Theory of Photon Emission in Electron Tunneling to Metallic Particles

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(Received 5 February 1992)

We consider photon emission in electron tunneling to a small metal particle. The radiative (dipole) plasmon mode of the particle can be excited resonantly by a tunneling electron either when it is in the barrier or else as a decay channel of the hot electrons injected into the particle via elastic tunneling. Analytical estimates show that for a particle with a few hundred angstrom radius the former process dominates over the latter by a factor of $\sim 10^3$, and that the integrated light intensity is $\sim 10^{-3}$ photon per tunneling electron under optimum conditions, in agreement with recent observations.

PACS numbers: 73.40.Gk

In 1976 Lambe and McCarthy [1] observed light emission when a current was drawn through a metal-oxide-metal tunnel junction. Appreciable light emission was found only if one of the electrodes was rough, e.g., a granular metal film. It was argued that the emitted light is mainly derived from the radiative decay of surface plasmons. Surface plasmons on a flat metal surface cannot decay via emission of a photon since such a process could not simultaneously conserve energy and momentum. On a rough electrode, however, translational invariance parallel to the surface is broken and photon emission can occur. Typically $\sim 10^{-5}$ to 10^{-6} photon per tunnel-injected electron were observed.

Theories of light emission in tunneling have been presented by Rendell and co-workers [2] and by Laks and Mills [3], based on the assumption that the surface plasmons are excited by fluctuations of the tunneling current. However, later experiments with junctions fabricated on sinusoidal gratings raised new issues [4]. The Laks-Mills theory extended to this rather well-defined situation could account neither for the much higher observed yield, nor for its reduction with counterelectrode thickness. This led Kirtley and co-workers [4] to propose that the radiative surface plasmons are excited by the injected hot electrons.

Interest in these issues has been revived by the observation of unusually intense light emission from condensed silver films (up to 10^{-3} photon per injected electron) in a scanning tunneling microscope (STM) [5]. Furthermore, the emitted light shows spatial intensity variations which correlate with nanometer surface features, e.g., grain boundaries, and the accessible spectral range is not limited by junction breakdown and extends into the field-emission range. Besides opening a door to a promising extension of STM, such experiments may help clarify how light is generated in tunnel junctions [6–8].

In this Letter we compare possible mechanisms of light emission in a model situation approximating the experimental one, yet simple enough so that the physics involved remains clear and competing radiative and nonradiative processes can be easily estimated. In this spirit we consider vacuum tunneling from an atomic s-like orbital at the apex of an STM tip into a spherical metallic particle. In an optimal case we estimate the yield of inelastic tunneling to be $\sim 10^{-3}$ photon per tunnel electron while the yield associated with hot-electron injection is estimated to be much smaller, of order $\sim 10^{-6}$. A real experimental situation is certainly much more complicated (and usually not fully known) than the simple model we study, but the order-of-magnitude estimates of the yields should be correct even in a realistic case. But the spectral and angular distribution of the emitted light cannot be realistically described by our model.

Let Ω be the resonance frequency of the dipole active surface plasmon mode of the metal particle ($\Omega = \omega_p/\sqrt{3}$ in the jellium model) and assume that $eV_t > \hbar\Omega$, so that a tunneling electron can excite the plasmon mode. The magnitude of the oscillating dipole moment associated with a single (quantized) surface plasmon can be estimated as follows: Just as for any harmonic oscillator, on the average half of the energy is stored in potential, and half in kinetic energy. Since the potential energy is stored in the electric field $\mathbf{E}$ we get $\hbar\Omega \sim \int d^3x\, E^2 \sim R^3E^2$, since the electric field extends over a volume $\sim R^3$. Hence the electric field must scale with R as $E \sim (\hbar\Omega R^{-3})^{1/2}$. The dynamic dipole moment p associated with the plasmon is related to E via $E \sim p/R^3$ so that $p \sim (\hbar\Omega R^3)^{1/2}$. For a spherical particle with the radius R, an exact calculation gives the *transition dipole moment*

