Application of the Orthogonality Theorem to the Motion of a Charged Particle in Metals. II

Kosaku Yamada, Akio Sakurai, Sasuke Miyazima and Hae Sun Hwang

Research Institute for Fundamental Physics
Kyoto University, Kyoto 606
*Department of Physics, Kyoto Sangyo University, Kyoto 603
**Department of Engineering Physics, Chubu University
Kasugai, Aichi 487
***Department of Physics, Dongeui University
San-24, Gaya-Dong, Busanjin-Ku, Busan 601, Korea

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The diffusion of charged heavy particles in metals is discussed by the method of the density matrix, extending the Kagan-Klinger theory to include electron-particle interaction. This method can be applied to both cases of band-like and hopping-like diffusions. The diffusion of the particles at low temperatures is determined by electron-particle scattering and the overlap integral between two electron clouds situated at different sites. The overlap integral between two electron clouds is extended to the system with two partial wave components of $T$-matrix at each site.

§ 1. Introduction

When a charged heavy particle moves in metals, electron clouds screening it play an essential role. This effect has been observed in the diffusion process of positive muons, $\mu^+$, in Cu and Al metals; at low temperatures the diffusion constant of muons is a decreasing function of temperature $T$. Recently Kondo and one of the authors have independently explained the temperature dependence as $T^{2K-1}$ ($K \leq 1/2$), in terms of overlap integral of electron clouds and electron-muon interaction. Here, $K$ is the exponent of the overlap integral between the initial $(i)$ and the final $(f)$ ground states in the conduction electron system, when the charged particle changes the position. The overlap integral is given by

$$|\langle f | i \rangle| = (\Delta_c / D)^K.$$  \hspace{1cm} (1.1)

This is a generalized Anderson orthogonality theorem, where $D$ is the band width of the conduction electrons and $\Delta_c$ is a cutoff parameter often replaced here by temperature $T$ (we use units of $\hbar = 1$ and $\hbar = 1$). We note that the exponent $K$ is generally expressed in terms of scattering matrices of a local potential at the Fermi surface, $\hat{S}(0)$, as

$$K = -\frac{1}{8\pi^2} \text{Tr} \log^2[\hat{S}_f(0)\hat{S}_i^+(0)],$$  \hspace{1cm} (1.2)

where $f$ and $i$ refer to the final and initial states, respectively.

Recently we have given a closed form solution for the hopping rate by extending the Nozières-Dominicis theory. The hopping rate in the system screened by conduction electrons with only $s$-symmetry is written as
Application of the Orthogonality Theorem

\[ \nu = \frac{\tilde{f}_0^2}{\sqrt{\pi} D} \left( \frac{\pi T}{D} \right)^{2K-1} \Gamma(K)/\Gamma\left(\frac{1}{2} + K\right), \]  

(1.3)

where \( \Gamma(x) \) and \( \tilde{f}_0 \) are the gamma function and the tunneling matrix element reduced by the particle-lattice coupling, respectively. \( K = 2K_0 \) is given by the following expression:

\[ K_0 = \frac{1}{\pi^2} \left\{ \tan^{-1}\frac{\sqrt{1-x^2}}{\sqrt{1+x^2}} \right\}^2, \]  

(1.4)

where \( \delta \) is the phase shift of s-wave at the Fermi energy; \( x = j_0^2(k_F a) \), \( j_0 \) being the spherical Bessel function with \( l = 0 \). If we expand \( K_0 \) given by (1.4) up to the second-order terms with respect to potential \( \rho V = -\tan\delta/\pi \), (1.3) coincides with that given by Kondo. 3) Expression (1.4) for \( K_0 \) coincides with our previous result 8) (hereafter referred to as I) obtained from the generalized expression (1.2), as expected. In connection with the problem of the macroscopic quantum coherence, one can obtain the same expression,9) assuming a boson-like dissipative term. However, if we treat correctly the electron clouds screening the charged particle, \( K \) should be written by the phase shift at the Fermi surface and its value is limited to be less than one-half for a particle with a unit charge of \( \pm e \). 4,8) In paper I, the condition for the localization of the charged particle was derived. The localization can be realized for the case \( K \geq 1 \), such as two-\( d \)-hole bound state in transition metals. 8)

In the previous papers 6,8) giving a closed form of \( K \), we have treated spherical symmetrical potentials by taking into account only one partial wave scattering. In this paper we extend our result to include another partial wave, which is firstly assumed relatively small. The lowest order contribution to \( K \) from the added scattering wave is obtained in a closed form (§ 2). Meanwhile, in calculating the expansion series of \( K \) we notice a partial-wave dependent factor which connects two scattering matrices at separated positions. Since a factor related to angular momentum dependence was overlooked in our previous result 8) for a single partial-wave scattering except the case \( l = 0 \), we correct it for the case \( l \neq 0 \), although the closed form expression giving \( K_0 \) remains unchanged.

