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Hybridization interaction between helium and a metal surface

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In order to calculate potentials for helium-atom diffraction from surfaces it is important to include the hybridization between the helium 1s orbital and the unoccupied states in the metal, since this term is strongly anticorrugating. In this paper we calculate the magnitude of the hybridization energy for helium near a jellium surface. This calculation shows that the hybridization is a large effect, and is sufficient to explain the anomalously small corrugations observed on clean metal surfaces. The calculation of the hybridization energy takes into account the effects of the surface image potential, which provides a large perturbation of the helium 1s orbital.

The development of low-energy atom scattering as an experimental surface probe[1,2] has stimulated a great deal of interest in the theory of inert-gas interactions with surfaces.[3–7] From the atom diffraction experiments it is possible to determine with high accuracy the whole potential energy function $U(\mathbf{r})$ of the atom near the surface. The corrugation in the repulsive region of the potential can be found from the intensities of the diffracted beams,[1] and the depth and approximate shape of the attractive well can be determined from observations of selective adsorption resonances.[8] For example, helium diffraction experiments on Ni(110), Cu(110), and Ag (110) (Refs. 9–12) have determined the corrugation, the energy dependence of the corrugation, the softness of the repulsive wall ($U^{-1}dU/dz$), and the attractive well depth (except Ni). The theoretical challenge is to calculate accurate atom-surface interaction potentials and hence to test models of surface structure with atom diffraction experiments.

There are two dominant effects that determine the shape of the atom-surface potential $U(\mathbf{r})$. At long range, the interaction is given by the van der Waals attraction. This arises because of the fluctuating dipole moment of the adatom which induces image charges in the metal surface.[13] At short range, the potential $U(\mathbf{r})$ becomes strongly repulsive because of overlap between the occupied adatom orbitals and occupied states in the metal. In order to orthogonalize to the adatom orbitals the metal states must increase their kinetic energy, thus giving rise to a repulsive energy. One can estimate this repulsive energy either by considering the energy to embed the adatom in a uniform electron gas[4] or by treating the adatom as a repulsive pseudopotential which scatters the metal electrons.[5] Both of these theoretical approaches come to the conclusion that for helium in the repulsive region the energy can be approximated by

$$U(\mathbf{r})=\alpha\rho(\mathbf{r}) , \qquad (1)$$

where $\rho(\mathbf{r})$ is the unperturbed metal charge density at the inert-gas atom position, and α is a constant. The charge density of a surface can be found by self-consistent linearized augmented-plane-wave (LAPW) calculations,[14] or can be approximated by a superposition of atomic charge densities,[15] and so Eq. (1) can be used to calculate the corrugations in helium potential. Theories differ over the exact value of α; the embedded atom calculations within the local density approximation[4,6,16] predict $\alpha\sim(200–300\ \text{eV})a_0^3$ for helium, while the pseudopotential approach[5] (based on Hartree-Fock calculations) gives $\alpha\sim(800\ \text{eV})a_0^3$. An alternative way to estimate α is provided by empirical helium-inert gas pair potentials,[17,18] giving $\alpha\sim(500\ \text{eV})a_0^3$. In general, there are also nonlocality correction terms to Eq. (1). These can be represented by averaging the charge density ρ over the adatom,[4] gradient terms in ρ,[18] or by replacing $\alpha\rho$ by an integral over the local density of states.[5] In practice, these corrections produce only minor changes in the corrugations of $U(\mathbf{r})$.

In the case of helium diffraction from smooth clean metal surfaces, there appear to be large and systematic discrepancies between the predictions of the theory and the experimental results. For example, on Ni(110) the helium potential corrugations calculated using Eq. (1) are a factor of 2 larger than those found experimentally.[9,14] This implies that the theory would predict much too large helium diffraction intensities. Another difficulty with Eq. (1) is that it predicts corrugations which always increase with helium energy. This contradicts the observations on Ni(110), which show that the helium potential corrugations are almost constant over a wide range of incident energies (20–240 meV) and even appear to decrease slightly at the higher energies. It is important to note that no reasonable modification of the value of α in Eq. (1) or of the surface charge density $\rho(\mathbf{r})$ would account for this observation. Another significant discrepancy is that the theory also predicts that the corrugations observed in neon diffraction should be smaller than those found in helium diffraction, since the value of α would be larger for neon than for helium.[19] Recent experimental results have shown the Ne-Ni(110) and Ne-Cu(110) potentials to be substantially more corrugated than the He-Ni(110) and He-Cu(110) potentials,[20,21] in contradiction to the theory. Discrepancies between theoretical and experimental helium corrugations also arise on other surfaces, for example on Ni(100).[22,23] For Cu(110) the situation is less clear; using an LAPW charge density and $\alpha \sim (200\ \text{eV})a_0^3$, Hamann and Tersoff[24] found helium corrugations too large, while on the other hand, using a superimposed Clementi-Roetti atom charge density and a larger value of α Garcia *et al.*[25] found agreement between theory and experiment.

In a previously written paper[26] we showed that these discrepancies for helium diffraction could be explained by assuming that, in addition to the van der Waals and overlap repulsion terms in the potential, a hybridization interaction was also taking place. This term would arise because of overlap between the occupied helium 1*s* orbital and unoccupied states in the metal. Hybridization, or charge transfer, between the helium and these metal states would give an additional attractive term in the potential. We showed that this hybridization energy would be larger at a top site than at a hollow site on the surface (because the unoccupied metal surfaces are predominantly antibonding in character and hence have nodes between atomic sites). This implies that the hybridization term would have an anticorrugating effect, i.e., would tend to reduce the surface corrugations, and hence would reconcile theory and experiment. Using a simple one parameter model for the hybridization, we showed that it was possible to obtain good agreement between theory and experiment, assuming reasonable values for the hybridization energy.

