Long-range excitation of electron-hole pairs in atom-surface scattering

James F. Annett

Cavendish Laboratory, Madingley Road, Cambridge CB3 OHE, United Kingdom

P. M. Echenique

Euskal Herriko Unbersitatea, Kimika Fakultatea, Apdo. 1072, S. Sebasitan 20080, Donostia, Euskadi, Spain

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The van der Waals potential of a neutral atom moving near a surface has both real and imaginary parts. The imaginary part corresponds to real excitations of the atom and of the surface. Because of this imaginary part, the van der Waals potential can give rise to inelastic processes in atom-surface scattering, for example excitation of electron-hole pairs or surface plasmons. Using a self-energy formulation of the complex van der Waals interaction we derive expressions for inelastic scattering probabilities of atoms or ions reflected from surfaces. In the case of ion or electron scattering from surfaces this reproduces a well-known result. We calculate the probabilities for inelastic scattering of neutral xenon atoms incident on metal surfaces at hyperthermal energies. A comparison of our results with the recent experimental measurements of electron-hole pair excitation for hyperthermal xenon scattering by Amirav and Cardillo shows that this long-range van der Waals coupling is only a small contribution to the total electron-hole pair excitation probability, which is mostly due to thermal excitation.

When an atom, molecule, or ion is scattered from a surface there are a number of possible inelastic processes. For example, the probe particle may lose energy by creating phonons, electron-hole pairs, surface plasmons, or any other elementary excitation of the surface. A fundamental understanding of these processes is necessary since they are related to a number of important phenomena such as the sticking of atoms to surfaces, and the microscopic nature of friction. In particular the relative importance of electron-hole pair excitation as opposed to phonon creation has been the subject of much theoretical interest in recent years.

The recent experiments of Amirav and Cardillo[1,2] have provided a way of directly measuring the electron-hole pair contribution to the inelastic scattering, thus providing an experimental test of the theories. The experiments involve scattering a beam of hyperthermal xenon atoms (2–15 eV energy) from the surface of a Ge or InP p-n junction. The p-n junction is reverse biased so that electron-hole pairs excited in the depletion region of the diode will produce a current transient. In this way Amirav et al.[2] were able to estimate the product of the electron-hole pair excitation probability and the collection efficiency as of the order of 10^{-4} for xenon atoms of about 9 eV energy. Furthermore, estimating the collection efficiency to within an order of magnitude, Amirav and Cardillo proposed that the electron-hole pair excitation probability was of the order of 0.2 per xenon atom at 9 eV. This large probability for electron-hole pair creation was interpreted in terms of thermal excitation in a "hot spot" region where the kinetic energy of the incoming atom causes a large local increase in temperature.

In this paper we shall discuss an alternative mechanism for energy loss from an atom incident on a surface,

namely losses due to long-range van der Waals–type coupling. It is well known that the van der Waals energy of an atom at rest outside a surface is due to virtual excitations of both the atom and the substrate. If the atom is moving, however, the same mechanism can give rise to real excitations, thus resulting in inelastic scattering. For a metallic substrate the excitations that can be created are electron-hole pairs and, if there is sufficient energy, surface plasmons. The surface plasmons created will decay into electron-hole pairs because of damping.

In the following sections we shall first derive a general self-energy expression for a particle outside a surface. In the case of a neutral atom this expression gives the van der Waals energy as its real part and the inelastic scattering rate as its imaginary part. In the case of an ion the real part of the corresponding expression gives the image potential. We shall show below that the imaginary part of the self-energy for ion or electron scattering from surfaces reproduces a well-known result, due to Evans and Mills,[3] for the inelastic scattering probabilities. In a later section we shall derive an analogous formula for the inelastic scattering of a neutral atom from a surface. Finally we shall apply this result to the scattering of hyperthermal xenon atoms from jellium surfaces, and compare our results with the experiments of Amirav and Cardillo.[1]

GENERAL FORMULATION

In order to calculate dynamical processes such as electron-hole pair excitation in atom-surface scattering it is necessary to go beyond the Born-Oppenheimer approximation for the atomic motion. We do this perturbatively in our calculation, starting with a Born-Oppenheimer wave function for the atomic motion and

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introducing the coupling to the surface as a perturbation. The perturbation parameter is the Coulomb coupling between the atom and the surface, which is essentially of order $1/z^3$ for a neutral atom distance z from the surface, and of order $1/z$ for an ion.

