Many-body effects in Auger deexcitation of atoms near solids*

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The role of many-body effects in the radiationless decay of an excited atom in the vicinity of a metallic surface is studied. In particular we calculate the decay rate for deexcitation by surface-plasmon emission and find it to be a rather likely process. The rate depends on the surface-plasmon dispersion relation and such atomic properties as the oscillator strength and the radiation frequency corresponding to the transition.

I. INTRODUCTION

Interest in Auger deexcitation of excited atoms in the vicinity of metallic surfaces has existed for some time. Early studies of the phenomenon were made by Massey,[1] Shekhter,[2] Cobas and Lamb,[3] and Hagstrum.[4] More recent investigations include the work of White and Tolk[5] and van der Weg and Bierman.[6] While experimental information concerning both neutral and ionic atoms is available it appears that the situation in the ionic case is considerably more involved. This is because the neutralization process is closely connected to the deexcitation process. In this paper we will only address ourselves to the neutral case.

The early experiments[7-11] involved directing metastable atoms at metallic surfaces and monitoring the Auger electrons emitted in the collision. Since the metastables owed their long life to spin-forbidden transitions linking the excited states to the ground state the deexcitation process was rather complicated. Either an exchange of electrons with the solid or a mutual spin flip was required before the atom could relax to the ground state. The more modern experiments[5] involving sputtering or collisions of incident ions to produce excited atoms are not just limited to metastable situations. Even optically decaying states can be studied in such an experiment.

The transition rate, $P(R)$, for deexcitation of an excited atom a distance R from the surface has been expressed in the form[4,5] $P(R)=Ae^{-aR}$. The parameters A and a are dependent on the details of the electronic structure. The quantity A/a is measured in the experiment. Thus, for the Cu 3247-Å line in the neighborhood of metallic copper it has been found that[5,6] $A/a=2\times10^6$ cm/sec.

The mechanism for the deexcitation has been analyzed as being a Coulomb collision between the atomic electron and the solid's electron. Since both tails of the electronic wave functions decay exponentially in space it seems reasonable that the deexcitation rate should also fall off exponentially. Thus a single-particle picture appears to be adequate in many cases.

In this paper we concern ourselves with the role played by many-body effects in the deexcitation process. In particular, we address ourselves to the case where an allowed transition has an energy greater than the surface-plasmon energy of the solid. In addition to the single-particle mode of decay one then has the possibility of a decay by means of surface-plasmon emission. Since the surface plasmon is a substantially extended object in many cases, this would give rise to a rather strong effect. As long as the transition frequency is close to the surface-plasmon frequency this mechanism is operative. If it greatly exceeds the surface-plasmon energy then the plasmon produced will probably be heavily damped. Alternatively the single-particle picture would then again be an appropriate one for analyzing the problem.

In Sec. II a theory for the deexcitation rate by plasmon coupling is developed. This is followed by a section (Sec. III) presenting results of the calculation.

II. THEORY

The surface plasmon is described by the scalar potential $\Phi(\vec{r})$. Expressed in second-quantized form one has the following expression[12] for Φ:

$$\Phi(\vec{r})=\sum_{\vec{k}_\perp} g(k_\perp)\,(a_{k_\perp}e^{-k_\perp|z|-i\vec{k}_\perp\cdot\vec{r}}+a_{k_\perp}^{\dagger}e^{-k_\perp|z|+i\vec{k}_\perp\cdot\vec{r}}). \quad (1)$$

Here $a_{k_\perp}$ and $a_{k_\perp}^{\dagger}$ denote annihilation and creation operators for a surface plasmon of wave vector $\vec{k}_\perp$. The surface is taken to be the plane $z=0$. The coupling coefficient $g(k_\perp)$ has been determined to be[12]

$$g(k_\perp)=[\pi\hbar\omega(k_\perp)/k_\perp A]^{1/2}, \quad (2)$$

where $\omega(k_\perp)$ is the surface-plasmon frequency and A is the area of the face of the crystal, which will be taken to be 1 for convenience.

An atom will interact with the surface-plasmon field through the Hamiltonian

$$H = H_0 + Ze\Phi(\vec{R}) - e\sum_{i=1}^{Z}\Phi(\vec{R}+\vec{r}_i). \tag{3}$$

Here H_0 is the free-atom Hamiltonian for an atom of nuclear charge Z. The nucleus is at position R and the electrons at position $\vec{r}_i$. The size of an atom is on the order of a Bohr radius while plasmon extents are typically the inverse of the Thomas-Fermi wave vector. Since the plasmon range is sufficiently large it is convenient to make a multipole expansion of Eq. (3) and truncate it at the dipole approximation. Thus we find

$$H = H_0 + \vec{\mu}\cdot\nabla\Phi(\vec{R}), \tag{4}$$

where the electric dipole moment of the atom has been denoted by $\vec{\mu}$.

