

Electron-hole-pair quenching of excited states near a metal

B. N. J. Persson*

*Institut für Festkörperforschung der Kernforschungsanlage Jülich, Postfach 1913,
D-5170 Jülich, West Germany*

N. D. Lang

IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

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We present a calculation of the nonradiative damping of a dipole outside a metal surface. The calculation uses a realistic surface potential for the metal conduction electrons in contrast to most earlier studies. A simple experiment is suggested to test the theoretical predictions.

I. INTRODUCTION

There has been a steadily increasing interest in dynamical processes at surfaces. Processes involving chemisorbed molecules, such as dissociation reactions¹ or vibrational damping,² are interesting but complicated. Processes involving molecules located well away from the surface are simpler because such molecules can interact with the metal only through the electromagnetic field. Interesting examples of this type include the van der Waals interaction between a molecule and a solid^{3,4} and the fluorescence decay of an excited molecule studied as a function of the distance to the surface.⁵⁻⁹

In this work we will consider problems of the latter type. We will concentrate on the lifetime of a vibrating dipole, but the results presented are more general than this, and can be used to determine, e.g., the friction force on a charged particle moving outside a metal surface.

Recently, several papers have been published in which the response of a metal to an external electromagnetic field has been studied.⁸⁻¹⁷ Most of these works treat the metal crudely, e.g., by using the infinite barrier model⁹ or even more approximate models.¹³⁻¹⁶ From the work by Feibelman it is now known that it is important to use a realistic surface potential such as the one obtained by Lang and Kohn.¹⁸ Feibelman's calculations indicate that the simpler models underestimate the probability of excitation of electron-hole pairs, while overestimating the probability for excitation of bulk plasmons.¹² However, Feibelman's calculations are limited to fields that vary slowly in space ($k \approx 0$) and rapidly in time ($\omega \gtrsim \omega_p/2$). In this work we will present results valid for $\omega \ll \omega_p$, which are ex-

pected to be at least as accurate as those of Feibelman. We will also use the surface potential obtained by Lang and Kohn. However, the response of the metal conduction electrons to an external electric field will not be treated within the random-phase approximation (RPA) (as Feibelman did) but more accurately.

In Sec. II, we present the basic model and its evaluation. In Sec. III, we discuss some numerical results and suggest an experiment to test the theory.

II. THEORY

Consider a vibrating dipole located at a distance d above a metal surface. We want to calculate the damping rate of the vibration due to excitation of electron-hole pairs in the metal. We treat the metal within the jellium approximation, i.e., the metal conduction electrons are assumed to move in a semi-infinite positive background obtained by smearing out the positive metal-ion cores (see Fig. 1). Let Ω be the vibration frequency of the dipole and assume that $\Omega \ll \omega_p$, where ω_p is the plasma frequency of the metal. Since $\Omega \ll \omega_p$, the metal conduction electrons can almost respond adiabati-

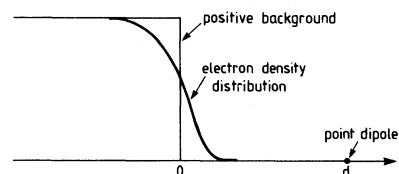


FIG. 1. Schematic representation of the density distributions.

cally to the slowly varying external field and thus almost adjust to the instantaneous static configuration. Thus to a good approximation, the screened dipole potential $\tilde{\phi}_{\text{dipole}}(\vec{x}, t)$ is obtained from a static calculation; for the jellium model such calculations have been performed by Lang and Kohn.¹⁹

The damping rate $1/\tau$, i.e., the rate at which the vibrationally excited state ($n=1$) decays to its vibrational ground state ($n=0$) while an electron is scattered from a level \vec{k} below the Fermi surface ($k < k_F$) to a level \vec{k}' above the Fermi surface ($k' > k_F$), is obtained from the golden-rule formula:

$$\frac{1}{\tau} = \frac{2\pi}{\hbar} \int d^3k d^3k' n_k (1 - n_{k'}) \times |\langle \vec{k}', n=0 | H' | \vec{k}, n=1 \rangle|^2 \times \delta(\epsilon_{k'} - \epsilon_k - \hbar\Omega). \quad (1)$$

