

Introductory Photoemission Theory

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An introductory review is presented on the basis of many-body scattering theory. Some fundamental aspects of photoemission theory are discussed in detail. A few applications are also discussed; photoelectron diffraction, depth distribution function and multi-atom resonant photoemission are also discussed briefly.

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1 Introduction

Photoemission spectroscopy has developed to one of the most powerful tools to study electronic and surface structures.¹ This review article discusses basic features of photoemission theory based on many-body scattering theory. More sophisticated theory can be developed on the basis of nonequilibrium Green's functions²⁻⁴ and quantum electrodynamics.⁵ These approaches are very powerful; however, they require more theoretical background. Here, we rather extensively use the simple and direct method; the many-body scattering theory⁶⁻⁹ is still widely applicable as demonstrated below. Also, we restrict to nonrelativistic framework. Relativistic photoemission theory is found in other references.^{10,11}

2 Basic Photoemission Theory

At first we introduce some formal scattering theory for later discussion.⁹ Let $|t\rangle$ be a solution of the Schrödinger equation (hereafter we use atomic units; $m_e = e = \hbar = 1$),

$$\left(i \frac{\partial}{\partial t} - H\right)|t\rangle = 0. \quad (1)$$

The total Hamiltonian $H = H_0 + V$ is assumed to be time independent, and the state $|t\rangle$ approaches to the unperturbed state $|t\rangle_0$ at $t \rightarrow -\infty$, which is a solution of the unperturbed

Schrödinger equation,

$$\left(i \frac{\partial}{\partial t} - H_0\right)|t\rangle_0 = 0. \quad (2)$$

Our problem is to relate $|t\rangle$ to $|t\rangle_0$. The Eq. (1) can also be written as

$$\left(i \frac{\partial}{\partial t} - H_0\right)|t\rangle = V|t\rangle. \quad (3)$$

For convenience, we introduce a retarded Green's function that satisfies an equation

$$\left(i \frac{\partial}{\partial t} - H_0\right)G^+(t-t') = \delta(t-t') \quad (4)$$

with the boundary condition $G^+(t-t') = 0$ ($t < t'$). Using the relation $d\theta(t-t')/dt = \delta(t-t')$, the Green's function is written as

$$G^+(t-t') = -i\theta(t-t')e^{-iH_0(t-t')}. \quad (5)$$

The desired integral equation is then given as

$$|t^+\rangle = |t\rangle_0 + \int_{-\infty}^{\infty} G^+(t-t')V|t'^+\rangle dt', \quad (6)$$

where the state $|t^+\rangle$ automatically satisfies the retarded boundary condition.

Now we substitute $|t^+\rangle = |a^+\rangle e^{-iEt}$ into Eq. (6) where $|a^+\rangle$ is a eigenstate of the full Hamiltonian H . The corresponding stationary state for the unperturbed Hamiltonian H_0 is $|a\rangle e^{-iEt}$.

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We should note that both $|a^+\rangle$ and $|a\rangle$ have the same energy eigenvalue E_a because they have continuous spectra

$$\begin{aligned} (H - E_a)|a^+\rangle &= 0, \\ (H_0 - E_a)|a\rangle &= 0. \end{aligned} \quad (7)$$

Then we have

$$\begin{aligned} |a^+\rangle &= |a\rangle - i \int_{-\infty}^0 \exp[i(H_0 - E_a)t'] V e^{iH_0 t'} |a^+\rangle dt' e^{iH_0 t}, \\ &= |a\rangle + \frac{e^{iH_0 t}}{E_a - H_0 + i\eta} V |a^+\rangle. \end{aligned} \quad (8)$$

When $e^{iH_0 t}$ replaced by 1, Eq. (8) is well known as the Lippmann-Schwinger equation:

$$|a^+\rangle = |a\rangle + G_0^+(E_a) V |a^+\rangle, \quad (9)$$

where the free Green's function G_0^+ is defined as

$$G_0^+(E) = \frac{1}{E - H_0 + i\eta}. \quad (10)$$

We have a formal solution for the state $|a^+\rangle$

$$\begin{aligned} |a^+\rangle &= |a\rangle + G^+(E_a) V |a\rangle \\ &= \frac{i\eta}{E_a - H + i\eta} |a\rangle, \end{aligned} \quad (11)$$

where the full Green's function G^+ is defined as

$$G^+(E) = \frac{1}{E - H + i\eta}. \quad (12)$$

Let consider the transition $a \rightarrow b$ ($a \neq b$). Because of the orthogonality $\langle b|a\rangle = 0$, we have an expression for the amplitude from Eq. (8),

$$\langle b|a^+\rangle = \langle b|G_0^+(E_a) V |a^+\rangle e^{iH_0 t}. \quad (13)$$

We thus can calculate the transition rate $w_{a \rightarrow b}$, in the limit $\eta \rightarrow 0$,

$$\begin{aligned} w_{a \rightarrow b} &= \frac{d}{dt} |\langle b|a^+\rangle|^2 \\ &\rightarrow 2\pi |\langle b|V|a\rangle|^2 \delta(E_a - E_b). \end{aligned} \quad (14)$$

We introduce the T matrix defined by

$$T(b, a) = \langle b|V|a^+\rangle = \langle b|T(E_a)|a\rangle \quad (15)$$

which simplifies Eq. (14)

$$w_{a \rightarrow b} = 2\pi |\langle b|T(E_a)|a\rangle|^2 \delta(E_a - E_b). \quad (16)$$

Substituting Eq. (11) into Eq. (15), we have an operator equation for T ,

$$\begin{aligned} T(E) &= V + VG^+(E)V \\ &= V + VG_0^+(E)V + VG_0^+(E)VG_0^+(E)V + \dots \\ &= V + VG_0^+(E)T(E) \end{aligned} \quad (17)$$

where we have used the relation between the full Green's function G and T

$$\begin{aligned} G^+ &= G_0^+ + G_0^+VG_0^+ + G_0^+VG_0^+VG_0^+ + \dots \\ &= G_0^+ + G_0^+VG^+ \\ &= G_0^+ + G_0^+TG_0^+. \end{aligned} \quad (18)$$

