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Calculation of transition probability for neutralization process of +1 ion based on the Nozières and Dominicis theory

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Abstract

We investigate the neutralization probability of a +1 ion moving parallel to a metal surface, mainly using the Nozières and Dominicis theory (ND theory), which was applied to the edge singularities in x-ray absorption and emission spectra in metals. In particular, we focus on the effects due to the sudden disappearance of the image potential in the neutralization process. From the analysis, we found that the neutralization probability is given by $P(i \rightarrow f) \propto \frac{\pi}{\Gamma(1-\alpha)} \left(\frac{D}{\Delta}\right)^\alpha$, where D and Γ are the band width and the gamma function. The factor $\alpha = 2\delta/\pi - (\delta/\pi)^2$ is given by the phase shift (δ : phase shift on Fermi surface), and the energy difference between the initial and final states, Δ , includes the kinetic energy of the ion and various other phenomenological factors. The singularity caused from the sudden disappearance of the image potential enhances or reduces the neutralization probability depending on the symmetry of atomic orbital of the ion. When the ion velocity is too fast to form an image potential, the neutralization process would proceed without the creation of an image potential, accompanying an excitation of a surface plasmon; as a result of plasmon excitation the ion velocity becomes slower than the plasma frequency because of screening effects. In this paper, we apply the ND theory to the case of slow ion motion and discuss the dynamics.

1. Introduction

The neutralization process of charged particles occurring in front of metal surface is an important issue in the field of surface science. Experimentally the neutralization process has been examined by various methods; they are analysis of the energy distribution of electrons ejected from the surface [1], the large-angle back-scattering technique for multi-charged ion neutralization [2–6], measurement of the number and charge state distribution of particles

formed after the reflection of the incident ions [7, 8] and spin-labelling techniques using electron-spin-polarized He^+ ions coupled with energy-resolved measurements of the ejected electron polarization [9–11].

If a multi-electron system plays a determining role in the neutralization process, the Auger transition process accompanying possible electron emission can be expected to appear [12–14]. Since this process is associated with the many-body problem, it seems very difficult to treat the Auger neutralization process theoretically. Accordingly various theoretical methods such as simplified electron wavefunctions [15–18], the inclusion of phenomenological screening [15, 17, 19] and the neglect of screening caused by electron–electron interaction [20] have been proposed to account for the Auger transition quantitatively. Recently Lorente calculated the Auger neutralization rate of He^+ and the de-excitation rates of excited He atoms above an Al surface [21], by developing a quantitative treatment of the Auger neutralization process; he introduced a self-consistent screening method for the electron–electron interaction using a self-consistent representation of the metal surface [22–24] and developed a full three-dimensional non-perturbative method regarding the metal state affected by the presence of the ion.

On the other hand, a resonant neutralization process appears when only one electron is associated with the neutralization process. The electron transferred from the metal surface usually occupies an excited state of the ion without the emissions of electrons following the de-excitation process. Borisov and Teillet-Billy proposed an effective theory of resonance neutralization which is in quantitative agreement with experiments [25, 26].

Nevertheless the neutralization process in the low energy levels remains an open problem both experimentally and theoretically. Certainly the Auger neutralization process has been commonly observed rather than the resonance neutralization process. For example, Akazawa and Murata proposed that the Auger neutralization process is dominant in a low-energy region of the neutralization processes of Ar^+ , N^+ , N_2^+ ions in front of a Pt(001) surface [27]. However, regarding the neutralization process of a He^+ ion with low energy in front of the solid surface, the resonance neutralization process was reported to be dominant [28–30] with the formation of an excited He atom (He^* atom), although this neutralization process had been generally considered to be an Auger process. Therefore it seems difficult to determine which neutralization process is dominant, because neutralization processes can be determined as a result of very complicated phenomena associated with the energy level of the vacant ionic orbital and that of the valence band of metal as well as a multi-electron system involving the many-body problem.

Shao, Nordlander and Langreth theoretically pointed out the appearance of the Kondo effect when a moving ion is approaching a surface with very low kinetic energy (i.e., sufficiently small velocity) [31]. However, the above theoretical analysis can be derived from the restricted assumption that the velocity of the moving ion is extraordinarily slow to cause the Kondo effect. When the kinetic energy of the moving ion is of the order of several hundred electron volts, theoretical and experimental studies have not been sufficiently developed. In addition, for a neutralization processes occurring in the vicinity of metal surface, there has been no theoretical treatment which takes into account the fact that the image potential due to the positive ion suddenly vanishes at the very moment of neutralization. Here we note that the image potential in a real situation represents the polarized charge near the metal surface induced by the ion.

Accordingly, in the present work, we investigate the neutralization probability of $+1$ ion in front of a metal surface, mainly based on the Nozières and Dominicis (ND) theory [32]. The ND theory has been used to account for the edge singularities in the x-ray absorption and emission spectra in metals. By using this theory, we consider the effects due to the sudden vanishing of surface charge at the neutralization process and apply these theoretical results to the analysis of

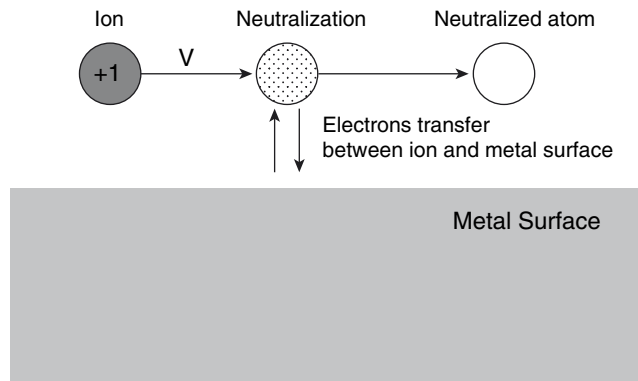


Figure 1. Schematic illustration for a +1 ion moving parallel to the metal surface and being neutralized as a result of electron transfer.

the neutralization process, focusing on the evaluation of the neutralization probability. In the following, we assume a resonance neutralization process. In addition, neutralized atoms are in excited states, not in the ground state, because of our assumption of resonance neutralization.

2. Theoretical methods

2.1. Perturbation method

Let us examine the physical process as shown in figure 1, where a +1 ion moving parallel to the metal surface with velocity \mathbf{V} is neutralized as a result of electron transfer from the metal surface to the ion. As is known from electromagnetism, the charge of $-e$ induced in the vicinity of surface, i.e., the image potential following the motion of +1 ion, is formed in the metal. Such a negative charge $-e$ can be formed as a result of the amassing of many electrons responding quickly to the motion of the positive ion. An illustration of the formation of surface charge is shown in figure 2. Based on the above discussion, we can easily infer that the formation of surface charge is impossible in the case of very fast ion velocity, because electrons cannot respond to the fast motion of ion. To screen the static potential due to the positive ion, we need electron-hole pair excitations in the vicinity of the Fermi surface. In that case electron-hole pair excitations possessing low excitation energy are realized in a macroscopic number of pairs. The electron Fermi surface and the hole Fermi surface should be overlapped. The condition is $q < 2k_F$. When $q > 2k_F$, it is impossible to realize electron-hole pair excitation because of low excitation energy.