Here

$$H' = e\tilde{\phi}_{\text{dipole}}(\vec{x}) \quad (2)$$

and

$$n_k = \begin{cases} 1 & \text{if } k < k_F, \\ 0 & \text{if } k > k_F. \end{cases}$$

$\langle \vec{x} | \vec{k} \rangle = \psi_{\vec{k}}(\vec{x})$ are the electronic wave functions

$$\frac{1}{\tau} \approx \frac{2\pi}{\hbar} \left[\frac{m}{\hbar^2} \right]^2 \hbar\Omega \int_{k_{||}, k'_{||} < k_F} d^2k_{||} d^2k'_{||} \frac{1}{(k_F^2 - k_{||}^2)^{1/2}} \frac{1}{(k_F^2 - k'_{||}{}^2)^{1/2}} |\langle \vec{k}', n=0 | H' | \vec{k}, n=1 \rangle|^2, \quad (3)$$

where it is implicitly understood that $k = k' = k_F$. In what follows we will only consider large d , namely, $d \gg \omega_F/\Omega k_F$. For such d the main contribution to the damping rate arises from the momentum supply from the surface, i.e., not from the momentum distribution of the near field itself.⁹ We must now calculate the screened dipole potential $\tilde{\phi}_{\text{dipole}}$, which enters the matrix element in Eq. (3). In the limit $\Omega \ll \omega_p$ and $d \gg \omega_F/\Omega k_F$ this is easily obtained as follows. If the metal is treated classically, then

$$\nabla^2 \tilde{\phi}_{\text{dipole}} = -4\pi\sigma(\vec{x}_{||})\delta(z), \quad (4)$$

where $\sigma(\vec{x}_{||})$ is the surface charge density. For a dipole located at $z=d$ (see Fig. 1) and oriented normal to the surface, $\sigma(\vec{x}_{||})$ is easily calculated

$$\sigma(x_{||}) = \frac{\mu_z}{(2\pi)^2} \int d^2q_{||} q_{||} e^{i\vec{q}_{||} \cdot \vec{x} - q_{||}d}. \quad (5)$$

A real metal does not have a steplike surface and the induced charge density is therefore not propor-

and $\epsilon_k = \hbar^2 k^2/2m$. We have calculated $\psi_{\vec{k}}(\vec{x})$ numerically using the potential $V_{\text{eff}}(z)$ obtained from a self-consistent local-density calculation.¹⁸

Note that the integrals over \vec{k} and \vec{k}' , in Eq. (1) are restricted to $k_z \geq 0$ and $k'_z \geq 0$ (since \vec{k} space is semi-infinite for a semi-infinite crystal when $\epsilon_k - \epsilon_F < W$, where W is the work function). It is convenient to introduce new integration variables, namely, $\epsilon = \hbar^2 k^2/2m$ and $\vec{k}_{||}$ (the projection of \vec{k} in the metal surface). Since

$$\int_{k_z \geq 0} d^3k = \int_0^\infty d\epsilon \int_{k_{||} \leq k} d^2k_{||} \frac{m}{\hbar^2} \frac{1}{(k^2 - k_{||}^2)^{1/2}},$$

we can write

$$\frac{1}{\tau} = \int_0^\infty d\epsilon \int_0^\infty d\epsilon' n_\epsilon (1 - n_{\epsilon'}) \times f(\epsilon, \epsilon') \delta(\epsilon' - \epsilon - \hbar\Omega)$$

$$= \int_0^{\epsilon_F} d\epsilon \int_{\epsilon_F}^\infty d\epsilon' f(\epsilon, \epsilon') \delta(\epsilon' - \epsilon - \hbar\Omega) \\ = \int_{\epsilon_F}^{\epsilon_F + \hbar\Omega} d\epsilon' f(\epsilon' - \hbar\Omega, \epsilon') \approx \hbar\Omega f(\epsilon_F, \epsilon_F),$$

where the last equality is valid if $f(\epsilon, \epsilon')$ varies slowly as a function of ϵ and ϵ' in an interval $\hbar\Omega$ near ϵ_F . Thus we have

tional to $\delta(z)$ but smoothed out in a way discussed in detail by Lang and Kohn.¹⁹ Thus Eq. (4) is replaced by

$$\nabla^2 \tilde{\phi}_{\text{dipole}} = -4\pi\sigma(\vec{x}_{||})f(z), \quad (6)$$

