Starting from a first principle many-body theory, we derive a general formula to describe overall features in core-level photoemission including plasmon losses and peak asymmetry due to X-ray singularity. In the high-energy region we can derive quantum Landau formula which is directly compared with the corresponding classical theory where electron propagation in solids is classically described. In this quantum Landau formula elastic scatterings before and after the loss are completely taken into account. The total photoemission intensity is factorized as (elastic part)\times (inelastic part). For the latter we have a quantum Landau formula. Explicit numerical calculations are also shown for rather high energy region, 7-10 KeV from Al 2p level. Although the interference term should drop out as a function of photoelectron energy, we find that the rate is very slow. [DOI: 10.1380/ejssnt.2008.263]

Keywords: XPS; Plasmon losses; Quantum Landau formula; Fluctuation potential; Optical potential

I. INTRODUCTION

Typical core-level X-ray photoemission spectra have plasmon loss bands in addition to a main sharp band. The loss of energy from the photoelectron to the remaining system may simultaneously occur in the excitation process (intrinsic loss) or when the photoelectron travels in the solid on its way out through the surface (extrinsic loss). The extrinsic losses were first discussed by Berglund and Spicer in their three step model, excitation, transport to the surface, and passage through the surface [1]. These two loss mechanisms are not possible to separate: They can interfere each other [2–7]. On the other hand the three step model has widely been used for practical purposes [8–11]. 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] plays a key role, where elastic scatterings before and after the loss are completely neglected. The Landau formula is originally derived for electron transport based on classical theory [12]. We thus have a convenient tool to directly compare the classical and the quantum approaches to the photoelectron transport in solids. Our main purpose is thus to derive a quantum Landau formula which fully considers elastic scatterings before and after the losses. Numerical calculations are also shown in rather high energy region, 7-10 KeV excited from Al 2p level.

II. NO-LOSS AND SINGLE-LOSS INTENSITIES

In this section we discuss overall spectral features of high-energy XPS spectra. Useful and practical many-body XPS theory has been developed by Hedin et al. based on many-body scattering theory [3, 6]. An alternative theoretical approach has also been developed on the basis of Keldysh nonequilibrium Green’s functions [13–16]. They provide quite a similar formula. Here we follow the latter approach.

Main XPS band (no loss band) measuring photoelectrons with momentum \( \mathbf{p} \) excited by X-ray photons with energy \( \omega \) is described in terms of the damping photoelectron wave function \( f_{\mathbf{p}} \) under the influence of the optical potential

\[
I(\mathbf{p}; \omega)^0 = 2\pi |\langle f_{\mathbf{p}} | \Delta | \phi_c \rangle S_0|^2 \times \delta(E_0 + \omega - E_{\mathbf{p}} - \varepsilon_\mathbf{p}). \tag{1}
\]

The intrinsic no-loss amplitude \( S_0 \) should be close to 1. The ground state energies with and without core hole are \( E_0^c \) and \( E_0 \). The amplitude \( |\langle f_{\mathbf{p}} | \Delta | \phi_c \rangle| \) can be calculated by using full multiple scattering formula [17, 18]

\[
|\langle f_{\mathbf{p}} | \Delta | \phi_c \rangle| = \sum_{\alpha} \exp \left( -i \mathbf{p} \cdot \mathbf{R}_\alpha \right) \times \exp \left( -\kappa d_\alpha(\mathbf{p}) \right) \sum_{L_L} Y_{L'}(\mathbf{p}) \left( 1 - X \right)^{-1} L_L^{\alpha c} \times M_{LL'}, \tag{2}
\]

\[
X^{\alpha\beta}_{LL'} = t_{L'}^{\alpha}(\mathbf{p})G_{LL'}(\mathbf{p}; \mathbf{R}_{\alpha\beta}) \exp(-\kappa \mathbf{R}_{\alpha\beta})(1 - \delta_{\alpha\beta}),
\]

where matrix \( X \) is labeled by a set of atomic site \( \alpha, \beta, \ldots \), and angular momentum \( L = l + m \), \( d_\alpha(\mathbf{p}) \) is the distance from the site \( \alpha \) to the surface along \( \mathbf{p} \). The photoexcitation matrix element \( M_{LL'} \) is weakly dependent on the energy. The full multiple scattering is taken into account by use of the inverse matrix \( (1 - X)^{-1} \). The damping of the photoelectron wave is taken into account from first principle theory, since \( f_{\mathbf{p}} \) is influenced by the non-Hermitian optical potential. The nonlocal optical potential \( \Sigma(\varepsilon_\mathbf{p}) \) have two different parts,

\[
\Sigma(\varepsilon_\mathbf{p}) = \Sigma_r(\varepsilon_\mathbf{p}) - i\Gamma(\varepsilon_\mathbf{p}).
\]