To comprehend and to analyse the preceding discussion, let us look at this problem from a different viewpoint. We take the coordinate fixed to the positive ion, where the metal moves by the velocity $-\mathbf{V}$. The virtual movement of electrons in the metal which is required in the relative relation to the ion, leads to the shift of the Fermi sphere. The shifted momentum $-\mathbf{q}$ from the original point $(0, 0, 0)$ in Fermi sphere is determined by

$$-\mathbf{q} = -m\mathbf{V}/\hbar, \quad (1)$$

where m is the mass of an electron. Owing to the shift of the Fermi sphere, the energy of each electron is replaced by $E_{\mathbf{k}-\mathbf{q}}$ instead of $E_{\mathbf{k}}$. As illustrated in figure 3(A), one can see that some electrons close to the Fermi surface exceed the Fermi energy E_F . In order to screen the

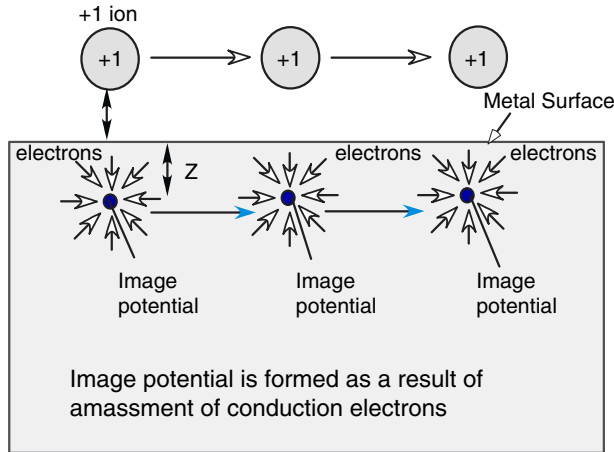


Figure 2. Schematic illustration of the formation of image potential.
(This figure is in colour only in the electronic version)

charge of the positive ion which is staying at origin, we need electron–hole pair excitation in the vicinity of the Fermi surface with $\mathbf{V} = 0$. The electron–hole pair excitation in the vicinity of the shifted Fermi surface contributes to the creation of negative charge potential. Therefore we need the overlap between two Fermi surfaces separated by q . However, as is shown in figure 3(B), the creation of negative charge potential is never realized physically, when the energy of all electrons inside the shifted Fermi sphere exceeds E_F and the two shifted Fermi surfaces do not overlap. Through a simple calculation concerning $E_{\mathbf{k}-\mathbf{q}} > E_F$, all electrons are found to exceed E_F in the case of $q(=|\mathbf{q}|) > 2k_F$ (see figure 3(B)). Thus we can conclude that the value of $q = 2k_F$ is the roughly estimated upper limit, beyond which induced charge cannot be formed. No induced charge appears if the ion velocity \mathbf{V} is larger than $2v_F$ (v_F : Fermi velocity). This result means in the real picture that electron–hole pairs in metal cannot follow the ion for $\mathbf{V} > 2v_F$.

The above conclusion is deduced from the viewpoint of excitation energy. To verify the above conclusion, let us discuss the upper limit of ion velocity in the light of plasma oscillation. Plasma frequency f_p in metal is given by

$$f_p = \frac{1}{2\pi} \sqrt{\frac{ne^2}{\varepsilon_0 m^*}}, \quad (2)$$

where n , e , ε_0 and m^* are the electron density per unit volume, charge of the electron, permittivity in vacuum and effective mass of the electron, respectively. To discuss this issue, we define L as the order of amplitude of plasma oscillation (0.5–1 nm), τ as the time when the positive ion traverses the distance L and τ_p as the period of plasma oscillation ($=1/f_p$).

Our idea is that no induced charge can be created if $\tau < \tau_p$ because electrons cannot have enough time to respond to the positive charge of the moving ion. Since $\tau = L/V$, no induced charge is observed in the metal when the ion velocity \mathbf{V} satisfies

$$\mathbf{V} > L/\tau_p = Lf_p = \frac{L}{2\pi} \sqrt{\frac{ne^2}{\varepsilon_0 m^*}}. \quad (3)$$

By using the above equation, we obtain $\mathbf{V} > 0.7v_F$ for $L \sim 0.5$ nm, $E_F = 3$ eV, and $\mathbf{V} > 1.9v_F$ for $L \sim 1$ nm, $E_F = 10$ eV. When evaluating \mathbf{V} , we adopt $m^* = m(9.108 \times 10^{-31}$ kg).

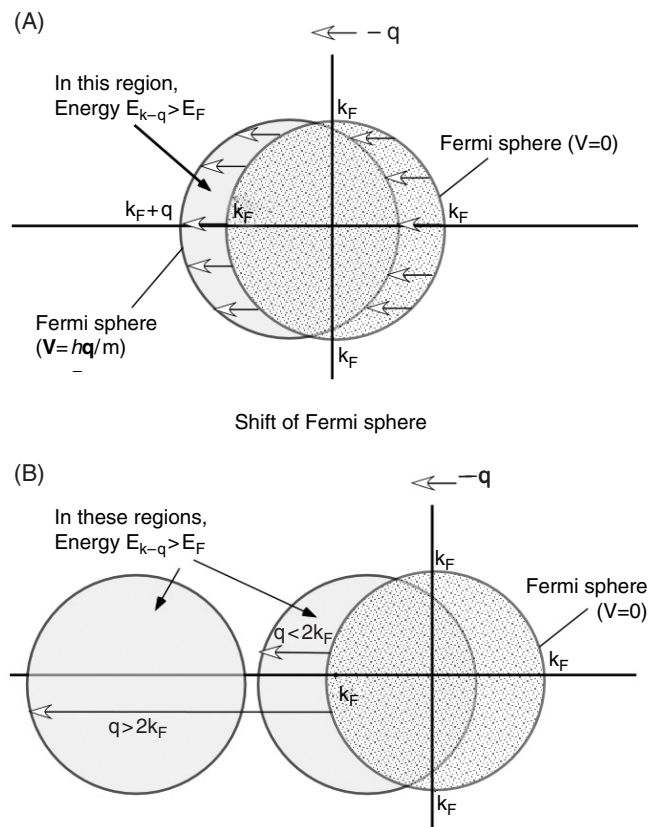


Figure 3. (A) The shift of the Fermi sphere due to the presence of momentum $-q$. (B) Schematic illustration of shifted Fermi sphere when $q(=|-q|)$ is more than $2k_F$ and less than $2k_F$, together with displaying each energy E_{k-q} .

Thus, from this approach, we can also obtain the same conclusion that no image potential is formed when $V > 2v_F$ and one can see that $V = 2v_F$ is the roughly estimated upper limit for conduction electrons to rearrange and form an image potential.