Consider an atom moving in the half-space $z > 0$, and assume the surface to occupy $z < 0$. Neglecting any coupling between the atom and the surface we can write many-body wave functions for the combined system as products of wave functions for the atom and the surface separately. The atom will have a Born-Oppenheimer wave function of the form

$$|\alpha\rangle = \phi_\alpha(\mathbf{R})\psi_\alpha(\mathbf{r}_1, \mathbf{r}_2, \ldots; \mathbf{R}) , \tag{1}$$

where $\mathbf{R}$ is the nuclear coordinate, and $\mathbf{r}_1$, etc., are the electronic coordinates. Similarly we let $|\beta\rangle$ denote the electronic state of the substrate, but we assume the nuclei in the solid are static. If we now introduce the Coulomb coupling $\hat{V}$ between the atom and the surface, then the transition rate between product state $|\alpha\beta\rangle$ and state $|\alpha'\beta'\rangle$ is simply given by Fermi's golden rule:

$$\Gamma_{\alpha\beta,\alpha'\beta'} = 2\pi |\langle\alpha\beta|\hat{V}|\alpha'\beta'\rangle|^2 \delta(\varepsilon_{\alpha'} + \varepsilon_{\beta'} - \varepsilon_\alpha - \varepsilon_\beta) . \tag{2}$$

Here ε_α is the energy of state $|\alpha\rangle$, etc. We assume atomic units $\hbar = 1$ throughout. The perturbation $\hat{V}$ is the Coulomb operator coupling the atom and the surface:

$$\hat{V} = \int \int d^3r \, d^3r' \frac{\hat{\rho}_a(\mathbf{r})\hat{\rho}_s(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} , \tag{3}$$

where $\hat{\rho}_a(\mathbf{r}), \hat{\rho}_s(\mathbf{r})$ are the charge-density operators for the atom and the surface, respectively, i.e.,

$$\hat{\rho}_a(\mathbf{r}) = Z\delta(\mathbf{r} - \mathbf{R}) - \sum_i \delta(\mathbf{r} - \mathbf{r}_i) , \tag{4}$$

and Z is the charge on the nucleus.

The scattering rate given by Eq. (2) can be related to the imaginary part of a self-energy which gives the van der Waals energy for an atom (or image potential for an ion) as its real part. This follows simply from the definition

$$\Sigma_{\alpha\beta} = - \sum_{\alpha',\beta'} \frac{|\langle\alpha\beta|\hat{V}|\alpha'\beta'\rangle|^2}{\varepsilon_{\alpha'} + \varepsilon_{\beta'} - \varepsilon_\alpha - \varepsilon_\beta - i\delta} , \tag{5}$$

where δ is a positive infinitesimal. The real part of this expression gives the change in energy of the state $|\alpha\beta\rangle$ due to the perturbation V, and this just gives the van der Waals energy for an atom outside a surface[4] (or the image potential for an ion). The imaginary part of the self-energy $\Sigma_{\alpha\beta}$ gives the total transition rate

$$-2\,\text{Im}(\Sigma_{\alpha\beta}) = \sum_{\alpha',\beta'} \Gamma_{\alpha\beta,\alpha'\beta'} . \tag{6}$$

Clearly the real part of Eq. (5) corresponds to virtual excitations of both the atom and the surface while the imaginary part is due to real excitations. We can thus use the same quantity to calculate both the van der Waals energy and the inelastic scattering rate. In addition this allows us to use methods which have been developed to treat the van der Waals problem in our calculations of inelastic scattering.

