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Interaction Potential between a Helium Atom and Metal Surfaces

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By employing an *S*-matrix theory for evanescent waves, we have calculated the repulsive potential between a helium atom and corrugated metal surfaces. *P*-wave interactions and intra-atomic correlation effects were found to be very important. The corrugation part of the interaction potential is much weaker than predicted by the effective-medium theory. Application to Cu, Ni, and Ag (110) surfaces gives good agreement with experiment without any adjustable parameters.

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The theory of the interaction of a helium atom and metal surfaces has been studied in recent years by many authors.[1-9] The basic framework was given in the papers by Zaremba and Kohn[1,2] who also made numerical application to He physisorption. The fact that the repulsive interaction was proportional to the unperturbed metal density was developed further in the so-called effective-medium theory,[3,4] in which the repulsive potential is written in the form

$$V_R(\mathbf{r}_a) = \alpha n^{(0)}(\mathbf{r}_a), \tag{1}$$

where $\mathbf{r}_a$ is the position of the atom, $n^{(0)}(\mathbf{r}_a)$ is the unperturbed metallic density, and α is a coefficient of proportionality. In the original publication[3] the value of α was given as 750 $\text{eV}\cdot a_\text{B}^3$ (a_B is the Bohr radius). Subsequent corrections and adjustments resulted in a variety of values, most recently about 200 $\text{eV}\cdot a_\text{B}^3$. Another approach[5] gave a value of about 1000 $\text{eV}\cdot a_\text{B}^3$. Nevertheless, recent diffraction experiments could not be explained by the form (1) of V_R, except with use of a value of $\alpha \approx 3500$ $\text{eV}\cdot a_\text{B}^3$ for Cu(110), which is quite unphysical.

We have reformulated the theory of Zaremba and Kohn[2] in terms of the *S* matrix for the evanescent wave functions of the metal electrons.[10] As a result of the crystalline character of the solid surface, the wave functions of the metal electrons outside the surface have the form

$$\psi^{(0)}_{\mathbf{k},E}(\mathbf{r}) = A_0(\mathbf{k},E)\exp(i\mathbf{k}\cdot\boldsymbol{\rho} - \kappa_0 z) + \sum_{\mathbf{g}\neq 0} A_{\mathbf{g}}(\mathbf{k},E)\exp[i(\mathbf{k}+\mathbf{g})\cdot\boldsymbol{\rho} - \kappa_g z], \tag{2}$$

where $\mathbf{k}$ is the reduced two-dimensional wave vector in the *x*-*y* plane, E is the energy, $\boldsymbol{\rho} = (x,y)$, $\mathbf{g}$ is a surface reciprocal lattice vector, and κ_0 and κ_g are given by $(\mathbf{k}^2 - 2E)^{1/2}$ and $[(\mathbf{k}+\mathbf{g})^2 - 2E]^{1/2}$, respectively, in atomic units. The corresponding density, $n^{(0)}(\mathbf{r})$, has the form

$$n^{(0)}(\mathbf{r}) = \sum_{\substack{\mathbf{k},E \\ \text{occupied}}} |\psi^{(0)}_{\mathbf{k},E}(\mathbf{r})|^2 = n_0(z) + \sum_{\mathbf{g}\neq 0} n_{\mathbf{g}}(z)\exp(i\mathbf{g}\cdot\boldsymbol{\rho}), \tag{3}$$

to first order in the coefficients $A_{\mathbf{g}}$. Similarly, again to first order in $A_{\mathbf{g}}$, the repulsive potential of the atom with the evanescent electrons has the asymptotic form

$$V_R(\mathbf{r}_a) = \alpha_0 n_0(z_a) + \sum_{\mathbf{g}\neq 0} \alpha_g n_g(z_a)\exp(i\mathbf{g}\cdot\boldsymbol{\rho}_a). \tag{4}$$