Recently, by using the linear response theory (LRT) and random phase approximation (RPA), the time response of induced screening charge in a two-dimensional electron gas was examined by Alducin *et al* [33]. From their theory, a time longer than 0.5 fs ($1 \text{ fs} = 10^{-15} \text{ s}$) is required so as to transit to the steady-state regime when an impurity charge is suddenly created in a 2D electron gas. Following the previous discussion, we can easily infer that the rearrangement of conduction electrons to screen a positive ion cannot be completed when $\tau < 0.5 \text{ fs}$. From this inequality, $V > 0.97v_F$ for $L \sim 0.5 \text{ nm}$, $E_F = 3 \text{ eV}$ and $V > 1.1v_F$ for $L \sim 1 \text{ nm}$, $E_F = 10 \text{ eV}$ are estimated.

Considering those discussions and estimations from the viewpoints of energy, plasma oscillation and the time response for induced screening, we can, therefore, conclude that the induced charge cannot follow the moving ion nor be created, when the velocity of positive ion V exceeds $2v_F$. However, it should be noticed that the value of $2v_F$ (or $2k_F$) does not mean such a critical point as the theoretically defined Curie temperature in magnetism but means a roughly defined threshold value. Thus this value ($2v_F$ or $2k_F$) is neither strictly defined nor proved but rather remains uncertain. Further experimental results are expected to verify our assumption.

Then we turn to the case of very slow motion of the ion ($V < 2v_F$), where a negative charge induced by the positive ion is formed to decrease the electromagnetic energy between the ion and electrons. In order to analyse this neutralization process theoretically and have the problem simplified, we assume that the charge distribution of the moving ion is isotropic and neutralization process is the resonance one. Then we can write down the perturbation Hamiltonian of the induced negative charge as follows:

$$\hat{H}'(\mathbf{q}) = \sum_{\mathbf{k}', \mathbf{k}, \sigma} V_{\mathbf{k}'\mathbf{k}}(\mathbf{q}) \hat{C}_{\mathbf{k}'\sigma}^+ \hat{C}_{\mathbf{k}\sigma}. \quad (4)$$

Based on the above discussion, we assume $V_{\mathbf{k}'\mathbf{k}}(\mathbf{q})$ satisfies

$$\lim_{q \rightarrow 2k_F} V_{\mathbf{k}'\mathbf{k}}(\mathbf{q}) \cong 0. \quad (5)$$

When the velocity of the ion is close to $2v_F$, the motion of electrons responding to the ion is considered not to be so effective as to compensate the positive charge; thus, the negative charge induced near the surface seems to decrease rapidly in the vicinity of $2q_F$ and finally reduces to almost 0 at $q = 2k_F$. Consequently $V_{\mathbf{k}'\mathbf{k}}(\mathbf{q})$ decreases rapidly as q approaches $2k_F$ and is almost 0 at $q = 2k_F$.

Next let us calculate the wavefunction when such a perturbation Hamiltonian of equation (4) is introduced into the system. Within the first-order perturbation, Φ is given by

$$\Phi = \Phi_0 + \Phi_1, \quad (6)$$

where Φ_0 represents the wavefunction of the unperturbed state. Using the perturbation method, we can express Φ_1 in the following form:

$$\Phi_1 = \sum_{\mathbf{K}', \mathbf{K}} D_{\mathbf{K}'\mathbf{K}}^{(\mathbf{q})} \hat{C}_{\mathbf{K}'}^+ \hat{C}_{\mathbf{K}} \Phi_0 \quad |\mathbf{K}'| > k_F, \quad |\mathbf{K}| < k_F. \quad (7)$$

$D_{\mathbf{K}'\mathbf{K}}^{(\mathbf{q})}$ can be determined by

$$D_{\mathbf{K}'\mathbf{K}}^{(\mathbf{q})} (E_{\mathbf{K}'} - E_{\mathbf{K}}) + \langle \mathbf{K}\mathbf{K}' | \hat{H}'(\mathbf{q}) | \Phi_0 \rangle = 0 \quad |\mathbf{K}'| > k_F, \quad |\mathbf{K}| < k_F, \quad (8)$$

where

$$|\mathbf{K}'\mathbf{K}\rangle = \hat{C}_{\mathbf{K}'}^+ \hat{C}_{\mathbf{K}} |\Phi_0\rangle.$$

In equation (8), the term $\langle \mathbf{k}\mathbf{k}' | \hat{H}'(\mathbf{q}) | \Phi_0 \rangle$ is given by

$$\langle \mathbf{K}\mathbf{K}' | \hat{H}'(\mathbf{q}) | \Phi_0 \rangle = V_{\mathbf{K}'\mathbf{K}}(\mathbf{q}). \quad (9)$$

Accordingly, $D_{\mathbf{K}'\mathbf{K}}^{(\mathbf{q})}$ is given by

$$D_{\mathbf{K}'\mathbf{K}}^{(\mathbf{q})} = \frac{-V_{\mathbf{K}'\mathbf{K}}(\mathbf{q})}{E_{\mathbf{K}'} - E_{\mathbf{K}}}. \quad (10)$$

Thus, within the first-order perturbation, we can obtain the wavefunction Φ as follows:

$$\Phi = \left(1 - \sum_{\mathbf{K}, \mathbf{K}'} \frac{V_{\mathbf{K}'\mathbf{K}}(\mathbf{q})}{E_{\mathbf{K}'} - E_{\mathbf{K}}} \hat{C}_{\mathbf{K}'}^+ \hat{C}_{\mathbf{K}} \right) \Phi_0 \quad |\mathbf{K}'| > k_F, \quad |\mathbf{K}| < k_F. \quad (11)$$

The normalized $\tilde{\Phi}$ is given by

$$\tilde{\Phi} = \frac{\Phi_0 + \Phi_1}{\sqrt{1 + |\Phi_1|^2}}.$$

Accordingly the overlap integral $\langle \Phi_0 | \tilde{\Phi} \rangle$ is written as

$$\langle \Phi_0 | \tilde{\Phi} \rangle = \frac{1}{\sqrt{1 + \rho^2 |\mathbf{V}_0|^2 |u(\mathbf{q})|^2 \ln N}}. \quad (12)$$

In the above equation, ρ and N denote the density of states of conduction electrons and the total number of conduction electrons, respectively. When deducing equation (12), we have assumed that $V_{\mathbf{k}'\mathbf{k}}(\mathbf{q}) = V_0 u(\mathbf{q})$ and ρ is flat.

Since $V_{\mathbf{k}'\mathbf{k}}(\mathbf{q}) \approx 0$ at $q = 2k_F$ as stated in equation (5), $|u(\mathbf{q})|$ is almost 0 at $q = 2k_F$. Therefore we can easily understand that Anderson's orthogonality theorem does not hold when q is larger than $2k_F$. In this case electron-hole pair excitations are impossible, because the velocity of the moving ion is too fast for the electrons in the metal to compensate the positive charge, and the neutralization process is expected to proceed without any formation of surface charge.

