledge of the surface electron density only.

There is a growing interest in helium diffraction from surfaces as an experimental technique for determining surface geometrical structures.² For the technique to be quantitative, it is crucial to be able to calculate the helium scattering potential from a given surface geometry. The diffraction intensities can then be calculated and compared with experiment. By continuing to vary the surface geometry until the best agreement with experiment is obtained, the atomic position of the surface atoms can be determined. In this connection it is important to know whether the local-density approximation is adequate to describe the helium-surface interaction, and whether the effective-medium theory gives an adequate approximation to this interaction. It obviously means an enormous simplification of the structure determination procedure if a full solution of the helium-surface interaction is not necessary for each geometry.

In the present calculations, the jellium model is used for the surface. This means that the metal ion cores are smeared out into a positive background over a half space. The metal is described by the average density n_0 or equivalently by r_s given by $\frac{4}{3}\pi r_s^3 = n_0^{-1}$. We have chosen $r_s = 3$ bohr, typical of

of the noble metals. At the distances far from the surface that are of interest here this should be a reasonable model to describe the interaction averaged parallel to the surface. Obviously the corrugation of the potential due to the atomic structure of the surface is not described. The calculational method employed is that of Lang and Williams.³ The same method has been applied successfully to the description of other rare-gas—surface systems.⁴

The results for the interaction energy as a function of distance from the surface are shown in Fig. 1. A shallow physisorption minimum with a depth around 7 meV is found, followed at smaller separations by a very steep repulsive wall. The well depth is typical of measured helium physisorption energies.⁵ This does not, of course, prove that the local-density approximation is valid here, but we note that similar good agreement between local-density results and experiment is found for the physisorption energy and dipole moment for other rare-gas adsorbates.⁴

Asymptotically, the helium-surface interaction has the van der Waals form⁶ $-C(z - z_{im})^{-3}$, where the (dynamical) image plane position z_{im} is $\lesssim 1$ bohr outside the positive background. This cannot be described in the local-density approximation, where the exchange-correlation hole is centered at the electron in question.⁷ The van der Waals interaction involves an average of the interaction with the nonlocal correlation hole (the image charge) over the extent of the rare-gas valence-electron orbit. Following Lang,⁴ for an adsorbed rare-gas atom at the equilibrium position, the inner part of the orbit is so close to the image plane that the nonlocal image interaction becomes doubtful. On the other hand, the local-density approximation usually works well close

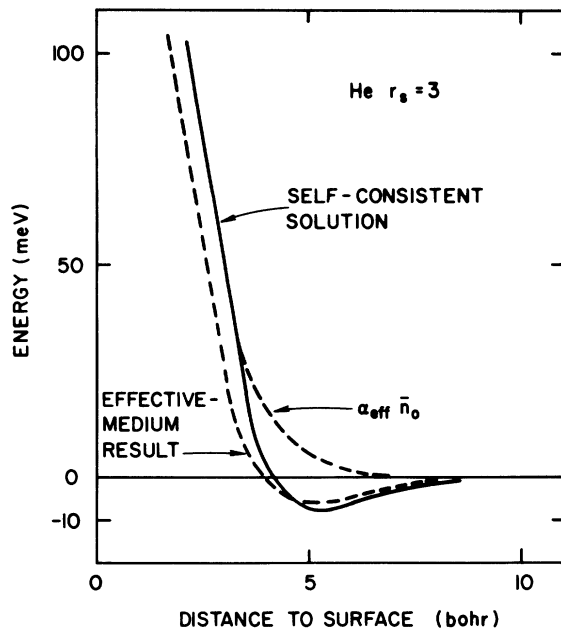


FIG. 1. Interaction energy of a helium atom with a jellium surface ($r_s=3$), calculated self-consistently using the local-density approximation for exchange and correlation. Comparison is made with results of the effective-medium theory. Distance is measured relative to the positive-background edge.

to the metal. On the outer part of the orbit the non-local image interaction will be most appropriate, but this part is much less important for the total interaction energy. This is expected to be the reason why the local-density approximation gives a reasonable description of rare-gas adsorption. These arguments of course work best for the heavier rare gases, which have the largest valence-electron orbit radii. The present results tend to indicate the validity of the arguments for physisorbed helium, too, and it is clear from Fig. 1 that for helium approaching the surface at energies between 20 and 150 meV (the usual energy range in a helium diffraction experiment) the classical turning point is so close to the surface that the local-density approach should be well justified in describing the scattering potential. On the other hand, the outer part of the physisorption well, which should approach the $-C(z-z_{im})^{-3}$ form asymptotically, has instead an exponential form in the local-density approximation. The uppermost vibrational levels, which have a considerable wave-function amplitude in this asymptotic region, are thus not expected to be well described here. This would also be true for any other property involving the outer part of the physisorption well in a central way.