To discuss the motion of a charged particle in metals in a more general way, we employ here the equation for the density matrix, which was applied by several authors 10,11) to the diffusion of heavy particles but without electron-particle interaction. Before applying the method of density matrix, we use a canonical transformation to eliminate the electron-particle coupling term with excitation energy larger than thermal energy \( T \). The purpose of employing the equation for the density matrix by Kagan-Klinger is to make possible to treat the both cases corresponding to band-like and hopping-like diffusions. The band (hopping)-like diffusion is defined here as the case where the mean free path of the particle is larger (smaller) than the lattice spacing \( a \). According to our result, the diffusion process changes continuously from band-like one to hopping-like one and is written in a unified expression (§ 3). It may be possible to observe the band-like diffusion in the systems with large tunneling matrix elements such as \( \mu^+ \) in Al and \( d \)-holes in transition metals. If tunneling matrix elements are fixed to a small value, the band-like diffusion can be realized when \( K \) is much smaller than unity. This point will be discussed in the last section (§ 4).
§ 2. Overlap integral between two electron clouds

The factor $K$ given by (1·2) can be expanded as

$$K = -\frac{1}{8\pi^2} \sum_{n=2}^{\infty} \sum_{m=1}^{n-1} \frac{(-1)^n(A\bar{B} + \bar{A} + \bar{B})^n}{m(n-m)},$$

where $\bar{A} = \bar{S}_f - 1$ and $\bar{B} = \bar{S}_i^+ - 1$. Here, by our assumption $S$-matrix $\bar{S}_i$ is spherical symmetric with respect to the center of site $i$ and $\bar{S}_f$ with spherical symmetry around site $f$ is the same operator as $\bar{S}_i$ displaced by $\alpha$.

As an example, we consider the following term:

$$\text{Tr} \bar{A}\bar{B} = \sum_{l,m} \langle flm|\bar{A}\bar{B}|flm\rangle = \sum_{l,m}(e^{2i\delta_i} - 1)\langle flm|\bar{B}|flm\rangle,$$

where $|flm\rangle$ represents spherical wave function $|fklm\rangle$ centered at site $f$ and $\delta_i$ is the phase shift of the spherical wave function with angular momentum $l$. Operator $\bar{B} = \bar{S}_i^+ - 1$ is centered at site $i$ and $\langle flm|\bar{B}|flm\rangle$ can be rewritten as

$$\langle flm|\bar{B}|flm\rangle = \sum_{Q_k} \langle flm|k\rangle e^{ik\cdot a} \sum_{l',m'} \langle k|il'm'\rangle (e^{2i\delta_{l'} - 1})$$

$$\times \sum_{Q_{k'}} \langle il'm'|k'\rangle e^{-ik'\cdot a} \langle k'|flm\rangle$$

$$= \sum_{l',m'} (e^{2i\delta_{l'}} - 1) \sum_{m'_{l'-l}} |X_{l'm'l'm'}|^2.$$ (2·3)

Here, the wave number $k$ for the plane wave $|k\rangle$ and spherical wave $|klm\rangle$ is fixed to that on the Fermi surface by (1·2). The factor $X_{lm,l'm'}$ is rewritten by spherical functions as

$$X_{lm,l'm'} = (-1)^l \sum_{i=0}^{\infty} i^{i+l'+l_1} (ka) \int_0^{\pi} d\theta_k \sin \theta_k \int_{-\pi}^{\pi} d\varphi_k Y_l^m(\theta_k, \varphi_k)$$

$$\times Y_l'^{m'}(\theta_k, \varphi_k) Y_{l_1}^0(\theta_k, \varphi_k) = X_{lm,l'm'} \delta_{m'm'}.$$ (2·4)