In the first-order approximation, the transition rate is represented by

$$w_{a \rightarrow b} \approx 2\pi |\langle b|V|a\rangle|^2 \delta(E_a - E_b) \quad (19)$$

which is known as Fermi's golden rule. The other solution of Eq. (1) is also important, the one that satisfies a different boundary condition: $|t^-\rangle$ approaches to the state $|t\rangle_0$ at $t \rightarrow \infty$. The corresponding stationary state $|a^-\rangle$ satisfies an equation similar to Eq. (11):

$$|a^-\rangle = \frac{-i\eta}{E_a - H - i\eta}. \quad (11')$$

3 XPS Theory Including Lifetime Effects

The basic formula Eq. (16) for the transition intensity is quite general. In this section, we apply it to study photoemission processes.

We consider a Hamiltonian which describes the electron-photon interaction in addition to electron-electron interactions, electron-nucleus interactions:

$$H = H_p + H_r + V(t). \quad (20)$$

H_p is the many-body Hamiltonian for the target, which is written as the sum of nuclear kinetic energy, T_N and the electronic Hamiltonian, H_e

$$\begin{aligned} H_p &= H_e + T_N, \\ H_e &= \sum_i \left(\frac{p_i^2}{2} + \sum_\alpha \frac{-Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} \right) + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} + \frac{1}{2} \sum_{\alpha \neq \beta} \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}}, \\ T_N &= \sum_\alpha \frac{P_\alpha^2}{2M_\alpha}. \end{aligned} \quad (21)$$

The Hamiltonian for the free photon field H_r is given in terms of the electric and magnetic field operators \mathbf{E} and \mathbf{B}

$$H_r = \frac{1}{8\pi} \int (\mathbf{E}^2(\mathbf{r}t) + \mathbf{B}^2(\mathbf{r}t)) d\mathbf{r}. \quad (22)$$

We now introduce the vector potential operator for a free photon field,

$$\mathbf{A}(\mathbf{r}t) = c \sum_{\mathbf{k}s} \sqrt{\frac{2\pi}{\omega_{\mathbf{k}}\Omega}} (a_{\mathbf{k}s} \mathbf{e}(\mathbf{k}s) e^{i(\mathbf{k}\cdot\mathbf{r} - \omega_{\mathbf{k}}t)} + h.c.), \quad (23)$$

where $h.c.$ means hermitian conjugation of the first term, and $\mathbf{e}(\mathbf{k}s)$ is the photon polarization vector of the wave vector \mathbf{k} and polarization s . From the transverse condition $\nabla \cdot \mathbf{A} = 0$, we have a relation

$$\mathbf{k} \cdot \mathbf{e}(\mathbf{k}s) = 0. \quad (24)$$

When a photon propagates in the direction $\hat{\mathbf{k}}$, the polarization vector \mathbf{e} is normal to \mathbf{k} ($s = 1, 2$). The volume of normalization box is Ω , $a_{\mathbf{k}s}$ and $a_{\mathbf{k}s}^\dagger$ are the photon annihilation and creation operators in the state $\mathbf{k}s$ which follow the boson commutation relations

$$\begin{aligned} [a_{\mathbf{k}s}, a_{\mathbf{k}'s'}] &= 0, \quad [a_{\mathbf{k}s}^\dagger, a_{\mathbf{k}'s'}^\dagger] = 0, \\ [a_{\mathbf{k}s}, a_{\mathbf{k}'s'}^\dagger] &= \delta_{\mathbf{k},\mathbf{k}'} \delta_{ss'}. \end{aligned} \quad (25)$$

We can rewrite Eq. (22) by the use of these operators

$$H_r = \sum_{\mathbf{k}} \omega_{\mathbf{k}} \left(a_{\mathbf{k}s}^\dagger a_{\mathbf{k}s} + \frac{1}{2} \right), \quad \omega_{\mathbf{k}} = ck. \quad (26)$$

In Eq. (20), $V(t)$ is the interaction operator between the target and photons. The nuclear masses are much heavier than the electron mass, so the direct nucleus-photon interaction can be neglected compared with the electron-photon interaction:

$$V(t) = \frac{1}{c} \sum_{\mathbf{i}} \mathbf{p}_{\mathbf{i}} \cdot \mathbf{A}(\mathbf{r}_{\mathbf{i}}t) + \frac{1}{2c^2} \sum_{\mathbf{i}} \mathbf{A}^2(\mathbf{r}_{\mathbf{i}}t). \quad (27)$$

Here the second quantized expression of the first term of Eq. (27) is also shown to clarify the physics used in it:

$$\begin{aligned} V_1(t) &= \frac{1}{c} \sum_{\mathbf{i}} \mathbf{p}_{\mathbf{i}} \cdot \mathbf{A}(\mathbf{r}_{\mathbf{i}}t) \\ &= \sum_{\mathbf{k}s} [T_r(\mathbf{k}s) a_{\mathbf{k}s} e^{-i\omega_{\mathbf{k}}t} + T_r^\dagger(\mathbf{k}s) a_{\mathbf{k}s}^\dagger e^{i\omega_{\mathbf{k}}t}], \end{aligned} \quad (28)$$

where we have used

$$\begin{aligned} T_r(\mathbf{k}s) &= \int d\mathbf{x} \psi^\dagger(x) \Delta_{\mathbf{k}s}(\mathbf{r}) \psi(x), \quad x = (\mathbf{r}, \sigma), \\ \Delta_{\mathbf{k}s}(\mathbf{r}) &= \sqrt{\frac{2\pi}{\omega_{\mathbf{k}} \Omega}} e^{i\mathbf{k} \cdot \mathbf{r}} \mathbf{e}(\mathbf{k}s) \cdot \mathbf{p}. \end{aligned} \quad (29)$$