The real (Hermitian) part \( \Sigma_r \) has substantial effects on the \( T \)-matrix \( t_\mathbf{p}(\mathbf{p}) \), and the imaginary (anti-Hermitian) part \( -i\Gamma \) is responsible for the photoelectron wave damping.
which is usually approximated by a constant. In order to
derive the multiple scattering formula (2), we apply the
site T-matrix expansion [18].
To apply the site T-matrix expansion, we have two dif-
ferent choices of the free propagators. The full propagator
\( g(\epsilon) \) can be expanded in terms of \( g_0(\epsilon) \) or \( g_0'(\epsilon) \)
\[
g(\epsilon) = \frac{1}{\epsilon - T_c - v - \Sigma_f + i\Gamma} \\
= g_0 + g_0(v + \Sigma_f)g_0 + \ldots \\
= g_0' + g_0'(v + \Sigma_f - i\Gamma)g_0' + \ldots
\]  
(3)
where \( v \) is the energy independent static potential and
\[
g_0(\epsilon) = \frac{1}{\epsilon - T_c + i\eta}, \\
g_0'(\epsilon) = \frac{1}{\epsilon - T_c + i\eta}(\eta \rightarrow +0),
\]  
(4)
where \( T_c \) is the kinetic energy operator. In the first ex-
ansion in Eq. (3), the muffin-tin constant \( v_0 \) is a real
constant value, whereas it is \( v_0 - i\Gamma \) in the second ex-
ansion in terms of \( g_0' \). The former choice makes unperturbed
plane wave have the complex wave number \( \tilde{p} \)
\[
\tilde{p} = \sqrt{2(\epsilon_p + i\Gamma)} = p_e + i\kappa; \quad (\tilde{p} \parallel p).
\]  
(5)
When we determine \( \Gamma \) as a muffin-tin constant which
is small enough in each atomic sphere, the phase shift cal-
culations are only influenced by the real potential. In the
high-energy region, we have the well-known formula
\[
k \approx \Gamma/p \approx -\text{Im}\Sigma/p.
\]
In the second expansion we cannot get rid of the re-
dundant scatterings from complex potential \(-i\Gamma\) in the inter-
stitial region. We thus should use the first expansion in
Eq. (3).
On the other hand single-loss XPS intensity whose loss
energy is \( \omega_m \), is written by [13]
\[
I(p; \omega) = 2\pi \sum_m \left| \langle \phi_p | E | \phi_m \rangle S_m \right|^2 \\
+ \langle \phi_p | v_m g(\epsilon_p + \omega_m) \Delta | \phi_m \rangle S_0 \\
x \delta(\omega_0 + \omega - \omega_m - \epsilon_p)
\]  
(6)
where \( v_m \) is the fluctuation potential responsible for in-
trinsic and extrinsic excitations and \( g \) is the causal Green’s
function. The intrinsic amplitude \( S_0 \), \( S_n (n > 0) \) are de-
fined by
\[
S_0 = \langle n^* | b | 0 \rangle, \quad S_n = \langle n^* | b | 0 \rangle,
\]  
(7)
where \( b \) (\( b^\dagger \)) is the annihilation (creation) operator asso-
ciated with the core state \( \phi_c \). To get more detailed infor-
mation, we introduce a well-known useful Hamiltonian to
describe core processes [12],
\[
H = H_v + \varepsilon_v b^\dagger b + V_e b^\dagger b^\dagger.
\]  
(8)
Here \( H_v \) is the full many-electron Hamiltonian for valence
electrons, \( V_e \) is the interaction between the core hole and
valence electrons, and \( \varepsilon_v \) is the core electron energy. The
