Analysis of Resonance Charge Transfer Neutralization on the Basis of Heisenberg Equations of Motion

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On the basis of Heisenberg equations of motion, we propose a new method to analyze the resonance charge transfer neutralization of an ion in front of a metal surface. The Hamiltonian of the system is taken to be a one-electron picture with time dependence. Our approach is directly derived from Heisenberg equations of motion without any approximation and we obtain the simultaneous differential equations to describe the time-dependent behaviors of electrons and ions. We show the derivation of equations and various numerical calculation results, including the case where an impurity potential is introduced into the nonperturbative Hamiltonian.

Subject Index: 340

§1. Introduction

Since Newns first discussed the chemical adsorption based on a model treating electron transfer between a metal surface and an atom (Anderson-Newns Model) in 1969,¹ many theoretical models based on the diagram methods and numerical calculations including cluster models have been reported and discussed extensively to explain the various and interesting surface phenomena.

In the various surface phenomena, the roles of resonant charge transfer (RCT) have been disclosed as a key to determine the surface dynamical processes such as neutralization, molecular dissociation, and chemisorption. In particular, the interpretation of secondary-ion mass spectroscopy (SIMS) data requires quantitative calculations of RCT neutralization rate; thus, extensive studies in both theoretical and experimental fields have been carried out in this area.²⁻¹⁹

Since RCT neutralization occurs as a result of the interaction between a discrete electronic level of an ion and the continuum of electronic states of a solid surface metal, the condition that causes RCT neutralization requires that the electronic level of the ion is close to that of the continuum of electronic states of the solid surface metal; thus, the conditions required for the appearance of RCT neutralization are considered to be very specific.²⁰⁻²²

However, it has recently been reported that the positive ion yield of Ne⁺ scattered off from the metal surface shows a strong dependence on metal work function φ,²³,²⁴ and the role of the RCT neutralization may not be so specific nor is it a

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minor neutralization pathway but rather important.

From the theoretical viewpoint of RCT neutralization, calculations of ion survival probabilities by analyzing the time-dependent Anderson-Newns model were first performed by Brako and Newns,\textsuperscript{4}) when an atom or ion is scattered from a metal surface. Starting from the equation of motion method proposed by Bloss and Hone,\textsuperscript{25}) they evaluated operators by solving the simultaneous differential equations while regarding operators (Q-number) as c-number. Following this study, Marston et al. extended and developed a theoretical analysis including the level crossing, excited neutrals, and negative ions.\textsuperscript{11}) In their research, firstly, the many-body wave functions $\Psi(t)$ including various quantum states are prepared, and the neutralization probability is obtained by solving the Schrödinger equation $i\hbar d\Psi(t)/dt = \hat{H}\Psi(t)$ numerically. Certainly, their method of solving the Schrödinger equation directly is very effective, but many quantum states are required.

Since the Keldish formalism\textsuperscript{26}) has been developed to calculate nonequilibrium states, this method has been applied to time-dependent dynamical systems such as quantum dot, point-conduct tunnel junction, spintronic devices, and surfaces. In particular, in the field of surface physics, the time-resolved two-photon photoemission from Cu(100)\textsuperscript{27}) was analyzed using this formalism. Recently, the formation of H- ions in collision with a Si surface has been investigated by García et al.\textsuperscript{28}) Ion fractions of hydrogen were calculated using the Keldysh Green function. The scanning tunneling microscopy (STM) tunneling current for ultrathin Pb on Si(111) substrate was also calculated on the basis of this formalism.\textsuperscript{29})

Although Green function methods have advantages in analyzing the various phenomena, integral schemes are essential in diagram methods (Dyson equation). Thus, calculations for complicated systems require considerable calculation times to evaluate the time-dependent behaviors of the system corresponding to experimental data. The calculation method proposed by Brako and Newns\textsuperscript{4}) is a very effective way of evaluating RCT neutralization probabilities and it provides a precise and complete image. However, their method also seems to require a long calculation time when the system is complicated, because integral schemes are involved.

In this article, therefore, we propose a new method that can be applied to complicated systems or to systems including a new perturbative Hamiltonian such as impurity potential. In §2, we show the theoretical framework on the basis of the Heisenberg equations of motion and derive simultaneous differential equations from the theoretical framework in the case of the Anderson-Newns Hamiltonian. In §3, to verify our proposed method, we apply it to three cases of resonance tunneling phenomena: comparison with Newn’s formula,\textsuperscript{4}) the case of the energy level of the ion being time-independent, and the case of energy shifts of the ion caused by the presence of an image potential of the surface. Through these cases, we obtain good results that do not contradict those reported and discussed. After confirming our calculations, we estimate the neutralization probability of a singly charged ion under the presence of the impurity potential of a surface, which is, as stated in the previous section, usually difficult to treat analytically and/or numerically using Green function or Newn’s formula.\textsuperscript{4}) Lastly, in §4 we conclude this paper and discuss the remaining problems and further developments.
§2. Theoretical approach

At first, let us start with the Heisenberg equations of motion, the equation for operator is given by

\[ i\hbar \frac{\partial}{\partial t} \hat{a}_i^+(t) = [\hat{a}_i^+(t), \hat{H}], \tag{2.1} \]

where operator \( \hat{a}_i^+(t) \) is in Heisenberg representation. By using Eq. (2.1), the differentiation of \( \hat{a}_i^+(t) \hat{a}_j(t) \) can be expressed as

\[ \frac{\partial}{\partial t} \hat{a}_i^+(t) \hat{a}_j(t) = \frac{1}{i\hbar} [\hat{a}_i^+(t), \hat{H}] \hat{a}_j(t) + \frac{1}{i\hbar} \hat{a}_i^+(t) [\hat{a}_j(t), \hat{H}]. \tag{2.2} \]

By taking the expectation value of each term, we obtain the following differential equation:

\[ \frac{d}{dt} \langle \hat{a}_i^+(t) \hat{a}_j(t) \rangle = \frac{1}{i\hbar} \langle [\hat{a}_i^+(t), \hat{H}] \hat{a}_j(t) \rangle + \frac{1}{i\hbar} \langle \hat{a}_i^+(t) [\hat{a}_j(t), \hat{H}] \rangle, \tag{2.3} \]

where \( \langle \cdots \rangle \) denotes the quantum-mechanical expectation value.

Next, let us apply the above equation to the RCT neutralization process, where a singly charged ion approaches a metal surface and moves away from it after the ion-surface collision. To describe the electronic interaction between a metal surface and an ion, we consider the following Anderson-Newns Hamiltonian while ignoring ion-surface collision. To describe the electronic interaction between a metal surface and an ion, we consider the following Anderson-Newns Hamiltonian while ignoring spin orientations:

\[ \hat{H} = \hat{H}_0 + \hat{H}', \tag{2.4} \]

\[ \hat{H}_0 = \sum_k E_k \hat{C}_{k}^+ \hat{C}_k + E_a(z) \hat{C}_{a}^+ \hat{C}_a, \tag{2.5} \]

\[ \hat{H}' = \sum_k (V_{ak}(z) \hat{C}_{a}^+ \hat{C}_k + V_{ka}(z) \hat{C}_{k}^+ \hat{C}_a). \tag{2.6} \]

In the above equations, \( E_k \) is the energy of a conduction electron with momentum \( k \). \( \hat{C}_{k}^+ \) and \( \hat{C}_k \) are creation and annihilation operators of a conduction electron with momentum \( k \). \( E_a(z) \) denotes the energy level of the ion and usually depends on the surface-ion distance \( z \). \( \hat{C}_{a}^+ \) and \( \hat{C}_a \) are creation and annihilation operators of a state of the ion, respectively. \( V_{ak}(z) \) is the electron transfer matrix element from the conduction electron \( k \) to a state of the ion and can be expressed as a function of the surface-ion distance \( z \). Since \( z \) can be expressed as a function of time, we use \( E_a(t), V_{ak}(t), \) and \( V_{ka}(t) \) instead of \( E_a(z), V_{ak}(z), \) and \( V_{ka}(z) \) hereafter.