$$p = (\hbar\Omega R^3/2)^{1/2}. \tag{1}$$

The scaling laws $E \sim R^{-3/2}$ and $p \sim R^{3/2}$ should remain valid for any compact particle of characteristic dimension R. For $R \sim 300$ Å and $\hbar\Omega \sim 2.5$ eV, Eq. (1) gives $p \sim 1500\, e$Å. Hence, for a particle with a radius of a few hundred angstroms, the large magnitude of the dynamical dipole moment associated with a surface plasmon makes the radiative decay channel quite effective, but it is still weaker than the nonradiative decay associated with excitation of an electron-hole pair. To see this, note that the radiative decay rate of an oscillating dipole is given by the classical formula [9] $w_{rad} = 4\Omega^3 p^2/3c^3\hbar$ which in the present case gives

$$w_{rad} \approx \tfrac{2}{3} R^3 \Omega^4/c^3.$$

This rate should be compared with the quenching rate of the surface plasmon due to the excitation of an electron-hole pair [10]

$$w_{e\text{-}h} = Cv_F/R\,,$$

where v_F is the Fermi velocity and C is a constant of order unity. This formula is valid for a jellium sphere and gives a lower bound of the nonradiative decay rate for a real metal. The ratio

$$P_{\rm rad} = \frac{w_{\rm rad}}{w_{\rm rad} + w_{e\text{-}h}} = \left[1 + \frac{3C}{2}\frac{v_F}{c}(kR)^{-4}\right]^{-1},$$

where $k = \Omega/c$, gives the probability for photon emission following excitation of the dipole mode, and corresponds to the last step in Figs. 1(a) and 1(b). (This formula is strictly valid only for $kR \ll 1$.) As an example, for an Ag particle, $P_{\rm rad} \sim 0.2$ if $kR = 0.2$ but only ≈ 0.01 if $kR = 0.1$. Figure 1 summarizes the R dependence of the decay rates as well as the branching ratios for the various decay processes, for a particle with a few hundred angstrom radius.

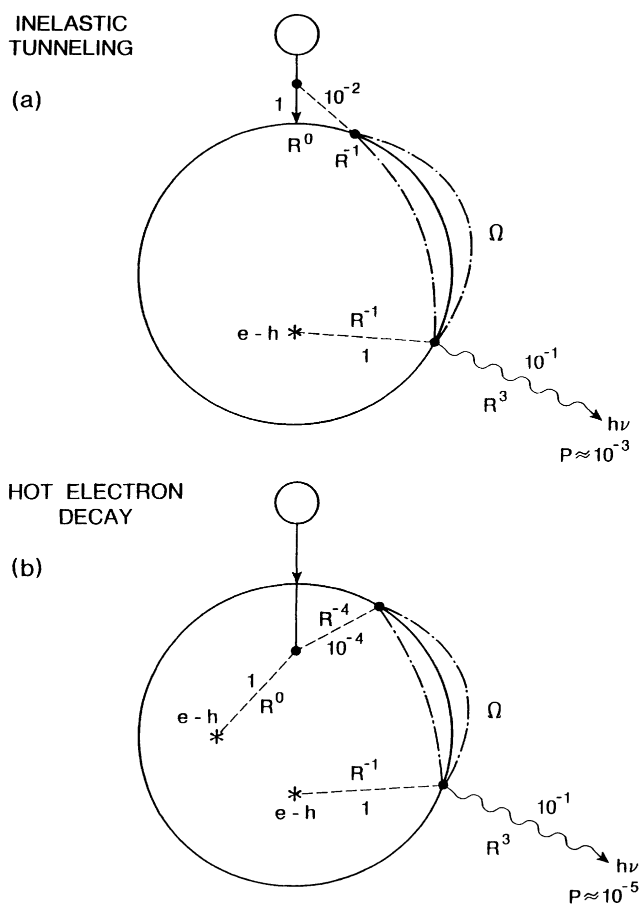

FIG. 1. A schematic picture of processes (a) and (b) discussed in the text. The dependence of competing decay processes on the radius R of the metallic particle is indicated together with relative branching ratios for a particle with $R \sim 200$ Å.

We now calculate the probability that a tunneling electron excites a surface plasmon in the first place. We distinguish between inelastic tunneling where the excitation occurs when the electron is in the vacuum barrier [Fig. 1(a)] and the hot-electron mechanism, where a tunneling electron injected in the particle excites the surface plasmon [Fig. 1(b)].