In this paper we shall calculate the hybridization energy of helium near a metal surface from first principles. This calculation is necessary since there has been some controversy[27] over whether the hybridization would be as large an effect as assumed in Ref. 26. The results of this paper show that the hybridization is indeed a large contribution to the energy and hence that it will have a significant anticorrugating effect on the potential. We shall show below that the large hybridization energy is a consequence of the image potential of the surface, which provides a substantial perturbation of the helium 1*s* orbital.

In the following sections of this paper we shall firstly define the hybridization energy, and show how it is related to the overlap repulsion and van der Waals attraction terms in the energy. Secondly, we shall derive a model for the electronic potential of the atom-surface system which includes the effects of the surface image potential. Using this model potential and accurate wave functions for the helium atom and the metal surface (treated in a jellium approximation we calculate the hybridization energy. The results of this calculation demonstrate that the hybridization is a large effect, supporting the conclusions of Ref. 26. Finally, as an example of how these results may be used to make parameter-free prediction of helium diffraction potentials, we present calculation of the leading corrugation coefficient of the Ag (110) surface.

CONTRIBUTIONS TO THE HELIUM ENERGY

In order to define the hybridization energy and to relate it to the other terms in the helium potential we shall discuss the density functional theory of the helium-surface interaction. Let us start from the single-particle Kohn-Sham equations of density-functional theory

$$\{-\tfrac{1}{2}\nabla^2+V\}\,|i\rangle=\varepsilon_i\,|i\rangle\ . \tag{2}$$

Here, the potential V is the sum of ionic, Hartree, and exchange-correlation contributions. The energy of the system is given by the sum of the one electron eigenvalues, ε_i, together with "double counting" terms due to the electron-electron interactions,

$$U=\sum_i \varepsilon_i-\tfrac{1}{2}\int\int\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3r\,d^3r' - \int V_{\text{xc}}\rho\,d^3r+E_{\text{xc}}[\rho]\ . \tag{3}$$

Here, $\rho(\mathbf{r})$ is the charge density, $E_{\text{xc}}[\rho]$ is the exchange-correlation functional, and V_{xc} is the exchange-correlation potential, defined as the functional derivative $\delta E_{\text{xc}}[\rho]/\delta\rho(\mathbf{r})$. Since the functional E_{xc} is not known in general, it is necessary to find some approximation for E_{XC} and hence for V_{xc}. Below we shall discuss various approximations that might be used for V_{xc} for the case of an atom near a surface, such as the local density approximation with or without self-consistency, Hartree-Fock exchange, or an image potential approximation. First we shall show how the energy changes due to the atom-surface interaction arise from the above equations.

Since the helium 1*s* eigenvalue lies below the bottom of the metal band, the eigenfunctions of 2 will consist of one localized solution, a perturbed helium 1*s* orbital $|H\rangle$, and a continuum of perturbed metal states $|k\rangle$. We can separate the calculation of the interaction energy into two distinct steps: Firstly, we freeze the helium orbital $|H\rangle$ in its unperturbed wave function $|H_0\rangle$ giving an energy U_1, and secondly we can relax the helium wave function into its perturbed state $|H\rangle$ with a change of energy U_2. This relaxation of the helium 1*s* orbital corresponds to the hybridization energy suggested in Ref. 26 and discussed above. To carry out this relaxation, we introduce projection operators onto and orthogonal to the unperturbed helium 1*s*, $P_H=|H_0\rangle\langle H_0|$ and $1-P_H$, respectively. This separates the basis into two subspaces: $|H_0\rangle$ and orthogonal states. The Hamiltonian can then be partitioned into terms which do not couple the two subspaces, i.e.,

$$\hat{H}_1=(1-P_H)(-\tfrac{1}{2}\nabla^2+V)(1-P_H) +P_H(-\tfrac{1}{2}\nabla^2+V)P_H$$

and into terms which couple the two subspaces, i.e.,

$$\hat{H}_2=P_H(-\tfrac{1}{2}\nabla^2+V)(1-P_H) +(1-P_H)(-\tfrac{1}{2}\nabla^2+V)P_H\ .$$

The energy U_1 is defined to be the energy of the system when these latter coupling terms are set to zero. We can then reintroduce the couplings in $\hat{H}_2$ as a perturbation, giving an energy change U_2 due to relaxation of the helium 1*s* orbital. We have therefore separated the total interaction energy into two contributions, U_1, which is the helium potential without hybridization and U_2, which is the hybridization energy. It is the latter of these terms, U_2 that we wish to calculate in this paper.

The "frozen-core" energy U_1 contains the overlap repulsion energy and the attractive well depth of the atom near the surface as we can see by the following argument. Denote by $|k_1\rangle$ the eigenstates of $\hat{H}_1$ in the space orthogonal to the helium 1*s*. In this subspace the helium atom will form a weak perturbation, as in pseudopotential theory, and we can take a zeroth-order approximation to the wave function as

$$|k_1\rangle=(1-|H_0\rangle\langle H_0|)|k_0\rangle/n_k \ , \qquad (4)$$

with $|k_0\rangle$ is an eigenstate of the unperturbed metal satisfying $\{-\frac{1}{2}\nabla^2+V_m\}|k_0\rangle=\varepsilon_k^0|k_0\rangle$, and $|H_0\rangle$ is the unperturbed helium 1*s* state satisfying $\{-\frac{1}{2}\nabla^2+V_H\}|H_0\rangle=\varepsilon_H^0|H_0\rangle$. n_k is a normalizing constant. This wave function is just the unperturbed metal state, orthogonalized to the helium 1*s* core, as in the orthogonalized plane wave (OPW) method of band-structure calculations. Using this approximation to the wave function, the shift in the eigenvalue is then found to be