The calculated charge density is shown in Fig. 2.

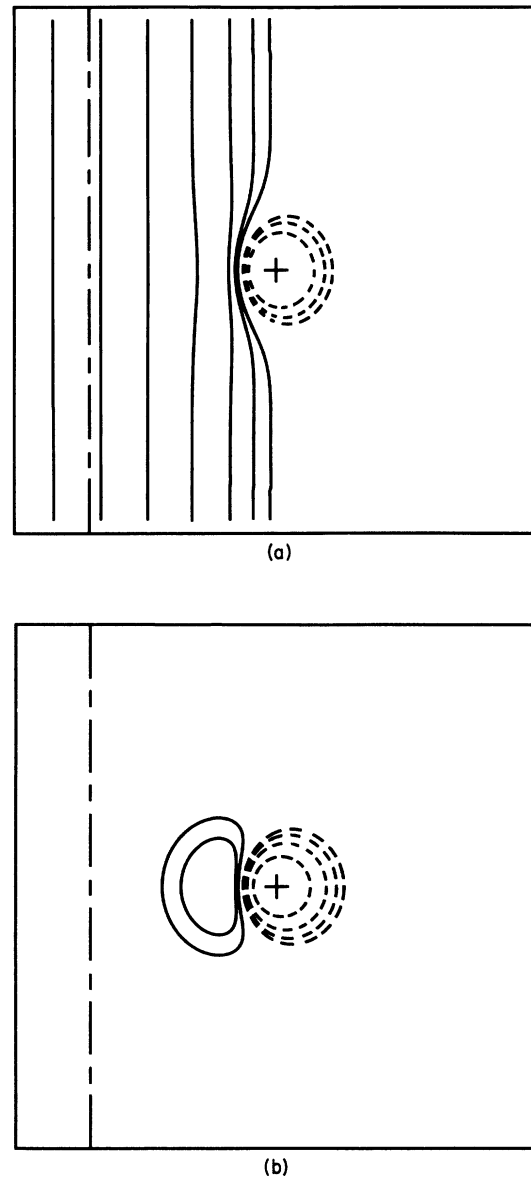


FIG. 2. Charge-density contours for a He atom at its equilibrium distance (5 bohr) from a jellium substrate ($r_s=3$). Maps are plotted in the plane normal to the surface containing the adatom nucleus (+). Metal is to the left; dash-dotted vertical line is positive-background edge. Contours in the immediate vicinity of the nucleus are deleted for clarity. Contour values shown are 0.0065, 0.003, 0.001, ± 0.0003 , ± 0.0001 , ± 0.00005 , and ± 0.00003 electron/bohr³ (solid line is positive, dashed line is negative). (a) Total charge density of He plus metal, minus that of the free He atom. This map shows how the He atom acts as a repulsive pseudopotential. (The binding arises from exchange-correlation effects.) (b) Charge density in the 1s state of the adsorbed He atom, minus that of the free atom. This shows the polarization of the 1s charge due to adsorption.

It is seen how the helium atom primarily acts as a repulsive pseudopotential pushing away the metal electrons.⁸ (The binding arises from exchange-correlation effects.) There is, however, a small net polarization which is primarily due to the polarization of the helium 1s bound state.⁹

Zaremba and Kohn⁶ have used the asymptotic van der Waals interaction to describe the surface-atom correlation effects for adsorbed rare gases, treating the repulsive part of the interaction in the Hartree-Fock approximation. Qualitatively the results are similar to ours, but typically the binding energies are smaller and the equilibrium distances larger.¹⁰

Our results also do not differ sharply from those obtained by Van Himbergen and Silbey¹¹ using the Gordon-Kim method.¹² The minimum for $r_s=3$ in this method (using the same bare-surface electron density as that employed here) is only about half as deep as ours, and the potential rises faster than ours with decreasing distance. This is probably because the method does not include the rearrangement of the metal electrons due to the repulsion from the 1s core that is evident from Fig. 2.

