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Author(s): Manninen, M. & Nørskov, J. K. & Puska, Martti J. & Umrigar, Cyrus

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Repulsive interaction of the helium atom with a metal surface

M. Manninen

Research Institute for Theoretical Physics, University of Helsinki,
SF-00170 Helsinki 17, Finland

J. K. Nørskov

Nordisk Institut for Teoretisk Atomfysik (NORDITA), Blegdamsvej 17,
DK-2100 Copenhagen Ø, Denmark

M. J. Puska

Laboratory of Physics, Helsinki University of Technology,
SF-02150 Espoo 15, Finland

Cyrus Umrigar

Laboratory of Atomic and Solid State Physics, Cornell University,
Ithaca, New York 14853

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The repulsive part of the helium scattering potential at a surface is approximately proportional to the surface electron density. The proportionality coefficient is shown to be a well-defined quantity, which can be related to the electron-helium scattering length. The spread in the values of the proportionality constant suggested in the literature is shown to be due to different definitions of the coefficient or due to inadequate calculational methods. The value calculated using the local density approximation with a self-interaction correction is in very good agreement with the electron-scattering-length measurements.

Using the effective-medium theory,[1,2] Esbjerg and Nørskov[3] showed that the leading repulsive term in the helium scattering potential from any electronic system is proportional to the local unperturbed electron density $n_0(\vec{r})$ of the host at the helium site:

$$V_R(\vec{r}) = \alpha n_0(\vec{r}) \ . \tag{1}$$

A more refined treatment[4] gives

$$V_R(\vec{r}) = \alpha_{\text{eff}} \bar{n}_0(\vec{r}) \ , \tag{2}$$

where $\bar{n}_0$ is the average of $n_0(\vec{r})$ over the electrostatic potential $\Phi_{\text{He}}(\vec{r})$ of the helium atom, and

$$\alpha_{\text{eff}} = \alpha - \int d^3r \, \Phi_{\text{He}}(\vec{r}) \tag{3}$$

is a new effective proportionality constant. Unfortunately, the value of α published in the original paper[3] was wrong due to numerical errors. This together with the occurrence of two constants α and α_{eff} and other approaches[5,6] for determining the coefficient has resulted in several values for α and has given an impression that theoretically α is not well defined or that the correct value is not known. This confusion is also increased by the fact that, keeping α as a free parameter, good agreement with the experimental results has been achieved for helium diffraction from metal surfaces.[7]

The purpose of the present Rapid Communication is to comment upon the differences between various values of the proportionality constant. We point out that α_{eff} is related to the scattering length for slow electrons on atomic helium. It can thus be determined experimentally. The α_{eff} used in the effective-medium theory is in good agreement with the experimentally determined value.

The density functional theory[8] expresses the ground-state energy as a functional of the total electron density of the system. In the effective-medium theory one goes a step

further and shows that the embedding energy of the helium atom in any electronic surrounding can be calculated as a functional of the unperturbed electron density of the host. Formally, one can always separate a local term from this functional and write

$$V_R(\vec{r}) = \Delta E(n_0(\vec{r})) + \Delta E_{\text{nl}} \ , \tag{4}$$

where $\Delta E(n_0)$ is the embedding energy of helium in a homogeneous electron gas of density n_0, $n_0(\vec{r})$ is the unperturbed surface electron density, and ΔE_{nl} includes all nonlocal terms. $\Delta E(n_0)$ is calculated by embedding the helium atom in a homogeneous electron gas with a compensating positive background charge.[9] In the low-density limit this gives $\Delta E(n)$ proportional to the density and thereby Eq. (1). We have calculated $\Delta E(n)$ for low electron densities using the local density approximation[10] (LDA) for the exchange and correlation energies with and without a self-interaction correction[11] (SIC). The corresponding slopes α are given in Table I.