From Eqs. (2.4)–(2.6), one finds

\[ [\hat{C}_a(t), \hat{H}] = E_a(t) \hat{C}_a(t) + \sum_k V_{ak}(t) \hat{C}_k(t), \tag{2.7} \]

\[ [\hat{C}_k(t), \hat{H}] = E_k \hat{C}_k(t) + V_{ka}(t) \hat{C}_a(t). \tag{2.8} \]

Accordingly, combining Eqs. (2.7) and (2.8) with Eq. (2.3), we obtain

\[ \frac{d}{dt} \langle \hat{C}_a^+(t) \hat{C}_a(t) \rangle = \frac{i}{\hbar} \sum_k V_{ka}(t) \langle \hat{C}_a^+(t) \hat{C}_k(t) \rangle - \frac{i}{\hbar} \sum_k V_{ak}(t) \langle \hat{C}_a^+(t) \hat{C}_k(t) \rangle, \tag{2.9} \]
\[
\frac{d}{dt} \langle \hat{C}_k(t) \hat{C}_a(t) \rangle = \frac{i}{\hbar} (E_k - E_a) \langle \hat{C}_k(t) \hat{C}_a(t) \rangle + \frac{i}{\hbar} V_{ak}(t) \langle \hat{C}_k(t) \hat{C}_a(t) \rangle \\
- \frac{i}{\hbar} \sum_{k'} V_{ak'}(t) \langle \hat{C}_k(t) \hat{C}_{k'}(t) \rangle.
\] (2.10)

\[
\frac{d}{dt} \langle \hat{C}_k(t) \hat{C}_{k'}(t) \rangle = \frac{i}{\hbar} (E_k - E_{k'}) \langle \hat{C}_k(t) \hat{C}_{k'}(t) \rangle + \frac{i}{\hbar} V_{ak}(t) \langle \hat{C}_a(t) \hat{C}_{k'}(t) \rangle \\
- \frac{i}{\hbar} V_{k'a}(t) \langle \hat{C}_k(t) \hat{C}_a(t) \rangle.
\] (2.11)

Now we define
\[
n_{ij}(t) \equiv \langle \hat{C}^+_i(t) \hat{C}_j(t) \rangle
\] (2.12)
and \(n_{ji}(t)\) is obtained from the relation \(n_{ji}(t) = (n_{ij}(t))^*\). By using Eq. (2.12), Eqs. (2.9)–(2.11) can be rewritten in the following forms:
\[
\frac{d}{dt} n_{aa}(t) = \frac{i}{\hbar} \sum_k V_{ka}(t)n_{ka}(t) - \frac{i}{\hbar} \sum_k V_{ak}(t)n_{ak}(t),
\] (2.13)

\[
\frac{d}{dt} n_{ka}(t) = \frac{i}{\hbar} (E_k - E_a)n_{ka}(t) + \frac{i}{\hbar} V_{ak}(t)n_{aa}(t) - \frac{i}{\hbar} \sum_{k'} V_{ak'}(t)n_{kk'}(t),
\] (2.14)

\[
\frac{d}{dt} n_{kk'}(t) = \frac{i}{\hbar} (E_k - E_{k'})n_{kk'}(t) + \frac{i}{\hbar} V_{ak}(t)n_{ak'}(t) - \frac{i}{\hbar} V_{k'a}(t)n_{ka}(t).
\] (2.15)

Furthermore, from Eqs. (2.13) and (2.15), we can easily obtain the following relation when \(k = k'\):
\[
\frac{d}{dt} n_{aa}(t) + \frac{d}{dt} \sum_k n_{kk}(t) = 0.
\] (2.16)

The above equation denotes that the total number of electrons is conserved at \(-\infty < t < \infty\).

Consequently, we obtain the simultaneous differential equations corresponding to the Hamiltonian of Eq. (2.4). The merit of this method is that by using computer codes one can obtain numerical solutions of Eqs. (2.13)–(2.15) under various initial conditions. The neutralization probability can be obtained without calculating the eigenstate for the above Hamiltonian or any estimation of the Green function.

To show the merits of our proposed method for the Hamiltonian of Eqs. (2.4)–(2.6), let us consider the neutralization, while focusing on the time-dependent Schrödinger equation \(i\hbar \partial \Psi(t)/\partial t = \hat{H}' \Psi(t)\). Since the Hamiltonian includes the interaction term \(\hat{H}'\), which expresses the interaction between the metal surface and the ion, the eigenstate \(\Psi\) is mixed with the quantum states of the ion and metal. Thus, the eigenstate can be expressed as the summation of linear combinations of many possible quantum states of the ion and metal, which requires complicated analytical and/or numerical processes to obtain \(\Psi\). Analysis based on the Schrödinger picture seems, therefore, unsuitable for evaluating the neutralization probability of the ion scattered on a metal surface. In addition, one-particle Schrödinger representation by Hartree-Fock and/or Hartree-Fock-Slater approximation is difficult because of the Hamiltonian of Eqs. (2.4)–(2.6) being a nonsteady state while showing time dependence.
On the other hand, on the basis of the conventional Green function method, we obtain the following Dyson equation using the diagram technique:

\[ G^R_{aa}(t, t') = G^{R0}_{aa}(t, t) + \frac{1}{\hbar^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} G^{R0}_{aa}(t, t_1) \Sigma^R_{aa}(t_1, t_2) G^R_{aa}(t_2, t') dt_1 dt_2 \quad (2.17) \]

and

\[ G^R_{ak}(t, t') = \frac{1}{\hbar} \int_{-\infty}^{\infty} G^{R0}_{aa}(t, t_1) V_{ak}(t_1) G^{R0}_{kk}(t_1, t') dt_1, \quad (2.18) \]

where the superscript \( R \) indicates the retarded Green function and \( G^{R0} \) is the unperturbed retarded Green function. \( \Sigma^R_{aa} \) denotes the retarded self-energy. Using the above Green functions, we can express the electron number, \( n_{aa}(t) \) on the atom at time \( t \), in the following form:

\[ n_{aa}(t) = n_{aa}(-\infty) |G^R_{aa}(t, -\infty)|^2 + \sum_k n_{kk}(-\infty) |G^R_{ak}(t, -\infty)|^2. \quad (2.19) \]