We now turn to the effective-medium estimate¹³⁻¹⁶ of the helium-surface interaction energy $V(\vec{r})$. The basic idea is to approximate the influence of the surface electrons on the helium atom by the influence of a homogeneous electron gas of a density equal to the surface electron density $n_0(\vec{r})$ at the atom position \vec{r} . The embedding energy of a helium atom in a homogeneous electron gas can be calculated once and for all. It rises linearly with electron gas density. This leads to a potential

$$V(\vec{r}) = \alpha n_0(\vec{r}). \quad (1)$$

Using helium in a homogeneous electron gas as the starting point, this simple result can be refined as shown in Ref. 16. In the region close to the atom

where the atomic potential dominates, the deviation of the surface electron density from homogeneity is treated in first-order perturbation theory. Similarly, in the region outside, the surface potential dominates and the influence of the atom is treated to first order. This gives a helium potential

$$V(\vec{r}) = \alpha_{\text{eff}} \bar{n}_0(\vec{r}) + \delta \Delta \sum_i \epsilon_i. \quad (2)$$

The new effective slope α_{eff} is given by

$$\alpha_{\text{eff}} = \alpha - \int_a \phi_a(\vec{r}) d\vec{r}, \quad (3)$$

where ϕ_a is the helium-atom electrostatic potential (the free-atom potential can be used here¹⁶), and the integration is over the atomic region a only. In Eq. (2) the surface electron density $n_0(\vec{r})$ is replaced by a density $\bar{n}_0(\vec{r})$ averaged over ϕ_a ,¹⁵

$$\bar{n}_0(\vec{r}) = \frac{\int n_0(\vec{r}') \phi_a(|\vec{r}' - \vec{r}|) d\vec{r}'}{\int \phi_a(\vec{r}') d\vec{r}'}. \quad (4)$$

In the local-density approximation, a value of $\alpha = 305 \text{ eV bohr}^3$ is found at the low electron densities of interest here. At higher densities a slightly lower value of $\alpha = 275 \text{ eV bohr}^3$ is found. The value of $\alpha_{\text{at}} = \int_a \phi_a(\vec{r}) d\vec{r}$ depends on the choice of the radius R_{cut} of the atomic region a . The distinction between region a and the rest is introduced to take care of the problems arising when the atom density starts overlapping the region close to the substrate cores. For jellium and far outside any metal surface this is not really important as illustrated by the fact that $\alpha_{\text{eff}} \bar{n}_0$ does not change with R_{cut} . This is simply because α_{eff} decreases and \bar{n}_0 increases simultaneously with increasing R_{cut} . For $R_{\text{cut}} = 2.5 \text{ bohr}$, which is the value used for helium in bulk metals, $\alpha_{\text{at}} = 129 \text{ eV bohr}^3$ and $\alpha_{\text{eff}} = 176 \text{ eV bohr}^3$. For $R_{\text{cut}} = \infty$, $\alpha_{\text{at}} = 145 \text{ eV bohr}^3$ and $\alpha_{\text{eff}} = 160 \text{ eV bohr}^3$.

The last term in Eq. (2),

$$\delta \Delta \sum_i \epsilon_i = \sum_i \epsilon_i(\text{He} + \text{surface}) - \sum_i \epsilon_i(\text{surface}) - \left[\sum_i \epsilon_i(\text{He} + \text{homogeneous electron gas}) - \sum_i \epsilon_i(\text{homogeneous electron gas}) \right], \quad (5)$$

involves the difference in the sum of the one-electron energies at the surface and in the homogeneous electron gas. This term describes the difference between the hybridization of the atomic levels with the real surface levels and with those of the homogeneous electron gas. For helium it is very small because the 1s level is far away in energy from any of the metal states. At distances far from the surface where the first term in Eq. (2) is small it

may, however, be important. In the Appendix we show how it can be approximated by the extra exchange-correlation energy of the atom at the surface relative to that in the homogeneous electron gas:

$$\delta \Delta \sum_i \epsilon_i = E_{\text{xc}}[n_0 + n_a] - E_{\text{xc}}[n_0] - (E_{\text{xc}}[\bar{n}_0 + n_a] - E_{\text{xc}}[\bar{n}_0]). \quad (6)$$

Here we have assumed that the atomic helium charge density n_a is the same in the homogeneous electron gas, at the surface, and in vacuum.