Now we use the following relation between spherical functions and 3-$j$ symbols which are related to the Clebsh-Gordan coefficients:

$$\int_0^{\pi} \sin \theta \int_{-\pi}^{\pi} d\varphi Y_l^m(\theta, \varphi) Y_{l_1}^{m_1}(\theta, \varphi) Y_{l_2}^{m_2}(\theta, \varphi)$$

$$= [(2l+1)(2l_1+1)(2l_2+1)/4\pi]^{1/2} \binom{l_1 \ l_2 \ l_3}{l_1 \ l_2 \ l_3} \binom{l \ l'}{m \ -m}.$$ (2·5)

By using (2·4) and (2·5), we represent $X_{lm,l'm'}$ by the 3-$j$ symbols.

$$X_{lm,l'm'} = \sum_{i=0}^{\infty} i^{i+l'-l_1} (2l+1) j_{i_1}(ka)$$

$$\times (-1)^m \sqrt{(2l+1)(2l'+1)} \binom{l \ l' \ l_1}{0 \ 0 \ m} \binom{l \ l' \ l_1}{m \ -m \ 0}. $$ (2·6)
In the above expression, \( l \) should satisfy the conditions to give finite contributions:
\[
l + l' + l = \text{even} \tag{2.7}
\]
and
\[
|l - l'| \leq l \leq (l + l') \tag{2.8}
\]
Hereafter, we discuss the two cases with \( l' = l \) and \( l' \neq l \). For the case with \( l' = l \), we put
\[
I_{l}^{m} = i^{l}j_{l}(ka)(2l+1)(2l+1)(1)^{m}
\begin{pmatrix}
l & l & l & l
0 & 0 & m & 0
\end{pmatrix},
\tag{2.9}
\]
\[
0 \leq l \leq 2l.
\tag{2.10}
\]
For example,
\[
I_{0}^{m} = j_{0}(ka),
\tag{2.11}
\]
\[
I_{2}^{m} = -15(-1)^{m}j_{2}(ka)
\begin{pmatrix}
1 & 1 & 2
0 & 0 & m & 0
\end{pmatrix},
\tag{2.12}
\]
\[
I_{2}^{1+1} = j_{2}(ka),
\tag{2.13}
\]
\[
I_{2}^{1-1} = -2j_{2}(ka),
\tag{2.14}
\]
where \( j_{l}(x) \) is a spherical Bessel function and \( k = k_{F} \). From (2.6), (2.9) and (2.10), \( X_{lm,lm} \) is given by
\[
X_{lm,lm} = \sum_{l=0}^{2l} I_{l}^{m}.
\tag{2.15}
\]
Here, we put
\[
x_{l}^{m} = |X_{lm,lm}|^{2} = \sum_{\vec{k}} \langle \vec{k} | e^{i\vec{k} \cdot \vec{a}} | \vec{k} | f_{l}^{m} \rangle \tag{2.16}
\]
They are given by
\[
x_{0}^{0} = j_{0}^{2}(ka),
\tag{2.17}
\]
\[
x_{1}^{\pm 1} = \{j_{0}(ka) + j_{2}(ka)\}^{2},
\tag{2.18}
\]
\[
x_{1}^{0} = \{j_{0}(ka) - 2j_{2}(ka)\}^{2}.
\tag{2.19}
\]
For the case with \( l' \neq l \), we put
\[
y_{lm}^{m} = |X_{lm,l'm'}|^{2} = \sum_{\vec{k}} \langle \vec{k} | e^{i\vec{k} \cdot \vec{a}} | \vec{k} | f_{l'm'} \rangle \tag{2.20}
\]
where \( X_{lm,l'm'} \) is given by (2.6). For example,
\[
X_{00,10} = \sqrt{3} j_{1}(ka)
\tag{2.21}
\]
and
\[
y_{01}^{0} = 3j_{1}^{2}(ka).
\tag{2.22}
Thus, we obtain the factor $<flm|\bar{B}|fl'm'>$ as

$$<flm|\bar{B}|fl'm'> = <lm|\bar{B}|l'm'>\delta_{mm'},$$

$$<lm|\bar{B}|l'm'> = \sum_{\tau_n}(e^{-2i\tau_n} - 1)X_{lm,l''m}X_{l''m,l'm'},$$

$$X_{l''m,l'm} = X^{*}_{l'm,l''m}.$$ \hfill (2·23) \hfill (2·24) \hfill (2·25)

In paper I, we discussed the case without coupled terms between the phase shifts with different symmetry. In that case, $K$ is given by

$$K = 2\sum_{l,m}K_0(x_{l,m}, \delta) ,$$ \hfill (2·26)

where $x_{l,m}$ is given by (2·16). In I, $K$ was given by $2(2l+1)K_0(x, \delta)$, which is correct for the case with $l=0$, but not for the case with nonzero $l$ and should be replaced by (2·26).