$$\begin{aligned}\Delta_1\varepsilon_k&=\langle k_1|-\tfrac{1}{2}\nabla^2+V|k_1\rangle-\varepsilon_k^0\\&=\langle k_0|\Delta V_m|k_0\rangle\\&\quad+s_k^2(\varepsilon_k^0-\varepsilon_H^0+\langle H_0|\Delta V_H|H_0\rangle)\\&\quad-2s_k\langle k_0|\Delta V_H|H_0\rangle \ ,\end{aligned} \qquad (5)$$

where $\Delta V_m=V-V_m$, $\Delta V_H=V-V_H$, and $s_k=\langle H_0|k_0\rangle$. This expression is essentially the same as the repulsive energy derived by Harris and Liebsch.[5] The energy change given by Eq. (5) is proportional to the square of the unperturbed metal wave function at the helium position, hence leading to a repulsive energy approximately of the form $\alpha\rho$ is in Eq. (1). It is possible to improve on the basic orthogonalized metal wave functions of Eq. (4) in various ways, for example, by including the coupling of the occupied metal states to the unoccupied ones or to the affinity levels of the adatom. However, these improvement make little difference to the basic form $U=\alpha\rho$ of the potential since the interaction energy still depends primarily on the local density of occupied metal states at the helium-atom position. For example, the calculations of Nordlander,[28] Zaremba and Kohn,[3] and Takada and Kohn[7,29] all improved on the basic orthogonalized wave functions of Eq. (4) but gave repulsion energies within 20% accuracy of the Harris-Liebsch result analogous to Eq. (5).

There will in general also be other contributions to the energy U_1 without hybridization: from the first-order shift in the helium eigenvalue,

$$\Delta_1\varepsilon_H=\langle H_0|\Delta V_H|H_0\rangle \ , \qquad (6)$$

and from the changes in the double counting terms. Whether these terms are important will depend on the approximation made for the exchange correlation potential V_{xc}. For example, it can be shown that in the Hartree-Fock approximation the leading order changes in the helium eigenvalue and in the double counting terms cancel.[3] On the other hand, Lang and Nørskov[6] showed that in the local density approximation most of the attractive well energy could be obtained with a frozen helium 1*s* wave function. We shall see below that if V_{xc} includes the asymptotic image potential of the surface then Eq. (6) gives the Lennard-Jones van der Waals potential.

The energy U_1 without hybridization has been extensively studied by other authors; in this paper we wish to concentrate on the contribution to the energy from relaxation of the helium 1*s* orbital, U_2. This energy can be obtained by reintroducing the terms in the Hamiltonian coupling the helium orbital $|H_0\rangle$ to orthogonal states, $\hat{H}_2$. Since the coupling will be weak we can find the eigenvalue change using straightforward perturbation theory. The energy change is given by:

$$U_2=\sum_k\frac{|M_k|^2}{\varepsilon_k^0-\varepsilon_H^0} \ , \qquad (7)$$

where the sum is taken over the unoccupied states of the metal. The matrix element M_k is taken by:

$$M_k=\langle k_1|-\tfrac{1}{2}\nabla^2+V|H_0\rangle \qquad (8a)$$

$$M_k\cong\langle k_0|\Delta V_H-\langle\Delta V_H\rangle|H_0\rangle \ , \qquad (8b)$$

with $\langle\Delta V_H\rangle=\langle H_0|\Delta V_H|H_0\rangle$. Equation (8a) is exact since the states $|k_1\rangle$ and $|H_0\rangle$ are the eigenstates of the Hamiltonian $\hat{H}_1$ before the coupling $\hat{H}_2$ is included. Equation (8b) is obtained by substituting the approximate wave functions of Eq. (4) into Eqs. (8a). The hybridization energy can therefore be evaluated from the unperturbed wave functions $|k_0\rangle$ and $|H_0\rangle$, once the perturbing potential ΔV_H is known.

The only significant approximation made in writing the hybridization energy in Eqs. (7) and (8b) is the use of the OPW metal wave functions $|k_1\rangle$ of Eq. 4. These wave functions should be a good approximation for most of the unoccupied metal states, the only exception being when the energy ε_k is close to that of an excited helium energy level, in which case resonances can occur. At these energies the eigenstates $|k_1\rangle$ will have a large component of the excited helium atomic wave function, which is not included in the approximation of Eq. (4). Since relatively few metal states will be resonant, these effects will not significantly alter hybridization calculated using Eq. (8b). Furthermore, since resonances would increase the amplitude of the metal wave function in the vicinity of the helium atom and hence increase $|M_k|^2$, our calculation give a lower bound on the hybridization energy.

THE ELECTRONIC POTENTIAL

In order to calculate the hybridization energy using Eq. (7), it is necessary to approximate the perturbing potential ΔV_H. This is defined as the difference between the full potential V of the atom-surface system, and the potential of the isolated helium atom, V_H. For example, one could use the local density approximation (LDA) to give the exchange correlation part of the potential, V_{xc}, either with a self-consistent charge density or with an approximate one. The LDA should be a good description when the helium is close to the surface but would break down at larger separations, since the LDA does not reproduce the correct asymptotic form of the surface potential.[30] Instead of the

LDA, we shall derive an expression for the potential ΔV_H which is valid in the limit of the helium being far from the surface. In this limit ΔV_H can be found using classical image charge arguments.

When the helium atom is far from the surface, the perturbation in electronic potential ΔV_H arises because of the formation of image charges in the metal. Consider a He^+ ion at a distance z_H from the surface image plane. This induces a negative image charge at $(0,0,-z_H)$, where we have taken the origin at the image plane and the z axis normal to the surface. If we now bring an electron from infinity to a point $\mathbf{r}=(x,y,z)$ the work done in the field of the image charges of the electron and the ion is

$$\Delta V_H = \frac{-1}{4z} + \frac{1}{[x^2+y^2+(z+z_H)^2]^{1/2}} \tag{9}$$

in Hartree atomic units. The effective potential of the electron thus arises from both the image of the electron itself and from the image of the positive nuclear charge. Note that the first term has a factor of $\frac{1}{2}$ which arises because the first image is induced by the electron itself. Equation (9) gives the extra potential energy of the electron due to the presence of the surface, which is therefore the perturbing potential ΔV_H that we require.