In inelastic tunneling the electron couples to the surface plasmon while in the barrier region. The electron-plasmon coupling is given by $e\hat{\phi}$ where $\hat{\phi}$ is the (quantized) electric potential from the surface plasmon at the position of the electron. Since $\hat{\phi} \sim p/R^2 \sim R^{-1/2}$ and since $\hat{\phi}$ enters squared in the rate of inelastic tunneling, we deduce that the probability of inelastic tunneling scales as R^{-1}, as indicated in Fig. 1(a). To estimate the branching ratio between inelastic and elastic tunneling, assume that the electrons tunnel from an orbital $|a\rangle$ on the tip to an orbital $|b\rangle$ on the particle. Elastic tunneling is described by

$$H' = tc_b^\dagger c_a + \text{H.c.}$$

The orbitals $|a\rangle$ and $|b\rangle$ are hybridized with the extended tip and particle states, respectively, forming resonances described by the projected density of states $\rho_a(\epsilon)$ and $\rho_b(\epsilon)$. The rate of elastic tunneling is given by Fermi's "golden rule" with H' as the perturbation

$$w_{\rm el} = \frac{2\pi}{\hbar}|t|^2 \int_{\epsilon_F - eV_t}^{\epsilon_F} d\epsilon\, \rho_b(\epsilon)\rho_a(\epsilon)$$

$$\approx \frac{2\pi}{\hbar}|t|^2 \rho_b(\epsilon_F)\rho_a(\epsilon_F) eV_t\,.$$

We have assumed that t and the densities of states $\rho_a(\epsilon)$ and $\rho_b(\epsilon)$ all vary slowly with the energy ϵ in the interval $\epsilon_F - eV_t < \epsilon < \epsilon_F$. This may not always be a good approximation and the nanoscale resolution observed in some STM light emission studies may in fact reflect atomic scale variations in the energy dependence of ρ_b. The rate of inelastic tunneling is given by the "golden rule" with the perturbation

$$e\hat{\phi} = e\hat{\mu}\frac{z}{r^3} = ep\langle b|\frac{z}{r^3}|a\rangle(B + B^\dagger)c_b^\dagger c_a + \text{H.c.}$$

$$\equiv t'(B + B^\dagger)c_b^\dagger c_a + \text{H.c.}\,,$$

where $\langle n=1|\hat{\mu}|n=0\rangle = p$ is the transition dipole moment and $B^\dagger$ and B the creation and annihilation operators of the surface plasmon mode. We get

$$w_{\rm inel} = \frac{2\pi}{\hbar}|t'|^2 \int_{\epsilon_F - eV_t + \hbar\Omega}^{\epsilon_F} d\epsilon\, \rho_b(\epsilon + eV_t)\rho_a(\epsilon)$$

$$\approx \frac{2\pi}{\hbar}|t'|^2 \rho_b(\epsilon_F)\rho_a(\epsilon_F)(eV_t - \hbar\Omega)\,.$$

The probability for an electron to tunnel inelastically by exciting a surface plasmon is therefore

$$P_{\rm inel} = \frac{w_{\rm inel}}{w_{\rm inel} + w_{\rm el}} \approx \frac{w_{\rm inel}}{w_{\rm el}} = \left|\frac{t'}{t}\right|^2 \left(1 - \frac{\hbar\Omega}{eV_t}\right). \qquad (2)$$

To simplify this expression, assume that both $|a\rangle$ and $|b\rangle$ are s orbitals. Using Bardeen's formula for the transfer matrix element t gives

$$t \approx (\hbar^2\kappa/ms)e^{-\kappa s}, \tag{3}$$

where s is the separation between the orbitals $|a\rangle$ and $|b\rangle$ and κ the radial decay constant determined by the barrier height $W=\hbar^2\kappa^2/2m$. Similarly one obtains

$$t'=ep\langle b|\frac{z}{r^3}|a\rangle \approx \frac{ep}{R^2}\langle b|a\rangle = \frac{ep}{R^2}e^{-\kappa s}, \tag{4}$$

since $z/r^3 \approx R^{-2}$ in the barrier region, assuming $s \ll R$. Using (1)-(4) gives

$$P_{\text{inel}} \approx \frac{\alpha}{8}\frac{\hbar\Omega}{W}\frac{\hbar c/R}{\hbar^2 s^{-2}/2m}\left(1-\frac{\hbar\Omega}{eV_t}\right),$$

where $\alpha = e^2/\hbar c \approx 1/137$ is the fine-structure constant. Hence the photon yield due to inelastic tunneling is