In this paper we include the coupled terms between two phase shifts $\delta_\ell$ and $\delta_\ell'(\delta_\ell \gg \delta_\ell')$, and obtain the expression for $K$ up to the first order term with respect to $\delta_\ell'$ as

$$K = 2\sum_{l,m}K_0(x_{l,m}, \delta_\ell) + 2\sum_{l,l',m}L(x_{l,m}, \delta_\ell)\gamma^{l_\ell'l_\ell'}\delta_\ell',$$ \hfill (2·27)

where we have included the spin degeneracy. $K_0(x, \delta)$ is given by (1·4). Here, we obtain $L(x, \delta)$ in a closed form with $\delta = \delta_\ell$ and $\delta' = \delta_\ell'$. Now, we put

$$A = <fl|\bar{A}|fl> = e^{2i\delta} - 1 ,$$ \hfill (2·28)

$$B = <il|\bar{B}|il> = e^{-2i\delta} - 1 = A^{*} ,$$ \hfill (2·29)

and

$$A' = <fl'|\bar{A}|fl'> = e^{2i\delta'} - 1 ,$$ \hfill (2·30)

$$B' = <il'|\bar{B}|il'> = e^{-2i\delta'} - 1 = A'^{*} ,$$ \hfill (2·31)

where $|A|, |B|, |A'|, |B'|$, by the assumption of $\delta \gg \delta'$. From (2·1), we obtain the coefficient of $y\delta'$ in the series expansion form of $x$ by using a similar method to that used in I. It is given up to the second order terms as

$$L(x, \delta)\gamma\delta' = \frac{y\delta'}{\pi x}\left\{-2\delta - x[\delta(1 + \tan^2\delta) - \tan\delta]
+x^2\left[\delta\left(-\frac{3}{4} + \frac{1}{2}\tan^2\delta - \frac{3}{4}\tan^4\delta\right) + \frac{3}{4}(1 + \tan^2\delta)\tan\delta\right] + \cdots\right\} .$$ \hfill (2·32)

On the other hand, $K_0(x, \delta)$ can be expanded in the series of $x$ as follows. \hfill (2·33)

$$K_0(x, \delta) = \frac{1}{\pi x}\left\{\delta^2 - \delta x \tan\delta - \frac{x^2}{4}\tan\delta[\delta(1 + \tan^2\delta) - \tan\delta]
+ \frac{x^3}{8}\tan\delta\left[\delta\left(-1 + \frac{2}{3}\tan^2\delta - \tan^4\delta\right) + (1 + \tan^2\delta)\tan\delta\right] + \cdots\right\} .$$

Comparing (2·32) with (2·33), we can obtain the following relation:

$$L(x, \delta) = -\frac{2}{\tan\delta}\frac{\delta}{dx}K_0(x, \delta) .$$ \hfill (2·34)
Application of the Orthogonality Theorem

This relation can be derived also by the following consideration: If \( K_0(x, \delta) \) is expanded with respect to \( \delta \), the lowest order term of the coefficient of \( x^n \) is given by \( a_n(x\delta^2)^n \). If we expand \( L(x, \delta)y\delta' \) in a similar way and put \( y = x \) and \( \delta' = \delta \), (2·32) should give \( 2na_n \) for the coefficient of \( (x\delta^2)^n \)-term. This relation can be derived from (2·34). Moreover, it should be noted that terms in the square bracket giving the coefficient of \( x^n \)-term begin with \( \delta^{2n-1} \)-term in the expansion form of (2·33). For example, \( x^2[\delta(1 - \tan^2 \delta) - \tan \delta] \) begins with \( x^2\delta^3 \). Combined with this result, the first order term of \( \tan \delta \) in front of the square bracket gives the \( \delta^{2n-1}x^n \)-term. If square brackets had lower order terms than \( \delta^{2n-1} \), the coefficient of \( x^n \) would begin with a lower order term than \( \delta^{2n} \). This result contradicts (2·1). Therefore, terms in square brackets should begin with \( \delta^{2n-1} \)-term. Thus, we can see that the factor \( \tan \delta \) in front of square brackets of (2·33) is the special one that gives the first order term in the expansion of \( \delta \), while terms with \( \tan \delta \) in brackets give rise to \( \delta^{2n-1} \)-term \((n \geq 2) \). We can assume this factor in front of square brackets remains as the first order terms of \( \delta' \) in (2·32) with the factor \( 2n \) from symmetry consideration. Thus, we obtain relation (2·34), which gives \( L(x, \delta) \) as