We can confirm that Eq. (9) gives the physically correct perturbing potential by a Taylor expansion for $\mathbf{r}\rightarrow(0,0,z_H)=\mathbf{r}_H$. We find,

$$\Delta V_H(\mathbf{r}) = \frac{+1}{4z_H} - \frac{x^2+y^2+2(z-z_H)^2}{16z_H^3} + \cdots , \tag{10}$$

confirming that there is no force on the electron when the two image charges are superimposed, since $\nabla[\Delta V_H(\mathbf{r})]=0$ at $\mathbf{r}=\mathbf{r}_H$. We can also see that the first-order energy shift of the adatom due to presence of the surface is given by

$$-\frac{\langle H_0 \,|\, (\mathbf{r}-\mathbf{r}_H)^2 \,|\, H_0 \rangle}{12z_H^3} , \tag{11}$$

since the first term in Eq. (10) is exactly canceled by the energy $-1/4z_H$ to bring the He^+ ion up to the surface. The interaction energy of Eq. (11) exactly corresponds to the van der Waals energy evaluated by Lennard-Jones.[13]

We can also derive the result of Eq. (9) by a quantum-mechanical method. When the helium is far from the surface, the image charges induced in the surface can be represented by a two-particle interaction between the charges of the helium atom. This interaction is

$$W(\mathbf{r},\mathbf{r}') = -[(x-x')^2+(y-y')^2+(z+z')^2]^{1/2} .$$

The many-body Hamiltonian for the helium atom can then be written as:

$$\hat{H} = \sum_{i=1}^{2} \{ -\tfrac{1}{2}\nabla^2{}_i - 2V(\mathbf{r}_i,\mathbf{r}_H) + \tfrac{1}{2}W(\mathbf{r}_i,\mathbf{r}_i) - 2W(\mathbf{r}_i,\mathbf{r}_H) \}$$
$$+ V(\mathbf{r}_1,\mathbf{r}_2) + W(\mathbf{r}_1,\mathbf{r}_2) + 2W(\mathbf{r}_H,\mathbf{r}_H) , \tag{12}$$

where $V(\mathbf{r},\mathbf{r}')=1/|\mathbf{r}-\mathbf{r}'|$. If we were to treat this Hamiltonian within the Hartree-Fock approximation we would find the single-particle potential,

$$\tfrac{1}{2}W(\mathbf{r},\mathbf{r}) - 2W(\mathbf{r},\mathbf{r}_H) + \int W(\mathbf{r},\mathbf{r}') \,|\, \phi_H(\mathbf{r}') \,|^2 d^3r' , \tag{13}$$

in addition to the Hartree-Fock potential of the isolated helium atom. To a good approximation, the last term in Eq. (13) is equal to $W(\mathbf{r},\mathbf{r}_H)$ and hence we recover the perturbation ΔV_H of Eq. (9). Clearly, for a hydrogen atom outside a metal surface Eq. (9) would be exact.

To go beyond the approximation of Eq. (9), we could include the frequency dependence of the metal surface response, giving $W(\mathbf{r},\mathbf{r}',\omega)$, and arrive at the effective potential via a calculation of the self-energy. In an appendix to this paper we show how the self-energy expression reduces to the image potential result of Eq. (9) under certain simplifying assumptions. The exact self-energy expression would give the exact van der Waals energy rather than the Lennard-Jones result of Eq. (11). In the present paper we shall use the approximation given by Eq. (9), which is exact in the limit of large surface-plasmon frequency. Including the details of the surface response would not qualitatively alter our results which establish the large magnitude of the hybridization energy, although the exact numerical value we obtain may be altered somewhat.

Equation (9) provides the perturbation on the helium atom when it is far from the image plane. When the helium is close to the image plane we must replace the classical image potential, which diverges at $z=0$, with the true quantum-mechanical surface potential $V_{\mathrm{im}}(z)$, which remains finite at the image plane. The potential $V_{\mathrm{im}}(z)$ is imagelike at large z and tends smoothly to the bulk density functional potential given by the LDA at small and negative z. We shall also correct the second term in Eq. (9), since the classical expression is discontinuous if either $z\rightarrow 0$ or $z_H\rightarrow 0$. We remove this discontinuity by introducing a screening function $\Theta(z)$, which gives the effective image charge as a function of z, i.e., $\Theta(z)=-4zV_{\mathrm{im}}(z)$ if $z>0$ and $\Theta(z)=0$ if $z<0$. We therefore take the perturbing potential ΔV_H to be:

$$\Delta V_H = V_{\mathrm{im}}(z) + \frac{\Theta(z)\Theta(z_h)}{[x^2+y^2+(z+z_H)^2]^{1/2}} . \tag{14}$$

