Theoretical Study of Plasmon Losses in Low-energy Photoemission Spectra*

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We study the energy- and angular-dependence of bulk and surface plasmon losses in low- and intermediate-energy region (< 1000 eV), and investigate the applicability of the quantum Landau formula which can explain overall plasmon loss features accompanied by core level photoemission. As an example, we calculate the Al 2s photoemission in the photoelectron kinetic energy range from 60 to 1000 eV measured at normal to the surface and at small take-off angles (10° and 30°). For the normal emission the quantum Landau formula gives quite similar results to those without the high-energy approximation even at 60 eV. On the other hand we observe the considerably large difference at the grazing angle emission (10°). Even at 30° we can safely apply the quantum Landau formula for the plasmon analyses above 250 eV.


Keywords: Photoemission; Plasmon losses; Al 2s; Quantum Landau formula

I. INTRODUCTION

Typical core-level X-ray photoemission spectra (XPS) have plasmon loss bands in addition to a main sharp band. The plasmon excitation processes by the core-hole potential are called intrinsic, which are contained in the one-electron spectral function [1]. Inelastic plasmon losses during photoelectron transport to the surface are called extrinsic. In the one-step model of the photoemission, we can expect the quantum mechanical interference between these two loss processes [2-7]. Recent experimental results for the plasmon losses demonstrate the importance of the quantum interference [7, 8]. On the other hand the three step model has been widely used for practical purposes [9, 10]. The photoemission is described as three-step process: (1) photo excitation, (2) transport to the surface, and (3) passage through the surface. In steps (2) and (3) the photoelectron could be scattered and lose its energy. These semi-classical approaches require much less computational cost.

In order to compare the quantum one-step calculations with the semi-classical ones, quantum Landau formula originally derived by Hedin et al. [6, 11] plays a key role, where elastic scatterings before and after the losses are completely neglected. So far Shinotsuka et al. have applied the quantum Landau formula to the plasmon loss spectra from Al 2p in a Al metal, and have investigated the relative importance of the interference [13]. Although the interference term should drop out as a function of the photoelectron energy, this term decays very slowly and is still important even at 5 keV. Later Fujikawa et al. have derived a quantum Landau formula which fully takes multiple elastic scatterings into account [12]: This formula is obtained by use of the approximations which work so well in the high-energy region.

It is thus important to study the applicability of the quantum Landau formula in the low-energy region. Landau formula is also derived in the classical trajectory approximation. If the quantum Landau formula is not applicable, we expect that the classical trajectory approach should be far from the practical application. Furthermore multi-plasmon losses can be described without introducing additional loss functions. We expect that the difference of plasmon loss features calculated by the direct (see Eq. (3)) and the quantum Landau approaches (see Eq. (9)) can be pronounced in those energy region. At first stage, we investigate the importance of path deviation due to inelastic scatterings within the approximate framework where no elastic scattering is considered.

II. THEORY

Main XPS band (no-loss band) measuring photoelectrons with momentum \( p \) excited by X-ray photons with energy \( \omega \) is described in terms of the damping photoelectron wave function \( \psi_p \) under the influence of the optical potential, the intrinsic no-loss amplitude \( S_0 (\approx 1) \) and the electron-photon interaction operator \( \Delta \):

\[
I(p, \omega)^0 = 2\pi|\langle \psi_p |\Delta|\phi_c \rangle S_0|^2 \delta(E_0 + \omega - E^*_0 - \varepsilon_p). \tag{1}
\]

The ground state energies with and without the core hole on \( \phi_c \) are \( E^*_0 \) and \( E_0 \). The amplitude \( \langle \psi_p |\Delta|\phi_c \rangle \) can be calculated by use of site-T-matrix expansion. We rather neglect elastic scatterings from surrounding atoms and have a simple relation

\[
\langle \psi_p |\Delta|\phi_c \rangle \approx \langle \phi_p |\Delta|\phi_c \rangle. \tag{2}
\]

The wave function \( \langle \phi_p |\Delta \rangle \) describes the photoelectron propagation emitted from a site A without suffering elastic scatterings from surrounding atoms [12].