hole state \( |n^* \rangle \) satisfies \( H^* |n^* \rangle = E_n^* |n^* \rangle \), \( (H^* = H_v + V_e) \), whereas \( |0 \rangle = |0_c \rangle \) stands for the ground state of the no-
hole Hamiltonian \( H_v + \varepsilon_v \). This approximate Hamiltonian
and conventional perturbation theory simplify those am-
plitudes,
\[
S_0 = \exp(-a/2), \quad S_n = -\frac{\langle c | v_n | c \rangle}{\omega_n} \exp(-a/2),
\]  
(9)
where \( v_n \) is the fluctuation potential associated with the
excitation \( 0_v \rightarrow n_v \) defined by
\[
v_n(r) = \int d\omega' v(r - r') \langle n_v | \psi^\dagger \psi \rangle |0_v \rangle.
\]  
(10)
The renormalization factor \( a \) is given by
\[
a = \sum_n \frac{|\langle c | v_n | c \rangle|^2}{\omega_n^2}.
\]  
(11)
The calculation of the extrinsic loss term is much more
difficult. Again we apply the site T-matrix expansion as
used to derive Eq. (2),
\[
\langle \phi_p | v_m g(\epsilon_p + \omega_m) \Delta | \phi_c \rangle = \langle \phi_p | \left( 1 + \sum_{\alpha} t_{\alpha 0} g_0 + \sum_{\alpha \neq \alpha'} t_{\alpha' 0} g_0 t_{\alpha 0} + \ldots \right) \Delta | \phi_c \rangle.
\]  
(12)
Here we use an abbreviation \( g_A' = g_A(\epsilon_p + \omega_m) \). The
damping plane wave \( \phi_p^0 \) has complex momentum \( p_z = \tilde{p} \)
defined by Eq. (5) and real parallel components \( p_{\parallel} = (p_x, p_y) \). The fluctuation potential \( v_m \) defined by Eq. (10)
can be specified by wave vector parallel to the surface
\( \mathbf{q} = (q_x, q_y, 0) \) with aid of translational symmetry parallel
to the surface
\[
v_m(r) = \exp(i \mathbf{q} \cdot \mathbf{r}) V_m(z).
\]  
(13)
We assume that the solid occupies the region \( z \leq 0 \).
The amplitude
\[
\tau_{ex}^{(0)}(\mathbf{p}) = \langle \phi_p^0 | v_m g_A' \Delta | \phi_c \rangle,
\]  
(14)
neglects whole elastic scatterings from surrounding atoms
before and after the loss. This amplitude is approximated by
\[
\tau_{ex}^{(0)}(\mathbf{p}) \approx -g_A^{(0)}(A; \mathbf{p}) \exp(-i\tilde{p}z_A)
\times \sqrt{\frac{2}{\pi}} \sum_L i^{-L} Y_L(Q') M_{LL'},
\]  
(15)
where \( Q' = (p_{\parallel} - \mathbf{q}, \kappa) \), and \( \kappa = \sqrt{p^2 + 2\omega_m} - (p_{\parallel} - \mathbf{q})^2 \).
We use \( M_{LL'} \) for the photoelectron energy \( \epsilon_p + \omega_m \), but
it slowly changes with energy. The loss amplitude during
the travel from the site \( A \) to the detector is given by
\[
g^{(n)}_{ex}(A; \mathbf{p})
= \frac{i}{\tilde{k}} \int_{-\infty}^{+\infty} dz \exp[-i(\tilde{k} - \tilde{p})(z - z_A)] V_m(z)
+ \int_{-\infty}^{+\infty} dz \exp[i(\tilde{k} - \tilde{p})(z - z_A)] V_m(z),
\]  
(16)
The derivation of Eqs. (15) and (16) is briefly shown in the Appendix. In the high-energy limit, both $\tilde{k}$ and $\tilde{p}$ should be large enough for the normal emission, and the rapidly oscillating first term has to be very small. We thus have an approximate formula where the electron wave propagates only out to solid surface:

$$ g_{ex}^m(A; \hat{p}) = \frac{i}{\hbar} \int_{z_0}^{\infty} dz \exp[i(\tilde{k} - \tilde{p})(z - z_0)] V_m(z). $$

(17)

In the similar way, we can obtain an practical formula which includes single-elastic scatterings before the loss,

$$ \tau_{ex}^{(1)}(\hat{p}) = \sum_{\beta} g_{ex}^m(\beta; \hat{p}) \exp[-i(\tilde{p}z_\beta + \mathbf{p}_\parallel \cdot \mathbf{R}_\beta)] $$

$$ \times \sqrt{\frac{2}{\pi}} \sum_{LL'} i^{-L} Y_{L'}(Q') \tilde{t}_F^p(p') G_{L'LL}(p' \mathbf{R}_\beta) M'_{LL'}. $$

(18)

For simplicity, we assume that the site of the core function $g_{ex}^m(\beta; \hat{p})$ is neglected, and we replace it by $g_{ex}^m(A; \hat{p})$. Furthermore in the high-energy near normal photoemission, we can safely put $\mathbf{Q'} \approx \hat{p}$. Let estimate the angular difference between $\mathbf{Q'}$ and $\hat{p}$ for $\omega_m = 2 \ a.u., \ q = 1 \ a.u.$ in the normal emission. When $\epsilon_p = 10 \ a.u.$, the difference is $12^{\circ}$, and when $100 \ a.u.$ it is $4^{\circ}$. The renormalization of the multiple scattering series before the loss is thus written by

$$ \tau_{ex}^{(0)}(\hat{p}) + \tau_{ex}^{(1)}(\hat{p}) + \ldots $$

$$ = -g_{ex}^m(A; \hat{p}) \sum_{\beta} \exp[-i(\tilde{p}z_\beta + \mathbf{p}_\parallel \cdot \mathbf{R}_\beta)] $$

$$ \times \sqrt{\frac{2}{\pi}} \sum_{LL'/\beta} i^{-L} Y_{L'}(p') [(1 - X)^{-1}]^{3A}_{LL'LL'} M'_{LL'}. $$

(19)

where $X$ is defined in Eq. (2).

We can rewrite the loss amplitude $g_{ex}^m(A; \hat{p})$ defined by Eq. (15) in the alternative form in terms of the damping propagator $g_0$ defined by Eq. (4);

$$ g_{ex}^m(A; \hat{p}) = $$

$$ -\frac{1}{(2\pi)^{3/2}} \int d\mathbf{r} \phi_0^*(\mathbf{r}) v_m(\mathbf{r}) g_0(\mathbf{r} - \mathbf{R}_A; \mathbf{p}'). $$

(20)

So far we have taken the full multiple scatterings into account before the loss. In the same way we can fully take them into account after the loss. The result is simple enough for the renormalized extrinsic losses,

$$ \tau_{ex}(\mathbf{p}) \approx (2\pi)^{3/2} (f_p^{-} |\Delta| \phi_c) $$

$$ \times \int d\mathbf{r} f_p^{-} (\mathbf{r}) v_m(\mathbf{r}) g_0(\mathbf{r} - \mathbf{R}_A; \mathbf{p}'). $$

(21)

In the high-energy photoemission, $(f_p^{-} |\Delta| \phi_c)$ can safely be replaced by $(f_p^{-} |\Delta| \phi_c)$ which yields an approximate extrinsic loss amplitude (the second term in $| \ldots |^2$ in Eq. (6))

$$ \langle f_p^{-} |v_m g(\epsilon_p + \omega_m) \Delta | \phi_c \rangle $$

$$ \approx \tau_{ex}^m(p) (f_p^{-} |\Delta| \phi_c), $$

$$ \tau_{ex}^m(p) = (2\pi)^{3/2} $$

$$ \times \int d\mathbf{r} f_p^{-} (\mathbf{r}) v_m(\mathbf{r}) g_0(\mathbf{r} - \mathbf{R}_A; \mathbf{p}'), $$

(22)

where $\mathbf{R}_A$ is the site of the core function $\phi_c$. In the low- and intermediate-energy region, say $\epsilon_p < 200-300 \ eV$, the above factorization is a poor approximation. We cannot use the approximations to arrive at Eq. (22).

### III. QUANTUM LANDAU FORMULA

To recover the lowest sum $I(p)^0 + I(p)^1$ and also satisfy the normalization condition, the overall photoemission profile is now written by the exponential form with aid of the approximation (22)

$$ I(p; \omega) = \left( \langle f_p^{-} |\Delta| \phi_c \rangle \right)^2 $$

$$ \times \int_{-\infty}^{\infty} dt \exp[i(\omega + \omega_0 - E_0 - \epsilon_p)t] $$

$$ \times \exp \left[ \int_0^{\omega} \frac{d\omega'}{\epsilon} e^{-\epsilon t} \right] $$

(23)

where we have defined an "asymmetric function" $\alpha(\omega)$

$$ \frac{\alpha(\omega)}{\omega} = \sum_m |\tau_m|^2 \delta(\omega - \omega_m), $$

$$ \tau_m(p) = \tau_{ex}^m(p) + S_m/S_0. $$

(24)

This exponential form (23) is known as Landau formula which was derived on the basis of classical transport theory [12]. Very similar quantum derivation is developed by Hedlin [19] where very simple time-reversed LEED function is used instead of renormalized damping photoelectron wave function $f_p^\pm$. This generalization is crucial to discuss quantum depth distribution function (DDF) [17]. It is important to note that $\tau_{ex}^m(p)$ depends on $p$ as shown by Eq. (22).