CALCULATION OF THE HYBRIDIZATION ENERGY

It is straightforward to calculate the hybridization energy given by Eq. (7) using the image potential perturbation derived above. Treating the metal as a semi-infinite jellium we can explicitly construct the unperturbed wave functions and thus evaluate the hybridization energy directly. First we numerically solve the Schrödinger equation for the metal electrons at the surface:

$$\{ -\tfrac{1}{2}\nabla^2 + V_{\mathrm{im}}(z) \} \phi_{k_\perp}(z)\exp(i\mathbf{K}\cdot\mathbf{R}) = \varepsilon_{\mathbf{k}}\phi_{k_\perp}(z)\exp(i\mathbf{K}\cdot\mathbf{R}) ,$$

where $\mathbf{r}=(\mathbf{R},z)$ with the z axis normal to the surface and $\mathbf{k}=(\mathbf{K},k_\perp)$. The wave function is matched onto a sine wave with wave vector $\mathbf{k}$ in the bulk. We take the unperturbed helium 1s wave function, ϕ_H, from the Herman-Skillman tables.[31] The surface barrier potential $V_{\mathrm{im}}(z)$ is approximated with a smooth interpolation between the image potential calculation of Appelbaum and Hamann[32] for large z and the self-consistent local density approximation potential of Lang and Kohn[33] for small and negative z. The image plane position was also taken from Appelbaum and Hamann. This defines all the quantities needed to calculate the matrix elements $M_{\mathbf{k}}$ of Eq. (8b),

$$M_{\mathbf{k}}=\int d^3r\,\phi_{k_\perp}(z)\exp(i\mathbf{K}\cdot\mathbf{R})\Delta V_H(\mathbf{r})\phi_H(\mathbf{r})\ ,$$

which we evaluate by a two-dimensional numerical integration (exploiting cylindrical symmetry). Finally, the hybridization energy can be evaluated by integrating over the unoccupied part of $\mathbf{k}$ space,

$$U_2=-2\int\frac{dk_\perp}{\pi}\frac{d^2K}{(2\pi)^2}\frac{|M_{\mathbf{k}}|^2}{\varepsilon_{\mathbf{k}}-\varepsilon_H}\ ,$$

which amounts to a further two-dimensional integration. The factor of 2 is due to spin degeneracy.

In these calculations we only include the contribution to the $\mathbf{k}$-space integral arising from the metal states which decay exponentially away from the surface. This is because any hybridization energy due to the unbound states will vary as an inverse power law with distance, and is thus a contribution to the van der Waals energy. On the other hand, the hybridization with bound states which are evanescent outside the surface gives an energy which varies exponentially with the atom-surface separation, which is not included in the van der Waals energy. It is this latter energy that resolve the discrepancies in the calculated corrugations for helium diffraction.

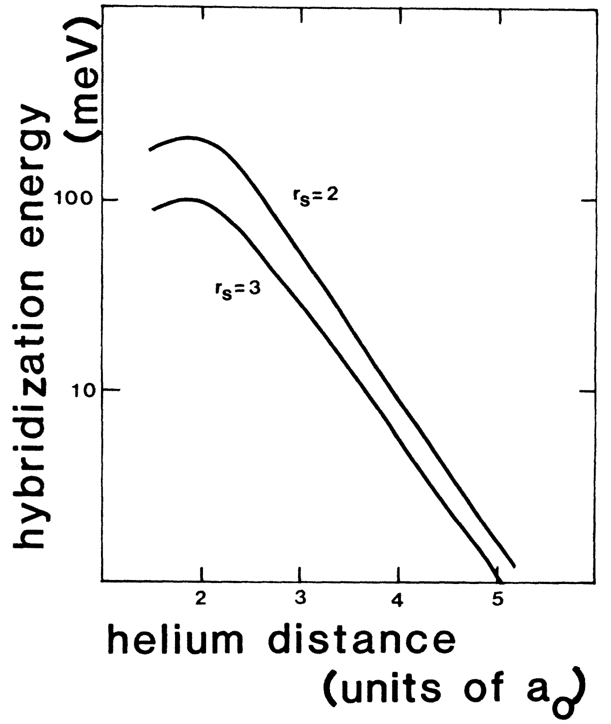

FIG. 1. Calculated hybridization energy for $r_s=2$ and $r_s=3$ jellium surfaces as a function of distance of the helium from the jellium edge.

RESULTS

Our results for the hybridization energy are shown in Fig. 1 for $r_s=2$ and $r_s=3$ jellium surfaces. These results demonstrate that the hybridization energy is a large effect, comparable in magnitude to other terms in the helium potential. For example, on $r_s=3$ jellium (corresponding to a silver surface) at a distance where the metal charge density is 5×10^{-4} a.u. (corresponding to the classical turning point a 100 meV helium atom), the hybridization energy is 77 meV. Clearly, if the hybridization were neglected, the helium potential would be significantly more repulsive than if it were included. If the hybridization energy were not included, the laterally averaged potential would be more repulsive by a change of (154 eV)a_0^3 in the effective Esbjerg-Nørskov parameter α. This is consistent with the larger values of α obtained by theories which neglect hybridization (such as Refs. 3 and 5) compared to calculations which do include some hybridization (e.g., Refs. 4 and 6).

We can compare the results of this calculation with the estimated values of the hybridization obtained in Ref. 26. In Ref. 26 the magnitude of the hybridization energy was parametrized with a single number γ for each surface. The values of γ were determined by fitting the calculated helium potential corrugations to experimental results; for example, for Ag(110) the hybridization parameter γ was estimated to have a value of (550 eV)a_0^3. We shall see below that the results shown in Fig. 1 give a prediction for the value of γ of (348 eV)a_0^3 for Ag(110). The calculation is within 40% accuracy of the original estimate, which is a good agreement given the simplicity of the model of the surfaces density of states used in Ref. 26. The calculation of Ref. 26 assumed metal wave functions which all decay into the vacuum at the same rate, determined by the Fermi level. The calculation here includes the full energy dependence of the wave functions and so gives a far more reliable estimate of the hybridization energy. The importance of the calculation presented here is that it shows that the hybridization has a large magnitude which will have a significant effect on the helium diffraction intensities.