$\psi(x)$ and $\psi^\dagger(x)$ are the annihilation and creation operators for the electron field. The operator V_1 describes a one-photon process such as X-ray absorption and emission, whereas the second term of Eq. (27),

$$V_2(t) = \frac{1}{2c^2} \sum_{\mathbf{i}} \mathbf{A}^2(\mathbf{r}_{\mathbf{i}}t) \quad (30)$$

describes two photon creation and annihilation because of $a_{\mathbf{k}s} a_{\mathbf{k}'s'}$, $a_{\mathbf{k}s}^\dagger a_{\mathbf{k}'s'}^\dagger$ terms, and X-ray scatterings because of $a_{\mathbf{k}s}^\dagger a_{\mathbf{k}'s'}$, $a_{\mathbf{k}s} a_{\mathbf{k}'s'}^\dagger$. Thus V_2 can be neglected in the photoemission analyses.

In order to apply the scattering theory developed in Sec. 2, we notice that

$$V_1(t) = e^{iH_0 t} V_1 e^{-iH_0 t}, \quad (31)$$

because the time dependence of the vector potential operator \mathbf{A} is simply $a_{\mathbf{k}s} e^{-i\omega_{\mathbf{k}}t}$. We thus can consider the Hamiltonian (20) as the interaction representation of the time-independent Hamiltonian

$$H_p + H_r + V_1. \quad (32)$$

Let specify the initial state and the final state: In the initial state a $(\mathbf{k}s)$ photon comes into the target (molecule or solid) in a ground state, $|0; \mathbf{k}s\rangle = a_{\mathbf{k}s}^\dagger |0\rangle$. In the final state, a photoelectron with momentum \mathbf{p} excited from a deep orbital c and the deep core hole state n^* which finally decays with fluorescence X-ray emission or Auger electron emission. In order to calculate the photoemission amplitude accompanying fluorescence emission with $\mathbf{k}'s'$ photon $\langle n^*, \mathbf{p}; \mathbf{k}'s' | T(E) | 0; \mathbf{k}s \rangle$, we introduce the projection operators, P_i : P_1 is the projector to the deep hole state, P_0 to the no hole state, P_2, P_3, \dots to the hole state shallower than the deep hole state. They satisfy

$$P_i P_j = \delta_{ij} P_j, \quad \sum_i P_i = 1. \quad (33)$$

And we also define a projection operator

$$Q_1 = 1 - P_1 \quad (34)$$

The projected states by Q_1 have free particles such as photons or scattering electrons. To apply partial sum technique, it is convenient to use the new unperturbed Hamiltonian H_0 and its perturbation V_d ,

$$H_0 = \sum_{\mathbf{i}} P_i H_p P_i + H_r, \quad (35)$$

$$V_d = Q_1 H_p P_1 + P_1 H_p Q_1 + V_1. \quad (36)$$

We should note that $Q_1 V_d Q_1 = P_1 V_d P_1 = 0$. Our calculations are reduced to $Q_1 T Q_1$ as discussed before:⁸

$$Q_1 T Q_1 = Q_1 V_d P_1 G^+ P_1 V_d Q_1. \quad (37)$$

By the use of Eq. (18) and of the fact that G_0 is the diagonal with respect to P_1 and Q_1 , we have by use of the abbreviations $V = V_d$ and $G_0 = G_0^+$

$$\begin{aligned} P_1 G^+ P_1 &= P_1 (G_0 + G_0 V G_0 + \dots) P_1 \\ &= P_1 G_0 \{ 1 + (V G_0)^2 + (V G_0)^4 + \dots \} P_1 \\ &= P_1 G_0 (1 - V G_0 V G_0)^{-1} P_1 \\ &= P_1 (G_0^{-1} - V G_0 V)^{-1} P_1 \\ &= P_1 \frac{1}{E - H_0 - \Sigma^+(E)} P_1, \end{aligned} \quad (38)$$

where we notice that for odd n , $P_1 (V G_0)^n P_1 = 0$, and $(AB)^{-1} = B^{-1} A^{-1}$. We define self-energy Σ^+

$$\begin{aligned} \Sigma^+(E) &= P_1 V Q_1 G_0 Q_1 V P_1 \\ &= \Delta(E) - \frac{i}{2} \Gamma(E). \end{aligned} \quad (39)$$

The second form of Eq. (39) is obtained by the use of the relation $(x + i\eta)^{-1} = P(1/x) - i\pi\delta(x)$. The real and imaginary part of Σ , Δ and Γ are the energy-dependent Hermitian operators, which describe the energy shift and lifetime width.

By the use of Eq. (38), we obtain the photoemission amplitude decaying to fluorescence emission

$$\begin{aligned} \langle n^*, \mathbf{p}; \mathbf{k}'s' | T(E) | 0; \mathbf{k}s \rangle &= \langle n^*, \mathbf{p} | a_{\mathbf{k}'s'} Q_1 V_1 P_1 G^+(E) P_1 V_1 Q_1 a_{\mathbf{k}s}^\dagger | 0 \rangle \\ &= \langle n^*, \mathbf{p} | a_{\mathbf{k}'s'} Q_1 V_1 \frac{1}{E - H_0 - \Sigma^+(E)} V_1 Q_1 a_{\mathbf{k}s}^\dagger | 0 \rangle. \end{aligned} \quad (40)$$