So far we should have detailed information on the fluctuation potentials $v_m$ for the calculations of $\tau_m$ in Eq. (24). In the exponential form (23) we only need $\alpha(\omega)/\omega$ defined by (24). To simplify it we note that both $\tau_{ex}^m$ and $S_m/S_0$ can be written in terms of the fluctuation potential $v_m$. From Eqs. (9) and (22) we have

$$ \tau_m(p) = \int f_A(r) v_m(r) dr, $$

(25)

$$ f_A(r) = - \frac{|\phi_c(r)|^2}{\epsilon} $$

$$ + (2\pi)^{3/2} f_p^{-} (r) g_0(\mathbf{r} - \mathbf{R}_A; \mathbf{p}'), $$

(26)

where $\epsilon = \omega + \omega_0 - E_0 - \epsilon_p$ is the excitation energy measured from the threshold. The first term of $f_A$ is
related to the intrinsic losses, whereas the second to the extrinsic losses. Assuming that all \( v_m \)'s are real, we thus obtain an alternative expression for \( \alpha(\omega)/\omega \),

\[
\frac{\alpha(\omega)}{\omega} = \int dr dr' f_A^* (r') f_A (r) \times \sum_m v_m(r') v_m(r) \delta(\omega - \omega_m) = -\frac{1}{\pi} \int dr dr' f_A^* (r') f_A (r) \times \text{Im} W (r, r'; \varepsilon),
\]

(27)

where \( W(\varepsilon) \) is the screened Coulomb propagator.

It is often reasonable to split \( \alpha(\omega) \) in a “low-energy” flat part \( \alpha_1(\omega) \) and a “high-energy” stronger part \( \alpha_2(\omega) \) [19],

\[
\alpha(\omega) = \alpha_1(\omega) + \alpha_2(\omega), \quad \alpha_1(\omega) = \alpha_0 \theta(\omega_0 - \omega).
\]

(28)

We thus have from Eq. (23)

\[
I(p; \omega)^c_{\infty} = \left| \left\langle f_p | \Delta \phi_c \right\rangle \right|^2 
\times 2\pi \int d\omega' \, D_1 (\varepsilon - \omega') \, D_2 (\omega') 
\times \exp \left[ -\int_0^\infty d\omega' \frac{\alpha(\omega')}{\omega'} \right],
\]

(29)

where low- \( D_1 \) and high-energy \( D_2 \) spectral functions are defined by \( (j = 1, 2) \)

\[
D_j (t) = \int_{-\infty}^{\infty} dt \, D_j (\omega) e^{-i \omega t} 
= \exp \left[ \int_0^\infty d\omega \, \frac{\alpha_j (\omega)}{\omega} e^{-i \omega t} \right].
\]

The low-energy spectral function \( D_1 (\omega) \) describes X-ray singularity for metallic systems [12] and recoil energy shift, broadening and asymmetry of the main photoemission band [20]. The high-energy spectral function \( D_2 (\omega) \) describes the plasmon losses taking both intrinsic and extrinsic ones into account, which can be expanded as

\[
D_2 (\omega) = \delta (\omega) + \beta (\omega) + \frac{1}{2!} (\beta * \beta) (\omega) + \ldots,
\]

(30)

\[
\beta (\omega) = \alpha_2 (\omega)/\omega,
\]

where \( (A * B) (\omega) = \int d\omega' \, A(\omega - \omega') B(\omega') \) is the convolution of \( A \) and \( B \). Substitution of Eq. (30) into (29) yields the photoemission intensity from the core site \( R_A \),

\[
I(p; \omega)^c_{\infty} = 2\pi \left| \left\langle f_p | \Delta \phi_c \right\rangle \right|^2 
\times \exp \left[ -\int_0^\infty d\omega \, \frac{\alpha(\omega)}{\omega} \right] 
\times \left[ D_1 (\varepsilon) + (D_1 * \beta) (\varepsilon) + \frac{1}{2!} (D_1 * \beta * \beta) (\varepsilon) + \ldots \right].
\]