\[
L(x, \delta) = -\frac{2}{\pi} \tan^{-1} \left[ \frac{\sqrt{1 - x\tan \delta}}{\sqrt{1 + x\tan^2 \delta}} \right] \sqrt{(1 - x)(1 + x\tan^2 \delta)}.
\]

(2·35)

This is shown in Fig. 1 as a function of \( \delta \) for typical values of \( x \).

§ 3. Diffusion of charged particles in metals

In this section we study the diffusion of charged heavy particles in metals. Fujii and Uemura\textsuperscript{11) }discussed the diffusion of muons in iron metal by using the density matrix for muons. They took into account the effects of the lattice distortion around muons and muon-phonon scattering, following the small polaron theory developed by Kagan and Klinger.\textsuperscript{10) }However, at low temperatures, the interaction between charged heavy particles and electrons plays an essential role\textsuperscript{21-24} and should be included in addition to the coupling with lattice distortion.

First, we neglect the coupling with lattice for the present and consider the interaction with conduction electrons. In this case, our system can be described by the following Hamiltonian:

\[
H = \varepsilon_0 \sum_n a_n^+ a_n + \sum_{n,m} J_{nm} a_n^+ a_m + \sum_{k,\sigma} \varepsilon_k c_{k\sigma}^+ c_{k\sigma} \\
+ \sum_{n,k,k',\sigma} V_{kk'} e^{i(k-k')R_n} c_{k\sigma}^{+} c_{k'\sigma} + \varepsilon_0 \sum_n a_n^+ a_n.
\]

(3·1)
Operator $a_m$ is the annihilation operator for the heavy particle at site $m$, which tunnels to another site $n$ with matrix element $J_{nm}$; $c_{k\sigma}$ is that for conduction electron with energy $\varepsilon_k$ and momentum $k$. The last term represents the intra-site Coulomb interaction between the particle and electrons. Now, to study the effect of conduction electrons on the diffusion of heavy particles, we use boson-approximation for the conduction electron system and then perform a canonical transformation to eliminate the boson-particle coupling term.\(^{(13)}\) We define boson operators for electron-hole pair excitations,\(^{(14)}\) as

\[
 b_k^+ = c_{k'}^+ c_{k}<, \tag{3·2}
\]

\[
 b_k = c_{k<}^+ c_{k'>}, \tag{3·3}
\]

\[
 \omega_k = \varepsilon_{k'} - \varepsilon_{k<}, \tag{3·4}
\]

where subscript $k'$ and $k<$ mean that $k'(k)$ is outside (inside) the Fermi surface. The index $\lambda$ stands for electron-hole pair with momentum $k'$ and $k<$ with spin $\sigma$. Then, (3·1) can be rewritten as

\[
 H = \varepsilon_0 \sum_n a_n^+ a_n + \sum_{n,m} J_{nm} a_n^+ a_m + \sum_\lambda \omega_\lambda b_\lambda^+ b_\lambda
 + \frac{1}{\sqrt{N}} \sum_{n,\lambda} \omega_\lambda X_\lambda^n a_n^+ a_n (b_\lambda^+ + b_{-\lambda}^+), \tag{3·5}
\]

where $\omega_\lambda X_\lambda^n$ is the particle-boson coupling constant.

To eliminate the particle-boson coupling term for $|\omega_\lambda| > T$, we use the following canonical transformation:\(^{(13)}\)

\[
 Q = U^+ q U, \tag{3·6}
\]

\[
 U = \exp \left[ \frac{1}{\sqrt{N}} \sum_{n,\lambda} X_\lambda^n a_n^+ a_n (b_\lambda^+ + b_{-\lambda}^+) \right]. \tag{3·7}
\]