where

$$\int_{-\infty}^\infty dz f(z) = 1. \quad (7)$$

Since the variation of $f(z)$ with z is much more rapid than the variation of $\sigma(\vec{x}_{||})$ with $\vec{x}_{||}$ (the ratio is $\sim 1/k_F d \ll 1$), we get

$$\tilde{\phi}_{\text{dipole}} \approx \sigma(\vec{x}_{||})A(z), \quad (8)$$

where

$$\frac{d^2 A}{dz^2} \approx -4\pi f(z). \quad (9)$$

Thus the screened dipole potential is obtained from Eq. (8) with $\sigma(\vec{x}_{||})$ given by Eq. (5) and $A(z)$ calcu-

lated from Eq. (9). Note that $f(z)$ entering the right-hand side of Eq. (9) is known; it is simply the induced charge-density profile, normalized to unit area, due to a uniform charged sheet located outside the metal surface. $f(z)$ has been calculated by Lang and Kohn in the jellium model.¹⁹

We can write the electronic wave functions as

$$\begin{aligned} \langle \vec{k}', n=0 | H' | \vec{k}, n=1 \rangle &= \frac{4\mu e}{(2\pi)^5} \int d^3x \int d^2q_{||} q_{||} e^{-q_{||}d} e^{i(\vec{k}_{||} - \vec{k}'_{||} + \vec{q}_{||}) \cdot \vec{x}} \psi_{k'_z}^*(z) A(z) \psi_{k_z}(z) \\ &= \frac{4\mu e}{(2\pi)^5} \int d^2q_{||} q_{||} e^{-q_{||}d} (2\pi)^2 \delta(\vec{k}_{||} - \vec{k}'_{||} + \vec{q}_{||}) \int dz \psi_{k'_z}^*(z) A(z) \psi_{k_z}(z) \\ &= \frac{4\mu e}{(2\pi)^3} |\vec{k}_{||} - \vec{k}'_{||}| e^{-|\vec{k}_{||} - \vec{k}'_{||}|d} \langle \psi_{k'_z} | A(z) | \psi_{k_z} \rangle, \end{aligned} \quad (11)$$

where $\mu = \langle 0 | \mu_z | 1 \rangle$ is the matrix element of the dipole moment operator, and

$$\langle \psi_{k'_z} | A | \psi_{k_z} \rangle = \int dz \psi_{k'_z}^*(z) A(z) \psi_{k_z}(z). \quad (12)$$

Now note that for large d

$$|\vec{k}_{||} - \vec{k}'_{||}|^2 e^{-2d|\vec{k}_{||} - \vec{k}'_{||}|} \approx N \delta(\vec{k}_{||} - \vec{k}'_{||}), \quad (13)$$

where N is a normalization factor chosen so that the two functions have the same area:

$$\int d^2q_{||} N \delta(\vec{q}_{||}) = N = \int d^2q_{||} q_{||}^2 e^{-2dq_{||}} = \frac{3\pi}{4d^4}. \quad (14)$$

Using Eqs. (3), (11), (13), and (14) gives

$$\begin{aligned} \frac{1}{\tau} &= \frac{\mu^2}{4d^3\hbar} \frac{\Omega}{\omega_F} \frac{1}{k_F d} \frac{3}{8\pi^2} \left[\frac{k_{TF}}{k_F} \right]^2 \\ &\times \int_0^{k_F} dk_z \frac{1}{k_z} |\langle \psi_{k_z} | A k_F^2 | \psi_{k_z} \rangle|^2, \end{aligned} \quad (15)$$

where $1/k_{TF}$ is the Thomas-Fermi screening length. Accounting for the electron spin [which introduces an extra factor of 2 in Eq. (15)], we can thus write

$$\frac{1}{\tau} = \frac{\mu^2}{4d^3\hbar} \frac{\Omega}{\omega_F} \frac{1}{k_F d} \xi(r_s), \quad (16)$$

where

$$\begin{aligned} \xi(r_s) &= \frac{3}{4\pi^2} \left[\frac{k_{TF}}{k_F} \right]^2 \\ &\times \int_0^{k_F} dk_z \frac{1}{k_z} |\langle \psi_{k_z} | A k_F^2 | \psi_{k_z} \rangle|^2. \end{aligned} \quad (17)$$

$$\psi_{\vec{k}}(\vec{x}) = \frac{1}{2\pi} \left[\frac{2}{\pi} \right]^{1/2} e^{i\vec{k}_{||} \cdot \vec{x}} \psi_{k_z}(z), \quad (10)$$

where

$$\psi_{k_z}(z) \rightarrow \sin(k_z z + \varphi_{\vec{k}}) \text{ as } z \rightarrow -\infty.$$