(31)

The first term \( D_1 (\varepsilon) \) describes the main band with no plasmon loss, and it also describes the recoil effects [20] and asymmetry due to the X-ray singularity [12]. The second term \( D_1 * \beta \) describes one-plasmon loss, and so on. As pointed out before \( \beta (\omega) \) depends on \( p \), so that plasmon loss bands show the angular dependence. At low energy prominent angular dependence of the plasmon loss spectra is observed, whereas no angular dependence is observed at high-energy excitation \( (\epsilon_p > 1 \text{ keV}) \) [7]. Some experimental results show that the relative plasmon loss intensity changes very slowly as a function of photoelectron energy [22, 23] in the high-energy region, but rapidly changes in the low-energy region. These results imply that \( \beta (\omega) \) should only depend on \( p \) in the high-energy region. Hedev et al. point out that the interference terms in \( \beta (\omega) \) drop out in the high-energy limit [6, 19]. Our numerical calculations [21], however, show that the rate of the drop out is very slow. Even at \( h\omega = 5 \text{ keV} \) for Al 2p excitation, the interference term still has considerably important contribution. In the energy range \( h\omega = 1-5 \text{ keV} \), the extrinsic amplitude is much larger than the intrinsic one.

IV. CALCULATED RESULTS

The previous paper by Uwatoko et al. has shown the plasmon loss bands associated with Al 2p excitation in low and intermediate energy region [7]. Destructive interference plays an important role especially at low energy \( (\omega = 125 \text{ eV}) \), in contrast to it extrinsic contribution is dominant at higher energy \( (\omega = 1486.6 \text{ eV}) \). Shinotsuka et al. have studied the plasmon losses at higher energy region up to 5 keV [21]. Here we show the plasmon losses as calculated in the previous papers for Al 2p excitation, whereas at higher energies, \( \omega = 7-10 \text{ KeV} \): X-ray is linearly polarized in the \( x \)-direction. Figure 1 shows the calculated results measured at take-off angle 60° in the \( zx \) plane, which are normalized to the maximum peak height of the total loss bands \( \beta (\varepsilon) \) in Eq. (31); the peak asymmetry in \( D_1 \) and elastic scatterings are neglected. The relative importance of the surface plasmon losses at 11.2 eV to the bulk ones at 15.8 eV decreases with the photon energy as expected. The calculated result shows that the interference in the bulk plasmon losses is much smaller than that in the surface plasmon losses. The integrated intensity of the interference term is still 8% of the total intensity even at 10 KeV. We thus realize that the rate of the drop out is very slow even at 10 KeV for both surface and bulk plasmon losses.

V. CONCLUDING REMARKS

Overall XPS spectral features are conveniently described by the exponential formula (Landau formula) which includes both the intrinsic, extrinsic terms and their interference in addition to X-ray singularities and recoil effects, even though we fully include elastic scatterings before and after the losses. This formula works well in the high-energy region, however we should investigate the border above which we can safely apply Eq. (29) or (31). For that purpose we have to study the depth dependence.
Photon energy is changed from 7 to 10 KeV. Reliable fluctuation potentials or screened Coulomb energy range. Numerical calculations show that the inter-

The author is grateful to Dr. H. Arai, Dr. L. Kövér for their useful comments on this paper.

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The propagator \( g_A(\mathbf{r}, \mathbf{r}') \) in the amplitude \( \tau_{ex}^{(0)} \) is given in the angular momentum representation

\[
g_A(\mathbf{r}, \mathbf{r}') = -2i\hbar \sum_L h_L(p' r_\geq) Y_L(\hat{\mathbf{r}}) R_l^A(p' r_<) \times Y_L^*(\hat{\mathbf{r}}') \exp(i\delta^A),
\]

where \( R_l^A \) is the regular radial solution for the spherically symmetric potential \( v_A \) at X-ray absorbing atom \( A \). As the core function \( \phi_c \) is strongly localized on the atom \( A \) at \( \mathbf{R}_A \), we can thus safely assume that the condition \( r > r' \) is always satisfied. It is convenient to use the integral representation,

\[
-2i\hbar h_L(p' r) Y_L(\hat{\mathbf{r}}) = \frac{i^{-l}}{\pi^2} \int d\mathbf{k} Y_L(\hat{\mathbf{k}}) \frac{\exp(i\mathbf{k} \cdot \mathbf{r})}{p'^2 - k^2 + 2i\Gamma}.
\]

