

## Inelastic scattering of rare-gas atoms from metal surfaces. Excitation of electron-hole pairs

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We have studied the inelastic scattering of rare-gas atoms from a metal surface due to the excitation of electron-hole pairs. By comparing with a quantum-mechanical calculation we show that a classical trajectory treatment of the rare-gas atom should in general be sufficient. From an *ab initio* calculation for He atoms scattered from a Cu surface, we conclude that the electronic mechanism is of little importance for inelastic scattering of rare-gas atoms.

### I. INTRODUCTION

The inelastic scattering of atoms from surfaces has recently attracted large interest, both experimentally<sup>1-4</sup> and theoretically.<sup>1,5-9</sup> A basic question is how the atoms lose their energy. It has been proposed that this occurs through the excitation of phonons<sup>5</sup> or electron-hole pairs.<sup>6-9</sup> There have been a number of model calculations,<sup>5-9</sup> which have given information about general features of these two mechanisms. However, it is often hard to calculate the parameters in these models, and for many systems there seems to be little conclusive evidence about the relative importance of the two mechanisms.

The electron-hole pair mechanism is expected to be particularly important if the incoming atom has a level close to the Fermi energy.<sup>7,9</sup> In most experiments, however, the scattering of rare-gas atoms has been studied. Since the levels of a rare-gas atom are far from the Fermi energy, one may expect the phonon mechanism to dominate. Nevertheless, certain aspects of the experimental results have given rise to speculations that the electronic mechanism is important even for rare-gas atoms. We have therefore performed a calculation for scattering of He atoms from a Cu surface. The He atom acts on the substrate electrons as an essentially repulsive pseudopotential, and the simplicity of this coupling makes a fairly realistic calculation possible.

Normally the incoming atom is treated as a classical particle.<sup>6,7,9</sup> In such a treatment it is assumed that the atom moves along a classical trajectory

and that it simply acts as an external perturbation on the substrate electrons. We have performed a full quantum-mechanical calculation, and the results are compared with a classical treatment of the rare-gas atom. The validity of the classical approximation is discussed.

In Sec. II we present the formalism and our model. The quantum-mechanical and classical treatment of the rare-gas atom are compared in Sec. III. The numerical results are presented in Sec. IV and the conclusions in Sec. V.

### II. QUANTUM-MECHANICAL FORMULATION AND MODEL

Although the scattered rare-gas atom moves slowly, the Born-Oppenheimer approximation is clearly not sufficient, since it would not allow for inelastic scattering due to electron-hole pair excitations. We are therefore interested in the nonadiabatic corrections. A general treatment of this problem has been given by Born and Huang<sup>10</sup> and others.<sup>11</sup> This formalism was first used by Brivio and Grimley<sup>8</sup> to treat the interaction of an atom with a surface.

Assuming that the ions of the substrate are rigid we write the Hamiltonian as

$$H = \sum_i \left[ -\frac{\hbar^2}{2m} \nabla_i^2 \right] + V(\vec{r}, \vec{R}) - \frac{\hbar^2}{2M} \nabla_{\vec{R}}^2$$

$$\equiv T_E + U + T_N, \quad (1)$$

where  $\vec{r}_i$  is the coordinate of electron  $i$ ,  $\vec{R}$  the atomic coordinate, and  $\vec{r}=(\vec{r}_1, \vec{r}_2, \dots)$ . The electron and nuclear masses are given by  $m$  and  $M$ , respectively. We expand the wave function  $\chi(\vec{r}, \vec{R})$  of the system in terms of the electronic eigenfunctions  $\phi_m(\vec{r}, \vec{R})$  and eigenvalues  $E_m(\vec{R})$  of  $T_E + U$  for a given  $R$  as

$$\chi(\vec{r}, \vec{R}) = \sum_m \psi_m(\vec{R}) \phi_m(\vec{r}, \vec{R}). \quad (2)$$