From Eqs. (2), (5), (8), and (10) we get

ξ depends only on the electron gas-density parameter r_s ; for $r_s=3$ we have calculated ξ numerically

$$\xi(r_s=3) = 1.2. \quad (18)$$

It is interesting to compare Eq. (16) (the surface contribution to the damping rate) with the volume contribution due to scattering of electrons against phonons, impurities, etc.⁶⁻⁹ The volume damping is given by⁶⁻⁸

$$\frac{1}{\tau} = \frac{\mu^2}{4d^3\hbar} 2 \text{Im} \frac{\epsilon - 1}{\epsilon + 1}, \quad (19)$$

where $\epsilon(\omega)$ is the bulk dielectric function. If $\epsilon(\omega)$ has a Drude form, i.e.,

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i/\tau')}, \quad (20)$$

and if $1/\tau' \ll \Omega \ll \omega_p$, one gets from Eqs. (19) and (20)

$$\begin{aligned} \frac{1}{\tau} &\approx \frac{\mu^2}{4d^3\hbar} \frac{\Omega}{\omega_F} \frac{1}{k_F l} \left[8 \frac{\omega_F^2}{\omega_p^2} \right] \\ &\approx \frac{\mu^2}{4d^3\hbar} \frac{\Omega}{\omega_F} \frac{1}{k_F l} (3.0), \end{aligned}$$

where $l = v_F \tau'$ is the mean free path, and where the last equality is valid for $r_s=3$. To summarize, for $r_s=3$, we have shown that

$$\frac{1}{\tau} = \frac{\mu^2}{4d^3\hbar} F, \quad (21)$$

where

$$\begin{aligned} F(\text{surface}) &\approx 1.2 \frac{\Omega}{\omega_F} \frac{1}{k_F d}, \\ F(\text{volume}) &\approx 3.0 \frac{\Omega}{\omega_F} \frac{1}{k_F l}. \end{aligned} \quad (22)$$

These two equations are both linear in Ω . On the other hand, they have a different distance dependence; $1/\tau(\text{surface}) \sim 1/d^4$ while $1/\tau(\text{bulk}) \sim 1/d^3$, which is known from several earlier works.^{8,10} For large enough d , the volume damping will therefore always dominate. For $d \lesssim \omega_F/\Omega k_F$, there will be, in addition to the surface and volume damping processes, a contribution where the needed momentum supply arises from the spatial variation of the dipole field itself.⁹ This contribution will have a more complicated distance dependence, presumably $\sim d^{-4} \ln k_F d$ (Refs. 20, 21, and 17). With respect to the relative magnitude of $F(\text{volume})$ and $F(\text{surface})$ it is obvious that for a transition metal as Ni or Pt, with a large density of levels at the Fermi energy and thus short mean free path of the electrons (typically $k_F l \sim 1$) the volume effect will dominate already for $d \sim 1$ Å. On the other hand, for a noble metal such as silver, below the onset of d -band transitions (i.e., $\hbar\Omega \lesssim 3.5$ eV) one has already at room temperature a very long mean free path, $l \sim 430$ Å.²² Thus the surface damping is expected to dominate for $d \lesssim 200$ Å. We will discuss this further in the next section.

III. DISCUSSION

The calculation presented in Sec. II is very simple and it is easy to extract some interesting physics from it. Note first that only electrons within a thin shell $\epsilon_F - \hbar\Omega < \epsilon < \epsilon_F$ near the Fermi surface can be excited without violating energy conservation. This does not mean that electrons in deeper lying levels are unimportant since they will give a contribution to the screening of the external potential. Of the electrons in the vicinity of the Fermi surface, only those which propagate normal or almost normal to the metal surface will couple to the screened dipole field. The reason is that $\tilde{\phi}_{\text{dipole}}$ vanishes very rapidly inside the metal. Thus for a metal electron to feel this potential, its wave function must penetrate far enough into the vacuum, and only electrons with a large velocity normal to the metal surface can do so. This is illustrated in Figs. 2 and 3. Figure 2 shows the screened potential $\tilde{\phi}_{\text{dipole}}$ as a function of z . Also shown are two conduction-electron wave functions, one corresponding to an electron propagating almost parallel to the surface ($k_z = 0.1k_F$), and the other normal to the surface ($k_z = k_F$), both with $\epsilon = \epsilon_F$. The latter wave function penetrates much further into the vacuum and will therefore couple much more strongly to $\tilde{\phi}_{\text{dipole}}$ than the former. The coupling strength is given by