Before we go on to apply Eq. (5) in our calculations, it is convenient to first rewrite it in terms of a surface dielectric function. When this is done the states $|\beta'\rangle$ of the substrate do not enter the equations explicitly and all the properties of the substrate enter only through this surface dielectric function. The surface dielectric function is defined by[4,5]

$$\text{Im}[g(q,\omega)] = \frac{2\pi}{q} \int d^2r_\parallel \int_{-\infty}^0 dz \int_{-\infty}^0 dz' \exp(qz + qz' - i\mathbf{q}\cdot\mathbf{r}_\parallel)\text{Im}[\chi(\mathbf{r}_\parallel, z, ', \omega)] , \tag{7}$$

where the density response function of the substrate is given by

$$\text{Im}[\chi(\mathbf{r}_\parallel - \mathbf{r}'_\parallel, z, z', \omega)] = \sum_{\beta'} \langle\beta|\hat{\rho}_s(\mathbf{r})|\beta'\rangle\langle\beta'|\hat{\rho}_s(\mathbf{r}')|\beta\rangle\pi\delta(\varepsilon_{\beta'} - \varepsilon_\beta - \omega) \tag{8}$$

for $\omega > 0$. Here $\mathbf{r} = (\mathbf{r}_\parallel, z)$. We assume translational invariance of the substrate in the x-y plane. The real part of the dielectric function $g(q,\omega)$ can be found by Kramers-Kronig analysis. The dielectric function $g(q,\omega)$ simply gives the linear response of the surface to a periodic external field of the form

$$\phi_{\text{exp}} = \phi_q \exp(i\mathbf{q}\cdot\mathbf{r}_\parallel + qz - i\omega t)$$

for $z < 0$, resulting in an induced field,

$$\phi_{\text{ind}} = -g(q,\omega)\phi_q \exp(i\mathbf{q}\cdot\mathbf{r}_\parallel - qz - i\omega t)$$

for $z > 0$. The surface dielectric function $g(q,\omega)$ has

been used in many studies of dynamical effects at surfaces (e.g., Refs. 5 and 6). Substituting this definition into our expression for the self-energy we obtain the following general result:

$$\Sigma_\alpha = \sum_{\alpha'} \int_0^\infty \frac{d\omega}{\pi} \int \frac{d^2q}{(2\pi)^2} \frac{2\pi}{q} \frac{|\langle\alpha|\hat{\rho}_q|\alpha'\rangle|^2}{\varepsilon_{\alpha'} - \varepsilon_\alpha + \omega - i\delta}$$
$$\times \text{Im}[g(q,\omega)] \tag{9}$$

with

$$\hat{\rho}_q = \int d^2r_\parallel \int dz \exp(-qz + i\mathbf{q}\cdot\mathbf{r}_\parallel)\hat{\rho}_a(\mathbf{r}) . \tag{10}$$

The subscript β has been dropped in Eq. (9), since the substrate is assumed to be in its ground state initially. Equation (9) gives our general result for the self-energy. It is applicable to a neutral atom or an ion near a surface, and includes both the wave functions for the electronic state and nuclear motion of the atom explicitly. The real part of Eq. (9) agrees with previous calculations of the static van der Waals interaction, while the imaginary part gives the inelastic scattering probabilities. In the following sections we shall apply Eq. (9) to a number of different atom or ion interactions with the surface.

ATOM MOVING PARALLEL TO A SURFACE

For a static atom located a distance z_0 outside a surface the self-energy of Eq. (9) is purely real and gives the van der Waals energy. In fact, in this case Eq. (9) reduces to a general expression for the van der Waals energy that we have derived previously,[6] using a similar self-energy approach. Let us consider an atom moving parallel to a surface at distance z_0 and with velocity v. The Born-Oppenheimer wave function for the atomic motion is

$$| z_0, \mathbf{v}_\parallel \rangle = \exp(i\mathbf{k}_\parallel \cdot \mathbf{r}_\parallel)\delta(z - z_0)\psi_0(\mathbf{r}_1, \dots, \mathbf{r}_N) ,$$

where $\mathbf{k}_\parallel = M\mathbf{v}_\parallel$. Since the atom is neutral the atomic charge density operator $\rho_a(\mathbf{r})$ is a dipole operator to leading order and we thus find the self-energy from Eq. (9):

$$\Sigma(z_0, \mathbf{v}_\parallel) = -\sum_n \frac{f_{n0}}{\omega_{n0}} \int_0^\infty \frac{d\omega}{\pi} \int \frac{d^2q}{(2\pi)^3} \frac{2\pi}{q} \frac{q^2 \text{Im}[g(q,\omega)]}{\omega + \omega_{n0} - \mathbf{q} \cdot \mathbf{v}_\parallel + q^2/2M - i\delta} , \qquad (11)$$