By use this amplitude, we can obtain the intensity measuring photoelectrons with momentum \mathbf{p} associated with fluorescence decay, after we sum over the all possible fluorescence and target states,

$$\begin{aligned} I_{\mathbf{k}s}^+(\mathbf{p}) &= 2\pi \sum_{\mathbf{n}, \mathbf{k}'s'} \left| \langle n^*, \mathbf{p}; \mathbf{k}'s' | T(E) | 0; \mathbf{k}s \rangle \right|^2 \delta(E_n^* + \omega_{\mathbf{k}'} + \varepsilon_{\mathbf{p}} - E) \\ &= 2\pi \sum_{\mathbf{n}, \mathbf{k}'s'} \langle 0 | T_r^\dagger(\mathbf{k}s) \frac{1}{E - H_0 - \Sigma^-(E)} T_r(\mathbf{k}'s') | n^*, \mathbf{p} \rangle \\ &\quad \times \langle n^*, \mathbf{p} | T_r^\dagger(\mathbf{k}'s') \frac{1}{E - H_0 - \Sigma^+(E)} T_r(\mathbf{k}s) | 0 \rangle \\ &\quad \times \delta(E_n^* + \omega_{\mathbf{k}'} + \varepsilon_{\mathbf{p}} - E), \end{aligned} \quad (41)$$

where Σ^\pm are approximated by c -numbers and $\Sigma^- = \Sigma^{*}$. The photoemission intensity $I_{\mathbf{k}s}^f$ includes the finite lifetime effects. We can rewrite Eq. (41) as the convolution of the photoemission intensity without lifetime effects $I_{\mathbf{k}s}^\infty$ (lifetime is ∞) and a Lorentzian,

$$I_{\mathbf{k}s}^f(\mathbf{p}) = \int \frac{d\omega}{2\pi} \frac{\Gamma_r I_{\mathbf{k}s}^\infty(\mathbf{p}, \omega)}{(\omega - \omega_k)^2 + \Gamma^2/4}, \quad (42)$$

$$I_{\mathbf{k}s}^\infty(\mathbf{p}, \omega) = 2\pi \sum_m \left| \langle m^*, \mathbf{p} | T_r(\mathbf{k}s) | 0 \rangle \right|^2 \delta(E_m^* + \varepsilon_p - E_0 - \omega), \quad (43)$$

where $\Gamma = \Gamma_r + \Gamma_A$, Γ_r and Γ_A are the lifetime broadenings contributed from fluorescence and Auger decays. In the above derivation, we assume that Γ is constant. In the case of Auger decay after the photoemission, we obtain $I_{\mathbf{k}s}^A(\mathbf{p})$ in the similar way; we use Γ_A in Eq. (42) instead of Γ_r . Summing over these two terms, we obtain the total photoemission intensity measuring photoelectrons with momentum \mathbf{p} ,

$$I_{\mathbf{k}s}(\mathbf{p}) = \int \frac{d\omega}{2\pi} \frac{\Gamma I_{\mathbf{k}s}^\infty(\mathbf{p}, \omega)}{(\omega - \omega_k)^2 + \Gamma^2/4}. \quad (44)$$

4 XPS Theory without Lifetime Effects

In this section we discuss a powerful technique to calculate the intensity $I_{\mathbf{k}s}^\infty$. The main ingredients are a damping photoelectron wavefunction under the influence of the optical potential. That intensity is directly calculated by the amplitude

$$T^\infty(m^*, \mathbf{p}; 0, \mathbf{k}s) = \langle m^*, \mathbf{p} | T_r(\mathbf{k}s) | 0 \rangle. \quad (45)$$

After the photoemission, the core hole potential V_c and the many-body Hamiltonian for the valence electrons H_v work to relax the valence electron states: $(H_v + V_c) | m_v^* \rangle = E_m^{v*} | m_v^* \rangle$. The photoelectron emission state $| m^*, \mathbf{p} \rangle$ is related to the unperturbed state as shown by Eq. (11'), and the amplitude is given in terms of the valence states of the target $| m_v^* \rangle$ influenced by the core hole

$$T^\infty(m^*, \mathbf{p}; 0, \mathbf{k}s) = \langle \phi_p^- | m_v^* \langle (1 + V_m G(E)) T_r(\mathbf{k}s) | 0 \rangle, \quad (46)$$

$$V_m = V_{es} - \langle m_v^* | V_{es} | m_v^* \rangle,$$

where V_{es} is the interaction between the photoelectron and particles in the solid. We define the Green's function

$$G(E) = \frac{1}{E - H + i\eta}, \quad (47)$$

$$E = E_0 + \omega_k = E_m^{v*} + \varepsilon_p,$$

where the total Hamiltonian H includes all interactions except for the those responsible for the lifetime effects. Photoelectron function ϕ_p^- is a solution of one-electron Hamiltonian h_c^m and satisfy the minus boundary condition. As discussed in Sec. 2, ϕ_p^- approaches to the plane wave ϕ_p^0 in the remote future. We thus have to use ϕ_p^- for the photoelectron wave function:

$$h_c^m \phi_p^- = \varepsilon_p \phi_p^-, \quad (48)$$

$$h_c^m = -\frac{\nabla^2}{2} - \sum_\alpha \frac{Z_\alpha}{|\mathbf{r} - \mathbf{R}_\alpha|} + \langle m_v^* | V_{es} | m_v^* \rangle,$$

where h_c^m is the Hermitian operator and cannot describe the damping of photoelectron propagation. The mean free path of

the photoelectrons is the smallest around 50 - 100 eV. We should go one step further to handle the photoelectron wave damping in solids.