The decay rate for the atom to go from state n to the ground state g is given by the Fermi golden rule

$$P(R) = (2\pi/\hbar)\sum_{\vec{k}_\perp} |\langle g, 1_{\vec{k}_\perp}|\vec{\mu}\cdot\nabla\Phi(\vec{R})|n, 0_{\vec{k}_\perp}\rangle|^2 \times \delta(E_n - E_g - \hbar\sigma(k_\perp)). \tag{5}$$

The energies of the atomic states have been denoted by E_n and E_g. States with no surface plasmons and one surface plasmon have been denoted by $|0_{\vec{k}_\perp}\rangle$ and $|1_{\vec{k}_\perp}\rangle$, respectively. If one wishes to include effects due to the finite lifetime of the surface plasmon one simply replaces the Dirac δ function of Eq. (5) by the Lorentzian function

$$\Delta(E_n - E_g - \hbar\sigma(k_\perp)) = \frac{1}{2\pi}\frac{\hbar\gamma(k_\perp)}{[E_n - E_g - \hbar\sigma(k_\perp)]^2 + [\frac{1}{2}\hbar\gamma(k_\perp)]^2},$$

where $\gamma(k_\perp)$ is the decay rate of the plasmon.

It is interesting that the only atomic parameters to enter Eq. (5) are dipole matrix elements and atomic frequencies—the same parameters which enter the radiative deexcitation process. Thus the quantities that the present theory will require from atomic physics have been thoroughly investigated. Insertion of Eq. (1) into Eq. (5) leads to the result

$$P(R) = \frac{2\pi}{\hbar}\int\frac{d^2k_\perp}{(2\pi)^2}\, g^2(k_\perp)\,[k_\perp^2|\langle g|\mu_z|n\rangle|^2 + |\langle g|\vec{\mu}_\perp|n\rangle\cdot\vec{k}_\perp|^2]\, e^{-2k_\perp R}\delta(E_n - E_g - \hbar\sigma(k_\perp)). \tag{6}$$

Let us limit our attention first to the case where plasmon lifetime effects are neglected.

Upon performing the angular integration, inserting Eq. (2), and performing the $k_\perp$ integration one obtains:

$$P(R) = \frac{\pi}{\hbar}\sum_{\text{Roots}} k_{gn}^2\sigma(k_{gn})\left|\frac{dk_{gn}}{d\sigma(k_{gn})}\right| e^{-2k_{gn}R} \times(|\langle g|\mu_z|n\rangle|^2 + \tfrac{1}{2}|\langle g|\mu_x|n\rangle|^2), \tag{7}$$

where k_{gn} is a root to the equation

$$\sigma(k_{gn}) = (1/\hbar)(E_n - E_g). \tag{8}$$

Henceforth we limit ourselves to the case where σ is a monotonic function of $k_\perp$, so at most one root can occur. Equation (7) is only valid if $\sigma(k_{gn})$ falls in the range

$$\sigma(0) \le \sigma(k_{gn}) \le \sigma(k_{\max}). \tag{9}$$

Here $\sigma(0)$ is the long-wavelength limit of the surface plasmon, which is $\omega_p/\sqrt{2}$, ω_p being the plasma frequency of the solid. The value of $k_\perp$ for which the surface plasmon becomes heavily damped due to decay to particle-hole pairs (Landau damping) is denoted by $k_{\max}$.

One notes that Eq. (7) is of the form

$$P(R) = Ae^{-aR}, \tag{10}$$

with

$$A = \frac{\pi}{\hbar}k_{gn}^2\sigma(k_{gn})\left|\frac{dk_{gn}}{d\sigma(k_{gn})}\right|(|\langle g|\mu_z|n\rangle|^2 + \tfrac{1}{2}|\langle g|\mu_x|n\rangle|^2), \tag{11}$$

and

$$a = 2k_{gn}. \tag{12}$$

In addition to Eq. (10) one should add the contribution arising from single-particle decay to obtain the total decay rate. The theory for this has been presented elsewhere so it won't be repeated here. Our attention will be focused solely on the surface-plasmon contribution. In order to make contact with atomic physics it is convenient to express Eq. (11) in terms of the oscillator strength for the transition

$$f_{gn} = \frac{2m\omega_{gn}}{e^2\hbar}|\langle g|\mu_z|n\rangle|^2. \tag{13}$$

Thus one has finally

$$A = \frac{3\pi e^2 k_{gn}^2 f_{gn}}{4m}\left|\frac{dk_{gn}}{d\sigma_{gn}}\right|. \tag{14}$$

The experimentally accessible number is

$$\frac{A}{a} = \frac{3\pi e^2 k_{gn} f_{gn}}{8m}\left|\frac{dk_{gn}}{d\sigma_{gn}}\right|. \tag{15}$$

Thus the quantity is fully determined by the oscillator strength, the atomic transition frequency and the surface-plasmon dispersion curve.