2.2. Calculation of transition probability by Nozières and Dominicis theory

Based on the above results and discussion, let us calculate the transition probability in the case of slow ion velocity ($V < 2v_F$). As pointed out in the previous paragraph, the neutralization process proceeds under the presence of induced surface charge. The transition probability $P(i \rightarrow f)$ of initial state i (ionic state) to final state f (neutralized state) is given by

$$P(i \rightarrow f) = \frac{2\pi}{\hbar} \sum_f |\langle f | \hat{H}' | i \rangle|^2 \delta(E_{\text{final}} - E_{\text{initial}}) \quad (13)$$

and

$$\hat{H}' = \sum_{\mathbf{Q}} (T_{\mathbf{Q}\mathbf{a}} \hat{C}_{\mathbf{Q}}^+ \hat{C}_{\mathbf{a}} + T_{\mathbf{a}\mathbf{Q}} \hat{C}_{\mathbf{a}}^+ \hat{C}_{\mathbf{Q}}), \quad (14)$$

where E_{final} and E_{initial} represent the energy of the final and initial states, respectively. $\hat{C}_{\mathbf{Q}}^+$ and $\hat{C}_{\mathbf{a}}^+$ are the creation operator of the conduction electron with momentum \mathbf{Q} and of the localized electron state $|a\rangle$. $T_{\mathbf{a}\mathbf{Q}}$ is the matrix element of electron transfer from state $|\mathbf{Q}\rangle$ to $|a\rangle$. The difference between E_{final} and E_{initial} is given by

$$E_{\text{final}} - E_{\text{initial}} = E_f - E_i + E_a + K_f - K_i. \quad (15)$$

In the above equation, E_f and E_i are energies of final and initial states of metal surface, E_a is the energy of the localized electron state $|a\rangle$. K_f and K_i are the kinetic energies of the moving ion in the final and initial states. Additionally, the final state of kinetic energy K_f includes the energy term related to the recoil effect arising from the scattering between the metal surface and moving ion.

Concerning the initial state, an impurity potential can be induced into the metal surface because of the presence of a positively charged ion above the metal surface; thus we can write the Hamiltonian \hat{H}_i to describe the initial state of the metal surface in the following form:

$$\hat{H}_i = H_i^0 = \sum_{\mathbf{k}} E_{\mathbf{k}} \hat{C}_{\mathbf{k}}^+ \hat{C}_{\mathbf{k}} + \sum_{\mathbf{k}', \mathbf{k}} V_{\mathbf{k}'\mathbf{k}}(\mathbf{q}) \hat{C}_{\mathbf{k}'}^+ \hat{C}_{\mathbf{k}}. \quad (16)$$

In equation (16), it should be noticed that $\lim_{q \rightarrow 2k_F} V_{\mathbf{k}'\mathbf{k}}(\mathbf{q}) \approx 0$ as stated in the previous section and that the final and initial Hamiltonian are same at $q = 2k_F$ because of annihilation of the image potential.

After the neutralization of the +1 ion through the electron transfer from the metal surface to the moving ion, the induced impurity potential vanishes; consequently the Hamiltonian \hat{H}_f corresponding to the final state is given by

$$\hat{H}_f = \sum_{\mathbf{k}} E_{\mathbf{k}} \hat{C}_{\mathbf{k}}^+ \hat{C}_{\mathbf{k}}. \quad (17)$$

\hat{H}_i and \hat{H}_f satisfy

$$\hat{H}_i |i\rangle = E_i |i\rangle \quad \text{and} \quad \hat{H}_f |f\rangle = E_f |f\rangle, \quad (18)$$

where states $|f\rangle$ and $|i\rangle$ denote eigenstates for \hat{H}_i and \hat{H}_f , respectively.

The factor $|\langle f|\hat{H}'|i\rangle|^2$ in $P(i \rightarrow f)$ of equation (13) can be expressed as

$$|\langle f|\hat{H}'|i\rangle|^2 = \langle f|\hat{H}'|i\rangle\langle i|\hat{H}'|f\rangle = \sum_{\mathbf{Q}} \sum_{\mathbf{Q}'} T_{a\mathbf{Q}} T_{\mathbf{Q}'a} \langle f|\hat{C}_a^+ \hat{C}_{\mathbf{Q}}|i\rangle \langle i|\hat{C}_{\mathbf{Q}'}^+ \hat{C}_a|f\rangle. \quad (19)$$

Concerning the above equation, two processes are involved: one is the transfer process of an electron with momentum \mathbf{Q} from the metal surface to the moving ion and the other is that of an electron from a neutralized atom to the metal surface with momentum \mathbf{Q}' . Consequently, considering these electron transfer processes, the transition probability of equation (13) can be expressed in the following form:

$$P(i \rightarrow f) = \frac{2\pi}{\hbar} \sum_{\mathbf{k}} \sum_{\mathbf{k}'} T_{a\mathbf{k}} T_{\mathbf{k}'a} \langle f|\hat{C}_a^+ \hat{C}_{\mathbf{k}}|i\rangle \langle i|\hat{C}_{\mathbf{k}'}^+ \hat{C}_a|f\rangle \delta(E_f - E_i + E_a + K_f - K_i). \quad (20)$$

Finally, using the Hamiltonians of \hat{H}_i , \hat{H}_f and eigenstates $|f\rangle$, $|i\rangle$ together with equation (18) and assuming the electron transfer matrix elements $T_{a\mathbf{k}}$ and $T_{\mathbf{k}a}$ to be constant, namely $T_{a\mathbf{k}} \rightarrow T_0$, we can write down the transition probability $P(i \rightarrow f)$ as follows:

$$P(i \Rightarrow f) = \frac{2}{\hbar} |T_0|^2 \text{Re} \left\{ \sum_{\mathbf{k}, \mathbf{k}'} \int_{-\infty}^0 dt \exp[i(E_a + K_f - K_i)t] \times \langle i|\hat{C}_{\mathbf{k}'}^+ \exp(iH_f t) \hat{C}_{\mathbf{k}} \exp(-iH_i^{\mathbf{Q}} t)|i\rangle \right\}. \quad (21)$$