In Fig. 1, the effective-medium estimate is also given. It is seen to approximate the full solution quite well both insofar as the depth of the physisorption well and the repulsive part of the potential are concerned. The first term in Eq. (2) giving a potential basically proportional to the surface charge density is also shown. It does very well for the repulsive part of the potential (the fact that it is right on top of the full solution at energies higher than 30 meV is only a coincidence). The physisorption minimum does, however, only appear if the (small) additional exchange-correlation energy due to the inhomogeneity of the surface is included. Note that this correction does not increase significantly for distances closer to the surface.

The polarization perpendicular to the surface of the helium 1s state is not included in the first-order effective-medium theory. The fact that the minimum is reproduced anyway suggests that this polarization is not important for the binding. We have checked this by freezing the helium 1s level in the full self-consistent calculation. This only decreased the binding energy by ~ 1 meV. The pushing away of metal electrons seen in Fig. 2 is to a large extent included in the effective-medium theory as a spherical average. Also the spherically symmetric part of the helium 1s polarization (the radial expansion or contraction of the 1s charge) is included.

In conclusion, the local-density approximation seems to give a reasonable description of the helium-surface interaction, and the effective-medium estimate is seen to be a good approximation to the full local-density calculation. This provides support for the effective-medium estimate, which is obviously much simpler than a full calculation at a real surface.¹⁷

APPENDIX

In this appendix we show how the one-electron energy difference Eq. (5) can be approximated by the exchange-correlation energy difference Eq. (6). We start by rewriting Eq. (6) using the assumptions behind the derivation of Eq. (2) (see Ref. 16)—that is, that $\delta n_0(\vec{r}) = n_0(\vec{r}) - \bar{n}_0$ is small in the atomic region a , and that the atom-induced electron density n_a is small in the region b outside. Furthermore, we assume that for the purpose of evaluating Eq. (6), n_a is the same at the surface, in the homogeneous electron gas, and in vacuum. This is a very good approximation for a closed-shell atom like helium because $\delta \Delta E_{xc}$ is a very small correction. Evaluating the total E_{xc} (or the total energy) in this manner is not a good approximation (cf. Fig. 2).

In the local-density approximation, we can split up the exchange-correlation energy into the part coming from the electrons in a (E_{xc}^a) and b (E_{xc}^b). We can then write Eq. (6) (here and throughout a subscript 0 denotes the system without the helium atom and a bar denotes the homogeneous electron gas) as

$$\begin{aligned} \delta \Delta E_{xc} = & (E_{xc}^a[n_0 + n_a] - E_{xc}^a[\bar{n}_0 + n_a]) \\ & - (E_{xc}^a[n_0] - E_{xc}^a[\bar{n}_0]) \\ & + (E_{xc}^b[n_0 + n_a] - E_{xc}^b[\bar{n}_0 + n_a]) \\ & - (E_{xc}^b[n_0] - E_{xc}^b[\bar{n}_0]). \end{aligned}$$

Using the definition of the exchange-correlation potential

$$V_{xc}(\vec{r}) = \frac{\delta E_{xc}[n]}{\delta n(\vec{r})},$$

and that $\delta n_0 = n_0 - \bar{n}_0$ is small in a and n_a is small in b , this gives

$$\delta \Delta E_{xc} = \int_a \{ V_{xc}[\bar{n}_0 + n_a(\vec{r})] - V_{xc}[\bar{n}_0] \} [n_0(\vec{r}) - \bar{n}_0] d\vec{r} + \int_b \{ V_{xc}[n_0(\vec{r})] - V_{xc}[\bar{n}_0] \} n_a(\vec{r}) d\vec{r}. \quad (\text{A1})$$