As shown above, \( n_{aa}(t) \) can be evaluated after Green functions are obtained. However, complicated analytical procedures are required to obtain the Green functions by solving the Dyson equation in comparison with coupled differential equations of (2.13)–(2.15). Accordingly, the neutralization probability based on the Green function method is estimated indirectly and we can only obtain calculation results for limited cases under some approximations; thus, analysis by Green function seems inconvenient for various experiments. Consequently, we can mention that the advantages of our proposed method are as follows:

1. We use not \( Q \)-number (operators) but \( c \)-number in the form of differential equations; thus, our method is very convenient to treat mathematically. By other methods, calculations are very difficult to perform when the electron transfer matrix is expressed as a function of wave number \( k \) and the density of states (DOS) is not flat. For example, let us consider the atomic level width \( \Gamma \), which is given by

\[ \Gamma = \frac{2\pi}{\hbar} \sum_k |V_{ak}|^2 \delta(E - E_k) = 2\Delta(E). \quad (2.20) \]

On the basis of both assumptions that the electron transfer matrix is independent of wave number \( k \) and DOS remains as a constant value of \( \rho_0 \), we can easily obtain the analytical expression for \( \Gamma \) as

\[ \Gamma = 2\pi \sum_k |V_{ak}|^2 \delta(E - E_k) = 2\pi |V_0|^2 \sum_k \delta(E - E_k) \]

\[ = 2\pi |V_0|^2 \int D(E')\delta(E - E')dE' = 2\pi |V_0|^2 \rho_0 (= 2\Delta) \Rightarrow \text{constant}. \quad (2.21) \]

However, it seems somewhat inadequate that both assumptions can be applied to most experimental cases; actually, only limited cases can be analyzed under \( \Gamma = \text{constant} \). Consequently, we can conclude that the condition of \( \Gamma = \text{constant} \) is inadequate if one hopes to analyze various experimental data more precisely. However, it should be noted that most of the analytical methods proposed previously
are mainly based on the assumption of $\Gamma = \text{constant}$. Moreover, Green function methods require $\Gamma = \text{constant}$ to obtain the analytical results. Thus, most of the theoretical methods can be applied to only limited cases such as wide band limit and we cannot apply these methods to various experimental data including nonflat DOS and/or electron transfer matrix showing wave number $k$ dependence. However, our developed methods do not require such an assumption of $\Delta = \text{constant}$ and it is possible to obtain numerical results by applying our methods to various experimental conditions.

2. On the basis of our proposed method, theoretical extension is easy because our analysis fundamentally combines the Heisenberg equation of motion with a differential form of product of operators $\hat{a}^+_i(t)\hat{a}_j(t)$, as shown below,

$$\frac{\partial}{\partial t}\hat{a}^+_i(t)\hat{a}_j(t) = \left[ \frac{\partial}{\partial t}\hat{a}^+_i(t) \right]\hat{a}_j(t) + \hat{a}^+_i(t)\left[ \frac{\partial}{\partial t}\hat{a}_j(t) \right] = \frac{1}{i\hbar}[\hat{a}^+_i(t), \hat{H}]\hat{a}_j(t) + \frac{1}{i\hbar}\hat{a}^+_i(t)[\hat{a}_j(t), \hat{H}]. \quad (2.22)$$

Accordingly, we can obtain an extended theoretical expression even if a new perturbation is introduced into the original Hamiltonian because $[\hat{a}^+_i(t), \hat{H}]$ or $[\hat{a}_j(t), \hat{H}]$ can be easily estimated. If other methods such as Green functions are applied to the system including a new perturbation Hamiltonian, theoretical extension is usually difficult and it requires complicated procedures and/or schemes to analyze Dyson equations. In addition, it should be noted that these differential equations can be derived directly from Heisenberg equations of motion, as far as the Hamiltonian can be written as one-body picture.

§3. Calculation results

3.1. Calculations on the assumption that $n_{kk'}(t)$ is independent of time

At first, for the purpose of verifying the above differential equations and of simplifying the discussions, let us consider the case of $n_{kk'}(t) = \delta_{kk'}$ while ignoring the imaginary part of $n_{kk'}(t)$. Here, $\delta_{kk'}$ denotes Kronecker delta. Thus, Eq. (2.14) is given by

$$\frac{d}{dt}n_{ka}(t) = \frac{i}{\hbar}(E_k - E_a(t))n_{ka}(t) + \frac{i}{\hbar}V_{ak}(t)(n_{aa}(t) - 1), \quad (3.1)$$

because $n_{ka}(-\infty) = 0$, $n_{ka}(t)$ is given by

$$n_{ka}(t) = \frac{i}{\hbar}\int_{-\infty}^{t} d\tau V_{ak}(\tau)[n_{aa}(\tau) - 1] \exp\left(-\frac{i}{\hbar}\int_{t}^{\tau}[E_k - E_a(x)]dx\right). \quad (3.2)$$

To simplify the calculations, we assume

$$V_{ak}(t) = V^0_{a}u(t), \quad \text{Im}u(t) = 0 \quad \text{and} \quad E_a(t) = E_a(\text{constant}). \quad (3.3)$$
By combining Eqs. (3·2) and (3·3) with Eq. (2·13), $dn_{aa}(t)/dt$ can be expressed as

$$
\frac{d}{dt}n_{aa}(t) = -\frac{2}{\hbar^2}|V_0^a|^2 u(t) \int_{-\infty}^{t} d\tau u(\tau) [n_{aa}(\tau) - 1] \sum_k \cos \left[ \frac{1}{\hbar} (E_k - E_a)(\tau - t) \right].
$$

(3·4)

Furthermore, we assume that DOS remains as a constant value $\rho_0$ (flat band) with bandwidth $D$ and that the Fermi level $E_F$ lies in the middle of the flat band (we set $E_F = 0$ eV). Finally, we obtain

$$
\frac{d}{dt}n_{aa}(t) =
\frac{4}{\hbar} |V_0^a|^2 u(t) \rho_0 \int_{-\infty}^{t} d\tau u(\tau) [1 - n_{aa}(\tau)] \frac{\cos \left[ \frac{1}{\hbar} (E_a + D/4)(\tau - t) \right] \sin \left[ \frac{1}{\hbar} D(\tau - t) \right]}{\tau - t}.
$$

(3·5)

In the above equation, we set $D = 6.0$ eV and $\rho_0 = 0.1$ eV$^{-1}$. In the calculation, we assume the gaussian type decay for $V_{ak}$ because we find it difficult to estimate numerical solutions of a series of differential equations of (2·13)–(2·15) and the above equation when adopting exponential decay for $V_{ak}$. Using the relation between metal surface-ion distance $z$ and ion velocity $v$, i.e., $z = v|t|$, we can express the gaussian decay in the following form:

$$
V_{ak} = V_0^a \exp(-\xi z^2) = V_0^a \exp(-\xi v^2 t^2) \quad \cdots \quad u(t) = \exp(-\xi v^2 t^2).
$$

(3·6)

Figure 1 shows the calculation results obtained by solving the above equations, where we set ion velocity $v = 2.0 \times 10^5$ cm/s and $\xi = 1.0 \text{ Å}^{-2}$. Since the velocity of the Cs$^+$ ion vertical to the surface ranges from $2.7 \times 10^5$ to $3 \times 10^6$ cm/s in the experiments of sputtering,$^6$ the value of ion velocity $v = 2.0 \times 10^5$ cm/s seems realistic from the viewpoints of experiments.