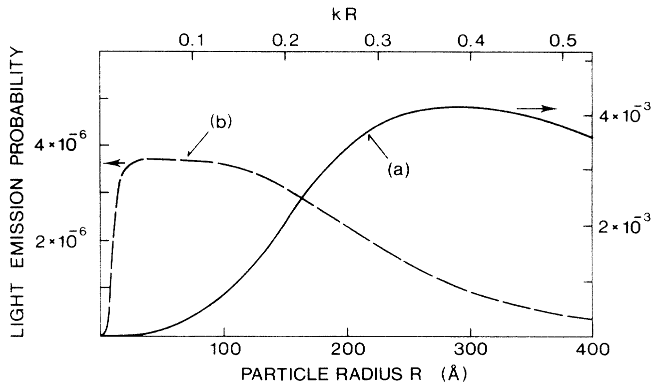

FIG. 2. The probability for light emission per tunneling electron as a function of the radius R of a metallic particle with a dipole resonance at $\hbar\Omega = 2.5$ eV for a tunneling voltage of 3 V. The solid and dashed lines correspond to processes (a) and (b) in Fig. 1. Note the difference between the left and right scales.

$$\eta_{\text{inel}} = P_{\text{inel}}P_{\text{rad}} \approx \frac{\alpha}{8}\frac{\hbar\Omega}{W}\frac{\hbar c/R}{\hbar^2 s^{-2}/2m}\left(1-\frac{\hbar\Omega}{eV_t}\right)\left(1+\frac{3C}{2}\frac{v_F}{c}(kR)^{-4}\right)^{-1}. \tag{5}$$

The solid line in Fig. 2 shows the variation of η_{inel} with the radius R of the particle, using $\hbar\Omega = 2.5$ eV, $s=6$ Å, $W=4$ eV, and $eV_t = 3$ eV. For $kR \sim 0.3$ (i.e., $R \sim 300$ Å), the yield is $\eta_{\text{inel}} \sim 4\times10^{-3}$. Equation (5) is derived under the assumption that the inelastic tunneling and the radiative decay of the excited surface plasmons occur independently. But treating the whole process coherently gives the same final result [6].

Consider now the photon yield from hot-electron injection. We first calculate the rate for a hot electron (with an energy $\epsilon_\alpha > \epsilon_F$) in the particle to decay to a lower energy level ϵ_β while exciting a surface plasmon. Inside the particle the electron is assumed to move in an effective one-particle potential $V(\mathbf{x})$, and $|\alpha\rangle, |\beta\rangle, \ldots$ denote the one-particle eigenstates. Using the "golden rule" we can calculate the desired rate to be

$$w = \frac{2\pi}{\hbar}\sum_\beta |\langle \beta, n=1|e\hat{\phi}|\alpha, n=0\rangle|^2 \delta(\epsilon_\beta + \hbar\Omega - \epsilon_\alpha). \tag{6}$$

The potential $\hat{\phi}$ associated with the surface plasmon is given by $\hat{\phi} = \hat{\mu}z/r^3$ for $r > R$ and $\hat{\phi} = \hat{\mu}z/R^3$ for $r < R$. The calculation of the matrix element and of the sum over β in (6) closely follows the calculation of the surface plasmon damping in Ref. [10] and here we only give the final result valid for a spherical-well model for the particle,

$$w = 2\sqrt{2}\frac{\epsilon}{\hbar}\left(\frac{\epsilon-\hbar\Omega}{\hbar\Omega}\right)^{1/2}\left(\frac{e^2/a_0}{\hbar\Omega}\right)^{5/2}\left(\frac{a_0}{R}\right)^4\left(1-\frac{3(\hbar\Omega)^2}{2U[(U-\epsilon)^{1/2}+(U+\hbar\Omega-\epsilon)^{1/2}]^2}\right)^2, \tag{7}$$

where a_0 is the Bohr radius, $\epsilon = \epsilon_\alpha$ is the energy of the hot electron, and $U = \epsilon_F + W$ is the well depth. Note that $w \sim R^{-4}$ as indicated in Fig. 1(b).