The coefficients α_0 and α_g are *all* expressible in terms of the elements S_l of the *S* matrix evaluated at the negative energy, $-\Phi$ (Φ is the work function):

$$\alpha_0 = \sum_{l=0}^{\infty} F_l \tag{5a}$$

and

$$\alpha_g = \sum_{l=0}^{\infty} F_l P_l((1 + \mathbf{g}^2/2\Phi)^{1/2}), \tag{5b}$$

where $P_l(s)$ is the Legendre function, analytically continued from $s \leq 1$ to $s > 1$, and F_l is defined by

$$F_l = \pi(2l+1)(-1)^l[S_l(i(2\Phi)^{1/2}) - 1]/(2\Phi)^{1/2}. \tag{6}$$

To obtain $n_0(z)$ and $n_g(z)$, we have followed previous authors in using superposition of atomic charge densities as calculated by Herman and Skillman.[11] Although this is somewhat questionable, it is supported by the fact that the asymptotic decay rates of n_0 and n_g are close to the correct values for the metals that we have studied.[12]

The *S*-matrix elements, S_l, were obtained by the following procedure. We have fitted, with an accuracy of 1%, the theoretical scattering phase shifts,[13] η_l, for electron-He scattering over the energy range $0 < E$

< 16.5 eV with a pseudopotential of the form

$$V(r)=\begin{cases}\sum_{l=0}^{\infty} V^{(l)}(r,E), & r<r_c,\\ -\alpha_p/2r^4, & r>r_c.\end{cases} \tag{7}$$

Here r_c is the "radius" of the He atom, $4.0a_\mathrm{B}$, containing 99.95% of the charge density[14] and α_p is the static polarizability of He, $1.384a_\mathrm{B}^3$. $V^{(0)}$ is very close to the Hartree-Fock potential, orthogonalized to the 1s core states. For $V^{(l)}$ with $l \geqslant 1$, and intra-atomic polarization potential of the form

$$V_p(r)=-\alpha_p/2(r^2+s^2)^2 \quad (s=1.20a_\mathrm{B}) \tag{8}$$

must be included to fit the calculated η_l. A linear dependence of $V_l(r,E)$ on E is sufficient for an accurate fit of the data.

To obtain the required S_l, we have solved the radial Schrödinger equations with the potentials $V_l(r,E)$, Eq. (7), evaluated at $E=-\Phi$. Scattering in the s channel was found to be strongly repulsive, while in the p and higher l channels, it is attractive. Figure 1 shows the values of F_l as a function of Φ.

The weak extra-atomic polarization potential of Eq. (7) was *not* included in the calculation of S_l. (It would lead to a divergence.) It is shown in Ref. 10 that its effect is largely included in the van der Waals attraction. In this connection, there are some unresolved questions about many-electron correlations. However, for He, which has a very small extra-atomic polarization potential, the remaining uncertainty is probably quantitatively unimportant.

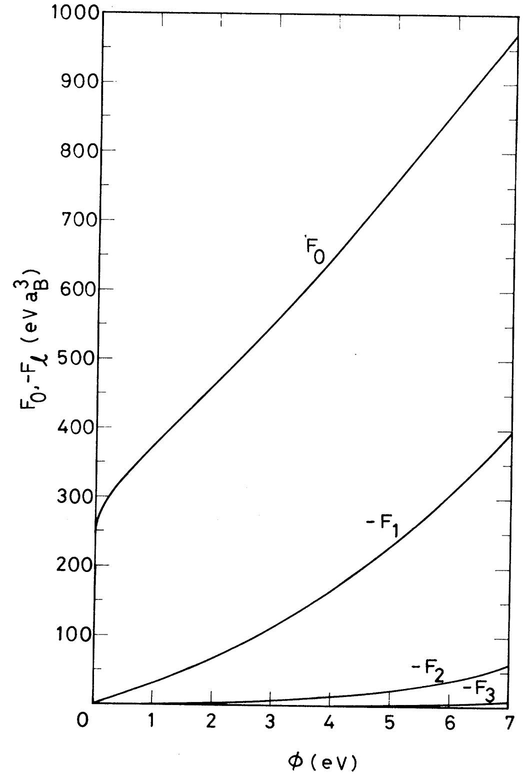

FIG. 1. Values of F_l in units of eV $\cdot\, a_\mathrm{B}^3$ as a function of the work function Φ.

In Table I, we list the values of the lattice constant a, of Φ, and of α_g for the (110) face of Cu, Ni, and Ag, including $g=0$ and the smallest nonvanishing g $(=2\pi/a)$. We note that α_0 is substantially constant ≈ 490 eV $\cdot\, a_\mathrm{B}^3$. The values of α_g are all considerably smaller than α_0 (as a result of the attractive scattering in the p and other channels) and differ from each other by as much as a factor of 1.7.