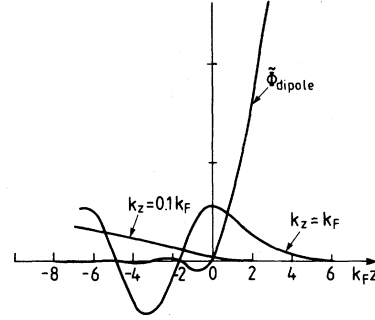


FIG. 2. Screened dipole potential $\tilde{\phi}_{\text{dipole}}$ and two electron wave functions $\psi_{k_z}(z)$ ($k_z = 0.1k_F$ and $k_z = k_F$), both with $\epsilon = \epsilon_F$, are shown as a function of $k_F z$. Electron density parameter $r_s = 3$.

the dimensionless quantity [see Eq. (15)]

$$P(k_z) = \frac{k_F}{k_z} |\langle \psi_{k_z} | A k_F^2 | \psi_{k_z} \rangle|^2$$

$$= \frac{k_F}{k_z} \left| \int dz |\psi_{k_z}(z)|^2 A(z) k_F^2 \right|^2.$$

Figure 3 shows $P(k_z)$, the relative probability for excitation of an electron on the Fermi surface with a given k_z . Obviously, only those electrons which propagate normal or almost normal to the surface have a non-negligible probability of being excited.

The damping function $F(\omega)$ can be related to the frequency-dependent image plane position $d_{\text{IP}}(\omega)$.¹⁰ To show this, let us consider a point particle with the polarizability $\alpha(\omega)$ located a distance d above a metal surface. Let E_0 be an external electric field (assumed normal to the surface) with the time dependence $\exp(-i\omega t)$. This field will induce a dipole moment in the particle given by

$$p = \alpha(E_0 + E_{\text{image}}), \quad (23)$$

where E_{image} is the electric field from the induced surface charge density (i.e., from the "image" dipole). If the metal could be described classically, then

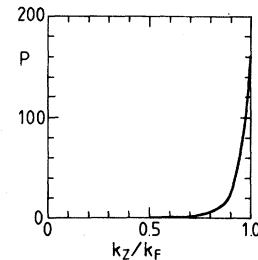


FIG. 3. Relative probability $P(k_z)$ for excitation of an electron on the Fermi surface ($\epsilon = \epsilon_F$) as a function of k_z .

$$E_{\text{image}} = \frac{p}{4d^3} \frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 1}. \quad (24)$$

Feibelman has shown that if the metal is treated microscopically (within the jellium model), then asymptotically for large d (actually $d \gg \omega_F/\omega k_F$), Eq. (24) has to be replaced by¹⁰

$$E_{\text{image}} = \frac{p}{4[d + d_{\text{IP}}(\omega)]^3} \frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 1}. \quad (25)$$

In general, d_{IP} is a complex number with the imaginary part associated with loss processes (electron-hole pairs). Substituting (25) in (23) gives

$$p = \frac{\alpha}{1 - \frac{\alpha}{4[d + d_{\text{IP}}(\omega)]^3} \frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 1}} E_0 \equiv \alpha_0 E_0.$$

Now if

$$\alpha = \frac{\alpha_1}{1 - \left[\frac{\omega}{\Omega} \right]^2},$$

then

$$\alpha_0(\omega) = \frac{\alpha_1}{1 - \left[\frac{\omega}{\Omega} \right]^2 - \frac{\alpha_1}{4[d + d_{\text{IP}}(\omega)]^3} \frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 1}}.$$