![Fig. 1](https://academic.oup.com/ptp/article-abstract/122/3/713/2938796)

Fig. 1. Plot of neutralization probability $n_{aa}(\infty)$ as a function of energy level of ion $E_a$ obtained by calculating Eq. (3·5), where $\rho(E) = \rho_0 = 0.1$ eV$^{-1}$, $\xi = 1 \text{ Å}^{-2}$, ion velocity $= 2 \times 10^5$ cm/s, and bandwidth $D = 6$ eV. •: $V_0^a = 0.5$ eV; □: $V_0^a = 0.2$ eV.
As illustrated in Fig. 1, \( n_{aa}(\infty) \) for \( V_a^0 = 0.5 \text{ eV} \) is almost unity in the entire range of \(-D/2 < E_a < 0\) because of bandwidth \( D = 6 \text{ eV} \) and Fermi level \( E_F \) lying in the middle of the band (\( E_F = 0 \text{ eV} \)).

On the other hand, \( n_{aa}(\infty) \) for \( V_a^0 = 0.2 \text{ eV} \) is less than unity because of the relatively small interaction between the metal surface and ion. However, both behaviors are very similar in the range of \(-D/2 < E_a < 0\); the neutralization rate remains constant and it markedly decreases in the vicinity of \( E_a = -D/2 \) and becomes 0. Such a marked decrease at the band edge is ascribed to the discontinuity of \( \rho(E) \) (= DOS of conduction electron) because of \( \rho(E) = \rho_0 \theta(D/2 - |E|) \), where \( \theta(x) \) is the step function. Since the metal surface-ion interaction has, as illustrated in Fig. 1, a strong effect on the resonance charge transfer neutralization, the neutralization rate is directly related to \( V_a^0 \). Accordingly, the fact that \( n_{aa}(\infty) \) remains constant at \(-D/2 < E_a < 0\) is due to the constant interaction \( V_a^0 \) without any energy dependence as well as constant \( \rho(E) \).

Figure 2 shows the comparison between our calculation result of Eq. (3-5) and Newns’s formula\(^1\) in the ground state (\( T = 0 \text{ K} \)), where Newns’s formula is expressed as

\[
n_{aa}(t) = n_{aa}(\infty) \exp \left( -\frac{2}{\hbar} \int_{-\infty}^{t} \Delta(t') \, dt' \right) + \frac{1}{\pi} \int dEf(E,T) \left| \frac{1}{\hbar} \int_{-\infty}^{\infty} dt' \sqrt{\Delta(t')} \exp \left( -\frac{i}{\hbar} Et' - \frac{1}{\hbar} \int_{t'}^{t} [iE_a(t'') + \Delta(t'')] \, dt'' \right) \right|^2.
\]

(3.7)

In the above equation, \( f(E,T) = 1/(1 + \exp((E - E_F)/k_BT)) \) is the Fermi function and

\[
\Delta(t) = \Delta|u(t)|^2, \quad \Delta = \pi|V_a^0|^2 \rho_0.
\]

(3.8)

As shown in Fig. 2, numerical agreements between the two methods are fairly good except for the range of \( E_a < -D/2 \) (= -3 eV), although theoretical derivation and backgrounds are utterly different. It should be noted that in our calculation bandwidth, \( D \) is 6 eV with \( E_F \) lying in the middle of the band, whereas Newns’s formula for \( n_{aa}(t) \) is derived on the basis of wide band limit (\( D \to \infty \)); thus \( n_{aa}(\infty) \) = 0 for \( E_a < -D/2 \) in our model. Consequently, we can conclude that our proposed method is working in comparison with previous theoretical results.

3.2. Numerical calculations of Eqs. (2.13)–(2.15)

In the previous section, we solved Eqs. (2.13)–(2.15) by introducing some approximations such as \( n_{kk'}(t) = \delta_{kk'} \) to treat many particle behaviors easily. The assumption that \( n_{kk'}(t) \) remains constant all the time seems to be a good approximation when the ion is far from the metal surface or the surface-ion interaction is relatively weak. However, the presence of the off-diagonal term of \( n_{kk'}(t) \) cannot be ignored when the ion-surface distance is very short, i.e., \( t \approx 0 \). Additionally, the application of the analytical form of Eq. (3.5) is very limited because it is derived under the assumption that DOS of conduction electrons, surface-ion interaction, and energy level of ion are constant. Considering that the energy level of ion \( E_a \) is strongly
We propose that a better way of interpreting experimental data is a numerical method based on the direct solutions of Eqs. (2·13)–(2·15) instead of the analytical form. At first, let us consider the simplest case of $N$-surface electrons affected by the surface-atom distance and that DOS of the conduction electron and surface-ion interaction usually show energy dependence, we need further analysis to explain the experimental data.

Since the application of the analytical method shown in Eq. (3·5) is considered to be very limited, we propose that a better way of interpreting experimental data is a numerical method based on the direct solutions of Eqs. (2·13)–(2·15) instead of the analytical form. At first, let us consider the simplest case of $N$-surface electrons

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Fig. 2. Comparison of neutralization probability $n_{aa}(\infty)$ together with theoretical results obtained by Brako and Newns where $\rho(E) = \rho_0 = 0.1 \text{ eV}^{-1}$, $\xi = 1 \text{ Å}^{-2}$, ion velocity $= 2 \times 10^5 \text{ cm/s}$ bandwidth $D = 6 \text{ eV}$. $\square$: theoretical results by Brako and Newns; $\bullet$: our calculation results (A) $V_0^a = 0.1 \text{ eV}$, (B) $V_0^a = 0.2 \text{ eV}$, (C) $V_0^a = 0.5 \text{ eV}$.
and a constant energy level of ion, i.e., $E_a(t) = E_a$. Then, Eqs. (2.13)–(2.15) are rewritten in the following form:

$$
\frac{d}{dt} n_{aa}(t) = \frac{i}{\hbar} \sum_{j=1}^{N} V_{ja}(t)n_{ja}(t) - \frac{i}{\hbar} \sum_{j=1}^{N} V_{aj}(t)n_{aj}(t),
$$

(3.9)

$$
\frac{d}{dt} n_{ja}(t) = \frac{i}{\hbar} (E_j - E_a(t))n_{ja}(t) + \frac{i}{\hbar} V_{aj}(t)n_{aa}(t) - \frac{i}{\hbar} \sum_{m=1}^{N} V_{am}(t)n_{jm}(t),
$$

(3.10)

$$
\frac{d}{dt} n_{jm}(t) = \frac{i}{\hbar} (E_j - E_m)n_{jm}(t) + \frac{i}{\hbar} V_{aj}(t)n_{am}(t) - \frac{i}{\hbar} \sum_{m=1}^{N} V_{ma}(t)n_{ja}(t).
$$

(3.11)

In the above equations, the subscripts “$j$” and “$m$” correspond to the momenta “$k$” and “$k'$”, respectively. As stated in the previous paragraph, we use $V_{aj}(t) = V_0^a \exp(-\xi v^2 t^2)$ without an imaginary part when calculating. Simultaneous differential equations obtained from Eqs. (3.9)–(3.11) are solved numerically under the initial conditions of $n_{aa}(-\infty) = 0$ and $n_{jm}(-\infty) = \delta_{jm}$ ($j, m = 1, 2, ..., N$), where $n_{jj}(-\infty)$ corresponds to the number of electrons occupying momentum $k$ at $t \to -\infty$ while $n_{aa}(-\infty) = 0$ to the complete ionic state at $t \to -\infty$. As stated previously, we assume that Fermi level $E_F$ remains in the middle of the band hereafter. In addition, we set $E_F = 0$ in all the calculations.