DISCUSSION

It is useful to compare these results for the hybridization energy with calculations which make different assumptions about the electronic potential ΔV_H. For example, rather than using the image potential approximation of Eq. (9), one could use the local density approximation (LDA) for the exchange-correlation potential. In the LDA the perturbing potential ΔV_H is essentially given by

$$\Delta V_H=V_{\mathrm{xc}}(\rho_{\mathrm{sc}})-V_{\mathrm{xc}}(\rho_H)\ ,$$

where $V_{\mathrm{xc}}(\rho)$ is the exchange-correlation potential of a uniform electron gas, ρ_{sc} is the self-consistently obtained charge density of the atom-surface system, and ρ_H is the charge density of the isolated helium atom. Lang and Nørskov[6] have carried out self-consistent LDA calculations for helium on $r_s=3$ jellium. They observed that at the equilibrium separation ($z=5a_0$) about 1 meV of the energy was due to relaxation of the helium 1s orbital.

From Fig. 1, at $z=5a_0$ the hybridization energy we calculate is also about 1 meV. This suggests that the two calculations are roughly in agreement, despite the different approximations used for the electronic potential.

Rather than a full self-consistent LDA calculation, one could make a further approximation by taking a charge density which is a superposition of the atom and surface densities. This gives the following form for the potential:

$$\Delta V_H = V_{\mathrm{xc}}(\rho_m+\rho_H)-V_{\mathrm{xc}}(\rho_H)\ ,$$

where ρ_m is the charge density of the metal surface. Using this potential we have calculated the hybridization energy given by Eq. (8b) using numerically generated surface wave functions as described above. This calculation gave 0.29-meV energy for helium $5a_0$ from $r_s=3$ jellium. Harris and Zaremba[27] also estimated the hybridization energy using this non-self-consistent LDS potential; at a charge density of $2.6\times10^{-5}\ a_0^{-3}$ (corresponding to $z=5a_0$), their estimates give a hybridization energy of order 0.2 meV, which is smaller than both our calculations and those of Lang and Nørskov. The discrepancy with the results shown in Fig. 1 can be attributed to the poor basis set in the calculation of Harris and Zaremba (consisting of only the helium $1s$ and $2p$ states) and to the lack of either self-consistency or the surface image potential in their calculation. We note that both self-consistency and the surface image potential allow for the response of the surface under the perturbation from the helium atom, which is not included in the non-self-consistent calculation.

It had been thought that in calculations using the Hartree-Fock approximation, any hybridization energy would be of a strictly smaller magnitude than other terms in the energy.[3] In an appendix to this paper we show that in fact this is not the case; within the Hartree-Fock approximation the hybridization energy is of the same order of magnitude as the other terms in the potential.

Our results for the hybridization energy are in qualitative agreement with the model Hamiltonian calculation of Drakova, Doyen, and Terentini,[34] who find significant terms in the helium potential due to interactions of the helium $1s$ with both the occupied and unoccupied states of the metal. They also find that the surface image potential plays an important role in determining these effects. However, the model of the metal surface that they use to calculate the helium corrugations is quite different from ours. For example, in our calculations the largest contribution to the corrugation in the helium potential is due to the metal *sp* band charge density, while in the calculation of Drakova, Doyen, and Terrentini the corrugations is due to the metal *d* band, the metal *sp* band being uncorrugated. If experimental helium corrugations could be observed on nearly free electron substrates, this would distinguish between the two theories.

CORRUGATION OF Ag(110)

To demonstrate how this hybridization energy influences the Fourier components of the helium potential, we have calculated the leading corrugation coefficient of the Ag (110) surface. The model helium potential that we use has been described elsewhere,[26] and is given by

$$U(\mathbf{r})=E(\rho)+\beta\nabla^2\rho-\gamma\rho_u\ . \tag{15}$$

Here, $\rho(\mathbf{r})$ is the charge density of the unperturbed surface and $\rho_u(\mathbf{r})$ is the density of unoccupied s-band states. The first two terms in Eq. (15) are derived from empirical helium-inert-gas pair-potential data and thus represent the helium potential without hybridization.[18,26] The last term in Eq. (15) gives the hybridization energy.

To calculate the helium potential it is necessary to calculate both the charge density ρ and the unoccupied state density ρ_u for a corrugated surface. The charge density ρ can be adequately approximated by a superposition of atomic charge densities. To calculate the unoccupied state density of the surface we introduce a tight-binding model for the local density of states. We adopt a basis consisting of a single atomic s orbital at each site, $|i\rangle$ at site i. In terms of this basis the Green-function matrix for the surface is given by:

$$\underline{G}(\varepsilon)=\underline{S}(\varepsilon\underline{I}-\underline{H})^{-1}\ ,$$

where $S_{ij}=\langle i\,|\,j\rangle$, $I=\delta_{ij}$, and $\underline{H}=\underline{S}^{-1}\underline{M}$ with $M_{ij}=\langle i\,|\,-\frac{1}{2}\nabla^2+V\,|\,j\rangle$. The overlap integrals are computed from the atomic orbitals, and the Hamiltonian $\underline{M}$ is assumed to consist of nearest-neighbor interactions only. The local density of states a point $\mathbf{r}$ is given by:

$$\rho(\varepsilon,\mathbf{r})=\frac{-1}{\pi}\mathrm{Im}[v_i^{*}G_{ij}(\varepsilon)v_j]\ , \tag{16}$$

where

$$v_i=(\underline{S}^{-1})_{ij}\langle j\,|\,\delta(\mathbf{r})\rangle\ .$$

The density of states in Eq. (16) can be efficiently evaluated using the recursion method,[35] which gives a continued fraction expansion for diagonal elements of the Green function G. We evaluate the recursion to five levels and terminate the continued fraction using standard methods. Finally, the unoccupied state density ρ_u is given by the integral of $\rho(\varepsilon,\mathbf{r})$ from the Fermi level to the top of the band. As we have explained elsewhere,[26] $\rho_u(\mathbf{r})$ is significantly less at a center site on the surface than at a top site, this is because the unoccupied states are essentially of antibonding character and hence have little weight between the surface atoms. This point explains why the hybridization energy has such a strong anticorrugating effect on the helium-surface potential.