In contrast to the no-loss band, the interference between the intrinsic and extrinsic losses is important for the loss band. The single-loss XPS intensity with loss

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energy $\omega_m$ is given by

$$I(p, \omega)^1 = 2\pi \sum_m \left| \langle \psi_p | \Delta | \phi_c \rangle S_m + \langle \psi_p | v_m g(\varepsilon_p + \omega_m) \Delta | \phi_c \rangle S_0 \right|^2 \times \delta(E_0 + \omega - E_0^* - \omega_m - \varepsilon_p),$$

(3)

where $v_m$ is the fluctuation potential associated with $0^\circ \rightarrow m^\circ$ excitation, $g$ is the damping one-electron Green’s function which describes the photoelectron propagation inside the solids. The intrinsic loss amplitude $S_m$ is now given by $S_m = \langle m^\circ | b | 0 \rangle$ in terms of the annihilation operator $b$ relating to the core state $\phi_c$. Equation (3) is obtained by use of Keldysh Green’s function’s approach [14, 15]. Very similar but slightly different formula can be obtained by use of many-body scattering theory [3, 6]. The first term in the absolute value in Eq. (3), $\tau_{in}$ describes the intrinsic loss and the second $\tau_{ex}$ the extrinsic loss amplitude. The fluctuation potential $v_m$ can be specified by the wave vector parallel to the surface $q = (k_x, q_y, 0)$

$$v_m(r) = \exp(i q \cdot r) V_m(z).$$

(4)

By use of Eq. (3), we thus obtain [12]

$$\tau_{in}(p) = \frac{\langle \phi_c | v_m | \phi_c \rangle}{\omega_m} \exp(-i p z_A) \times \sum_L Y_L(p) M_{L_L} \exp(-a/2),$$

(5)

$$\tau_{ex}(p) = -v_m^{\ast}(A; p) \exp(-i p z_A) \times \sum_L Y_L(Q) M_{L_L}^\prime \exp(-a/2),$$

(6)

$$a = \sum_m \left| \frac{\langle \phi_c | v_m | \phi_c \rangle}{\omega_m} \right|^2, \quad \bar{p} = \sqrt{p^2 + 2\Gamma},$$

(7)

where $\Gamma$ is the imaginary part of the optical potential. We also used $Q = (p || q, \kappa)$, $\kappa = \sqrt{p^2 + 2\omega_m - (p || q)^2}$, and $M_{L_L}$, and $M_{L_L}^\prime$ are the atomic core excitation matrix elements for the photoelectron energy $\varepsilon_p$ and $\varepsilon_p + \omega_m$ which weakly depend on the energy. The transition $L_0 \rightarrow L$ is dominated by the dipole transition. The amplitude $g_{ex}^{m\ast}$ in Eq. (6) describes the extrinsic loss during the travel from the site A to the detector and is given by

$$g_{ex}^{m\ast}(A; p) = \frac{i}{\bar{\kappa}} \int_{-\infty}^{\infty} dz \exp[-\tilde{p}(z - z_A) + i\kappa |z - z_A|] \times V_m(z),$$

(8)

In the high-energy region ($\varepsilon_p \gg \omega_m$), the difference between $Q'$ and $p$, and also that between $M_{L_L}$ and $M_{L_L}^\prime$ are small enough so that we have a simplified approximate formula

$$I(p, \omega)^1 = 2\pi \sum_L \left| Y_L(\tilde{p}) M_{L_L} \right|^2 \exp(-a) \times \sum_m \left| \frac{\langle \phi_c | v_m | \phi_c \rangle}{\omega_m} + g_{ex}^{m\ast}(A; p) \right|^2 \times \delta(E_0 + \omega - E_0^* - \omega_m - \varepsilon_p).$$

(9)

To recover the lowest sum $I(p, \omega)^0 + I(p, \omega)^1$ and also satisfy the normalization condition, the overall photoemission profile is written by the exponential form called Landau formula [6, 12]. The difference between $I(p, \omega)^1$ and $I(p, \omega)^1$ can be pronounced in low energy region. We thus carefully investigate the energy and angular dependence of the single plasmon loss intensities $I(p, \omega)^1$ and $I(p, \omega)^1$.

For the practical calculations we have to use a reliable but tractable fluctuation potential $v_m$ in Eq. (4). So far several ones have been proposed. In this work we use the one proposed by Bechstedt et al. [16].

### III. RESULTS AND DISCUSSION

![Al(001) polarized X-ray photoelectron spectrum](image)