which is precisely the result derived in Ref. 6. Here f_{n0} is the dipole oscillator strength for a transition from atomic state 0 to n, with frequency ω_{n0}. In the low-velocity limit the van der Waals potential given by Eq. (11) has an asymptotic $-C_3/z_0^3$ behavior, in agreement with the standard results.[4] In addition, Eq. (11) has the advantage that it gives a well-behaved result for all atom-surface separations z_0. The standard asymptotic series approach to the van der Waals potential diverges at small separations. The origin of the divergence can be traced to a small-q expansion of the surface dielectric function $g(q,\omega)$; here we do not make any such small-q expansion. The spatial dispersion of the dielectric function $g(q,\omega)$ limits the surface response at short wavelengths, and is sufficient to keep the van der Waals potential finite. We have shown in Ref. 6 how Eq. (11) gives a van der Waals energy which becomes saturated from its $-C_3/z^3$ asymptotic form when the atom is close to the surface, giving a reduction in physisorbtion well depths compared to the unsaturated van der Waals calculation.

The self-energy given in Eq. (11) has zero imaginary part unless $|\mathbf{v}_\parallel| > 2M\omega_{n0}$. This implies that for low atomic velocities there is no friction for an atom moving parallel to a surface. This is in agreement with the observations of Schaich and Harris[7] and of Sols, Flores, and Garcia.[8] To obtain a nonzero friction coefficient it is necessary to take the calculation to higher orders of perturbation theory in the atom-surface coupling $\hat{V}$. The reason for this is that the leading-order theory requires a dipolar atomic transition, this must necessarily leave the atom in an excited state, and hence by energy conservation a high beam energy is necessary. This difficulty can only be surmounted if more than one transition takes place, which requires a higher order of perturbation theory. Because van der Waals forces are intrinsically weak, such high-order processes have an extremely low

cross section, giving only very small electron-hole pair excitation probabilities. Since these higher-order terms are small, we shall only discuss the leading-order processes in this paper. This means that we shall have to restrict our attention to high-energy atomic beams for which there is sufficient energy to excite real atomic transitions.

ION SCATTERED FROM A SURFACE

Let us now apply the general result of Eq. (9) to the problem of an ion scattered from a surface. In this case we can compare our self-energy approach with previous work on inelastic electron or ion scattering from surfaces. In fact we shall show that for ion or electron scattering our approach reproduces the well-known results of Evans and Mills.[3]

For the case of an atom or ion scattered from a surface the appropriate Born-Oppenheimer wave function is given by

$$| \mathbf{k} \rangle = \sqrt{2} \sin(k_z z) \exp(i\mathbf{k}_\parallel \cdot \mathbf{R}_\parallel)\psi_0(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) , \qquad (12)$$

where $\mathbf{k} = (\mathbf{k}_\parallel, k_z)$ and $\mathbf{R} = (\mathbf{R}_\parallel, z)$. Here we are assuming that the particle moves in zero potential for $z > 0$ and encounters a perfectly reflecting wall at $z = 0$. We are neglecting the effect of the van der Waals or image potential on the nuclear motion, since this is consistent with our treatment of the particle-surface coupling to lowest order in perturbation theory. If the probe particle is an ion the atomic density operator $\hat{\rho}_a(\mathbf{r})$ is a monopole, and we do not have to have dipolar transitions as in the neutral atom case. Substituting this wave function and density operator into the general self-energy expression of Eq. (9) we can calculate the inelastic scattering rate. Dividing by the incident flux of particles $k_z/(M\sqrt{2}) = v_\perp/(\sqrt{2})$ we can convert this to a scattering probability. We obtain the following result

for the probability of scattering from initial state $\mathbf{k}$ to final state $\mathbf{k}'$:

$$P(\mathbf{k},\mathbf{k}') = \frac{2}{\pi^2} \frac{Q^2}{qv_\perp} \left[\frac{q}{q^2 + (k_z - k_z')^2} - \frac{q}{q^2 + (k_z + k_z')^2} \right]^2 \text{Im}[g(q,\omega)],$$

(13)

where the parallel momentum transfer $q = \mathbf{k}_\parallel - \mathbf{k}_\parallel'$, and the energy loss is $\omega = k^2/2M - k'^2/2M$. Equation (13) applies equally to ions or electrons scattered from surfaces. The result is well known in the theory of inelastic scattering of electrons,[3,9] where it is used in analyzing electron energy-loss spectra (EELS) of surfaces[5,10,11] (usually the second term in the large parentheses is neglected since it is much smaller than the first for small energy losses). It is a useful check of our theory that it should reproduce this standard result. In the following section we shall generalize this result to the case of a neutral atom scattered from a surface.