Figure 3 shows $n_{aa}(\infty)$ as a function of the energy level of ion $E_a$. In the calculation, we define the energy level $E_j$ of surface electrons as $E_j = -D_j/2N$ [eV] ($N = 10, 20, 40, 60, j = 0, 1, 2, ..., N$) and set the bandwidth $D = 0.8$ eV. As shown

![Fig. 3. Plot of neutralization probability $n_{aa}(\infty)$ as a function of energy level of ion for different energy intervals of surface electrons, where $\xi = 1$ Å$^{-2}$, ion velocity $= 3 \times 10^5$ cm/s, bandwidth $D = 0.8$ eV, $V_0^a = 1.2$ eV, and $E_j = -D_j/2N$ eV, $j = 0, ..., N$. ◆: $N = 10$, ○: $N = 20$, △: $N = 40$, ×: $N = 60$.](https://academic.oup.com/ptp/article-abstract/122/3/713/2938796)
in the above definition, $N$ is proportional to the reciprocal of the energy interval from the relation of the energy interval $= D/2N$. As shown in this figure, one can easily see that the neutralization almost seems independent of the energy intervals of surface electrons although the neutralization rate somewhat decreases with $N$.

Since $n_{aa}(\infty)$ denotes the number of electrons occupying the atomic energy state $E_{a}$ when the projectile is moving far away after the collision with the surface, the neutralization probability can be determined from the value of $n_{aa}(\infty)$; $n_{aa}(\infty) \approx 1$ corresponds to the neutralization state, whereas $n_{aa}(\infty) \approx 0$ corresponds to the ionization state. As shown in Fig. 3, the neutralization occurs in the range of about $-0.4$ to $0.0$ eV, the range of which corresponds to the occupied bandwidth because of $D/2 = 0.4$ eV. Furthermore, it should be noted that $n_{aa}(\infty)$ shows a peak when the energy level of the ion, i.e., $E_{a}$, is lying in the middle of the occupied band ($-0.2$ eV in this case); thus, this implies that the neutralization could easily occur in the case of $E_{a}$ being in the middle of the occupied band. However, our estimation is based on the calculation results using the constant DOS of surface electrons. Actually, it seems reasonable that the neutralization can easily proceed when $E_{a}$ exists in the high DOS, usually in the vicinity of the Fermi level.

3.3. Numerical calculations including dependence of ion energy level on ion-metal distance

In §§3.1 and 3.2, we calculated the neutralization probabilities under the condition that the energy level of the ion remains a constant value $E_{a}$ to simplify the calculations. However, the atomic level of the ion actually fluctuates because of electron transfer between the surface and ion when the ion is close to the surface; thus, calculations including such a deviation are required. The dependence of ion level $E_{a}$ on the surface-ion distance $z$ can be expressed as below in the atomic unit,

$$E_{a} = E_{a}(z) = E_{a}(t) = \phi - I + \frac{1}{4(z - z_{im})},$$

(3.12)

where $\phi$, $I$, and $z_{im}$ are work function, ionization potential, and the location of image potential (we take $z_{im} = -2a_B$ and $I = 3$ eV in calculations hereafter, $a_B$: Bohr radius).

$n_{aa}(\infty)$ as a function of work function $\phi$ is shown in Fig. 4, where each energy level of surface electron $E_{j}$ is the same as previously defined in §3.2 and bandwidth $D$ is 0.8 eV. From the values of $n_{aa}(\infty)$, it is found that the RCT is numerically confirmed in the range of $N \geq 30$, while numerical instabilities arise when $N \leq 20$, which denotes that the energy interval of each surface electron has an effect on the numerical calculation results and that such a dependence on energy intervals is different from the calculation result obtained in §3.2: a large interval will cause instabilities during calculation. Although such instabilities arise when $N$ is small, the neutralization range is constant at $N \geq 30$. Consequently, we can conclude that reliable results are obtained provided that we take a large $N$ even when the calculations include the term related to Eq. (3.12).
Fig. 4. Plot of neutralization probability $n_{aa}(\infty)$ as a function of work function $\phi$ for different
energy intervals of surface electrons, where $\xi = 1$ Å, $E_j = -D_j/2N$ eV, ion velocity $= 2 \times 10^5$ cm/s, ionization potential $I = 3$ eV, $V_a^\prime = 1.2$ eV and bandwidth $D = 0.8$ eV. : $N = 10$, $

3.4. Neutralization process in the presence of impurity potential

We have discussed the RCT neutralization occurring on the clean surface without
impurity scattering. However, in actual crystals, there are some impurity atoms and
lattice defects such as point defects, dislocations, and voids. One can see that these
have effects on electrons on the surface regarded as impurity potential. The terms of
impurity scattering, therefore, should be estimated to simulate the behaviors of the
actual crystal surface. Then let us consider the case where the impurity potential
exists on the crystal surface. The Hamiltonian is expressed as

$$\hat{H} = \hat{H}_0 + \hat{H}', \quad (3.13)$$

$$\hat{H}_0 = \sum_k E_k \hat{C}_k^+ \hat{C}_k + E_a(t) \hat{C}_a^+ \hat{C}_a + \sum_k (V_{ak}(t) \hat{C}_a^+ \hat{C}_k + V_{ka}(t) \hat{C}_k^+ \hat{C}_a), \quad (3.14)$$

$$\hat{H}' = \sum_{kk'} V_{kk'} \hat{C}_k^+ \hat{C}_{k'}. \quad (3.15)$$

Equation (3.15) denotes the impurity scattering on the surface. Concerning $E_a(t)$,
we take the same expression as Eq. (3.12). On the basis of the above Hamiltonian,
we obtain the following equations:

$$\frac{d}{dt} n_{aa}(t) = i \hbar \sum_k V_{ka}(t) n_{ka}(t) - i \hbar \sum_k V_{ak}(t) n_{ak}(t), \quad (3.16)$$

$$\frac{d}{dt} n_{ka}(t) = i \hbar (E_k - E_a(t)) n_{ka}(t) + \frac{i}{\hbar} V_{ak}(t) n_{aa}(t)$$

$$- \frac{i}{\hbar} \sum_{k'} V_{ak'}(t) n_{kk'}(t) + \frac{i}{\hbar} \sum_{k'} V_{kk'}^* n_{k'a}(t), \quad (3.17)$$
\[
\frac{d}{dt}n_{kk'}(t) = \frac{i}{\hbar}(E_k - E_{k'})n_{kk'}(t) + \frac{i}{\hbar}V_{kk'}(t)n_{kk'}(t) - \frac{i}{\hbar}V_{k'a}(t)n_{ka}(t) + \frac{i}{\hbar}\sum_{k''}V_{kk''}^*n_{k''k'}(t) - \frac{i}{\hbar}\sum_{k''}V_{k''k}n_{kk''}(t).
\]