The pole of $\alpha_0(\omega)$ defines the complex resonance frequency $\omega = \bar{\omega}$, thus

$$\left[\frac{\bar{\omega}}{\Omega} \right]^2 - 1 + \frac{\alpha_1}{4[d + d_{\text{IP}}(\bar{\omega})]^3} \frac{\epsilon(\bar{\omega}) - 1}{\epsilon(\bar{\omega}) + 1} = 0$$

or, if $\alpha_1/d^3 \ll 1$,

$$\bar{\omega} \approx \Omega \left[1 - \frac{\alpha_1}{8[d + d_{\text{IP}}(\Omega)]^3} \frac{\epsilon(\Omega) - 1}{\epsilon(\Omega) + 1} \right].$$

With the substitution of $\alpha_1 = 2\mu^2/\hbar\Omega$ we get

$$-\text{Im}\bar{\omega} \approx \frac{\mu^2}{4\hbar d^3} \left[\text{Im} \frac{\epsilon(\Omega) - 1}{\epsilon(\Omega) + 1} - 3 \text{Re} \frac{\epsilon(\Omega) - 1}{\epsilon(\Omega) + 1} \text{Im} d_{\text{IP}}(\Omega)/d \right]. \quad (26)$$

The first term in this expression is identical with Eq. (19), except for a factor of 2. This difference is simply a consequence of $1/\tau$ being the rate of energy transfer from the particle to the metal while $-\text{Im}\bar{\omega}$ is the damping rate for the amplitude p . These two rates are, of course, related by a factor of

2. Comparison of (26) with (16) gives

$$-\text{Im}k_F d_{\text{IP}}(\Omega) = \frac{1}{6} \frac{\Omega}{\omega_F} \xi(r_s), \quad \Omega \ll \omega_p. \quad (27)$$

The position of the image plane $d_{\text{IP}}(\omega)$ can be related to two other surface response functions, $d_{\perp}(\omega)$ and $d_{\parallel}(\omega)$, also introduced by Feibelman¹⁰:

$$d_{\text{IP}}(\omega) = \frac{\epsilon d_{\perp}(\omega) + d_{\parallel}(\omega)}{\epsilon + 1}.$$

For $\omega \ll \omega_p$, we have $d_{\text{IP}}(\omega) \approx d_{\perp}(\omega)$; thus Eq. (27) can alternatively be written

$$-\text{Im}k_F d_{\perp}(\Omega) = \frac{1}{6} \frac{\Omega}{\omega_F} \xi(r_s), \quad \Omega \ll \omega_p.$$

For $\omega < \omega_p$, $d_{\perp}(\omega)$ is simply the centroid of the induced charge-density profile (which in general is a complex number).¹⁰

The response function $d_{\perp}(\omega)$ [or equivalently, the damping function $F(\omega)$] is very important because it determines the influence of the metal surface on practically all processes occurring well away from it ($d \gg \omega_F/\omega k_F$). Here we only mention a few examples.²³

- (1) Damping of a vibrating dipole as discussed above;
- (2) the friction force on a charged particle moving above a metal surface²⁰;
- (3) the van der Waals interaction between a particle and a metal^{4,12,17};
- (4) surface plasmon dispersion^{12,17};
- (5) the surface photoelectric effect.^{24,12}

Thus a large number of phenomena are closely related and can be expressed in a unified way using the surface response function $d_{\perp}(\omega)$ [or, equivalently, the damping function $F(\omega)$]. Therefore, a detailed knowledge of $d_{\perp}(\omega)$, as a function of ω , is very important. Feibelman has calculated $\text{Im}d_{\perp}(\omega)$ for $\omega \gtrsim \omega_p/2$, see Fig. 4. Also shown in this figure is our own result for $\omega \ll \omega_p$. It is satisfying to see that it is possible to smoothly interpolate between the low- and high-frequency results. Recall that Feibelman's calculation is done within the RPA while we treat the screening process more accurately. Since it is possible to interpolate smoothly between the two calculations, the RPA might be a reasonable approximation for the present problem.