A much more likely decay process of a hot electron is excitation of an electron-hole pair. This process has been originally studied by Quinn [11] for an infinite electron gas, but his results also hold approximately for a metallic particle if the radius R is large compared to a typical electron wavelength. In the limit $\epsilon - \epsilon_F \ll \epsilon_F$, he obtained the following decay rate:

$$w' \approx \beta(r_s)\frac{e^2}{a_0\hbar}\left(\frac{\epsilon}{\epsilon_F}-1\right)^2, \tag{8}$$

where $\beta(r_s)$ only depends on the electron gas density parameter r_s. For $r_s = 3$ (silver), $\beta = 0.018$ and if $\epsilon - \epsilon_F = 2$ eV, Eq. (8) gives $w' \sim 10^{14}$ s^{-1}, corresponding to a hot-electron mean free path of about 100 Å. For a particle of radius $R = 200$ Å, Eq. (7) gives $w \sim 10^9$ s^{-1} which is smaller by ~ 5 orders of magnitude than the rate of e-h pair excitation. This is the reason why the hot-electron mechanism is quite ineffective. The branching ratio for a hot electron to excite a plasmon is given by $P_{\text{pl}} = w/(w+w')$ and is indicated in Fig. 1(b) for a particle with $R \sim 200$ Å. The corresponding photon emission yield $\eta_{\text{hot}} = P_{\text{pl}}P_{\text{rad}}$ is shown, as a function of R, by the dashed line in Fig. 2, assuming $\epsilon = 8$ eV, $\epsilon_F = 5$ eV, and $\hbar\Omega = 2.5$ eV. Note that the yield reaches $\sim 4\times10^{-6}$ for R between 20 and 100 Å, and for $R \sim 200$-300 Å it is ~ 3 orders of magnitude smaller than the yield from inelastic tunneling. But for very small particles, $R < 15$ Å, the hot-electron injection gives the dominating contribution to light emission but the overall yield is now very small, of order $\sim 10^{-6}$.

For $eV_t < \hbar\Omega$ no excitation of real plasmons can occur, but photon emission is still possible: As an electron tunnels between the tip and the particle, screening charges will appear on the tip and particle surfaces. If we assume a grounded sphere the tunneling electron and the induced charges give rise to a dipole moment $p \sim es$, which is "turned on" for a time of order τ, where $\tau = s(m/2W)^{1/2}$ is the so-called traversal time [12] for a barrier of height W and width s. This gives rise to a spectral distribution $p(\omega) \sim es\tau$ of bandwidth $\sim 1/\tau$. The probability for photon emission is easily calculated to be $P \approx (s/a_0)^4 (eV_t)^4 / [W(mc^2)^2 e^2/a_0] \approx 10^{-7}$ where we have used $W = 4$ eV, $s = 5$ Å, and $eV_t = 2$ eV.

Another direct light emission process is also possible: If the mean free path of the hot electrons injected in the particle is large enough, they can ballistically propagate to the back surface of the particle. If we consider a hot electron as a wave packet, then as long as it is inside the particle, it cannot emit any photons since the electric field of the electron is almost completely screened out by the other electrons and also because the electron is not likely to be decelerated (negligible bremsstrahlung). However, when the wave packet reaches the surface the electron is partly unscreened and gives rise to a fluctuating surface dipole. Using the jellium model we have estimated the probability for photon emission and found it to be extremely small, typically of order $P \sim 10^{-10}$. Nevertheless, this process may be involved in light emission from planar metal-oxide-metal tunneling junctions when the top electrode is relatively thick and very smooth [13].

To summarize, we have discussed in detail the yield of photon emission for a very simple model, where the contribution from various processes can be estimated analytically. If eV_t is larger than the energy of the dipole active surface plasmon mode, most of the emitted light results from inelastic tunneling. The maximum yield is found to be $\sim 10^{-3}$ in agreement with recent STM studies.

We thank R. Berndt, J. H. Coombs, J. Kirtley, D. Pohl, and especially J. K. Gimzewski for useful discussions. One of us (B.P.) acknowledges the IBM Zürich Research Laboratory for enabling his stay there as a visiting scientist.

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