By this transformation, (3·5) is rewritten as

\[
 H = \sum_n \varepsilon_n A_n^+ A_n + \sum_{n,m} J_{nm} A_n^+ A_m \theta_n^+ \theta_m
 + \sum_\lambda \omega_\lambda B_\lambda^+ B_\lambda + \frac{1}{\sqrt{N}} \sum_{n,\lambda} \omega_\lambda X_\lambda^n A_n^+ A_n (b_\lambda^+ + b_{-\lambda}^+), \tag{3·8}
\]

where

\[
 A_n = U^+ a_n U, \tag{3·9}
\]

\[
 A_n^+ A_n = U^+ a_n^+ a_n U = a_n^+ a_n, \tag{3·10}
\]

\[
 B_\lambda = U^+ b_\lambda U, \tag{3·11}
\]
Application of the Orthogonality Theorem

\[ \theta_n = \exp \left[ -\frac{1}{\sqrt{N}} \sum_{|\omega_k| > T} X_k^n (B_k - B_{-k}) \right] \]  

(3.12)

and

\[ \tilde{\varepsilon}_n = \varepsilon_n - \frac{1}{N} \sum_{|\omega_k| > T} \omega_k |X_k^n|^2. \]  

(3.13)

The last term of (3.8) corresponds to the following electron-particle interaction in the original system:

\[ \sum_{k,k',\sigma} V_{kk'} e^{i(k-k')\cdot r_n} c_{k,\sigma}^+ c_{k',\sigma} A_n^+ A_n. \]  

(3.14)

We have assumed in the boson representation for conduction electrons that the electron-particle interaction can be divided into two parts depending on its excitation energy compared with thermal energy \( T \). This division is natural and can be understood in the following way. Electron-hole pair excitations with lower energy than thermal energy \( T \) cannot follow the tunneling motion of particles and gives rise to a non-adiabatic potential to the particles through thermal fluctuations. On the other hand, excitations with higher energy than \( T \) follows the tunneling motion of particles through the electron-particle coupling. This effect increases the effective mass of the particles. But it remains to be a finite value, because the overlap integral of electron clouds does not vanish due to the finite cutoff parameter \( T \). Thus, we can generally divide the effects of conduction electrons on the diffusion of charged particles into the reduction of tunneling matrix element and the non-adiabatic electron-particle interaction.

Combining the particle-electron interaction discussed above and the coupling with lattice distortion treated by Kagan-Klinger, we obtain the following Hamiltonian:

\[ H = H_0 + H', \]  

(3.15)

\[ H_0 = \sum_n \tilde{\varepsilon}_n |n\rangle \langle n| + \sum_{n, g \neq 0} |n + g\rangle \langle \tilde{\beta} (T) | n\rangle + H_E + H_L, \]  

(3.16)

\[ H' = \sum_n (|n\rangle \langle \tilde{\beta} (\tau T^e) + \tilde{\beta} (\tau T^e) \rangle + \sum_{g \neq 0} |n + g\rangle \langle \tilde{\beta} (T) - \tilde{\beta} (T)\rangle | n\rangle. \]  

(3.17)

A charged particle \(|n\rangle\) at site \( n \) with effective energy \( \tilde{\varepsilon}_n \) tunnels to nearest sites \( n + g \) with effective matrix element \( \tilde{\beta} (T) \), accompanying the lattice distortion and electron cloud. The Hamiltonians \( H_E \) and \( H_L \), corresponding to the third term of (3.8), are those for conduction electron and lattice systems with their distortions around the particle, respectively. The first term \( \tilde{\beta} (\tau T^e) \) of (3.17) shows a non-adiabatic intra-site interaction between conduction electrons and the charged particle, which is given by (3.14). The second term \( \tilde{\beta} (\tau T^e) \) is that for phonons, which was derived by Kagan-Klinger. The second term of (3.16) represents the coherent tunneling of the charged particle without any excitations, while the last term of (3.17) denotes incoherent tunneling accompanying simultaneous excitations in the electron and/or phonon systems. By using the adiabatic
approximation for electron clouds with excitation energy higher than $T$ and lattice distortion, we obtain the effective tunneling matrix element $\tilde{J}(T)$ reduced by the coupling with lattice distortions and electron clouds; it is given by

$$\tilde{J}(T) = J_0 e^{-S(T)}(T/D)\kappa,$$

(3.18)

where $\exp[-S(T)]$ is the overlap integral between neighboring lattice distortions and tends to a finite value at low temperatures. The factor $(T/D)\kappa$ represents the overlap integral between electron clouds situated at neighboring sites, and corresponds to thermal average of $\langle \theta_n^+ \theta_m^- \rangle$ of (3.8) in the boson approximation. Here we have put $\Delta_c = T$ in (1.1) giving the overlap integral of electron clouds, since the Fermi surface broadening due to thermal fluctuation is the largest cutoff parameter in the usual case. If $\tilde{J}(T)$ is larger than $T$ at very low temperatures it can be the largest cutoff parameter, as discussed in the final section.