When calculating Eqs. (3-16)–(3-18), we assume \( V_{kk'} = V_0 \) (constant \( \text{Im}(V_0) = 0 \)) for shortening the calculation time and simplifying the calculation scheme. Furthermore, yielding to the notation using \( j, j' \) instead of \( k, k' \) written in Eqs. (3-9)–(3-11) previously, we can rewrite Eqs. (3-16)–(3-18) in the following forms:

\[
\frac{d}{dt}n_{aa}(t) = \frac{i}{\hbar}\sum_{j=1}^{N} V_{ja}(t)n_{ja}(t) - \frac{i}{\hbar}\sum_{j=1}^{N} V_{aj}(t)n_{aj}(t),
\]

\[
\frac{d}{dt}n_{ja}(t) = \frac{i}{\hbar}(E_j - E_a(t) - V_0)n_{ja}(t) + \frac{i}{\hbar}V_{aj}(t)n_{aa}(t) - \frac{i}{\hbar}\sum_{j'=1}^{N} V_{aj'}(t)n_{jj'}(t)
\]

\[
+ \frac{i}{\hbar}V_0\sum_{j'=1}^{N} n_{ja}(t),
\]

\[
\frac{d}{dt}n_{jj'}(t) = \frac{i}{\hbar}(E_j - E_{j'}(t))n_{jj'}(t) + \frac{i}{\hbar}V_{aj}(t)n_{aj'}(t) - \frac{i}{\hbar}V_{j'a}(t)n_{ja}(t)
\]

\[
+ \frac{i}{\hbar}V_0\sum_{j''=1}^{N} n_{j''j'}(t) - \frac{i}{\hbar}V_0\sum_{j''=1}^{N} n_{jj''}(t).
\]

The corrective term "\(- V_0" of the right-hand side of Eq. (3-20) is introduced owing to the impurity potential \( \tilde{H}' \).

Figures 5(A) and 5(B) show the calculation results for \( V_0 = \mp 20 \text{ meV} \). Concerning the energy level of surface electrons, we take the same expression used in Fig. 3 and fix the bandwidth \( D = 0.6 \text{ eV} \). In both cases, the calculation results show the differences among \( N = 10, 20 \) and 30; the peak of \( n_{aa}(\infty) \) shifts leftward with increasing \( N \) when \( V_0 = -20 \text{ meV} \), whereas it shifts rightward when \( V_0 = 20 \text{ meV} \). In addition, it is found that the value of the peak of \( n_{aa}(\infty) \) tends to decrease with \( N \) in both cases. Thus, the energy interval of surface electrons seems important for the calculation results.

Figures 6(A) and (B) show the calculated \( n_{aa}(\infty) \) for the various values of \( V_0 \): the results of \( V_0 \leq 0 \) are shown in Fig. 6(A), while those of \( V_0 \geq 0 \) are shown in Fig. 6(B). As for the energy level of surface electrons, we take the same expression of \( D = 0.6 \text{ eV} \) and \( N = 30 \) as used in Figs. 5(A) and (B); thus, the energy interval is 10 meV. As illustrated in this figure, it should be noted that a value of \( V_0 \) as small as \( \pm 10 \text{ meV} \) strongly affects the neutralization. Accordingly, we conclude that the RCT neutralization is very sensitive to impurity scattering, which, we suppose, directly leads to the experimentally observed fact that the RCT neutralization is strongly affected by small defects on the surface. Furthermore, in both figures, with increasing \( |V_0| \), the neutralization range shifts leftwards for \( V_0 < 0 \), while it shifts rightwards for \( V_0 > 0 \). Thus, it can be hypothesized that the neutralization range
Fig. 5. Plot of neutralization probability $n_{aa}(\infty)$ as a function of work function $\phi$ for different energy intervals of surface electrons under the condition of impurity potential being a constant value of $V_0$, where $\xi = 1\, \text{Å}^{-2}$, $E_j = -Dj/2N\, \text{eV}$, ion velocity $= 2 \times 10^5\, \text{cm/s}$, ionization potential $I = 3\, \text{eV}$, $V^0_a = 1.2\, \text{eV}$ and bandwidth $D = 0.6\, \text{eV}$. $\times$: $N = 10$, $\triangle$: $N = 20$, $\blacksquare$: $N = 30$.

shifts to the left or right if the impurity atom on the surface has an attractive or repulsive interaction between surface electrons. Additionally, the broadening of the neutralization range is observed with the increase in $|V_0|$ for both figures.

Now let us consider the reason why an impurity potential as small as $\pm 10\, \text{meV}$ has a considerable effect on the neutralization. Then we focus on the following Hamiltonian $\hat{H}_{\text{surface}}$ to describe the surface state in the presence of impurity potential:

$$
\hat{H}_{\text{surface}} = \sum_k E_k \hat{C}_k^+ \hat{C}_k + \sum_{kk'} V_{kk'} \hat{C}_k^+ \hat{C}_{k'} = \sum_k E_k \hat{C}_k^+ \hat{C}_k + V_0 \sum_{kk'} \hat{C}_k^+ \hat{C}_{k'}
$$
\[
= \sum_{j=1}^{N} E_j \hat{C}_j^+ \hat{C}_j + V_0 \sum_{j=1, j' \neq 1}^{N} \sum_{j=1, j' \neq 1}^{N} \hat{C}_j^+ \hat{C}_{j'}.
\]

In the above equation, \(N\) denotes the total number of surface electrons. Thus, matrix \(H_{\text{surface}}\) (\(H_{\text{surface}} = [H_{\text{surface}}(i, k), i, k = 1, 2, \ldots N] = \langle i | \hat{H}_{\text{surface}} | k \rangle\)) is expressed as

\[
H_{\text{surface}} = \begin{pmatrix}
E_1 & V_0 & \cdots & V_0 \\
V_0 & E_2 & \cdots & V_0 \\
\vdots & \vdots & \ddots & \vdots \\
V_0 & V_0 & \cdots & E_N
\end{pmatrix}.
\]

Consequently, we can obtain eigenvalues for this Hamiltonian by diagonalizing the above matrix. Figure 7(A) shows the calculation results of eigenvalues of Hamiltonian for different impurity potentials, where \(\xi = 1 \text{ Å}^{-2}, E_j = -D_j/2N \text{ eV} (N = 30)\), ion velocity = \(2 \times 10^5 \text{ cm/s}\), ionization potential \(I = 3 \text{ eV}\), \(V_0^a = 1.2 \text{ eV}\) and bandwidth \(D = 0.6 \text{ eV}\). (A) \(\bullet: V_0 = -20 \text{ meV}, \triangle: V_0 = -10 \text{ meV}, \bigcirc: V_0 = 0 \text{ meV}\). (B) \(\square: V_0 = 20 \text{ meV}, \blacktriangle: V_0 = 10 \text{ meV}, \bigcirc: V_0 = 0 \text{ meV}\).
tonian $\hat{H}_{\text{surface}}$ for $V_0 = 0, -10, \text{and} -20$ meV, whereas those for $V_0 = 0, 10, \text{and} 20$ meV are shown in Fig. 7(B), where we take the same expression of $E_j$ as the case of Fig. 6. When $V_0 = -10$ or $-20$ meV, as shown in Fig. 7(A), the lowest energy level seems utterly different although other energy levels are similar to the case of $V_0 = 0$. In contrast, when $V_0 = 10$ and $20$ meV, as shown in Fig. 7(B), the location of the highest energy level is exceptionally high in comparison with other levels. Thus, the appearance of localized states — lowest level in Fig. 7(A) and highest level in Fig. 7(B) — as a result of the presence of the impurity potential seems to play a very important role in determining the neutralization.