Furthermore, we redefine

$$t \rightarrow t - t', \quad t' > t. \quad (22)$$

Then, equation (21) is rewritten as

$$P(i \rightarrow f) = \frac{2}{\hbar} |T_0|^2 \text{Re} \left\{ \int_{-\infty}^0 d(t - t') \exp[i(E_a + K_f - K_i)(t - t')] \times \sum_{\mathbf{k}, \mathbf{k}'} \langle i|\hat{C}_{\mathbf{k}'}^+(t') \hat{S}(t', t) \hat{C}_{\mathbf{k}}(t)|i\rangle \right\} = \frac{2}{\hbar} |T_0|^2 \text{Re} \left\{ \int_{-\infty}^0 d(t - t') F(t - t') \right\}, \quad (23)$$

where

$$\hat{S}(t', t) \equiv \exp(i\hat{H}_i^{\mathbf{Q}} t') \exp(i\hat{H}_f(t - t')) \exp(-i\hat{H}_i^{\mathbf{Q}} t) \quad (24)$$

$$\hat{C}_{\mathbf{k}'}^+(t') \equiv \exp(i\hat{H}_i^{\mathbf{Q}} t') \hat{C}_{\mathbf{k}'}^+ \exp(-i\hat{H}_i^{\mathbf{Q}} t') \quad (25)$$

$$\hat{C}_{\mathbf{k}}(t) \equiv \exp(i\hat{H}_i^{\mathbf{Q}} t) \hat{C}_{\mathbf{k}} \exp(-i\hat{H}_i^{\mathbf{Q}} t) \quad (26)$$

$$F(t - t') \equiv \sum_{\mathbf{k}, \mathbf{k}'} F_{\mathbf{k}'\mathbf{k}}(t - t') \quad (27)$$

$$F_{\mathbf{k}'\mathbf{k}}(t - t') \equiv \exp[i(E_a + K_f - K_i)(t - t')] \langle i|\hat{C}_{\mathbf{k}'}^+(t') \hat{S}(t', t) \hat{C}_{\mathbf{k}}(t)|i\rangle. \quad (28)$$

To simplify further calculation, we introduce the following variable:

$$\xi \equiv E_a + K_f - K_i. \quad (29)$$

Next, we define the Green function $\varphi_{\mathbf{k}'\mathbf{k}}(\tau\tau', tt')$ as follows:

$$\varphi_{\mathbf{k}'\mathbf{k}}(\tau\tau', tt') \equiv \frac{\langle i|\mathbf{T}[\hat{C}_{\mathbf{k}'}^+(\tau) \hat{C}_{\mathbf{k}}(\tau') \hat{S}(t', t)]|i\rangle}{\langle i|\hat{S}(t', t)|i\rangle}. \quad (30)$$

Finally, using the Green function and variable defined in equation (29), $F(t - t')$ can be expressed as

$$F(t - t') \equiv \sum_{\mathbf{k}, \mathbf{k}'} F_{\mathbf{k}'\mathbf{k}}(t - t') = e^{i\xi(t-t')} \langle i|\hat{S}(t', t)|i\rangle \lim_{\substack{\tau \rightarrow t' \\ \tau' \rightarrow t}} \sum_{\mathbf{k}'\mathbf{k}} \varphi_{\mathbf{k}'\mathbf{k}}(\tau\tau', tt'). \quad (31)$$

The Green function defined in equation (30) satisfies the following Dyson equation.

$$\varphi_{\mathbf{k}\mathbf{k}}(\mathbf{q} : \tau\tau', tt') = G_{\mathbf{k}\mathbf{k}}^0(\tau - \tau') + i \int_t^{\tau'} d\tau'' \sum_{\mathbf{Q}\mathbf{Q}'} G_{\mathbf{k}\mathbf{Q}'}^0(\tau - \tau'') \mathbf{V}_{\mathbf{Q}\mathbf{Q}'}(\mathbf{q}) \varphi_{\mathbf{Q}\mathbf{k}}(\tau''\tau', tt'), \quad (32)$$

where

$$G_{\mathbf{k}\mathbf{k}}^0(\tau - \tau') = \langle i | \mathbf{T} \hat{C}_{\mathbf{k}}^+(\tau) \hat{C}_{\mathbf{k}}(\tau') | i \rangle. \quad (33)$$

Furthermore, assuming $\mathbf{V}_{\mathbf{Q}\mathbf{Q}}^{(\mathbf{q})} = \mathbf{V}_0 u(\mathbf{q})$ as used in equation (12), we can write down the Dyson equation of (32) in the simplified form,

$$\varphi_{\tau\tau'}(\tau, tt') = G^0(\tau - \tau') + i \mathbf{V}_0 u(\mathbf{q}) \int_t^{\tau'} d\tau'' G^0(\tau - \tau'') \varphi(\tau''\tau', tt'), \quad (34)$$

where

$$\varphi(\tau\tau', tt') = \sum_{\mathbf{k}\mathbf{k}'} \varphi_{\mathbf{k}\mathbf{k}'}(\tau\tau', tt'), \quad (35)$$

$$G^0(\tau - \tau') = \sum_{\mathbf{k}\mathbf{k}'} G_{\mathbf{k}\mathbf{k}'}^0(\tau - \tau'). \quad (36)$$

As shown in equations (34)–(36), we introduced local Green functions $\varphi(\tau\tau', tt')$ and $G^0(\tau - \tau')$. Actually virtual photon emission associated with the momentum of $\mathbf{k}\mathbf{k}'$ could possibly appear because of the vector potential caused by the moving ion current. However, we assume that the velocity of the moving ion is not so fast as to cause such an emission; thus our treatment which introduces $\varphi(\tau\tau', tt')$ and $G^0(\tau - \tau')$ instead of $\varphi_{\mathbf{k}\mathbf{k}'}(\tau\tau', tt')$ and $G_{\mathbf{k}\mathbf{k}'}^0(\tau - \tau')$ is reasonable.

Accordingly, $F(t - t')$ is written in a very simple form,

$$F(t - t') = e^{i\xi(t-t')} \langle i | \hat{S}(t', t) | i \rangle \lim_{\substack{\tau \rightarrow t' \\ \tau' \rightarrow t}} \varphi(\tau\tau', tt'). \quad (37)$$

Our goal is to calculate the transition probability through the calculation of the Green function. For the purpose of estimating the Green function $\varphi_{\mathbf{k}\mathbf{k}}(\tau\tau', tt')$, we introduce the following operators defined as follows:

$$\hat{C}_{\mathbf{k}}^{0+}(\tau) \equiv \exp(i\hat{H}_0\tau) \hat{C}_{\mathbf{k}}^+ \exp(-i\hat{H}_0\tau), \quad (38)$$

$$\hat{C}_{\mathbf{k}}^0(\tau') \equiv \exp(i\hat{H}_0\tau') \hat{C}_{\mathbf{k}} \exp(-i\hat{H}_0\tau'), \quad (39)$$

and

$$\hat{H}_0 = \sum_{\mathbf{k}} E_{\mathbf{k}} \hat{C}_{\mathbf{k}}^+ \hat{C}_{\mathbf{k}}. \quad (40)$$

As has been already shown in equation (17), $\hat{H}_0 = \hat{H}_f$. Thus $\langle i | \mathbf{T} \hat{C}_{\mathbf{k}}^{0+}(\tau) \hat{C}_{\mathbf{k}'}^0(\tau') | i \rangle$ is given by

$$\begin{aligned} \xi_{\mathbf{k}\mathbf{k}'}^0(\tau - \tau') &\equiv \langle i | \mathbf{T} \hat{C}_{\mathbf{k}}^{0+}(\tau) \hat{C}_{\mathbf{k}'}^0(\tau') | i \rangle \\ &= \delta_{\mathbf{k}\mathbf{k}'} \exp[i(\tau E_{\mathbf{k}} - \tau' E_{\mathbf{k}'})] \{ \theta(\tau - \tau') \theta(k_F - |\mathbf{k}|) - \theta(\tau' - \tau) \theta(|\mathbf{k}| - k_F) \}. \end{aligned} \quad (41)$$