Results for the dispersion curve of the surface plasmon for small wave numbers are generally presented in the form[13]

$$\sigma(k_\perp) = (\omega_p/\sqrt{2})(1 + \alpha k_\perp + \cdots). \tag{16}$$

In the present treatment we neglect the lifetime broadening of the surface plasmon and take a to be a real number. Combining Eq. (16) with Eq. (15) results in an equation which is valid at small $k_\perp$:

$$\frac{A}{a}=\frac{3\pi e^2 f_{gn}}{4m\omega_p^2\alpha^2}\left(\sigma(k_{gn})-\frac{\omega_p}{\sqrt{2}}\right). \tag{17}$$

At larger wave numbers the more general expression of Eq. (15) is to be used.

We now extend the results of this section to the case where the finite lifetime of the surface plasmon cannot be disregarded. Inspection of Eq. (15) shows that the point $(dk/d\sigma)_{gn}=0$ requires special attention. In the neighborhood of the resonance one then has

$$\sigma(k_\perp)=\sigma_{gn}+\tfrac{1}{2}(k_\perp-k_{gn})^2\left(\frac{d^2\sigma}{dk^2}\right)_{gn}+\cdots. \tag{18}$$

The δ function in Eq. (6) must be replaced by a Lorentzian function. The peaked nature of this function may still be exploited. In particular, one need only have need to know the surface-plasmon damping rate at the resonance itself. Thus, in place of the previous integration

$$\int_0^\infty dk_\perp\,\delta(E_n-E_g-\hbar\sigma(k_\perp))=\frac{1}{\hbar}\left(\frac{dk}{d\sigma}\right)_{gn}$$

one now has

$$\int_0^\infty dk_\perp\,\frac{\hbar\gamma(k_{gn})/2\pi}{[\frac{1}{2}\hbar(k_\perp-k_{gn})^2(d^2\sigma/dk^2)_{gn}]^2+[\frac{1}{2}\hbar\gamma(k_{gn})]^2}$$

$$=\frac{1}{\hbar}\left(\frac{2}{\gamma(k_{gn})\,|(d^2\sigma/dk^2)_{gn}|}\right)^{1/2}. \tag{19}$$

Thus Eq. (15) reduces to

$$\frac{A}{a}=\frac{3\pi e^2 k_{gn} f_{gn}}{8m}\left(\frac{2}{\gamma(k_{gn})\,|(d^2\sigma/dk^2)_{gn}|}\right)^{1/2}. \tag{20}$$

In a similar fashion one may extend the above to the case where a finite number of σ vanish at the resonance point.

III. RESULTS AND DISCUSSION

Considerable debate exists in the literature as to what the actual surface-plasmon dispersion formula is.[14] Rather than attempt to sort out the confusion that is prevalent in the theoretical estimates we illustrate the application of the formula by resorting to experimental information about the surface plasmon dispersion curve.[13,15] For aluminum (111) surfaces it has been found that the surface plasmon obeys the relation

$$\sigma'' = 10.5 + 2k_\perp, \tag{21}$$

where the wave vector is measured in Å^{-1} and the energy is measured in eV.

While many atomic lines can be found from the tables of Charlotte Moore[16] whose energy is slightly greater than the 10.5 eV needed, we perform the calculation for the simplest of cases—the Lyman β line of atomic hydrogen (12.1 eV). The oscillator strength[17] is known to be $f=0.0791$ for this transition. One then finds $A/a=6.12\times10^7$ cm/sec for hydrogen on aluminum.

Before one can genuinely make a comparison of theory with experiment one must include effects of direct Coulomb collisions between the atomic electron and the solid's electron. The total decay rate is then described by a function of the form

$$P(R)=Ae^{-aR}+A'e^{-a'R}, \tag{22}$$

where the unprimed parameters refer to plasmon processes and the primed parameters to Coulombic effects. The probability that an excited atom will escape from the influence of the metal without suffering a radiationless deexcitation is given by

$$S=\exp\left[-\frac{1}{v_g}\left(\frac{A}{a}+\frac{A'}{a'}\right)\right], \tag{23}$$

where v_g is the component of atomic velocity perpendicular to the surface of the metal. The experimentally observed quantity is now $A/a+A'/a'$. By subtracting out the many-body effect one then has a measure of the Coulombic effect. If it turns out that the many-body effect dominates, then valuable information concerning the surface plasmon may be obtained from Eq. (20).

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