To examine the localized states as shown in both Figs. 7(A) and (B) in detail,
we introduce a new operator $\tilde{C}_i$ defined in the linear combinations of operator $\hat{C}_j$,

$$\tilde{C}_i = \sum_{j=1}^{N} \Gamma_{ij} \hat{C}_j.$$  \hspace{1cm} (3.24)

Using the above operator, we can transform the Hamiltonian $\hat{H}_{\text{surface}}$ of Eq. (3.22) into the simplified form,

$$\hat{H}_{\text{surface}} = \sum_{j=1}^{N} E_j \hat{C}_j^+ \hat{C}_j + V_0 \sum_{j=1, j' \neq j}^{N} \hat{C}_j^+ \hat{C}_{j'} = \sum_{j=1}^{N} E^{(j)} \hat{C}_j^+ \hat{C}_j,$$  \hspace{1cm} (3.25)

where matrix $\Gamma$ composed of element $\Gamma_{ij}$ satisfies

$$\Gamma \Gamma^+ = \Gamma^+ \Gamma = 1 \left( \begin{array}{cccc} 1 & 0 & \cdots & 0 \\ 0 & 1 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & 1 \end{array} \right)$$  \hspace{1cm} (3.26)

and

$$\Gamma H_{\text{surface}} \Gamma^{-1} = \begin{pmatrix} E^{(1)} & 0 & \cdots & 0 \\ 0 & E^{(2)} & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & E^{(N)} \end{pmatrix},$$  \hspace{1cm} (3.27)

Thus, instead of the form of Eqs. (3.13)–(3.15), we can obtain the simplified Hamiltonian having no terms related to the impurity potential and can express it in the following form:

$$\hat{H} = \hat{H}_0 + \hat{H}'$$

$$\begin{align*}
&= \hat{H}_{\text{surface}} + E_a \hat{C}_a^+ \hat{C}_a + V_a^0 u(t) \sum_{j=1}^{N} (\hat{C}_a^+ \hat{C}_j + \hat{C}_j^+ \hat{C}_a) \\
&= \sum_{j=1}^{N} E^{(j)} \hat{C}_j^+ \hat{C}_j + E_a(t) \hat{C}_a^+ \hat{C}_a + V_a^0 u(t) \sum_{j=1}^{N} (g_j \hat{C}_a^+ \hat{C}_j + g_j^* \hat{C}_j^+ \hat{C}_a), \hspace{1cm} (3.28)
\end{align*}$$

where $g_j$ is

$$g_j = \sum_{i=1}^{N} \Gamma_{ij}^+ = \sum_{i=1}^{N} x_i^{(j)},$$  \hspace{1cm} (3.29)

and

$$H_{\text{surface}} \mathbf{x}^{(j)} = E^{(j)} \mathbf{x}^{(j)},$$

$$\mathbf{x}^{(j)} = \begin{pmatrix} x_1^{(j)} \\ \vdots \\ x_i^{(j)} \\ \vdots \\ x_N^{(j)} \end{pmatrix}. \hspace{1cm} (3.30)$$
As illustrated in the above equations, the obtained Hamiltonian is very similar to the form composed of Eqs. (2·4)–(2·6) except for the term of $g_j$. Table I shows a list of $j$, $E^{(j)}$, and $g_j$ ($j = 1, 2, ..., N$) for $V_0 = 0$, $\mp 10$ meV when $N = 30$. It should be noted that the value of $g_j$ is anomalously large (more than 5) compared with others ($-0.3 \sim 0.3$) when the corresponding $E^{(j)}$ is markedly high or low. Since a large $g_j$ denotes the strong interaction with the ion, it can be hypothesized that such a markedly high or low energy level (impurity level) easily caused by an impurity potential has a strong interaction with the ion and therefore has a considerable effect on the neutralization. On the basis of the above speculation, the broadening of the neutralization range with increasing $|V_0|$, as illustrated in Figs. 6(A) and (B), can be explained from the relative location of the impurity level and corresponding $g_j$: a large $g_j$ and a distant impurity level will broaden the neutralization range. Furthermore, the leftward shift or rightward shift of the neutralization range depending on the sign of impurity potential — rightward shift in case of positive (repulsive) impurity potential and leftward shift in case of negative (attractive) impurity potential as found in Figs. 6(A) and (B) — can also be ascribed to the location of the impurity level. Since the impurity level having a strong interaction with the ion is above the Fermi level ($E_F$) for $V_0 > 0$ and is below $E_F$ for $V_0 < 0$, the rightward shift of the neutralization range is considered to be due to the impurity level $> E_F$, whereas the leftward shift to the impurity level $< E_F$.

Additionally, the energy interval seems to play an important role in causing such an anomalous state shown in Figs. 7(A) and (B). In our calculation, the energy intervals of surface electrons are as large as 10 meV. However, on the basis of further calculation results treating the case of the impurity potential value $V_0$ being less than the energy interval of surface electrons, these results do not show such anomalous states. Actually, the energy interval in the vicinity of the Fermi level is considered to be on the order of $D/N_A$ ($D$: bandwidth, $N_A$: number of electrons consisting of the band $\sim 10^{22}/\text{cm}^3$ order); consequently, it is considered that even a small impurity potential can easily cause an anomalous state above or below the Fermi surface and that such new states on the surface have strong effects on the neutralization. However, the above computational results are mainly discussed from the viewpoints of the local effects of adsorbates; thus, it should be noted that a nonlocal effect associated with a macroscopic surface property has a considerable effect on the RCT neutralization. Actually, it has been found that adsorbates such as alkali metal play very important roles in the reduction of the surface work function because the presence of a dipole layer created by small coverages of alkali atoms on metal considerably modifies the surface work function. Since the RCT neutralization strongly depends on the relative energy position between the atomic and Fermi level, the reduction of the surface work function due to the presence of the alkali metal dipole layer causes a change in the relative energy position between the two, which easily leads to the direction of the RCT neutralization. Indeed, it is reported that such a reduction of the surface work function can markedly enhance the negative ion formation. Consequently, further calculations including local and nonlocal effects are necessary to explain various RCT neutralization experiments.
**Analysis of RCT by Heisenberg Equations of Motion**

Table I. Values of $E^{(j)}$ and $g_j$ for $V_0 = 0$, $-10$, and $10$ meV.

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§4. Conclusion

We have examined the neutralization process, focusing particularly on the values of $n_{aa}(\infty)$ under various conditions. To evaluate these values, we have proposed a new method, that is, simultaneous differential equations directly derived from Heisenberg equations of motion that can accurately simulate the time-dependent behaviors of electrons and ions.