Therefore we can obtain

$$\xi^0(\tau - \tau') \equiv \sum_{\mathbf{k}} \sum_{\mathbf{k}'} \xi_{\mathbf{k}\mathbf{k}'}^0(\tau - \tau') = \frac{\rho}{i(\tau - \tau')} [1 - \exp(-iD|\tau - \tau'|)], \quad (42)$$

where D and ρ are the band width and density of states of conduction electrons, respectively. In addition, we assume that the band is flat without energy dependence. Then the Dyson equation for $G^0(\tau - \tau')$ is

$$G^0(\tau - \tau') = \xi^0(\tau - \tau') - i \mathbf{V}_0 u(\mathbf{q}) \int_{-\infty}^{+\infty} d\tau'' \xi^0(\tau - \tau'') G^0(\tau'' - \tau'). \quad (43)$$

By applying a Fourier transformation to equation (43), we obtain

$$G^0(\tau - \tau') = \frac{\rho}{i(1 + \mathbf{V}_0^2 u^2(\mathbf{q}) \rho^2 \pi^2)} \frac{1}{\tau - \tau'} - i \frac{\mathbf{V}_0 u(\mathbf{q}) \rho^2 \pi^2}{1 + \mathbf{V}_0^2 u^2(\mathbf{q}) \rho^2 \pi^2} \delta(\tau - \tau'). \tag{44}$$

Substituting the above result into equation (34), we can obtain the following Dyson equation:

$$\varphi(\tau \tau'; tt') = \frac{G^0(\tau - \tau')}{1 - \mathbf{V}_0 \Lambda} - \frac{\tan \delta}{\pi} \int_t^{\tau'} P\left(\frac{1}{\tau - \tau''}\right) \varphi(\tau'' \tau'; tt') d\tau'', \tag{45}$$

where

$$\Lambda \equiv \frac{\mathbf{V}_0 u(\mathbf{q}) \rho^2 \pi^2}{1 + \mathbf{V}_0^2 u^2(\mathbf{q}) \rho^2 \pi^2} \quad \text{and} \quad \tan \delta \equiv -\pi \rho \mathbf{V}_0 u(\mathbf{q}). \tag{45'}$$

The solution of the above equation, based on the Muskhelishvili method [34], is given by

$$\varphi(\tau \tau'; tt') = G_a(\tau - \tau') \left[\frac{(\tau' - t')(t - \tau)}{(\tau - t')(t - \tau')} \right]^{\frac{\delta}{\pi}}, \tag{46}$$

where

$$G_a(\tau - \tau') = -i\rho \left[P\left(\frac{1}{\tau - \tau'}\right) + \pi \tan \theta \delta(\tau - \tau') \right] \quad \text{and} \quad \tan \theta \equiv -\frac{1}{\pi \rho \mathbf{V}_0 u(\mathbf{q})} - \cot \delta. \tag{46'}$$

The above equation (46) shows singularities in the limit of $\tau \rightarrow t'$ or $\tau' \rightarrow t$ because of our approximation of the Green function; thus, we define a parameter $-i/D$ as $t' - \tau = \tau' - t = -i/D$ in the limit of $\tau \rightarrow t'$ and $\tau' \rightarrow t$ to correct our calculation. Consequently, the exact solution is given by

$$\lim_{\substack{\tau \rightarrow t' \\ \tau' \rightarrow t}} \varphi(\mathbf{q} : \tau \tau', tt') = \varphi(t't; tt') = -i\rho \frac{(i(t' - t)D)^{\frac{2\delta}{\pi}}}{t' - t}. \tag{47}$$

Next let us evaluate the S matrix. The S matrix is defined as

$$\hat{S}(t', t) = T \left[\exp \left(-i \int_t^{t'} \hat{H}'(\tau) d\tau \right) \right], \tag{48}$$

where

$$\hat{H}'(\mathbf{q}) = - \sum_{\mathbf{k}, \mathbf{k}'} \mathbf{V}_{\mathbf{k}\mathbf{k}'}(\mathbf{q}) \hat{C}_{\mathbf{k}}^+ \hat{C}_{\mathbf{k}'}. \tag{49}$$

We introduce $g(t', t)$ for further calculation; $g(t', t)$ is given by

$$g(t', t) \equiv \langle i | \hat{S}(t', t) | i \rangle. \tag{50}$$

To calculate equation (50), we assume that $\mathbf{V}_{\mathbf{k}\mathbf{k}'}(\mathbf{q})$ is multiplied by λ , that is

$$\mathbf{V}_{\mathbf{k}\mathbf{k}'}(\mathbf{q}) \Rightarrow \lambda \mathbf{V}_{\mathbf{k}\mathbf{k}'}(\mathbf{q}). \tag{51}$$

Then, the following equation can be deduced:

$$\frac{\partial}{\partial \lambda} g(t', t) = i \sum_{\mathbf{k}, \mathbf{k}'} \mathbf{V}_{\mathbf{k}\mathbf{k}'} \langle i | \hat{S}(t', t) | i \rangle \int_t^{t'} \varphi_{\mathbf{k}\mathbf{k}'}(\tau \tau_{+0}; tt') d\tau. \tag{52}$$

Next, we define $C(t, t')$ as

$$C(t', t) = \ln g(t', t). \tag{53}$$

Consequently $\frac{\partial}{\partial \lambda} C(t', t)$ is

$$\frac{\partial}{\partial \lambda} C(t', t) = iV_0 u(\mathbf{q}) \sum_{\mathbf{k}\mathbf{k}'} \int_t^{t'} \varphi_{\mathbf{k}\mathbf{k}'}(\tau \tau_{+0}; tt') d\tau = iV_0 u(\mathbf{q}) \int_t^{t'} \varphi(\tau \tau_{+0}; tt') d\tau. \quad (54)$$

The Green function $\varphi_{\mathbf{k}\mathbf{k}'}(\tau \tau_{+0}, tt')$ can be expanded into the following form:

$$\varphi(\tau \tau_{+0}; tt') = \varphi^e(\tau \tau_{+0}; tt') = G^a(\tau - \tau') \left(1 + \frac{\delta}{\pi} (\tau - \tau') \left[\frac{1}{\tau' - t} + \frac{1}{t' - \tau'} \right] + \dots \right). \quad (55)$$