This leads to an equation<sup>10</sup> for  $\psi_m(\vec{R})$

$$[T_N + E_n(\vec{R}) - E] \psi_n(\vec{R}) = \sum_m A_{nm}(\vec{R}, \nabla_{\vec{R}}) \psi_m(\vec{R}), \quad (3)$$

where

$$A_{nm}(\vec{R}, \nabla_{\vec{R}}) = \frac{\hbar^2}{2M} \int d^3r \phi_n^*(\vec{r}, \vec{R}) \times [\nabla_{\vec{R}}^2 \phi_m(\vec{r}, \vec{R}) - \phi_m(\vec{r}, \vec{R}) \nabla_{\vec{R}}^2]. \quad (4)$$

Introducing a Green's function which satisfies the scattering boundary conditions defined below,

$$\left[ -\frac{\hbar^2}{2M} \nabla_{\vec{R}}^2 + E_n(\vec{R}) - E \right] G_n(\vec{R}, \vec{R}', E) = \delta(\vec{R} - \vec{R}'), \quad (5)$$

we find for the inelastic part

$$\psi_n(\vec{R}) = \sum_m \int d^3R' G_n(\vec{R}, \vec{R}', E) A_{nm}(\vec{R}', \nabla_{\vec{R}}) \psi_m(R'). \quad (6)$$

The scattering experiments are usually performed with particle energies in the meV range. Rare-gas atoms can therefore only penetrate the outermost tail of the electron density where the lateral inhomogeneity is very small. We therefore assume that  $E_n(\vec{R})$  only depends on the coordinate perpendicular to the surface,  $Z$ . Since we shall consider delocalized electronic excitations only, it is reasonable to assume that all the curves  $E_n(R)$  are parallel, i.e.,

$$E_n(R) = V(Z) + \epsilon_n. \quad (7)$$

Then a Green's function with outgoing scattered-wave boundary conditions is given by

$$G_n(R, R', E) = \frac{1}{(2\pi)^2} \int d^2k e^{i\vec{k}_{\parallel}(\vec{R}_{\parallel} - \vec{R}'_{\parallel})} \times \tilde{g} \left[ E - \epsilon_n - \frac{\hbar^2 \vec{k}_{\parallel}^2}{2M}, Z, Z' \right], \quad (8)$$

with

$$\tilde{g}(E, Z, Z') = \frac{2\pi M}{\hbar^2 k} f(k, Z_{<}) g(k, Z_{>}), \quad (9)$$

where  $k = \sqrt{2ME}/\hbar$ ,  $Z_{<}$  ( $Z_{>}$ ) is the smaller (larger) of  $Z$  and  $Z'$ . The function  $f(k, Z)$  is the regular and  $g(k, Z)$  is an irregular solution (unbounded for  $Z \rightarrow -\infty$ ) of

$$\left[ -\frac{\hbar^2}{2M} \frac{d^2}{dZ^2} + V(Z) - E \right] \phi(Z) = 0, \quad (10)$$

with the boundary conditions

$$\lim_{Z \rightarrow \infty} f(k, Z) = \sqrt{2/\pi} \sin(kZ + \phi_k), \quad (11)$$

$$\lim_{Z \rightarrow \infty} g(k, Z) = \frac{1}{\sqrt{2\pi}} e^{i(kZ + \phi_k)},$$

for some value of  $\phi_k$ . The positive  $Z$  axis points towards the vacuum side. This result follows from standard techniques for calculating the Green's function for a linear second-order differential equation,<sup>12</sup> which simplifies to the form (9) if the Wronskian is a constant.

We now assume that electron-electron interaction effects are included in an effective exchange-correlation potential.<sup>13</sup> We write

$$V(\vec{r}, \vec{R}) = \sum_i [w(\vec{r}_i) + v(\vec{r}_i - \vec{R})], \quad (12)$$

where  $w(r_i)$  describes the effective potential in the absence of the rare-gas atom and  $v(r_i - R)$  is the pseudopotential of the rare-gas atom. In analogy with Eq. (7) we assume that  $w(r)$  only depends on the  $Z$  coordinate. Equation (12) reduces the electronic problem to a one-body problem and the excited states are characterized by the occupied states above the Fermi energy  $\epsilon_F$  and the unoccupied states below  $\epsilon_F$ . The interaction between the helium atom and the substrate electrons is not very strong. For instance, the  $t$  matrix for a plane wave with  $\vec{k}=0$ ,  $t_0$ , is only a factor 2 smaller than the result in the Born approximation.<sup>14</sup> We therefore assume that lowest-order perturbation theory is valid. Since the range of  $v(r)$  is fairly short, of the order  $2-3a_0$ , we can partly include higher-order effects by making the replacement

$$\int d^3x \phi_{\mu}^*(\vec{x}) v(\vec{x} - \vec{R}) \phi_{\nu}(\vec{x}) \rightarrow \phi_{\mu}^*(\vec{R}) \phi_{\nu}(\vec{R}) t_0. \quad (13)$$