We thus have

\[
\tau_{ex}^{(0)}(\mathbf{p}) = \sum_{\mathbf{k}} \frac{i^{-l} (2\pi)^{1/2}}{\pi^2} \exp(-i\mathbf{p}z_A) \int d\mathbf{k}_z \frac{Y_L(\hat{\mathbf{k}}')}{k^2 - k'^2 + 2i\Gamma} \int_{-\infty}^{\infty} dz V_m(z) \exp[i(k z - \bar{p})(z - z_A)],
\]

\( k' = (p_\parallel - q, k_z) \).

We can calculate the integral

\[
\int d\mathbf{k}_z \frac{\exp[i k_z (z - z_A)]}{k^2 - k'^2 + 2i\Gamma} = -\frac{\pi i}{k} \exp \left( i\kappa [z - z_A] \right),
\]

where \( \kappa = \sqrt{k^2 + 2i\Gamma} \).

Substituting this into Eq. (34), we obtain the formula (15) for \( \tau_{ex}^{(0)} \).

\[\text{FIG. 1: Calculated Al 2p plasmon losses (bulk at 15.8 eV and surface at 11.2 eV) at off-normal emission, take-off angle is 60°, in the } xz \text{ plane; X-ray is linearly polarized in the } x \text{-direction. Photon energy is changed from 7 to 10 KeV.}\]

of the loss amplitude from the site \( \beta, g_{\alpha}^{(0)}(\beta) \) for wide energy range. Numerical calculations show that the interference terms drop out very slowly with the photoelectron energy.

For quantitative studies it is important to obtain reliable fluctuation potentials or screened Coulomb propagator which should explicitly take the surface effects into account.

\[\text{Acknowledgments}\]

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\[\text{Appendix}\]

\[\text{The propagator } g_A(\mathbf{r}, \mathbf{r}') \text{ in the amplitude } \tau_{ex}^{(0)} \text{ is given in the angular momentum representation}\]

\[
g_A(\mathbf{r}, \mathbf{r}') = -2i\hbar \sum_L h_L(p' r_\geq) Y_L(\hat{\mathbf{r}}) R_l^A(p' r_<) \times Y_L^*(\hat{\mathbf{r}}') \exp(i\delta^A),
\]

where \( R_l^A \) is the regular radial solution for the spherically symmetric potential \( v_A \) at X-ray absorbing atom \( A \). As the core function \( \phi_c \) is strongly localized on the atom \( A \) at \( \mathbf{R}_A \), we can thus safely assume that the condition \( r > r' \) is always satisfied. It is convenient to use the integral representation,

\[
-2i\hbar h_L(p' r) Y_L(\hat{\mathbf{r}}) = \frac{i^{-l}}{\pi^2} \int d\mathbf{k} Y_L(\hat{\mathbf{k}}) \frac{\exp(i\mathbf{k} \cdot \mathbf{r})}{p'^2 - k^2 + 2i\Gamma}.
\]

We thus have

\[
\tau_{ex}^{(0)}(\mathbf{p}) = \sum_{\mathbf{k}} \frac{i^{-l} (2\pi)^{1/2}}{\pi^2} \exp(-i\mathbf{p}z_A) \int d\mathbf{k}_z \frac{Y_L(\hat{\mathbf{k}}')}{k^2 - k'^2 + 2i\Gamma} \int_{-\infty}^{\infty} dz V_m(z) \exp[i(k z - \bar{p})(z - z_A)],
\]

\[\text{Because of the factor } (k^2 - k'^2 + 2i\Gamma)^{-1}, \text{ the main contribution to the above integral over } k_z \text{ comes from very small region near } \kappa, \text{ and we can replace the slowly varying function } Y_L(k') \text{ by } Y_L(Q') \text{ where } Q' = (p_\parallel - q, k_z). \text{ Thus we can calculate the integral}\]

\[
\int d\mathbf{k}_z \frac{\exp[i k_z (z - z_A)]}{k^2 - k'^2 + 2i\Gamma} = -\frac{\pi i}{k} \exp \left( i\kappa [z - z_A] \right),
\]

where \( \kappa = \sqrt{k^2 + 2i\Gamma} \).

Substituting this into Eq. (34), we obtain the formula (15) for \( \tau_{ex}^{(0)} \).

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