Let us again introduce the projection operators $P = | m_v^* \rangle \langle m_v^* |$ and $Q = 1 - P$. We can rewrite

$$V_m = (P + Q)V_m(P + Q) = QV_mQ + PV_mQ + QV_mP \quad (PV_mP = 0). \quad (49)$$

This relation yields from Eq. (46)

$$P(1 + V_m G) = P(1 + V_m G)(P + Q) = P(1 + V_m G)P + PV_mGQ. \quad (50)$$

Here we use a new unperturbed Hamiltonian \tilde{H} and its perturbation \tilde{V} ,

$$H = \tilde{H} + \tilde{V} \\ \tilde{H} = H_v + V_c + QV_mQ + h_c^m \\ \tilde{V} = PV_mQ + QV_mP. \quad (51)$$

The inelastic fluctuation potential \tilde{V} is an important factor to describe the extrinsic losses. Green's function corresponding to the Hamiltonian \tilde{H} is defined as

$$\tilde{G}(E) = \frac{1}{E - \tilde{H} + i\eta}. \quad (52)$$

By the use of relations, $PV_m = PV_mQ = P\tilde{V}$ and $G = \tilde{G} + \tilde{G}\tilde{V}\tilde{G} + \dots$, we have

$$P(1 + V_m G) = P(1 + \tilde{V}\tilde{G} + (\tilde{V}\tilde{G})^2 + \dots)P(1 + \tilde{V}\tilde{G}Q). \quad (53)$$

Only the even powers of \tilde{V} in the first bracket on the right side are non-vanishing; they give rise to

$$P(1 + V_m G) = P\tilde{G}^{-1}(\tilde{G}^{-1} - \tilde{V}\tilde{G}\tilde{V})^{-1}P(1 + \tilde{V}\tilde{G}Q) \\ = (\varepsilon_p - h_c^m + i\eta) \frac{1}{\varepsilon_p - h_c^m - \Sigma_m(E)} P(1 + \tilde{V}\tilde{G}Q), \quad (54)$$

where Σ_m is the optical potential defined similar to Eq. (39)

$$\Sigma_m(E) = \langle m_v^* | \tilde{V}\tilde{G}\tilde{V} | m_v^* \rangle. \quad (55)$$

The left side of the transition amplitude (46) is thus written,

$$\langle \phi_p^- | \langle m_v^* | (1 + V_m G) \\ = i\eta \langle \phi_p^- | \frac{1}{\varepsilon_p - h_c^m - \Sigma_m(E)} \langle m_v^* | (1 + \tilde{V}\tilde{G}Q) \\ = \langle \psi_p^- | \langle m_v^* | (1 + \tilde{V}\tilde{G}Q), \quad (56)$$

where a new one-electron function $|\psi_p^- \rangle$ is defined as

$$|\psi_p^- \rangle = \frac{-i\eta}{\varepsilon_p - h_c^m - \Sigma_m(E)} |\phi_p^- \rangle. \quad (57)$$

This one-electron wave function is the solution of the equation,

$$[h_c^m + \Sigma_m(E)] |\psi_p^- \rangle = \varepsilon_p |\psi_p^- \rangle, \quad (58)$$

which satisfies the minus boundary condition, and damps under the influence of the non-Hermitian operator Σ_m . In the transition amplitude (46) we have

$$T_r(\mathbf{k}s)|0\rangle \approx \Delta_{\mathbf{k}s}|c\rangle|0_v\rangle, \quad (59)$$

where $|0_v\rangle$ is the valence electron state which is not affected by the core-hole potential. We thus obtain a practical formula for the transition amplitude (46)

$$\begin{aligned} T^\infty(m^*, \mathbf{p}; 0, \mathbf{k}s) &= \langle \psi_{\mathbf{p}}^- | \langle m_v^* | (1 + \tilde{V}\tilde{G}) | 0_v \rangle \Delta_{\mathbf{k}s} | c \rangle \\ &= \sum_n \langle \psi_{\mathbf{p}}^- | \langle m_v^* | (1 + \tilde{V}\tilde{G}) | n_v^* \rangle \Delta_{\mathbf{k}s} | c \rangle S_n, \end{aligned} \quad (60)$$

where S_n is the intrinsic amplitude defined by use of the annihilation operator b for the deep core level c ,

$$S_n = \langle n_v^* | 0_v \rangle = \langle n_v^* | b | 0 \rangle. \quad (61)$$

The operator $\langle m_v^* | 1 + \tilde{V}\tilde{G} | n_v^* \rangle$ works on the photoelectron during the extrinsic transitions $n_v^* \rightarrow m_v^*$. For example, the main photoemission peak is described by the amplitude

$$\begin{aligned} T^\infty(0^*, \mathbf{p}; 0^*, \mathbf{k}s) &= \\ &= \langle \psi_{\mathbf{p}}^- | \Delta_{\mathbf{k}s} | c \rangle S_0 + \sum_{n \neq 0} \langle \psi_{\mathbf{p}}^- | \langle 0_v^* | \tilde{V}\tilde{G} | n_v^* \rangle \Delta_{\mathbf{k}s} | c \rangle S_n. \end{aligned} \quad (62)$$

The first term describes the direct photoemission from the deep core orbital $|c\rangle$ where valence electrons relax to the state $|0_v^*\rangle$ influenced by the core hole potential V_c ($S_0 \approx 1$). The photoelectron wave $|\psi_{\mathbf{p}}^- \rangle$ propagates to the surface and out to a detector with momentum \mathbf{p} . The second term describes the second order processes where first the target is simultaneously excited to n th state with the amplitude S_n , and then deexcited from the n th state to the 0th state during the propagation in the solid. We can usually neglect the second term because it is of the order of 10^{-2} of the first term. In case of the loss band, the intrinsic and the extrinsic amplitudes are in the same order, and the strong interference is expected. Please refer to a recent work.¹²

5 X-ray Photoelectron Diffraction Theory

To discuss the main photoemission peak, one needs to calculate only the first term of Eq. (62). In this section we discuss multiple scattering theory to calculate the amplitude $\langle \psi_{\mathbf{p}}^- | \Delta_{\mathbf{k}s} | c \rangle$. The damping photoelectron function $\langle \psi_{\mathbf{p}}^- |$ is related to $\langle \phi_{\mathbf{p}}^0 |$ from Eq. (11)

$$\langle \psi_{\mathbf{p}}^- | = \langle \phi_{\mathbf{p}}^0 | [1 + \sum_0 (E_0^{v*} + \varepsilon_p) g(\varepsilon_p)]. \quad (63)$$