This procedure is well-known in the theory of neutron scattering. We need to know how the one-particle functions  $\phi_{\mu}(\vec{x}, \vec{R})$  vary with  $\vec{R}$ . To lowest order we have

$$\phi_{\mu}(\vec{x}, \vec{R}) = \phi_{\mu}(\vec{x}) + \sum_{\nu \neq \mu} \frac{\phi_{\mu}(\vec{x}) \int d^3x' \phi_{\mu}^*(\vec{x}') v(\vec{x}' - \vec{R}) \phi_{\nu}(\vec{x}')}{\epsilon_{\mu} - \epsilon_{\nu}}, \quad (14)$$

where  $\phi_{\mu}(\vec{x})$  and  $\epsilon_{\mu}$  are calculated without the perturbation from the helium atom. From (14) we can easily obtain  $A_{nm}(\vec{R})$  which is inserted in Eq. (6). Since we are only interested in the lowest-order effect the summation over  $m$  is limited to  $m=0$ , which is the label of the elastic scattering function  $\psi_0(\vec{R})$ . We now consider the limit when  $\vec{R}$  is far outside the surface. In this limit we can perform partial integrations to obtain

$$\lim_{Z \rightarrow \infty} \psi_{\mu\nu}(\vec{R}) = -\frac{1}{(2\pi)^2} \int d^2k_{\parallel} e^{ik_{\parallel} \cdot R_{\parallel}} e^{ik_{\perp}^f Z} m_{\mu\nu}(k_{\parallel}), \quad (15)$$

with

$$m_{\mu\nu}(\vec{k}_{\parallel}) = \frac{2M}{\hbar^2 k_{\perp}^f} \int d^3R d^3r e^{-i\vec{k}_{\parallel} \cdot \vec{R}} \int f(k_{\perp}^f, Z) v(\vec{r} - \vec{R}) \phi_{\mu}^0(\vec{r})^* \phi_{\nu}^0(\vec{r}) \psi_0^0(\vec{R}), \quad (16)$$

where  $k_{\perp}^f(k_{\perp}^i)$  is the perpendicular momentum of the scattered (incoming) atom and  $\psi_0^0(\vec{R}) = f(k_{\perp}^i, Z) \times \exp(i\vec{k}_{\parallel}^i \cdot \vec{R}_{\parallel})/2\pi$ . This first-order result could also have been obtained from the distorted-wave Born approximation.<sup>15</sup> We now make the replacement (13) and write the electronic wave functions as  $\phi_{\mu}(\vec{r}) = h_{k_{\perp}^{\mu}}(z) \exp(i\vec{k}_{\parallel}^{\mu} \cdot \vec{r}_{\parallel})/2\pi$ . Then we perform the  $\vec{R}_{\parallel}$  integral in (16) which produces the parallel momentum conservation delta function. Inserting into (15) yields

$$\lim_{Z \rightarrow \infty} \psi_{\mu\nu}(\vec{R}) = -\frac{e^{i(\vec{k}_{\parallel}^i - \vec{k}_{\parallel}^{\nu} + \vec{k}_{\parallel}^{\mu}) \cdot \vec{R}_{\parallel}}}{2\pi} e^{ik_{\perp}^f Z} m_{\mu\nu}, \quad (17)$$

with

$$m_{\mu\nu} = \frac{1}{(2\pi)^2} t_0 \frac{2M}{\hbar^2 k_{\perp}^i} \int_{-\infty}^{\infty} dZ f(k_{\perp}^f, Z) h_{k_{\perp}^{\mu}}^*(Z) h_{k_{\perp}^{\nu}}(Z) f(k_{\perp}^i, Z).$$