In the region outside a metal surface sampled by a low-energy (< 500 meV) helium atom there are no positive charges. Also, the surface electron density has non-negligible gradients. In the refined treatment, Eqs. (2) and (3), the former problem is taken into account by subtracting from Eq. (1) the electrostatic interaction of the helium atom with the homogeneous background [Eq. (3)]. This results in the new proportionality constant α_{eff} in Eq. (2), which is also given in Table I.[15] The use of an averaged surface electron density $\bar{n}_0(\vec{r})$ in Eq. (2) is the lowest-order inclusion of nonlocality. Outside a metal surface we typically find $\bar{n}_0(\vec{r}) \simeq 1.3 \ n_0(\vec{r})$ fairly independent of $\vec{r}$ for the range of positions of relevance for low-energy helium scattering. This means that we can define a third proportionality constant

$$\bar{\alpha}_{\text{eff}} = [\bar{n}_0(\vec{r})/n_0(\vec{r})]\alpha_{\text{eff}}$$

TABLE I. Proportionality constants for the helium-metal scattering potential.

	α (eV a_0^3)	α_{eff} (eV a_0^3)	$\bar{\alpha}_{\text{eff}}$ (eV a_0^3)
Effective-medium approach			
LDA	305	160	208
LDA-SIC	329	196	255
Harris-Liebsch approach			
First-order (Ref. 5)		517	1000
Second-order (Ref. 12)			~ 500
Scattering length			
Calculation (Ref. 13)		203	
Experimental (Ref. 14)		191, . . . , 203	

so that

$$V_R(\vec{r}) = \bar{\alpha}_{\text{eff}} n_0(\vec{r}) \ . \tag{5}$$

$\bar{\alpha}_{\text{eff}}$ is also included in Table I. It should be stressed that $\bar{\alpha}_{\text{eff}}/\alpha_{\text{eff}}$ depends on the kind of system considered and that $\bar{\alpha}_{\text{eff}}$ in Table I is only applicable for helium-metal surface interactions over a limited range of distances.

Following Zaremba and Kohn,[16] Harris and Liebsch[5] have shown that, to first order in the overlap between the surface and helium states, the repulsive part of the helium-surface potential can be written

$$V_R(\vec{r}) = \int_{-\infty}^{\epsilon_F} d\epsilon\, g(\epsilon) n_0(\epsilon, \vec{r}) \ , \tag{6}$$

where $g(\epsilon)$ is a universal function of energy only, and $n_0(\epsilon, \vec{r})$ is the local density-of-states function of the bare surface. Formally Eq. (6) can be written

$$V_R(\vec{r}) = g(\bar{\epsilon}) n_0(\vec{r}) \ , $$

where $\bar{\epsilon}$ in principle depends on $\vec{r}$. We have made explicit calculations within the local density approximation, using the linear augmented plane-wave method for a five-layer Ni(110) slab,[17] which show that in reality $\bar{\epsilon}$ is basically constant for the range of distance of interest here [$n_0(\epsilon, \vec{r})$ is dominated by energies close to the Fermi energy]. This has also been argued by Harris and Liebsch[5] based on jellium-surface calculations. The Harris-Liebsch value for $\bar{\alpha}_{\text{eff}}$ is thus $g(\bar{\epsilon})$ and again $\bar{\alpha}_{\text{eff}}$ will depend on the kind of system studied. For a low-density homogeneous electron gas the Harris-Liebsch approach gives $\alpha_{\text{eff}} = g(0)$. The Harris-Liebsch values for $\bar{\alpha}_{\text{eff}}$ and α_{eff} calculated within the Hartree-Fock approximation are shown in Table I. In the table we include both the originally published values (first order in the helium pseudopotential) and the most recent ones by Nordlander and Harris.[12] The latter are calculated to second order in the helium pseudopotential and the energy argument in $g(\epsilon)$ is replaced by $\epsilon - v_0(\vec{r})$, where $v_0(\vec{r})$ is the host one-electron potential at the helium position.[12] The Harris-Liebsch approach is not designed for the problem of helium in a uniform electron gas, and the perturbation theory which involves a polarizability does not converge well[18] as the electron gas density and bandwidth go to zero. We therefore have not included any second-order value for α_{eff} in Table I (treated in all orders of the perturbation theory the Harris-Liebsch approach would lead to the exact value extracted from the scattering length; see below). It is

seen how the value $\bar{\alpha}_{\text{eff}}$ differs dramatically from the effective medium value, which is rather independent of the approximation used for the treatment of exchange and correlation effects. Most of this difference is found again in α_{eff}.