In equation (55), the superscripts e and a represent 'emission' and 'absorption', respectively. By substituting equation (55) into (54), $\frac{\partial}{\partial \lambda} C(t', t)$ can be expressed as

$$\frac{\partial}{\partial \lambda} C(t', t) = iV_0 u(\mathbf{q}) \left[(t' - t) G_\lambda^a(\tau - \tau_{+0}) - 2i \frac{\rho \delta(\lambda)}{\pi} \ln[i(t' - t)D] \right], \quad (56)$$

where $\delta(\lambda)$ satisfies

$$\tan \delta(\lambda) = -\lambda \pi \rho V_0 u(\mathbf{q}). \quad (57)$$

Integrating equation (56) over λ , we obtain

$$C(t', t) = i(t' - t) V_0 u(\mathbf{q}) \int_0^1 G_\lambda^a(\tau - \tau_{+0}) d\lambda - \left(\frac{\delta}{\pi} \right)^2 \ln[i(t' - t)D]. \quad (58)$$

In equation (58), we redefine $\delta \equiv \delta(\lambda = 1)$. Finally $g(t', t)$ can be given by

$$\begin{aligned} g(t', t) &= \langle i | \hat{S}(t', t) | i \rangle \\ &= (i(t' - t)D)^{-\left(\frac{\delta}{\pi}\right)^2} \exp \left[i(t' - t) V_0 u(\mathbf{q}) \int_0^1 G_\lambda^a(\tau - \tau_{+0}) d\lambda \right]. \end{aligned} \quad (59)$$

By combining the above result with equation (47), we can express $F(t - t')$ as follows:

$$F(t - t') = e^{i(t-t')(\xi - \Theta)} \left(\frac{-i\rho}{t' - t} \right) (i(t' - t)D)^\alpha, \quad (60)$$

where

$$\alpha \equiv 2 \frac{\delta}{\pi} - \left(\frac{\delta}{\pi} \right)^2 \quad \text{and} \quad \Theta \equiv V_0 u(\mathbf{q}) \int_0^1 G_\lambda^a(\tau - \tau_{+0}) d\lambda. \quad (61)$$

In the above equation, Θ represents the energy shift due to the potential: this term indicates the decrease of the initial state energy, which is induced by the screening of the image potential by conduction electrons. Substituting equations (60) and (61) into equation (23), we can write down the transition probability in the following form:

$$\begin{aligned} P(i \rightarrow f) &= \frac{2|T_0|^2}{\hbar} \text{Re} \left\{ \int_{-\infty}^0 d(t - t') e^{i(t-t')(\xi - \Theta)} \left(\frac{-i\rho}{t' - t} \right) (i(t' - t)D)^\alpha \right\} \\ &= \frac{2|T_0|^2}{\hbar} \rho D^\alpha \text{Re} \left\{ \int_0^\infty dt e^{-i(\xi - \Theta)t} \left(\frac{-i}{t} \right) (it)^\alpha \right\} \quad t' - t \rightarrow t, \end{aligned} \quad (62)$$

where $\xi \equiv E_a + K_f - K_i$ as has been defined in equation (29).

From the phenomenological viewpoint, the decay due to various physical processes should be considered; hence the mathematical term to represent this decay ($\exp(-\gamma t)$) should be involved and inserted in the above result. Finally we can express the transition probability as follows:

$$\begin{aligned}
P(i \rightarrow f) &= \frac{2|T_0|^2}{\hbar} \rho D^\alpha \operatorname{Re} \left\{ \int_0^\infty dt e^{-(\gamma+i(\xi-\Theta))t} \left(\frac{-i}{t}\right) (it)^\alpha \right\} \\
&= \frac{2|T_0|^2}{\hbar} \rho D^\alpha \operatorname{Re} \left\{ -i (i)^\alpha \frac{\Gamma(\alpha)}{(\gamma+i(\xi-\Theta))^\alpha} \right\} \\
&= \frac{2|T_0|^2 \rho}{\hbar} \Gamma(\alpha) \left(\frac{D}{R}\right)^\alpha \sin\left(\frac{\pi}{2} - \phi\right) \alpha, \tag{63}
\end{aligned}$$

where $\Gamma(x)$ is the gamma function,

$$R = \sqrt{\gamma^2 + (\xi - \Theta)^2} \quad \text{and} \quad \tan \phi = \frac{\xi - \Theta}{\gamma} \left(-\frac{\pi}{2} \leq \phi \leq \frac{\pi}{2} \right). \tag{63'}$$

In particular, in the limit of $\gamma \rightarrow 0$, which corresponds to the absence of phenomenological decay, the transition probability can be given by

(i) $\Theta - \xi < 0$.

From equation (63')

$$\lim_{\gamma \rightarrow +0} \tan \phi = \lim_{\gamma \rightarrow +0} \frac{\xi - \Theta}{\gamma} = +\infty \quad \therefore \lim_{\gamma \rightarrow +0} \phi = \pi/2. \tag{64}$$

Hence we can deduce the following result by substituting equation (64) into (63):

$$P(i \rightarrow f) = 0 \tag{65}$$

(ii) $\Theta - \xi > 0$.

From equation (63')

$$\lim_{\gamma \rightarrow +0} \tan \phi = \lim_{\gamma \rightarrow +0} \frac{\xi - \Theta}{\gamma} = -\infty \quad \therefore \lim_{\gamma \rightarrow +0} \phi = -\frac{\pi}{2}. \tag{66}$$

Accordingly, the transition probability is

$$\begin{aligned}
P(i \rightarrow f) &= \frac{2|T_0|^2 \rho}{\hbar} \Gamma(\alpha) \left(\frac{D}{\Theta - \xi}\right)^\alpha \sin \pi \alpha = \frac{2|T_0|^2 \rho}{\hbar} \left(\frac{D}{\Theta - \xi}\right)^\alpha \frac{\pi}{\Gamma(1 - \alpha)} \\
&= \frac{2|T_0|^2 \rho}{\hbar} \frac{\pi}{\Gamma(1 - \alpha)} \left(\frac{D}{K_i - K_f - E_a + \Theta}\right)^\alpha. \tag{67}
\end{aligned}$$

Figures 4(A) and (B) illustrate the transition probability calculated on the basis of equations (63)–(67): singularity is revealed at the threshold ($\Theta - \xi = 0$) when $\gamma = 0$ (figure 4(A)). On the other hand, an asymmetric peak is observed without showing a singularity when $\gamma \neq 0$ (figure 4(B)). The calculated transition probability of $\gamma \neq 0$ is similar to those observed in experiments of soft x-ray absorption and emission spectra of metals [35–37] and of photoelectron spectroscopy on metal surfaces by the single-shot x-ray laser-induced time-of-flight method [38]. We expect the neutralization probability to be expressed in the form of figure 4(B), but experimental results have not been reported and/or obtained yet because of the experimental difficulty of measuring a neutralization process occurring parallel to the metal surface as illustrated in figure 1. However, we expect that our proposed experiments (the measurement of neutralization probability versus $\Theta - \xi (= K_i - K_f - E_a + \Theta)$) will become possible in the future, considering further development of the time-of-flight technique and the measurement of the energy distribution of electrons together with x-ray photoemission spectroscopy.