To calculate the probability  $P_{\vec{k}_{\perp}^{\mu} \rightarrow \vec{k}_{\perp}^{\nu}}$  of exciting an electron from the state  $\vec{k}^{\mu}$  to the state  $\vec{k}^{\nu}$  we have to take the ratio of outgoing to ingoing flux. With the normalization of  $f(k_{\perp}^i, Z)$  the incoming flux is  $(1/2\pi)^2 k_{\perp}^i/4$  and the total outgoing (non-angular-resolved) flux follows from (17) as  $(1/2\pi)^2 k_{\perp}^f |m_{\mu\nu}|^2$ . So we have

$$P_{\vec{k}_{\perp}^{\mu} \rightarrow \vec{k}_{\perp}^{\nu}} = \frac{4k_{\perp}^f}{k_{\perp}^i} |m_{\mu\nu}|^2. \quad (18)$$

The probability that the atom losses the energy  $\epsilon$  and momentum  $\vec{k}_{\parallel}$  is then

$$P(\epsilon, \vec{k}_{\parallel}) = 2 \int d^3k^{\mu} \int d^3k^{\nu} P_{k^{\mu} \rightarrow k^{\nu}} f(\epsilon_{\mu}) [1 - f(\epsilon_{\nu})] \delta(\epsilon + \epsilon_{\mu} - \epsilon_{\nu}) \delta(\vec{k}_{\parallel} + \vec{k}_{\parallel}^{\mu} - \vec{k}_{\parallel}^{\nu}), \quad (19)$$

where  $f(\epsilon) = 1/[1 + \exp(\beta\epsilon)]$  is the Fermi function and  $T = 1/\beta$  is the temperature. To calculate the inelastic scattering probability (19) we have to specify the potential  $V(Z)$  [Eq. (7)] felt by the incoming atom and the potential  $w(r)$  felt by the electrons. The potential  $V(Z)$  is obtained from the calculation by Zaremba and Kohn<sup>16</sup> and for the  $w(r)$  we use the step barrier model

$$w(r) = \begin{cases} 0, & z \leq 0 \\ \epsilon_F + \phi \equiv \Delta\phi, & z > 0 \end{cases} \quad (20)$$

where  $\phi$  is the work function. The electronic-wave functions are given by

$$\phi_{\mu}(r) = e^{i\vec{k}_{\parallel}^{\mu} \cdot \vec{r}_{\parallel}} h_{\mu}(z), \quad (21)$$

where

$$h_{\mu}(z) = \frac{2}{\sqrt{\pi}} \times \begin{cases} \sin(k_{\perp}^{\mu} z + \phi_{\mu}) \\ \frac{k_{\perp}^{\mu}}{\sqrt{\Delta\phi}} e^{-\kappa_{\mu} z}, \end{cases} \quad (22)$$

where  $\hbar k_{\perp}^{\mu} = \sqrt{2m\epsilon_{\mu}}$  and  $\hbar\kappa_{\mu} = [2m(\Delta\phi - \epsilon_{\mu})]^{1/2}$ . Then we obtain

$$P(\epsilon, \vec{k}_{\parallel}) = \frac{1}{4\pi^6} \int d^2k'_{\parallel} \int_0^{\infty} dk'_{\perp} P_{k' \rightarrow k''} f(\epsilon_{k'}) [1 - f(\epsilon_{k'} + \epsilon)] \frac{1}{k'_{\perp}} \quad (23)$$

where  $k' = (\vec{k}'_{\parallel}, k'_{\perp})$  and  $k''$  is determined by conservation of energy and parallel momentum. We are interested in energy transfers and temperatures which are very small on the scale of electronic energies. Therefore, for a given  $\vec{k}'_{\parallel}$ , the product of the two Fermi functions is non-negligible only for a very small interval of  $k'_{\perp}$  values. If we assume that the other quantities do not change over this interval, the  $k'_{\perp}$  integral can be evaluated and

$$P(\epsilon, \vec{k}_{\parallel}) = \frac{1}{8\pi^6} \frac{\epsilon}{1 - \exp(-\beta\epsilon)} \times \int_{|\vec{k}'_{\parallel}| \leq k_F} d^2k'_{\parallel} \frac{P_{k' \rightarrow k''}}{k'_{\perp} k'_{\parallel}}, \quad (24)$$

where  $\epsilon_{k'}$  and  $\epsilon_{k''}$  are now assumed equal to  $\epsilon_F$ .