NEUTRAL ATOM SCATTERED FROM A SURFACE

For a neutral atom scattered from a surface it is straightforward to extend the theory we have derived for ion scattering in the previous section. The only difference is that the probe particle no longer has a monopole contribution to the charge-density operator and we must take a dipole term as the leading contribution. Since we must have dipole transitions, we have to consider transitions from nuclear motion state $\mathbf{k}$ to $\mathbf{k}'$ and from electronic state 0 to n. Evaluating the self-energy of Eq. (9), taking the imaginary part, and dividing by the incident flux we obtain the following result for the inelastic scattering probability:

$$P_{0n}(\mathbf{k},\mathbf{k}') = \frac{f_{n0}}{\omega_{n0}} \frac{2}{\pi^2} \frac{q}{v_\perp} \left[\frac{q}{q^2 + (k_z - k_z')^2} - \frac{q}{q^2 + (k_z + k_z')^2} \right]^2$$

$$\times \text{Im}[g(q,\omega)] ,$$

(14)

where the energy loss is

$$\omega = k^2/2M - k'^2/2M - \omega_{n0} .$$

(15)

f_{n0} is the dipole oscillator strength for transition from electronic state 0 to n. Equation (16) constitutes our basic result. The formula is essentially a generalization of the well-known ion(electron)-surface scattering result of Eq. (13) to the case of a neutral atom.

A consequence of Eq. (14) is that there is no inelastic scattering if the initial kinetic energy $k^2/2M$ is less than the atomic excitation frequency ω_{n0}. As we discussed above, this is because we must have a dipole transition which leaves both the atom and the surface in an excited state. For instance, in the case of xenon-atom scattering

from a metal surface, Eq. (14) would give energy losses only above the excitation energy of about 9 eV. It is only possible to have electron-hole pair excitations for smaller incident energies by carrying the calculation to higher orders of perturbation theory. It is then possible to have a second-order process, where the atom is first virtually excited in a dipole transition, and is then deexcited via a second dipole transition while creating a real electron-hole pair or surface plasmon in the solid. Such transitions can occur whatever the incident energy of the atom, however, Sols, Flores, and Garcia[8] have investigated these higher-order effects for helium-surface scattering, and concluded that such terms make a negligible contribution. Another possibility is coupling via the short-range repulsion forces, rather than by the long-range dispersion force. Gunnarsson and Schönhammer[12] have found that the probability of electron-hole pair excitation due to the these overlap forces is a small effect.

In the following section we shall calculate the electron-hole pair excitation probability in xenon-surface scattering using Eq. (14). The treatment is thus restricted to beam energies of more than the excitation threshold for xenon, ~ 9 eV. This is certainly an experimentally feasible beam energy using seeded molecular beam techniques. It should also prove possible to observe the electron-hole pair production given by Eq. (9) at smaller beam energies using probe particles with a lower excitation threshold than xenon. An interesting example might be a heteropolar diatomic molecule where this mechanism could lead to vibrational excitation via the molecular dipole moment.

A self-energy method similar to ours has been employed by Manson and Ritchie.[13,14] These authors define a self-energy $\Sigma(Z)$ which depends on the position of the probe particle and its velocity. The imaginary part of their self-energy has two contributions: one is dissipative and gives energy losses when integrated along the particle trajectory, and the other contribution is nondissipative, and gives zero contribution when integrated along the particle trajectory. In our approach, this distinction between dissipative and nondissipative contributions does not arise; the imaginary part of our self-energy is always dissipative. This is because the integration over the particle trajectory is already included in our definition of the self-energy [Eq. (9)] which explicitly depends on the Born-Oppenheimer wave function for the particle motion.