As shown in the above equation, the cut-off energy is $\Theta - \xi (= K_i - K_f - E_a + \Theta)$. However, life-time broadening of the excited atomic level and other factors should be considered and involved; thus it seems a better description to replace $K_i - K_f - E_a + \Theta$ by Δ which denotes

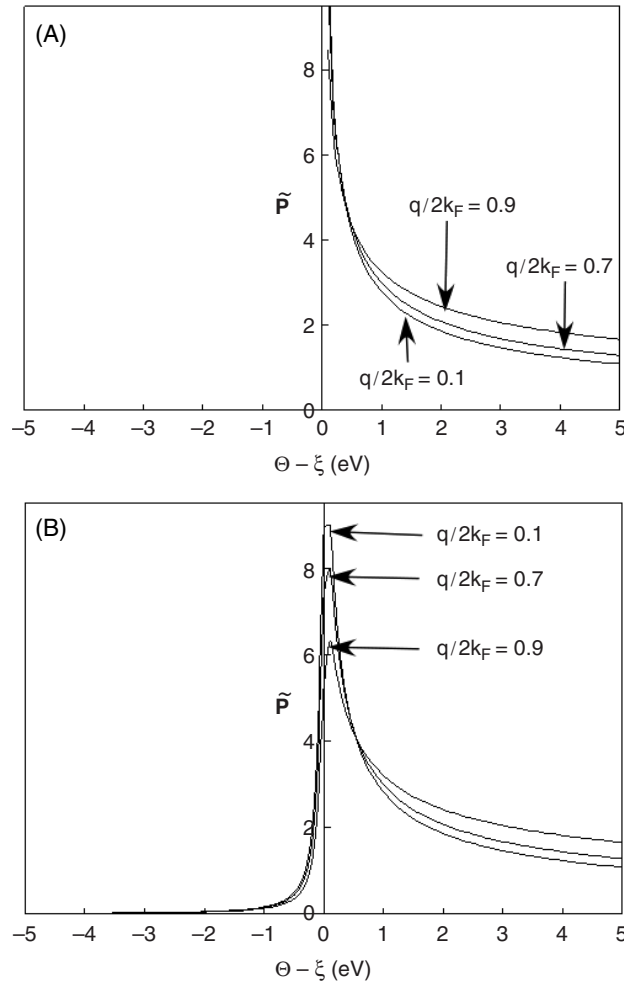


Figure 4. Schematic illustration of calculated transition probability, where $\xi = E_a + K_f - K_i$ (E_f , E_i and E_a are the energies of the final and initial states of the metal surface, and of the localized electron of state $|a\rangle$). We set $T = 0$ K. As shown in equation (62), $\Theta \equiv V_0 \int_0^1 G_\lambda^\alpha(\tau - \tau_{+0}) d\lambda$. For convenience of calculation, we define probability = $P(i \rightarrow f) \hbar / 2 |T_0|^2 \rho$ with no dimension and $u(q) = \sqrt{1 - (q/2k_F)^2}$. (A) $\gamma = 0$ eV, $D = 3$ eV, $V_0 = 2$ eV, $\rho = 1/D$ (B) $\gamma = 0.1$ eV, $D = 3$ eV, $V_0 = 2$ eV, $\rho = 1/D$.

various broadening factors. Consequently the transition probability of equation (67) can be modified and given in the following form:

$$P(i \rightarrow f) = \frac{2|T_0|^2 \rho}{\hbar} \frac{\pi}{\Gamma(1 - \alpha)} \left(\frac{D}{\Delta} \right)^\alpha. \quad (68)$$

As we have discussed in the previous paragraph, when $V > 2v_F$, the neutralization process is supposed to be proceeding without any formation of induced surface charge. In such a case, the Landau-Zener formalism probably would be considered. Further detailed analysis including the Landau-Zener process and virtual photon emission caused by the high velocity of the ion will be needed.

3. Conclusion

We have investigated the transition probability of a +1 ion being neutralized in the vicinity of a metal surface, based on the Nozières and Dominicis theory which was proposed to account for the edge singularities in the x-ray absorption and emission spectra in metals, mainly focusing on the effects due to the sudden disappearance of induced surface charge at the very moment of neutralization. First, we have calculated the quantum state within the first-order perturbation theory; thus it is disclosed that Anderson's orthogonality theorem cannot hold when $|q| > 2k_F$ because the induced charge cannot follow the ion motion. Secondly, referring to the theoretical results obtained from the first-order perturbation calculation, we evaluated the transition probability on the basis of the Nozières and Dominicis theory. When the atomic excited level E_a has s-wave symmetry ($l = 0$), the transition probability is enhanced. For the case where the phase shift δ with $l = 0$ is dominant, α is given by

$$\alpha = 2\frac{\delta}{\pi} - \left(\frac{\delta}{\pi}\right)^2 - \left(\frac{\delta}{\pi}\right)^2 = 2\frac{\delta}{\pi} - 2\left(\frac{\delta}{\pi}\right)^2,$$

where we have included \uparrow and \downarrow spin parts. For example, if we set $\frac{\delta}{\pi} = \frac{1}{2}$, then $\alpha = \frac{1}{2}$ is obtained. Accordingly the transition probability is, as shown below, found to be enhanced:

$$P(i \rightarrow f) \propto \left(\frac{D}{\Delta}\right)^{\frac{1}{2}}$$

In figure 4(B), we show the enhanced case with s-wave symmetry. Near the threshold, the neutralization probability is enhanced, as shown in this figure. This enhancement becomes clear with decreasing velocity of the ion. When the atomic level has $l \neq 0$ symmetry and $\delta_l = 0$, α is usually given by $\alpha = -2\left(\frac{\delta}{\pi}\right)^2$. If we set $\frac{\delta}{\pi} = \frac{1}{2}$, then $\alpha = -\frac{1}{2}$ is obtained. The transition probability is reduced.

$$P(i \rightarrow f) \propto \left(\frac{D}{\Delta}\right)^{-\frac{1}{2}} = \left(\frac{\Delta}{D}\right)^{\frac{1}{2}}.$$

This result can be explained as follows. When the screening cloud near the surface induced by the positive ion possesses the same symmetry as the atomic orbital, the transition probability is enhanced. In our calculation we have assumed the coordinate where the moving ion is static. Accordingly induced charge which follows the moving ion should also be supposed to be static; thus we assume the induced potential is s-symmetry out of sphere charge distribution of moving ion, as we have assumed in section 2.1. In addition, the distance between the ion and the metal surface is large enough to assume spherical induced charge. On the other hand, when the atomic orbital has different symmetry from the screening induced cloud, the probability is reduced owing to the small overlap integral. In the latter case, a drastic rearrangement of electron cloud in the final state is necessary to screen the charge.

When the ion velocity is very fast, induced charge cannot be formed. The neutralization process is supposed to proceed without the presence of induced charge. A fast ion can excite the plasmon and reduce its energy to lower than the plasma frequency.

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