### III. COMPARISON WITH CLASSICAL TREATMENT

It is often assumed that the scattered atom can be treated as a classical particle. A general discus-

sion of this assumption has been given by, e.g., Child<sup>17</sup> for intermolecular scattering. Here we give a more explicit and quantitative discussion for scattering of rare-gas atom from a surface by choosing the potential  $V(Z)$  in Eq. (7) in such a way that the problem can be solved analytically. Since the van der Waals attraction of a helium atom is weak, we neglect it for the moment and assume that the potential is purely repulsive. We expect the potential to have a steep almost exponential growth and assume

$$V(Z) = \begin{cases} 0, & Z > Z_0 \\ \infty, & Z \leq Z_0 \end{cases} \quad (25)$$

where  $Z_0$  is the classical turning point. From Eq. (18) we obtain the quantum mechanical transition probability

$$P_{\mu \rightarrow \nu}^{\text{QM}} = c^2 \frac{k_{\perp}^f}{k_{\perp}^i} \left[ \frac{\hbar\alpha v_{\perp}^i}{(\hbar^2\alpha^2/2M)^2 + \hbar^2\alpha^2 \frac{1}{2}(v_{\perp}^{i2} + v_{\perp}^{f2}) + [\epsilon - \hbar\vec{k}_{\parallel} \cdot \frac{1}{2}(\vec{v}_{\parallel}^i + \vec{v}_{\parallel}^f)]^2} \right]^2, \quad (26)$$

where  $c = 2t_0 k_{\perp}^{\mu} k_{\perp}^{\nu} e^{-\alpha Z_0} / \Delta\phi$ ,  $\alpha = \kappa_{\mu} + \kappa_{\nu}$  and  $v_{\perp}^i$  ( $v_{\perp}^f$ ) is the perpendicular part of the velocity of the rare-gas atom in the initial (final) state. The classical result is obtained from

$$P_{\mu \rightarrow \nu}^{\text{cl}} = \frac{1}{\hbar^2} \left| \int_{-\infty}^{\infty} dt \langle \nu | v[r - R(t)] | \mu \rangle e^{i\epsilon t/\hbar} \right|^2, \quad (27)$$

where  $R(t)$  describes the classical trajectory. We find

$$P_{\mu \rightarrow \nu}^{\text{cl}} = c^2 \left[ \frac{\hbar\alpha v_{\perp}}{(\hbar\alpha v_{\perp})^2 + (\epsilon - \hbar\vec{k}_{\parallel} \cdot \vec{v}_{\parallel})^2} \right]^2, \quad (28)$$

where  $v_{\perp}$  and  $\vec{v}_{\parallel}$  can be taken to be  $v_{\perp}^i$  and  $\vec{v}_{\parallel}^i$ , respectively.

We can see immediately that if the energy and momentum transfers are small the classical description is valid if

$$v_{\perp} \gg \frac{\hbar\alpha}{2M}, \quad (29)$$

or if

$$\lambda \equiv \frac{2\pi\hbar}{Mv_{\perp}} \ll \frac{4\pi}{\alpha}. \quad (30)$$

This means that the classical description is valid if the wave function  $f(k_{\perp}, Z)$  of the rare-gas atom has many oscillations over the region  $4\pi/\alpha$ , which is essentially the range over which the particle interacts with the substrate. For a helium atom with the energy 0.025 eV we find

$$\frac{2Mv_{\perp}}{\hbar\alpha} \sim 6, \quad (31)$$

and the condition (29) is fairly well satisfied. We have calculated  $\alpha$  under the assumptions that electronic states close to the Fermi energy with  $\vec{k}_{\parallel} = 0$  are excited and that the helium atom has normal incidence. As expected the classical description be-

comes better if, for fixed velocity, the mass is increased or if the velocity is increased for a fixed mass.