To the repulsive potential, Eq. (4), we must add the van der Waals attraction. This consists of a long-range z^{-3} term[1] and an exponentially decreasing oscillatory term,[1,9] given approximately by

$$V_\mathrm{VW}(\mathbf{r}_a)=-\frac{C_\mathrm{VW}}{(z_a-z_\mathrm{VW})^3}=\sum_{\mathbf{g}\neq 0} C_g\frac{ag^2}{4}\left(\frac{\pi}{g}\right)^{1/2}\frac{\exp[-g(z_a+\sqrt{2}a/8)]}{(z_a+\sqrt{2}a/8)^{5/2}}\exp(i\mathbf{g}\cdot\boldsymbol{\rho}_a). \tag{9}$$

Here C_VW and z_VW, for Cu and Ag, are given in Ref. 1 and listed in Table I and are very similar for both metals. For Ni, we have tentatively chosen the same values as for Cu. The coefficient C_g has been discussed by Hill, Hal-

TABLE I. Lattice constant, work function, and potential parameters for the He–metal-surface interaction for several metals.

Metal	a (a_B)	Φ (eV)	α_0 (eV $\cdot\, a_\mathrm{B}^3$)	α_g (eV $\cdot\, a_\mathrm{B}^3$)	C_VW (eV $\cdot\, a_\mathrm{B}^3$)	z_VW (a_B)
Cu	6.83	4.48	484	213	1.52	0.417
Ni	6.65	5.15	503	173	1.52[a]	0.417[a]
Ag	7.72	4.00	471	287	1.68	0.371

[a] These values have been assumed to be identical to those for Cu.

TABLE II. Comparison of experimental and theoretical corrugation amplitudes, Δz_g (Å).

	Cu(110)			Ni(110)			Ag(110)		
Incident energy (meV)	Expt. (Ref. 15)	Th(1)[a]	Th(2)[a]	Expt. (Ref. 16)	Th(1)[b]	Th(2)[b]	Expt. (Ref. 17)	Th(1)	Th(2)
21	0.111	0.109	0.102	0.074	0.071	0.068	0.238	0.246	0.232
63	0.136	0.137	0.129	0.080	0.085	0.082	0.271	0.313	0.296
120	0.163	0.167	0.157	0.072	0.098	0.094	⋯	⋯	⋯
240	0.202	0.230	0.215	⋯	⋯	⋯	⋯	⋯	⋯

[a] Th(1) and Th(2) correspond, respectively, to the choices $C_g = C_{\mathrm{VW}}$ and $C_g = 1.5C_{\mathrm{VW}}$.

[b] The theoretical results are more tentative, partly because C_{VW} and z_{VW}, in the absence of theoretical calculations, were assumed to be equal to the values for Cu, and partly because the atomic configuration was assumed to be $3d^8 4s^2$ rather than $3d^9 4s^1$.

ler, and Celli[9] for Ag. Its value is not precisely known but should be in the range of about $(1-1.5) \times C_{\mathrm{VW}}$. Its effect is much smaller than the effect of the oscillatory term in V_R. In Table II, we list results corresponding to both extremes of C_g, which will be seen not to be very different.

The experimental diffraction data have been summarized in terms of the corrugation amplitude Δz_g,[18] defined as the maximum difference across the x-y plane of the classical turning point, $z(x,y)$, corresponding to $V_R + V_{\mathrm{VW}}$. Comparison of experimental and theoretical results for different energies of incidence are given in Table II.

We make the following comments. We note that for higher energies the theoretical results tend to be larger than the experimental ones. This is probably due, at least in part, to the unphysical singularity of the van der Waals potential, Eq. (9), at $z_a = z_{\mathrm{VW}}$. Thus, it appears that at the high-energy turning points, V_{VW} is seriously in error. We note further that since the experimental data can be characterized by a single function $\Delta z(E)$, and the expression for the total potential involves seven parameters [α_0, α_g, C_{VW}, z_{VW}, C_g, and two decay constants characterizing $n_0(z)$ and $n_g(z)$], it is clear that a phenomenological fit of the data is far from unique. This emphasizes the importance of *a priori* theoretical calculations for diffraction scattering.

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