FIG. 1: Calculated bulk (15.8 eV) and surface (11.2 eV) plasmon loss bands excited by soft X-rays from Al 2s level. The X-ray is linearly polarized normal to the surface. The photoelectrons are measured at small take-off angle $10^\circ$ for different kinetic energies in the range 60-1000 eV at main no-loss bands. The solid lines show the loss bands calculated by use of $I(p, \omega)^1$ (see Eq. (3)), and the dashed lines show those by the quantum Landau formula $I(p, \omega)^1$ (see Eq. (9)).
We thus observe the large difference between $\hat{\phi}$ angle inelastic scatterings can take place, whereas small-
ent from to the X-ray polarization (see Eq. (6)); $Q$
The extrinsic excitation amplitude $\tau$
ion because $p$
emission amplitude $I$
Landau formula $\hat{\phi}$ electrons are measured normal to the surface for different ki-
X-ray is linearly polarized normal to the surface. The photo-
surface because they mainly travel through bulk region.
suffer bulk plasmon losses before they come out of the
Surface plasmon loss intensities are much smaller than the
in Fig. 1: Here we detect the normal photoemission in-
served but the bulk/surface loss intensity ratio is nearly
500 eV). Even at 1000 eV, prominent difference is still ob-
served but the bulk/surface loss intensity ratio is nearly
the same.
Figure 2 shows the similar loss bands to those shown in Fig. 1: Here we detect the normal photoemission in-
tensities. In contrast to the results shown in Fig. 1, the
surface plasmon loss intensities are much smaller than the
the corresponding bulk plasmon loss intensities in particular
high-energy excitation. In this setup the photoelectrons
bulk plasmon losses before they come out of the
surface because they mainly travel through bulk region.
In this mode the quantum Landau formula $\hat{I}(p, \omega)_1$ gives
quite similar loss bands to $I(p, \omega)_1$. $\hat{\phi}$
In the small take-off angle ($10^\circ$) mode the intrinsic pho-
toemission amplitude $\tau_{\text{in}}(p)$ has quite a small contribu-
tion because $p$ is nearly normal to the X-ray polarization.
The extrinsic excitation amplitude $\tau_{\text{ex}}(p)$, however, can
have appreciable contribution when $Q'$ is nearly parallel
to the X-ray polarization (see Eq. (6)); $Q'$ is quite differ-
ent from $p$ in this case. In the low energy region, large-
angle inelastic scatterings can take place, whereas small-
angle losses are only allowed in the high-energy region.
We thus observe the large difference between $\hat{I}(p, \omega)_1$ and
$\hat{I}(p, \omega)_1$ in this grazing emission mode. On the other
hand, in the normal emission where the X-ray polariza-
tion is also normal to the surface as shown in Fig. 2, we
expect important contribution only when $Q' \approx p$. We
thus observe the small difference.
Figure 3 shows the same ones except the take-off an-
gle; in this case it is $30^\circ$. The surface sensitivity is low
compared with the grazing emission ($10^\circ$) so that the
surface plasmon loss intensities are comparable with the bulk
plasmon loss intensities in the energy range, $\varepsilon_p \leq 500$ eV.
For rather high-energy photoemission the bulk loss in-
tensity is much stronger than that for the surface loss.
In this setup both $\hat{I}(p, \omega)_1$ and $\hat{I}(p, \omega)_1$ yield nearly the
same loss shapes. In low energy region $\varepsilon_p \leq 100$ eV, the
small difference is still observed but they agree well above
250 eV.

IV. CONCLUSION

We theoretically study the plasmon loss features in low-
and intermediate-energy region (60-1000 eV) for three dif-
ferent detection modes; 10, 30, 90$^\circ$ measured from the
surface. Except for the nearly forbidden direction ($10^\circ$),

![FIG. 2: Calculated bulk (15.8 eV) and surface (11.2 eV) plasmon loss bands excited by soft X-rays from Al 2s level. The X-ray is linearly polarized normal to the surface. The photoelectrons are measured normal to the surface for different kinetic energies in the range 60-1000 eV at main no-loss bands. The solid lines show the loss bands calculated by use of $I(p, \omega)_1$ (see Eq. (3)), and the dashed lines show those by the quantum Landau formula $\hat{I}(p, \omega)_1$ (see Eq. (9)).](image1)

![FIG. 3: Calculated bulk (15.8 eV) and surface (11.2 eV) plasmon loss bands excited by soft X-rays from Al 2s level. The X-ray is linearly polarized normal to the surface. The photoelectrons are measured at 30$^\circ$ measured from the surface for different kinetic energies in the range 60-1000 eV at main no-loss bands. The solid lines show the loss bands calculated by use of $I(p, \omega)_1$ (see Eq. (3)), and the dashed lines show those by the quantum Landau formula $\hat{I}(p, \omega)_1$ (see Eq. (9)).](image2)
the one-plasmon loss functions obtained from the quantum Landau formula works so well even at rather low energy; 60 eV for 90°, and 250 eV for 30°.

In this work we have neglected the elastic scatterings of the photoelectrons from surrounding atoms. Very recently Kazama et al. have succeeded in calculating the plasmon loss bands incorporating elastic scatterings in the framework of the quantum Landau formula [17]: The elastic scatterings play some important roles. In the forthcoming work we are going to discuss this problem.

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