We now assume for a moment that  $\vec{k}_{\parallel}=0$  but that  $\epsilon$  is non-negligible. From Eq. (27) we can see that in the classical description the probability for an energy transfer  $\epsilon$  is substantially reduced if

$$\frac{|\epsilon|}{\alpha v_{\perp}} \equiv |\epsilon| T \gg 1, \quad (32)$$

where  $T=1/(\alpha v_{\perp})$  is the time during which the perturbation is large. If the condition (32) is fulfilled there is a large destructive interference in (27). In the quantum-mechanical description the relation  $|\epsilon| \lesssim \alpha v_{\perp}$  is less obvious, since there is no classical trajectory and the velocity plays a less conspicuous role. Nevertheless we can see from Eq. (17) that the functions  $f(k_{\perp}^f, Z)$  and  $f(k_{\perp}^i, Z)$  interfere destructively over the range of  $h_{\mu}^*(z)h_{\nu}(z)$ , that is the matrix element is small, if

$$|k_{\perp}^i - k_{\perp}^f| \gg \alpha. \quad (33)$$

Multiplying by  $v_{\perp}$  it becomes clear that Eqs. (32) and (33) are essentially the same. That the energy dependence is very similar can also be seen directly from Eqs. (26) and (28), which are also shown in Fig. 1. For large energy losses, however, the results are different because of the prefactor  $k_{\perp}^f/k_{\perp}^i$  in the quantum mechanical expression. This prefactor prevents, for the given  $V(Z)$  [Eq. (25)], energy losses larger than the initial energy, which would be unphysical.

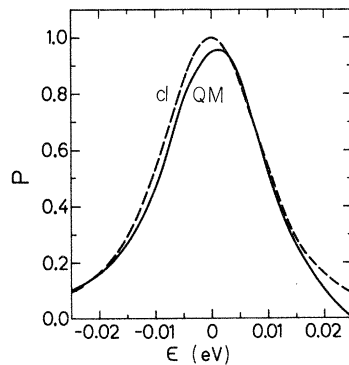


FIG. 1. Probability of exciting an electron-hole pair with energy  $\epsilon$  as a function of  $\epsilon$ . The results for a quantum-mechanical (solid line) and a classical (dashed line) treatment of the scattered atom are compared. We have considered a helium atom with the initial energy 25 meV and assumed normal incidence without parallel momentum transfer. The curves have been normalized so that the classical result for  $\epsilon=0$  is unity.

Finally, we discuss the case of a more realistic  $V(Z)$  which increases gradually. In a classical description there is, in general, no difference between matrix elements for a gain and for a loss process [see Eq. (27)]. In the quantum-mechanical description, however, the final-state wave function  $f(k_{\perp}^f, Z)$  penetrates deeper into the surface if the “perpendicular” energy  $\hbar^2 k_{\perp}^2/2M$  is increased instead of decreased. Therefore, the interaction with the electronic states becomes stronger and the matrix element larger. Thus, although the Fermi factors in Eq. (19) tend to suppress the energy gain events the matrix elements tend to have the opposite effect. In certain situations the energy gain events can therefore dominate in the quantum-mechanical treatment.

#### IV. RESULTS

We first consider the work of Mason and Williams<sup>4</sup> on the scattering of helium from a Cu surface. For the theoretical description we use the He-Cu adiabatic potential of Zaremba and Kohn<sup>16</sup> and the He electron  $t$  matrix of Jortner *et al.*<sup>14</sup> The initial energy of the He atoms is 22.6 meV and the temperature is 16 K. In Fig. 2 we show the probability for inelastic scattering as a function of the