The photoelectron function $\langle \phi_{\mathbf{p}}^0 |$ is related to the plane wave $\langle \phi_{\mathbf{p}}^0 |$, ($T_c = -\nabla^2/2$),

$$\begin{aligned} \langle \phi_{\mathbf{p}}^- | &= \langle \phi_{\mathbf{p}}^0 | [1 + V_0 \hat{g}(\varepsilon_p)], \\ \hat{g}(\varepsilon_p) &= \frac{1}{\varepsilon_p - T_c - V_0 + i\eta}, \end{aligned} \quad (64)$$

where the kinetic energy and the averaged static potential V_0 from the target state $|0_v^*\rangle$ with a deep hole on c are used,

$$V_0 = \langle 0_v^* | V_{cs} | 0_v^* \rangle - \sum_{\alpha} \frac{Z_{\alpha}}{|\mathbf{r} - \mathbf{R}_{\alpha}|}. \quad (65)$$

The relation between $\langle \psi_{\mathbf{p}}^- |$ and $\langle \phi_{\mathbf{p}}^0 |$ is obtained by using the relation $g = \hat{g} + \hat{g}\Sigma_0 g$,

$$\langle \psi_{\mathbf{p}}^- | = \langle \phi_{\mathbf{p}}^0 | [1 + \{V_0 + \sum_0 (E_0^{v*} + \varepsilon_p)\} g(\varepsilon_p)]. \quad (66)$$

We can safely approximate the imaginary part of the optical potential Σ_0 as a constant $-i\gamma_c/2$ when the photoelectron energy is large enough. Within this approximation, we have

$$\begin{aligned} V_0 + \sum_0 &= V_0 + \text{Re}\Sigma_0 - i\frac{\gamma_c}{2} \\ &= V_T - i\frac{\gamma_c}{2}, \quad V_T = V_0 + \text{Re}\Sigma_0, \end{aligned} \quad (67)$$

where V_T is the Hermitian part of the total potential for the photoelectrons. Going back to the process to derive Eq. (66), we obtain the relation between $\langle \psi_{\mathbf{p}}^- |$ and the damping plane wave $\phi_{\mathbf{p}}'$

$$\langle \psi_{\mathbf{p}}^- | = \langle \phi_{\mathbf{p}}' | [1 + V_T(\varepsilon_p) g(\varepsilon_p)]. \quad (68)$$

One-electron Green's function with damping is defined as

$$g_0(\varepsilon) = \frac{1}{\varepsilon - T_c + i\gamma_c/2}. \quad (69)$$

By using the relation $g = g_0 + g_0 V_T g$ and the T matrix,

$$\begin{aligned} V_T g &= V_T (g_0 + g_0 V_T g) \\ &= V_T (g_0 + g_0 V_T g_0 + g_0 V_T g_0 V_T g_0 + \dots) \\ &= (V_T + V_T g_0 V_T + \dots) g_0 \\ &= T g_0. \end{aligned} \quad (70)$$

Therefore we can simplify the relation Eq. (68) as

$$\langle \psi_{\mathbf{p}}^- | = \langle \phi_{\mathbf{p}}' | [1 + T g_0]. \quad (71)$$

In order to obtain multiple scattering series, it is useful to express the total potential V_T as the sum of each atomic potential V_{α} . By use of the relation $T = V_T + V_T g_0 V_T + \dots$, we have

$$T = \sum_{\alpha} V_{\alpha} + \sum_{\alpha\beta} V_{\alpha} g_0 V_{\beta} + \sum_{\alpha\beta\gamma} V_{\alpha} g_0 V_{\beta} g_0 V_{\gamma} + \dots \quad (72)$$

The second and higher terms have scattering terms on the same site, like $V_{\alpha} g_0 V_{\alpha}$. We now define site- t matrix on the site α

$$t_{\alpha} = V_{\alpha} + V_{\alpha} g_0 V_{\alpha} + V_{\alpha} g_0 V_{\alpha} g_0 V_{\alpha} + \dots \quad (73)$$

By use of the site- t matrix, the total T matrix given by Eq. (72) can be rewritten

$$T = \sum_{\alpha} t_{\alpha} + \sum_{\alpha \neq \beta} t_{\alpha} g_0 t_{\beta} + \sum_{\alpha \neq \beta \neq \gamma} t_{\alpha} g_0 t_{\beta} g_0 t_{\gamma} + \dots \quad (74)$$

The deep core orbital c is strongly localized on the X-ray absorbing site A : The excited photoelectrons propagate to the surrounding sites. We thus pick up the site- t matrix expansion

$$1 + T g_0 = 1 + t_A g_0 + \sum_{\alpha (\neq A)} t_{\alpha} g_A + \sum_{\beta \alpha (\neq A)} t_{\beta} g_0 t_{\alpha} g_A + \dots, \quad (75)$$

where g_A is the one-electron Green's function that fully includes the potential effects on the site A :

$$g_A(\varepsilon) = g_0(\varepsilon) + g_0(\varepsilon)t_A g_0(\varepsilon). \quad (76)$$