Now we want to point out that there is a more direct way of determining the coefficient α_{eff}. In the extreme low-density limit the interaction of electrons with a helium atom can be calculated from scattering theory. For N electrons in a volume V (without the positive background) the embedding of a helium atom increases the total energy of the electrons by

$$\Delta E = \frac{4\pi\hbar^2}{2m} a_s \frac{N}{V} \ , \tag{7}$$

where a_s is the scattering length. A comparison with Eq. (1) gives directly

$$\alpha_{\text{eff}} = \frac{2\pi\hbar^2}{m} a_s \ . \tag{8}$$

This approximation for the electron-helium interaction has conventionally been used in studying the electron-induced bubbles in liquid helium (see Ref. 19 and references therein). The advantage is that the scattering length can be computed by solving a three-electron problem and a more elaborate many-body theory can be applied. The α_{eff} values determined from theoretical and experimental scattering lengths are included in Table I. A comparison shows that the LDA gives good results and LDA-SIC give excellent results for the helium interaction with the low-density electron gas. The results of Table I do, however, indicate some problems with the Harris-Liebsch value for α_{eff}. There are two possible explanations of the too-large value. It may be that the expansion in the helium-metal overlap or the perturbation theory in the helium pseudopotential is not converged. The other possibility is the difference in the treatment of exchange and correlation effects between the Hartree-Fock (HF) and LD approximations used in the two approaches. In the HF approximation of the Harris-Liebsch approach,[5,12] no correlation effects are included, whereas in the LD approximation and, in particular, when the self-interaction correction is included, correlation effects are treated to a certain approximation. The LDA value of $\bar{\alpha}_{\text{eff}}$ is therefore less repulsive than the Hartree-Fock value. If the too-large value of α_{eff} in the Harris-Liebsch-Nordlander treatment is due to a lack of correlation effects in the HF treatment, this need not invalidate the approach for calculat-

ing the He-surface interaction. All correlation effects are in principle included in the zeroth order contribution to the interaction potential in the overlap expansion which is the van der Waals attraction. In praxis the asymptotic form of the van der Waals interaction is added to the HF repulsive potential Eq. (6). Such a procedure gives, for instance, a reasonable description of the physisorption minimum when compared to experiment. In the effective-medium approach, on the other hand, the exchange-correlation energy of the helium atom in a homogeneous electron gas is already included in the repulsive part V_R of the potential, and only the extra exchange-correlation energy due to the inhomogeneity of the surface electron density must be added. Model calculations for jellium surfaces show that this is a small effect which is important only far from the surface, where V_R is small. With the inclusion of the extra exchange-correlation energy the effective-medium approach provides a good description of the helium-jellium–surface potential including the physisorption minimum, when compared to a fully self-consistent calculation within the local density approximation.[4,20]

Providing the overlap expansion is converged, the choice of the value for the proportionality constant $\bar{\alpha}_{\text{eff}}$ in the repulsive part of the helium-surface potential thus depends on the choice of the treatment of the exchange and correlation effects. If the asymptotic form of the van der Waals interaction is included, the corresponding large (HF) value of $\bar{\alpha}_{\text{eff}}$ must be used. This description is clearly the most appropriate far from the surface. Closer in, care must be taken with the divergence of the asymptotic van der Waals form.[12] If a local density description of the exchange and correlation is chosen, the small value of $\bar{\alpha}_{\text{eff}}$ should be used and only the extra exchange-correlation energy due to the inhomogeneity of the surface electron density added. This correction is small. The local density description is expected to work better the closer the He atom is to the surface.

ACKNOWLEDGMENTS

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