We can determine the parameter γ using the calculated values of the hybridization energy shown in Fig. 1. To do this we adjust the value of γ is to give a hybridization energy of 77 meV in the laterally averaged potential at the distance from the surface where the laterally averaged charge density is 5×10^{-4} a.u. This procedure gave a value of γ of $(348\ \mathrm{eV})a_0^3$ for Ag (110). We are therefore using quantities calculated from the helium-jellium interaction in order to predict the Fourier components of the potential for a corrugated surface.

Our results for the Ag(110) corrugations are shown in Fig. 2. The three potentials shown are the following: the Esbjerg Nørskov potential of Eq. (1) with $\alpha=(176\ \mathrm{eV})a_0^3$, the potential of Eq. (15) with no hybridization ($\gamma=0$), and

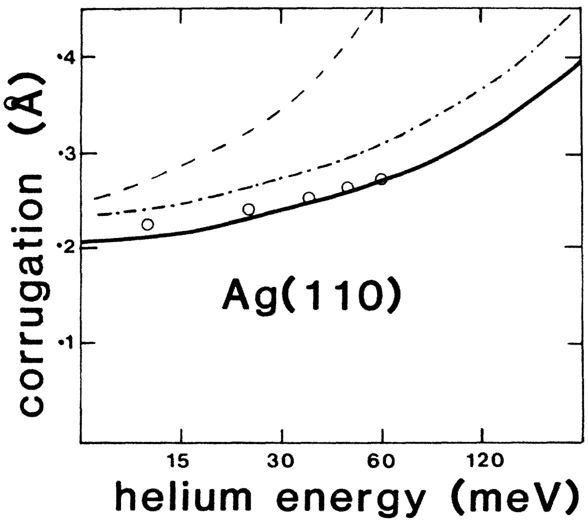

FIG. 2. Calculated and experimental corrugations of Ag(110). The corrugation shown in the leading Fourier coefficient ξ_{10} of the helium isopotential surface, taken in the direction across the close packed atomic rows. ξ_{10} is normalized so that it corresponds to the maximum corrugation height if higher coefficients are negligible. The theoretical corrugations shown are calculated with the Esbjerg Nørskov potential $U=\alpha\rho$ with $\alpha=176\ \text{eV})a_0^3$ (dashed line), the model potential of Eq. (15) with no hybridization, i.e., with $\gamma=0$ (dotted line), and the potential of Eq. (15) including hybridization with $\gamma=(348\ \text{eV})a_0^3$ (solid line). The experimental points are taken from Luntz *et al.*[11]

the potential of Eq. (15) including the hybridization [with $\gamma=(348\ \text{eV})a_0^3$]. The experimental points are taken from the work of Luntz *et al.*,[11] and were determined from a soft wall fit to the experimental helium diffraction intensities. Clearly, Fig. 2 shows an excellent agreement between the calculated potential and the experiment, while the other theories give corrugations that are too large. We have also calculated the corrugation coefficient along the close packed rows ξ_{01}, and we find a maximum corrugation height of a 0.02 Å in this direction at typical energies.

We have therefore shown that by including the calculated hybridization energy we can obtain good agreement with experimental corrugations, while if the hybridization is neglected, the corrugations obtained are substantially larger.

CONCLUSION

To conclude, we have shown that the hybridization energy is a large effect which should certainly be included in calculations of potentials for helium diffraction. The size of the hybridization energy is a consequence of the long-ranged nature of the surface image potential which provides a large perturbation of the helium 1*s* orbital. We have explicitly calculated the hybridization energy as a function of helium position outside $r_2=2$ and $r_s=3$ jellium surfaces. These calculations are in agreement with other estimates of the hybridization energy obtained by fitting the experimental helium corrugations. Using the hybridization energy calculated for jellium surfaces, it is possible to make parameter-free calculations of the helium potential which fully includes the anticorrugating effect of the hybridization. We illustrate this by a calculation of the leading corrugation coefficient of the Ag(110) surface, which is in excellent agreement with experiment. Although the hybridization is an added term in the theory of the helium potential, it should not make comparison of theory and experiment much more difficult.

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APPENDIX A

In this appendix we show how the electronic potential ΔV_H may be defined from the self-energy, and how this definition reduces to the straightforward image potential results under the usual decomposition of the self-energy into Coulomb hole and screened exchange contributions.

In the self-energy formalism the effective single-particle potential ΔV_H may be defined as follows:

$$\Delta V_H(\mathbf{r})\phi_H(\mathbf{r}) = \int d^3r'\,\Sigma(\mathbf{r},\mathbf{r}',\varepsilon_H^0)\phi_H(\mathbf{r}') \,, \tag{A1}$$

where ϕ_H is the unperturbed helium orbital with energy ε_H^0. This definition of the effective potential has been used in many calculation of the van der Waals energy.[36,37]

The self-energy is given by the *GW* approximation of Hedin and Lundqvist:[38]

$$\Sigma(\mathbf{r},\mathbf{r}',\omega) = \frac{i}{2\pi}\int G(\mathbf{r},\mathbf{r}',\omega+\omega')W(\mathbf{r},\mathbf{r}',\omega')e^{i\delta\omega'}d\omega' \,, \tag{A2}$$

where *G* is the single-particle Green function and *W* is the screened interaction. δ is a positive infinitesimal. As shown by Hedin and Ludqvist, this expression can be approximately divided into two types of terms. Firstly the poles of *W* give a Coulomb hole term and secondly the poles of *G* give a screened exchange energy. In our case these two terms give

$$\Sigma(\mathbf{r},\mathbf{r}',\varepsilon_H^0) = \tfrac{1}{2}W(\mathbf{r},\mathbf{r}',0)\delta(\mathbf{r}-\mathbf{r}') - \phi_H(\mathbf{r})\phi_H^*(\mathbf{r}')W(\mathbf{r},\mathbf{r}',0) \,.$$

Substituting into the expression for the effective potential we find, to a good approximation,

$$\Delta V_H(\mathbf{r}) = \tfrac{1}{2}W(\mathbf{r},\mathbf{r},0) - W(\mathbf{r},\mathbf{r}_H,0) \,,$$

and this is precisely the result found by image potential arguments as given in Eq. (9).