Now return to the one-electron energy difference Eq. (5). For the purpose of evaluating this small energy difference we can assume that the helium and host wave functions are changed similarly when the atom is outside the surface and when it is in the homogeneous electron gas. This is well justified since hybridization of the helium 1s state with the surface or homogeneous electron-gas states will be very small, both because the overlap is small at the distances outside the surface (or at the low corresponding homogeneous electron gas densities) of interest here and because the 1s state is far away in energy from any of the surface or homogeneous electron-gas states. The kinetic energy terms in the one-electron energy sums of Eq. (5) will then cancel out and we have

$$\begin{aligned} \delta \Delta \sum_i \epsilon_i = & \left[\int_a [n_0(\vec{r}) + n_a(\vec{r})] V_{\text{eff}}(\vec{r}) d\vec{r} - \int_a n_0(\vec{r}) V_{\text{eff}}^0(\vec{r}) d\vec{r} \right] - \left[\int_a [\bar{n}_0 + n_a(\vec{r})] \bar{V}_{\text{eff}}(\vec{r}) d\vec{r} - \int_a \bar{n}_0 \bar{V}_{\text{eff}}^0(\vec{r}) d\vec{r} \right] \\ & + \left[\int_b [n_0(\vec{r}) + n_a(\vec{r})] V_{\text{eff}}(\vec{r}) d\vec{r} - \int_b n_0(\vec{r}) V_{\text{eff}}^0(\vec{r}) d\vec{r} \right] - \left[\int_b [\bar{n}_0 + n_a(\vec{r})] \bar{V}_{\text{eff}}(\vec{r}) d\vec{r} - \int_b \bar{n}_0 \bar{V}_{\text{eff}}^0(\vec{r}) d\vec{r} \right]. \end{aligned}$$

Here $V_{\text{eff}}(\vec{r}) = \phi(\vec{r}) + V_{\text{xc}}(\vec{r})$ is the sum of the electrostatic (Hartree) potential ϕ and the exchange-correlation potential V_{xc} . In Ref. 16 it is discussed how the assumptions behind Eq. (2) (δn_0 small in a and n_a small in b) are equivalent to assuming $V_{\text{eff}}(\vec{r}) = \bar{V}_{\text{eff}}(\vec{r})$ in region a , and $V_{\text{eff}}(\vec{r}) = V_{\text{eff}}^0(\vec{r})$ in region b . This means that

$$\delta\Delta \sum_i \epsilon_i = \int_a [n_0(\vec{r}) - \bar{n}_0][\bar{V}_{\text{eff}}(\vec{r}) - \bar{V}_{\text{eff}}^0(\vec{r})] d\vec{r} + \int_b n_a(\vec{r})[V_{\text{eff}}^0(\vec{r}) - \bar{V}_{\text{eff}}^0] d\vec{r}. \quad (\text{A2})$$

The average density \bar{n}_0 is defined by^{15,16}

$$\int_a [n_0(\vec{r}) - \bar{n}_0][\bar{\phi}(\vec{r}) - \bar{\phi}^0] d\vec{r} = 0. \quad (\text{A3})$$

This means that we can replace V_{eff} by V_{xc} in the first integral in Eq. (A2). Furthermore, at the distances outside the surface of relevance to the He + surface problem, the surface electrostatic potential ϕ^0 is negligible. This means that V_{eff} can also be replaced by V_{xc} in the second integral. The right-hand sides of Eqs. (A2) and (A1) are thus the same and

$$\delta\Delta \sum_i \epsilon_i = \delta\Delta E_{\text{xc}}.$$

We note that this term is very small, 10–20 meV at all distances from the surface, and it therefore is not important, for example, for helium atoms dissolved inside a metal or for atoms making chemical bonds with the surface, since in these cases all other energies in the problem will be much larger. The \bar{n}_0 dependence of Eq. (6) does give rise to a very slight R_{cut} dependence of $\delta\Delta \sum_i \epsilon_i$. Changing R_{cut} from ∞ to 2.5 bohr increases $\delta\Delta \sum_i \epsilon_i \sim 1$ meV. In Fig. 1, $R_{\text{cut}} = \infty$ is used.

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¹⁰There can be several reasons why these results differ

from ours, in addition to the differences in the treatment of the exchange-correlation effects. First of all, the approach of Zaremba and Kohn does not treat the attractive and repulsive contributions to the energy on the same footing. This may cause some inaccuracy, since the small physisorption energy is a difference between two larger numbers. Also, these authors assume that the helium 1s level is nonpolarizable and that the higher-lying helium levels (2s and 2p) do not interact with the metal conduction-band states.

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