To date, the jellium theory for surface screening has its strongest experimental support in the surface photoelectric experiment by Levinson, Plummer, and Feibelman.²⁴ Here we would like to suggest

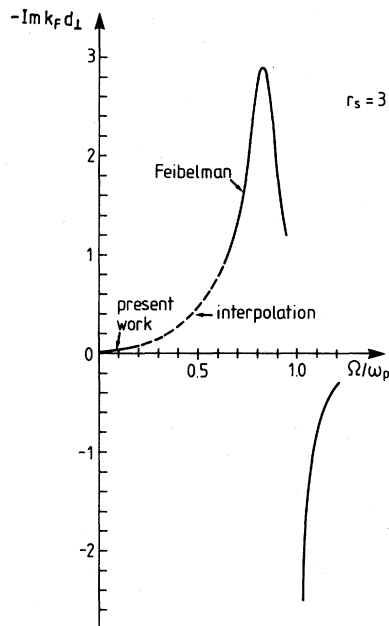


FIG. 4. Imaginary part of the surface response function $d_L(\omega)$ as calculated by Feibelman ($\omega \geq 0.6\omega_p$) and from this work ($\omega \ll \omega_p$). The dashed line is an interpolation between the two calculations.

another experiment that adds a further test of the theory, and that is of interest in its own right.²⁵ We propose that one should measure the lifetime of an excited molecule located at various distances d above a silver surface. Curve *A* in Fig. 5 shows the volume contribution to the damping function $F(\Omega)$ for silver at room temperature. The strong increase in $F(\text{volume})$ at $\hbar\Omega \approx 3.5$ eV is due to the onset of transitions from the d band that cause strong damping (incidentally, the sharp peak at $\hbar\Omega \approx 3.5$ eV is due to the excitation of surface plasmons). $F(\text{volume})$ is very small for $\hbar\Omega \leq 3.5$ eV, and for $\hbar\Omega \leq 2$ eV, it is well-approximated by Eq. (21) with $l \approx 430$ Å.²² Thus the surface contribution to F will dominate over the volume damping if $d \leq 200$ Å and $\hbar\Omega \leq 2$ eV. We therefore suggest that one should study the variation of the lifetime as a function of d (e.g., using layers of argon as spacers between the molecule and the metal²⁶) and determine whether the lifetime varies as d^3 (volume damping) or d^4 (surface damping). In case the damping has the latter distance dependence (as expected), it

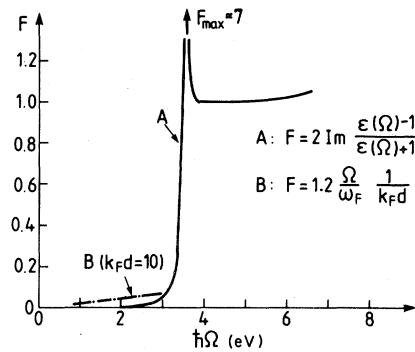


FIG. 5. Curve *A* is the volume contribution to the damping function calculated from Eq. (19), using the full dielectric function $\epsilon(\Omega)$ for silver, as measured by Johnson and Christy (Ref. 22). Curve *B* is the surface contribution to the damping function calculated from Eq. (16) with $k_F d = 10$ and $r_s = 3$, which is the electron gas-density parameter of silver.

would be of great interest to calculate the actual proportionality constant $c, \tau = cd^4$, and compare it with the theoretical prediction, Eq. (16).

Finally, let us emphasize that the theory presented in Sec. II is valid only if $d \gg \omega_F / \Omega k_F$. However, this inequality imposes a negligible restriction on d in the study of the lifetime of an electronically excited molecule above a metal surface, because for $\hbar\Omega \sim 2$ eV one has $\omega_F / \Omega k_F \sim 2$ Å. Thus there will be a large interval in d (say, $10 < d < 100$ Å) where the theory is applicable. On the other hand, the theory cannot be used in discussing, e.g., the dipole contribution to the damping rate of a vibrationally excited molecule *adsorbed* on a metal surface, since typically $\hbar\Omega \sim 0.25$ eV for vibrations and thus $\omega_F / \Omega k_F \sim 20$ Å while for an adsorbed molecule $d \sim 1$ Å.

Note added in proof. This work is the first in a proposed series of three concerning the dynamical properties of metal surfaces. In the second work we plan to present some powerful sum rules for surface response functions and illustrate their use. In the third paper we plan to extend the formalism of this work by treating the response of a metal surface to external fields which varies arbitrarily rapidly in space (i.e., removing the restriction $d \gg \omega_F / \omega k_F$).

*Present address: IBM Thomas J. Watson Research Center, Yorktown Heights, N.Y. 10598.

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