XENON-SURFACE SCATTERING

As an example of the use of Eq. (14) for calculations of inelastic scattering probabilities we have applied it to xenon atoms reflected from simple metal surfaces. We approximate the surface dielectric function with the well-known specular reflection model of Ritchie and Marusak,[15] which gives

$$g(q,\omega) = \frac{1 - \varepsilon_s(q,\omega)}{1 + \varepsilon_s(q,\omega)} ,$$

(16)

with

$$\varepsilon_s(q,\omega)=\frac{q}{\pi}\int_{-\infty}^{\infty}dk_z\frac{1}{(k_z^2+q^2)\varepsilon(k,\omega)} , \qquad (17)$$

with $k^2=k_z^2+q^2$. For the bulk dielectric function $\varepsilon(k,\omega)$ we use the Mermin dielectric function,[16] which is a generalization of the usual Lindhard dielectric function. The Mermin dielectric function includes electron-hole pairs, plasmons, and also damping. The damping allows the plasmons to decay into electron-hole pairs, and gives the plasmon line a finite width. The Mermin dielectric function given by

$$\varepsilon(k,\omega)=1+\frac{(\omega+i\Gamma)[\varepsilon_L(k,\omega)-1]}{\omega+i\Gamma[\varepsilon_L(k,\omega)-1]/[\varepsilon_L(0,\omega)-1]} , \qquad (18)$$

where the parameter Γ measures the plasmon damping. $\varepsilon_L(k,\omega)$ is the usual Lindhard dielectric function, and is the $\Gamma\rightarrow0$ limit of the Mermin function.

Figure 1 shows our results for the total inelastic scattering probability of xenon atoms at normal incidence, over the energy range from 0 to 30 eV. The surface was taken at $r_s=2$ jellium. As we have already discussed, our leading-order calculation gives no electron-hole pair excitation except for incident energies above the atomic threshold of 9 eV, as can be seen in Fig. 1. Above the threshold energy the inelastic scattering probability rises rapidly with beam energy. The inelastic scattering probability is typically 10^{-5}, which is substantially smaller than the experimental estimates of Amirav and Cardillo.[1] Figure 1 also shows that the results are relatively insensitive to the magnitude of the plasmon damping parameter Γ, values of $\Gamma=0.05$, 0.2,
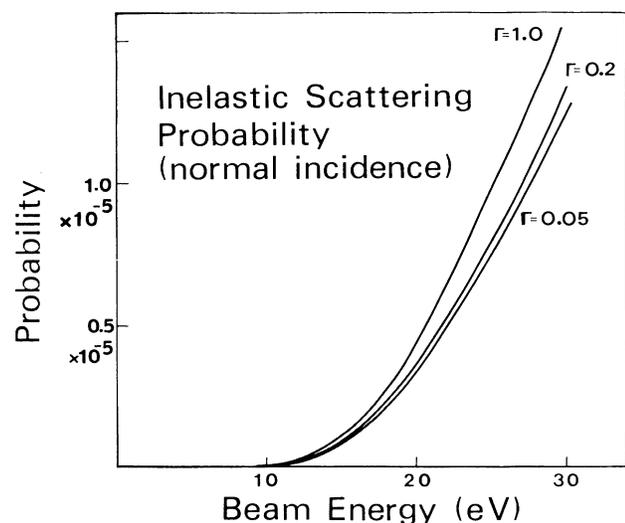
and 1.0 (in units of the Fermi energy, 12.5 eV for $r_s=2$) giving very similar results. This indicates that the dominant excitations produced are electron-hole pairs, not surface plasmons.

Away from normal incidence the inelastic scattering probability falls off quickly with the beam angle. This is demonstrated in Fig. 2 where we plot the total inelastic scattering probability for 15-eV xenon atoms. For comparison we also plot the loss probability of atoms at normal incidence with an energy $E_\perp=E_0\cos^2(\theta_i)$, $E_0=15$ eV. This demonstrates that the loss intensity scales very accurately with $E_\perp$, and that the motion parallel to the surface is relatively unimportant. As expected, the loss intensity shown in Fig. 2 drops almost to zero when E falls below the atomic excitation threshold ω_{n0}. For such large angles of incidence the only available loss processes involve a large momentum transfer to the solid with $q\gg2k_f$, a regime where the surface response function $\text{Im}[g(q,\omega)]$ is very small.