There are three points that confirm the physical validity of this potential: Firstly, the leading change in the adatom energy gives the Lennard-Jones-van der Waals potential. Secondly, there is no net force on the electron when the two image charges are superimposed, since $\nabla(\Delta V_H)=0$ at $\mathbf{r}=\mathbf{r}_H$. Thirdly, the adatom eigenvalue is shifted upwards by an amount $+1/4z_H+\cdots$ [see Eq. (10)] implying that the energy to remove an electron from the atom to infinity is given by $-\varepsilon_H^0-1/4z_H+\cdots$. This is the correct electron removal energy since there is a positive ion left behind at z_H.

APPENDIX B

In this appendix we shall discuss the hybridization energy that would be obtained in the Hartree-Fock approximation. Zaremba and Kohn[3] argued that within the Hartree-Fock approximation the perturbation of the helium 1*s* wave function would be of order $S(\sim|\phi_q(z_H)|^2)$, and hence that any hybridization energy would be of order S^2, negligible compared to the other terms. Here we shall reexamine this question, and come to the conclusion that in fact the perturbation in the helium wave function is of order $S^{1/2}$ and hence the hybridization energy is of order S, which is the same order as the overlap repulsion energy.

Let us start with a basis of an unperturbed helium 1*s* orbital ϕ_H, and orthogonalized metal states, $\phi_k-s_k\phi_H$, as in Eq. (4) $(s_k=\langle\phi_k|\phi_H\rangle)$. The perturbation in the helium wave function is of order M_k, where M_k is defined by Eq. (8b), and the energy change is of order M_k^2, as in Eq. (7). In the Hartree-Fock approximation, the perturbing potential ΔV_H is given by the exchange potential of the metal states. To leading order in the overlap this gives

$$M_k=\sum_q\int\int\frac{\phi_k(\mathbf{r}')\phi_q(\mathbf{r}')\{\phi_q(\mathbf{r})-s_q\phi_H(\mathbf{r})\}\phi_H(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d^3r\,d^3r'\,, \tag{B1}$$

summed over all the occupied metal states ϕ_q. Consider first the $\mathbf{r}'$ integral in Eq. (B1); this is dominated by the region inside the metal and is therefore of order S^0. On the other hand, the $\mathbf{r}$ integral is dominated by the region near the helium atom (because ϕ_H is strongly localized) and is of order $S^{1/2}$. To prove this we can make a multipole expansion of $|\mathbf{r}-\mathbf{r}'|^{-1}$ for $|\mathbf{r}'|\gg|\mathbf{r}|$, taking the helium nucleus as the origin. The first nonzero term in the integral is then:

$$\int\frac{\phi_q(\mathbf{r})rP_1[\cos(\theta)]\phi_H(\mathbf{r})}{(r')^2}d^3r\sim\phi_q(0)\int e^{-qz}\frac{z}{(r')^2}\phi_H(\mathbf{r})d^3r\,, \tag{B2}$$

which is of order $S^{1/2}$ for any $q\neq0$. We have therefore shown that the hybridization matrix element M_k is of order $S^{1/2}$ and hence that the hybridization energy is of order S in the Hartree-Fock approximation.

Our proof differs from that of Zaremba and Kohn[3] only in the choice of basis set used to expand the perturbation of the helium wave function. But clearly the order of magnitude of the hybridization energy cannot depend on the basis set; therefore let us reconsider our derivation using the basis set of Zaremba and Kohn. Zaremba and Kohn expanded the perturbation of the helium 1*s* in terms of the excited orbitals of the helium atom, $\phi_{H'}$. In this basis set the relevant matrix element is $M_{H'}$, which is given by

$$M_{H'}=\sum_q\int\int\frac{\phi_{H'}(\mathbf{r}')\{\phi_q(\mathbf{r}')-s_q\phi_H(\mathbf{r}')\}\{\phi_q(\mathbf{r})-s_q\phi_H(\mathbf{r})\}\phi_H(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d^3r\,d^3r'\,. \tag{B3}$$

Clearly the $\mathbf{r}$ integral in this expression gives a result of order $S^{1/2}$ by the same reasoning as above. It would appear at first sight that the $\mathbf{r}'$ integral is also of order $S^{1/2}$ by the same argument and hence that $M_{H'}$ is of order S; however this is not correct. This is because the $\mathbf{r}'$ integral is not dominated by the region inside the helium atom as the $\mathbf{r}$ integral was. To see this note that $\phi_{H'}$ is localized like $e^{-br'}$ near the helium, where $-\frac{1}{2}b^2=E_{H'}$, while the metal state behaves like $e^{-qz'}$ near the helium, with $\frac{1}{2}q^2=\Phi$ and with Φ the work function of the metal. Thus the integral over r' behave like

$$\int\exp(-qz')\exp(-br')d^3r'$$

near the helium. This integral will only be dominated by the region near the helium if $b>q$, or if $-E_{H'}>\Phi$; a condition which is not satisfied since each excited state of the helium lies above the metal work function. Therefore in Eq. (B3) the $\mathbf{r}'$ integral is of order S^0, and the $\mathbf{r}$ integral of order $S^{1/2}$, giving an overall matrix element of order $S^{1/2}$ and thus an energy shift of order S. We can conclude therefore that even in the Hartree-Fock approximation there is a large contribution to the helium energy due to relaxation of the helium 1*s* orbital under the perturbation of the surface.

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