When calculating, we usually have a fixed bandwidth $D$ with varying $N$ as illustrated in Figs. 3–5. From these results, it is disclosed that the energy interval of surface electrons is a key to make the calculation scheme convergent and smooth. An energy interval of less than 10 meV seems to lead to convergent and stable results from our experience. Furthermore, it is considered that more precise and credible results will be given under the condition that $N$ is sufficiently large (order of $10^3$) and the energy interval of surface electrons is less than about 1 meV.
On the basis of our proposed model, it is possible to evaluate \( n_{aa}(\infty) \) numerically even when the new perturbative Hamiltonians such as impurity potential are introduced into the nonperturbative Hamiltonian composed of Eqs. (2.4)–(2.6). Additionally, complicated calculations including time-dependent terms such as \( E_a(t) \) or \( V_a(t) \) are possibly performed without any integral procedures. Since our theoretical approach, as stated in the previous section, is based on the transformation of the Heisenberg operators (\( Q \)-number) into \( c \)-number such as \( \langle \hat{a}^+_i(t)\hat{a}_j(t) \rangle \) after combining the Heisenberg equations of motion with the differential form of \( \hat{a}^+_i(t)\hat{a}_j(t) \), the merit of our proposed method can, therefore, be easily applied to the calculations of \( n_{aa}(\infty) \) including a new perturbative Hamiltonian or complicated time-dependent terms because it is written not in integral forms but in simultaneous differential equations. Numerical solutions can be obtained by solving these differential equations after substituting analytically evaluated terms of \([\hat{a}^+_i(t), \hat{H}]\) and \([\hat{a}_j(t), \hat{H}]\) into Eq. (2.3).

Concerning the theoretical method using the same differential form, we can also mention the electronic bath approach proposed by McDowell,\(^{35}\) which is to divide the orbitals into three parts, those for an ion, a primary zone, and an electronic bath. In this approach, differential equations corresponding to an electronic bath are removed using an approximated memory kernel and driving term. This method yields accurate results for a semi-infinite Hückel chain; however, it also seems that this approach requires complicated analytical procedures for calculation of the system including a perturbative Hamiltonian.

Additionally, from the theoretical viewpoint to treat RCT neutralization and the Landau-Zener process, it seems important to refer to the work of Tsuneyuki et al.\(^{36}\) They investigated the finite band effect of target states on the charge exchange process at the solid surface on the basis of the semiclassical time-dependent Anderson Hamiltonian. By carrying out numerical calculations of a set of independent integro-differential equations to be derived by introducing the time development operator \( \tilde{U}(t, t_0) \), they concluded that the width and DOS of the surface band have considerable effects on the charge-transfer process. In particular it is disclosed that the scattering time \( T \) plays a very important role in the entire process of RCT. To compare their work with ours, we investigated the velocity dependence on RCT assuming a timeindependent energy level of a singly charged ion, because the velocity of ion \( v \) is associated with the scattering length \( L \) in the following equation, \( vT \cong 2L \). Although both calculation methods are utterly different, we obtain results similar to theirs: some oscillations are observed in the case of the narrow surface band while no oscillations are observed in the wide band. Through such comparisons, our proposed methods are shown to work.

On the basis of our calculations, it is disclosed that an impurity potential \( V_0 \) as small as \( \pm 10 \) meV has considerable effect on the RCT neutralization, which is considered to be consistent with many experimental results, that is, the RCT neutralization is very sensitive to even small defects or impurities on the surface. The neutralization range shifts leftwards when \( V_0 < 0 \), while it shifts rightwards when \( V_0 > 0 \). Thus, the direction of the shift in the neutralization range may be determined by whether the impurity atom on the surface has an attractive or
repulsive interaction between surface electrons. In addition, the broadening of the neutralization range is observed regardless of the sign of $V_0$. By examining the surface Hamiltonian $\hat{H}_{\text{surface}}$, the strong sensitivity to impurity potential seems to be mainly ascribed to the localized state caused by even slight perturbation of $V_0$. Since such a presence of localized state usually disappears when the energy interval of surface electrons is larger than $V_0$, the strong sensitivity is associated with the relationship between the energy intervals of surface electrons and the value of $V_0$. Actually, the energy intervals of surface electrons in metal are much smaller than our setting value; the localized states in the vicinity of the Fermi surface caused by slight perturbation such as lattice defects or a trace amount of impurity atoms on the surface may have a strong effect on the RCT neutralization. The screening effects as pointed out by Kondo\textsuperscript{37} seem to play important roles in the RCT neutralization. However, as stated in the previous section, it should be noted that we mainly examined the local effects such as impurity potential caused by adsorbates. Nonlocal effects that reduce the work function on the surface should be considered in further calculations because even a small amount of alkali metal adsorbates easily forms dipoles on the surface resulting in a marked reduction of the work function.

Concerning the reoccupation of new energy level schemes after RCT neutralization, it should be noted that holes in the band structure are mainly formed in the vicinity of the incoming ion level. Such a readjustment in electron occupation after scattering is considered as the result of resonance tunneling neutralization. Additionally, Eq. (2·16) as shown below, can be applicable to all the cases we have investigated in this study,

$$\frac{d}{dt}n_{aa}(t) + \frac{d}{dt} \sum_k n_{kk}(t) = 0.$$  

This means that the total number of electrons after neutralization is preserved even in the presence of impurity potential.

Finally, as already stated in the preceding paragraph, small energy intervals of surface electrons can yield accurate and reliable calculation results. Additionally, calculations under various DOS seem possible if we are able to take large $N$; thus simulations can possibly explain the experimental results quantitatively. However, it should be noted that we are usually required to solve $(N + 1)^2$ simultaneous differential equations when the system consists of $N$ surface electrons and an ion. For example, $(N + 1)^2 = 10,201$ simultaneous differential equations have to be solved numerically if we examine the time-dependent behaviors of a system composed of 100 surface electrons and a singly charged ion.

Actually, let us consider the experimental case of the neutralization of $K^+$ scattered from Cs/Cu(110) ⟨110⟩ by Kimmel et al.\textsuperscript{9} As shown in their report, the ion survival probability, i.e., ISP is less than unity within the range of $2.6 \, \text{eV} < \phi < 4.6 \, \text{eV}$ ($\phi$ : work function); thus, the number of band electrons required to perform the precise simulation of $K^+$ behavior in the range of $2.6 \, \text{eV} < \phi < 4.6 \, \text{eV}$ is roughly estimated to be more than $(4.6-2.6) \, \text{eV}/0.01 \, \text{eV} = 200$ because of the energy intervals of band electrons being less than 10 meV in our calculations. This means that more than $200^2 \sim 40,000$ simultaneous differential equations have to be solved.
numerically. However, it is impossible to evaluate such a huge number of simultaneous differential equations (more than 40000 simultaneous differential equations) using our computer because of the long calculation time and the computer’s capacity; accordingly, we focused on a very small number of electrons in this article for the purpose of mainly investigating the trend of the neutralization under various conditions. Consequently, a fast algorithm to solve a huge number of simultaneous differential equations accurately such as FFT is strongly desirable from the viewpoints of more accurate simulations.

References
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