The overall magnitude of the electron-hole pair excitation probability that we calculate is of order 10^{-5}, which is much smaller than estimated experimentally by Amirav and Cardillo[1] (0.2 per xenon atom). Of course, the experiments were performed on semiconducting surfaces while our calculations were for metals, but this is unlikely to explain such a large discrepancy. For frequencies above the energy-gap region the semiconductor dielectric function should not be very different from the metallic one we used, since Ge and InP are weak pseudopotential materials with nearly-free-electron bands. Furthermore, both the semiconductor and the metal dielectric functions satisfy the same f sum rule:

$$\frac{2}{\pi}\int_0^\infty\omega\,\text{Im}\left|\frac{1}{\varepsilon(k,\omega)}\right|d\omega=-4\pi n ,$$

FIG. 1. Calculated inelastic scattering probabilities, for xenon atoms at normal incidence on an $r_s=2$ surface. The atomic excitation threshold is at about 9 eV. Calculations are shown with the Mermin plasmon damping parameter Γ at 0.05, 0.2, or 1.0 in units of the Fermi energy (12.5 eV for $r_s=2$).
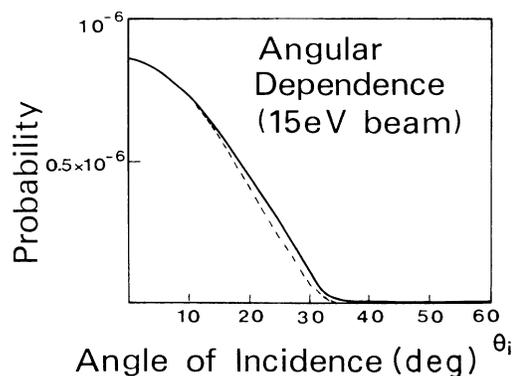
FIG. 2. Solid curve: loss probability vs angle of incidence for a 15-eV xenon atom (taking $\Gamma=0.2E_F$). Dashed curve: loss probability for xenon atoms at normal incidence with energy $E_\perp=E_0\cos^2(\theta_i)$, $E_0=15$ eV. This demonstrates good scaling with the kinetic energy of motion normal to the surface and the relative unimportance of parallel motion. At the critical angle of 38° the kinetic energy due to normal motion $E_0\cos^2(\theta_i)$ is less than ω_{n0}, the atomic excitation threshold.

where n is the average electron density, which is essentially the same for $r_s = 2$ jellium and Ge or InP. Thus it seems that some other electron-hole pair excitation mechanism must be important in Amirav and Cardillo's experiment; the long-range van der Waals coupling provides too weak an effect to account for the data. For example, one possible mechanism is electronic excitation at short range due to the overlap force.[12] Alternatively, formation of local "hot spots" may occur, as proposed by Amirav and Cardillo.[1] In this case the xenon atom first loses large amounts of energy to the substrate phonons, creating a region of high temperature from which electron-hole pairs can be thermally excited.

To conclude, we have developed a self-energy approach to the long-range interaction of an atom or an ion with a surface. This self-energy gives the van der Waals potential for an atom (or the image potential for an ion) as its real part and gives an inelastic scattering rate as its imaginary part. Our expression agrees with previous calculations of the van der Waals energy, and with standard results for the inelastic scattering of ions or electrons from surfaces. In the case of neutral-atom–surface scattering we give a general result for the excitation probabilities of electron-hole pairs and of surface plasmons (if there is sufficient energy). The simple first-order loss mechanism that we propose only occurs at incident energies above the atomic excitation threshold, since the atom must undergo a dipole transition. For example, this loss mechanism would be applicable to the scattering of hyperthermal atomic beams from surfaces. Comparison with available experimental results suggests, however, that this long-range coupling gives only a minor contribution to the inelastic scattering probability. Therefore the dominant electron-hole pair excitation mechanism for hyperthermal atom scattering cannot be long-range van der Waals coupling, but must be attributed to some other process, for example, the formation of local hot spots as proposed by Amirav and Cardillo.[1]

ACKNOWLEDGMENTS

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