We obtain the photoemission amplitude

$$\begin{aligned} \langle \psi_p^- | \Delta_{\mathbf{k}s} | \phi_c \rangle &= \langle \phi_{\bar{A}p}^- | \Delta_{\mathbf{k}s} | \phi_c \rangle \\ &+ \sum_{\alpha(\neq A)} \langle \phi_p' | t_{\alpha} g_A \Delta_{\mathbf{k}s} | \phi_c \rangle \\ &+ \sum_{\alpha\beta(\neq A)} \langle \phi_p' | t_{\beta} g_0 t_{\alpha} g_A \Delta_{\mathbf{k}s} | \phi_c \rangle + \dots, \\ \langle \phi_{\bar{A}p}^- | &= \langle \phi_p' | (1 + t_A g_0), \end{aligned} \quad (77)$$

where $\langle \phi_{\bar{A}p}^- |$ is the photoelectron wave function for the potential on the X-ray absorbed atom A . The first term of Eq. (77) describes the direct photoemission amplitude without suffering any elastic scattering (direct term). The second term is the single scattering amplitude scattered from the site α (single scattering term). The third term describes the double elastic scattering at α and β (double scattering term). For practical purposes we write each of them in angular momentum representations. The direct term Z_1 is explicitly written by

$$\begin{aligned} Z_1 &= \langle \phi_{\bar{A}p}^- | \Delta_{\mathbf{k}s} | \phi_c \rangle \\ &= \sum_L Y_L(\hat{\mathbf{k}}) M_{LL_c}, \end{aligned} \quad (78)$$

where L is the abbreviated form of the pair of angular momentum, $L = (l, m)$. In the dipole approximation, the photoexcitation matrix element M_{LL_c} excited by linearly polarized light parallel to the z axis is given by

$$\begin{aligned} M_{LL_c} &= \sqrt{\frac{2}{\pi}} i^{-l} e^{i\delta_l^A} \rho(l)_c G(L_c 10 | L), \\ \rho(l)_c &= \int R_l(kr) R_{l_c}(r) r^3 dr, \end{aligned} \quad (79)$$

where δ_l^A is the phase shift of l th partial wave at site A , and $R_l(kr)$ and R_{l_c} are the radial parts of $\phi_{\bar{A}p}^-$ and ϕ_c labeled by the orbital angular momentum l and l_c . Gaunt integral $G(L_c 10 | L) = \int Y_{L_c}(\hat{\mathbf{r}}) Y_{10}(\hat{\mathbf{r}}) Y_L^*(\hat{\mathbf{r}}) d\hat{\mathbf{r}}$ is responsible for the angular momentum selection rule of the photoexcitation. The single-scattering term Z_2 is explicitly written by

$$\begin{aligned} Z_2 &= \sum_{\alpha(\neq A)} \langle \phi_p' | t_{\alpha} g_A \Delta_{\mathbf{k}s} | \phi_c \rangle \\ &= \sum_{\alpha(\neq A)} e^{-i\mathbf{k}\cdot\mathbf{R}_{\alpha A}} \sum_{LL'} Y_L(\hat{\mathbf{k}}) t_l^{\alpha}(k) G_{LL'}(k\mathbf{R}_{\alpha A}) M_{LL_c}, \end{aligned} \quad (80)$$

where $\mathbf{R}_{\alpha A}$ is the position vector of the scatterer α measured from the emitter A . The angular momentum representation of the site- t matrix $t_l^{\alpha}(k)$ at site α is given by

$$t_l^{\alpha}(k) = -\frac{e^{2i\delta_l^{\alpha}} - 1}{2ik} \quad (81)$$

in terms of the phase shift δ_l^{α} at site α and the photoelectron wave number k . The propagator $G_{LL'}(k\mathbf{R}_{\alpha A})$ describes electron propagation from the site A with L to the site α with L' . In terms of $X = tG$, we obtain the general renormalized multiple scattering XPD amplitude,

$$\begin{aligned} M(\mathbf{k}) &= \sum_{\alpha} e^{-i\mathbf{k}\cdot\mathbf{R}_{\alpha A}} \sum_{LL'} Y_L(\hat{\mathbf{k}}) \times [1 + X + X^2 + X^3 + \dots]_{LL'}^{\alpha A} M_{LL_c} \\ &= \sum_{\alpha} e^{-i\mathbf{k}\cdot\mathbf{R}_{\alpha A}} \sum_{LL'} Y_L(\hat{\mathbf{k}}) [(1 - X)^{-1}]_{LL'}^{\alpha A} M_{LL_c}, \end{aligned} \quad (82)$$

$$X_{LL'}^{\alpha A} = t_l^{\alpha}(k) G_{LL'}(k\mathbf{R}_{\alpha A}) (1 - \delta^{\alpha\beta}), \quad (83)$$

where X is a square matrix, in which a matrix element is labeled by a set of atomic sites (A, α, β, \dots) and angular momentum L , whose matrix dimension is $N(l_{\max} + 1)^2$ for the cluster of N atoms and maximum angular momentum l_{\max} . The full multiple scattering is taken into account by use of the inverse matrix $(1 - X)^{-1}$.

In order to calculate the amplitude (82), we have to use sophisticated optical potential Σ_0 (see Eq. (55)) for which some approximations have been developed, such as the Hedin-Lundqvist potential¹³ and its nonlocal version.¹⁴

6 Depth Distribution Function

In this section, we apply the XPD theory developed in the previous section to calculate the mean free path and depth distribution functions (DDF).¹⁵ The imaginary part, γ_c , of the nonlocal potential Σ_0 is responsible for the photoelectron damping, which typically weakly depends on the space. The expansion in terms of Eq. (69) naturally describes the photoelectron wave propagation with damping. The complex momentum \mathbf{k}' is thus defined by the principal value

$$k' = \sqrt{2(\varepsilon_k + i\Gamma_0)} \equiv k_r + i\kappa, \quad (\mathbf{k}' \parallel \mathbf{k}). \quad (84)$$

In the high energy region ($\varepsilon_k \gg \gamma_c$), κ is approximated by

$$\kappa = \frac{\gamma_c}{k} \sim \frac{1}{k} \text{Im} \Sigma_0. \quad (85)$$

The expression gives the widely used inelastic mean free path (IMFP) formula.⁷

We can calculate the DDF starting from the first principle many-body quantum mechanical multiple scattering theory by use of *ab initio* optical potential. Figure 1 shows the DDF calculated from cylindrical bcc models, where all multiple scatterings inside these cylindrical clusters are fully taken into account. Incident X-ray polarization is parallel to the surface normal. The intensity from the third layer in the cylinder models is much larger than that from the chain model. The calculated DDF converges at the eighth sheet. This result clearly shows that the chain models successfully predict a peak in DDF due to focusing elastic scatterings, whereas they are poor in describing the decay profile of the DDF, in particular at $z > 10 \text{ \AA}$. The asymptotic behavior of $\phi(z)$ at large z is well described by a simple exponential law

$$\phi(z) \sim \phi_0 e^{-z/\lambda_d},$$

where λ_d is the dressed IMFP, which effectively includes the elastic scattering effects. This law does not work at small z , as seen before.