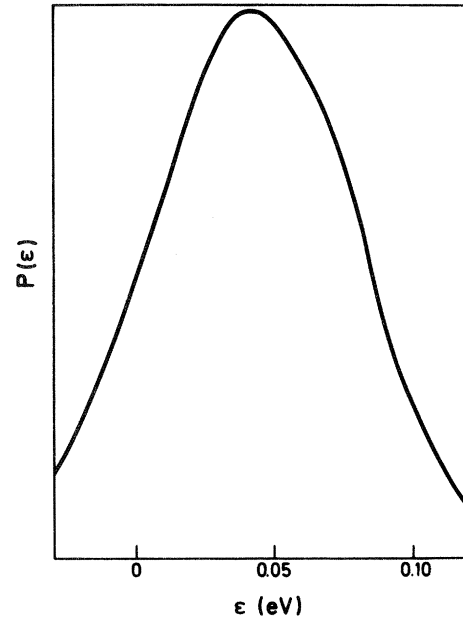


FIG. 2. The probability

$$P(\epsilon) = \frac{1}{2(\pi)^2} \int d^2 k_{\parallel} P(\epsilon, \vec{k}_{\parallel})$$

that the helium atom loses an energy  $\epsilon$  to electron-hole pair excitations.

energy transfer  $\epsilon$ . The integrated probability for inelastic scattering is  $10^{-5}$ . We note that this intensity is much smaller than the experimental result. We can also extract results for the energy accommodation coefficient<sup>1</sup>

$$\alpha = \frac{E_r - E_i}{E_s - E_i}, \quad (34)$$

where  $E_i$  is the energy of the incident atoms,  $E_r$  the average energy of the scattered atoms, and  $E_s = k_B T_s$  is the energy of atoms in thermal equilibrium with the surface. We find  $\alpha \approx 1 \times 10^{-6}$  which is about 4 orders of magnitude smaller than experiment.<sup>1</sup> These results are in agreement with the interpretation that the phonon mechanism dominates. We also consider the experiment by Feuerbacher and Willis<sup>3</sup> for Ne atoms scattered from a Ni surface. Although both the  $t$  matrix and the rare-gas-atom—metal-surface interaction are different, these differences should not be large enough to change the qualitative result. We therefore use the same model as before but change the initial energy of the rare-gas atom to 64.5 meV and use the temperature 300 K. We calculate the total inelastic scattering probabilities to be  $2 \times 10^{-4}$ . Feuerbacher and Willis<sup>3</sup> observed inelastic events corresponding to an energy transfer of 15–45 meV, which occurred for almost zero parallel momentum transfer. Since there have been some speculations that these events are due to electron-hole pair excitations we show in Fig. 3 the inelastic scattering probability as a function of the absolute value of the parallel momentum transfer for a given energy transfer. This probability basically decreases with increasing value of  $|\vec{k}_{\parallel}|$ . However, this decrease is much too slow to explain the data of Feuerbacher and Willis,<sup>3</sup> and the figure gives no support for the interpretation that the electron-hole pair mechanism is important for Ne-Ni scattering. In passing we note that the initial increase in  $P(\epsilon, k_{\parallel})$  in Fig. 3 can be understood from, e.g., Eq. (26), since a finite  $\vec{k}_{\parallel}$  with an appropriate direction reduces the last term in the denominator. This effect does not occur for  $\epsilon \sim 0$ . Finally, we note the electron-hole pairs could also in principle be excited by long-range van der Waals forces. However, Schaich and Harris<sup>18</sup> have found this effect to be negligible.

## V. DISCUSSION

To understand the amazingly small result for the energy accommodation coefficient in Sec. IV, we

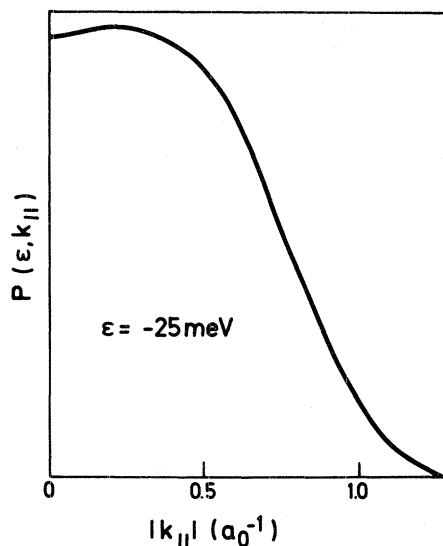


FIG. 3. The angular average of  $P(\epsilon, k_{\parallel})$  over the directions of  $\vec{k}_{\parallel}$  as a function of  $|\vec{k}_{\parallel}|$ . The initial energy is 64.5 meV and the figure shows results for events where the incident atom gains an energy 25 meV.

make a connection to our previously presented boson formalism<sup>9</sup> and perform a “back of the envelope” calculation.

We have shown<sup>9</sup> that for systems where the interaction mainly takes place via one adsorbate level the energy transfer can be written as

$$E_i - E_r = \frac{2}{\pi} \int_{-\infty}^{\infty} \left| \frac{d}{dt} \delta(t) \right|^2 dt. \quad (35)$$

The phase shift  $\delta(t) = \pi \Delta n(t)$  is directly related to the occupancy  $\Delta n(t)$  of the adsorbate level and the spin degeneracy has been taken into account. For simplicity, we assume that the He atom can be treated as a hard-core pseudopotential, where the core radius  $r_c$  is chosen so that the correct  $t$  matrix is obtained.<sup>14</sup> The unperturbed substrate density  $n(r)$  has to be excluded from the hard core and as an estimate of the induced charge we use

$$\Delta n(t) \approx - \int_{|r - R(t)| \leq r_c} n(r) d^3r, \quad (36)$$

which gives an approximation to  $\delta(t)$  if we assume that mainly one adsorbate level is involved. For the adsorbate trajectory we assume

$$R(t) = Z_0 + v_0 |t|, \quad (37)$$

where  $Z_0$  is the classical turning point according to the potential energy curve of Zaremba and Kohn<sup>16</sup> and  $v_0$  is the initial velocity. We interpolate the results of Land and Kohn<sup>19</sup> for the jellium model to the density of copper ( $r_s = 2.67$ ) and find

a simple analytic form

$$n(r) = n_0 e^{-\alpha z} \quad (38)$$

approximately valid in the density tail far from the surface. Equations (36)–(38) give the phase shift

$$\delta(t) = -N n_0 e^{-\alpha Z_0} e^{-\alpha v_0 |t|} \quad (39)$$

where

$$N = 2\pi^2 [\alpha r_c (e^{\alpha r_c} + e^{-\alpha r_c}) - (e^{\alpha r_c} - e^{-\alpha r_c})] / \alpha^3.$$

This leads to the energy transfer

$$E_r - E_i = \frac{2}{\pi} (N n_0)^2 e^{-2\alpha Z_0} \alpha v_0 \quad (40)$$

and the energy accommodation coefficient is  $0.6 \times 10^{-6}$ , which differs by about a factor 2 from the more accurate calculations in Sec. IV. Considering that a change of  $r_c$  by about 10% would be enough to obtain the “correct” result, this is a good agreement.

We can now see that the main reason for the small energy transfer is the small maximum value of  $\delta(t) \sim 10^{-3}$ . The reason is that the substrate charge density is very small even at the turning point of the He atom. We can see from Eq. (39) that if the He atom could move to the jellium edge ( $Z_0 = 0$ ) the energy transfer would increase by almost 4 orders of magnitude.

For a chemically reactive molecule, with an adsorbate level close to the Fermi energy, the energy

transfer would be larger for several reasons. The attractive forces would bring the molecule in closer contact with the substrate (smaller  $Z_0$ ) and they would increase the velocity  $v_0$ . In addition, the fact that the level is close to the Fermi energy would tend to increase the occupancy  $\Delta n$ . For certain systems the adsorbate level may actually cross the Fermi energy.<sup>7</sup> In that case we would get  $\delta \sim \pi$ . Since  $E_r - E_i \sim \delta^2$  this fact alone would tend to increase our result by about 7 orders of magnitude.

## VI. CONCLUSIONS

We have studied the inelastic scattering of rare-gas atoms from metal surfaces. By comparing with a full quantum-mechanical calculation, we have found that for small energy and momentum transfers a classical treatment of the rare-gas atom is sufficient except for very small initial velocities. We have also calculated the total inelastic scattering probability and studied the dependence on the momentum transfer. The results show that the electron-hole pair mechanism should *not* be important for rare-gas atom scattering. Finally, we want to emphasize that the model used here is not applicable to atoms or molecules which react chemically with the surface and our conclusion does therefore not apply to such systems.

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