7 Resonant Photoemission Theory

In this section we study resonant photoemission. The direct approach described above is not easily available to discuss these processes, and an alternative approach is more useful to study the resonant processes. As the alternative approach, first-principle XPS theories based on Keldysh Green's functions have been developed.^{4,16} These theories give formally exact perturbation expansions of the photoemission intensity.

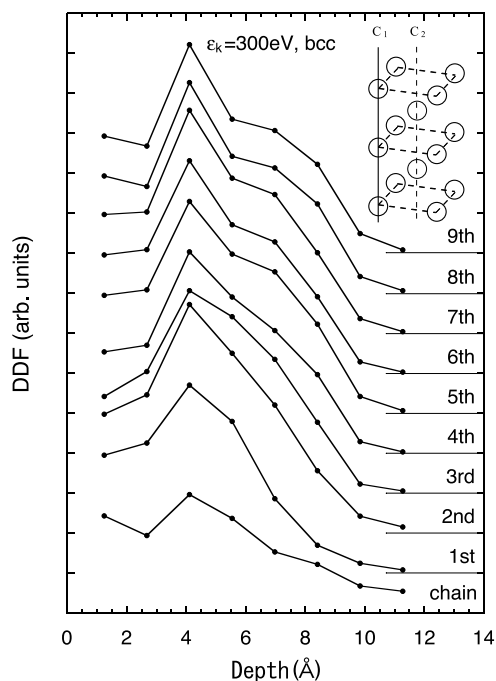


Fig. 1 Calculated DDFs from Fe(001) surface where we use cylindrical bcc models. In the inset, two different types of chains C_1 and C_2 are shown.¹⁵ Up to 9th surrounding chains are taken into account in these calculations.

The present authors have used skeleton expansion in terms of renormalized one-electron Green's functions. Further refinements to include radiation field screening are also proposed.⁵ We obtain the photoemission intensity including the radiation field screening vertex,

$$I \propto \left| \langle f_p^- | \Delta | g_n \rangle + i \langle f_p^- | X(\omega) | g_n \rangle + i \langle f_p^- | Z(\omega) | g_n \rangle \right|^2 \times \delta(\epsilon_p + E_n(N-1) - \omega - E_0(N)), \quad (86)$$

where the hole and particle Dyson orbitals g_n and f_p^- and the resonant operators $X(\omega)$ and $Z(\omega)$ are defined in our previous paper.¹⁷ The scattering particle Dyson orbital f_p^- is basically the same as the damping photoelectron wave function ψ_p^- used in the above sections. We note that the first term is corresponding to the photoemission amplitude Eq. (77). The second and the third term describe the resonant effects. We also note that the third term is the contribution from the radiation field screening.

By using this framework, we can systematically study, in particular, not only the radiation field screening but also the dynamically polarized part in the screened Coulomb propagator. They play a crucial role in the resonant processes. In particular, multi-atom resonant photoemission (MARPE) is a good example to study these effects. MARPE occurs when photon energy is tuned to be a core-level absorption edge of an atom neighboring to the absorbing atom A , so that MARPE permits direct determination of near-neighbor atomic identities.^{18,19} In MARPE calculations we can neglect the second term of Eq. (86) because of the small overlap between emitter and surrounding atoms. The polarization part W_p of the screened Coulomb interaction ($W = v + W_p$) depends on energy, where v is the bare Coulomb potential, which is energy-independent. We demonstrated the importance of W_p to obtain intense MARPE values comparable with the observed one.¹⁹ Figure 2 shows the O 1s MARPE

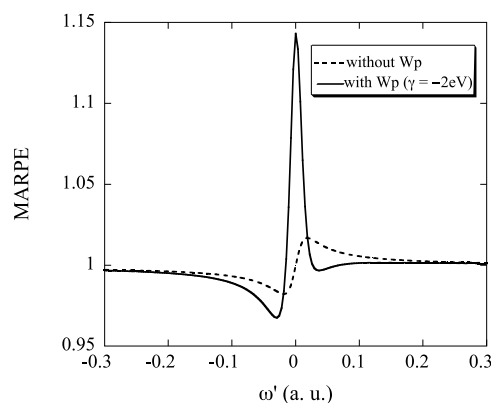


Fig. 2 Calculated O 1s MARPE near the Mn 2p threshold.¹⁶

spectra calculated near the Mn L-edge. The broken line calculated without W_p gives weak MARPE whose relative intensity to the main photoemission band is about 2%. In contrast to this result, the solid line calculated with W_p gives a prominent peak comparable with the experimental one (~12%),¹⁹ and still shows a Fano-like asymmetric shape. In this case we have used the parameter $\gamma = -2$ eV to obtain a good agreement with the experimental result. We have also demonstrated the importance of the structure surrounding the emitter. For example, high symmetric local structure such as O_h symmetry around the X-ray absorbing atom gives rise to no MARPE signal.¹⁶ The detailed discussion is found in our previous papers.^{16,20}

8 Concluding Remarks

We review the photoemission theory based on the general scattering theory which provides lifetime effects, mean free path, and multiple scattering series from first principles. We should stress the importance of a consistent many-body theory to explain, for example, the mean free path and the electron yield calculations in consistent ways.

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