Now, we derive the equation of motion for density operator $\rho_{nm}$ for a charged heavy particle in a site-representation. The standard equation for the density matrix is given by

$$\dot{\rho} = [H_0 + H', \rho].$$

(3.19)

Here, we use an adiabatic approximation for electron clouds and lattice distortion. After taking the trace over conduction electron and phonon variables, we obtain the following result within the second-order in $H'$:

$$\frac{\partial \rho_{lm}}{\partial t} + i\tilde{J} \sum_{g \neq 0} (\rho_{l+gm} - \rho_{lm+g}) = -\mathcal{Q}_{lm} \rho_{lm}, \quad (l = m)$$

(3.20)

$$\frac{\partial \rho_{ll}}{\partial t} + i\tilde{J} \sum_{g \neq 0} (\rho_{l+gl} - \rho_{ll+g}) = -I_{ll}.$$ (3.21)

$\mathcal{Q}_{lm}$ is a damping factor for the site-offdiagonal element of the density matrix. It is determined by the average square fluctuation of the relative position of energy levels in neighboring well due to the intra-site electron-particle and phonon-particle interactions. $^{10}$

$$\mathcal{Q}_{lm} = \pi \sum_{\nu, \beta} \delta(E_\nu - E_\beta) \{ |\tilde{V}_{\nu}^\beta|^2 + |\tilde{V}_{\nu}^\beta|^2 - 2 \tilde{V}_{\nu}^\beta \tilde{V}_{\nu}^\beta \tilde{V}_{\nu}^\beta \tilde{V}_{\nu}^\beta \},$$

(3.22)

where $\tilde{V}_{\nu} = \tilde{V}_{\nu}^e + i \tilde{V}_{\nu}^i$ and $\nu$ and $\beta$ represent excitations in electron and phonon systems.

The right-hand side of (3.21), $I_{ll}$, gives the damping term of diagonal element of $\rho$ and gives rise to the so-called incoherent diffusion at high temperatures near the Debye temperature. It is given by $^{10,11}$

$$I_{ll} = \sum_{\nu, \beta, g} 2\pi H_{\nu, g}^* H_{\nu, g} (\rho_{ll} - \rho_{l+gl+g}) \delta(E_\nu - E_\beta) = 2\Gamma(T) \sum_{g} \langle \rho_{ll} - \rho_{l+gl+g} \rangle = I.$$ (3.23)

This equation defines $\Gamma(T)$, which is discussed in the Appendix.

To solve (3.20) and (3.21), we define $\rho_n(\mathbf{k})$ as the Fourier transform of $\rho_{ll-n}$.

$$\rho_n(\mathbf{k}) = \frac{1}{N} \sum_{l} e^{-ik\cdot l} \rho_{l-n}.$$ (3.24)
In such a mixed representation, \( (3\cdot20) \) for \( \mathbf{n} = \mathbf{g} \) can be written as

\[
\frac{\partial \rho_{\mathbf{g}}}{\partial t} + i \mathcal{J} \rho_{\mathbf{g}}(\mathbf{h}) [e^{-i \mathbf{k} \cdot \mathbf{g}} - 1] + i \mathcal{J} \sum_{\mathbf{g} \neq \mathbf{g}} \rho_{\mathbf{g} + \mathbf{g}'}(\mathbf{h}) [e^{i \mathbf{k} \cdot \mathbf{g}' - 1}] = -\mathcal{Q} \rho_{\mathbf{g}}(\mathbf{h}) ,
\]

where we have put \( \mathcal{Q} = \mathcal{Q}_{\mathbf{g}} \). If the density matrix in \( (3\cdot25) \) is determined by waves with \( |\mathbf{k}| \ll a^{-1} \) and the characteristic time of the density matrix evolution is large compared with \( \mathcal{Q}^{-1} \), the following relation between \( \rho_{\mathbf{g}}(\mathbf{h}) \) and \( \rho_{\mathbf{0}}(\mathbf{h}) \) can be derived from \( (3\cdot25) \),

\[
\rho_{\mathbf{g}}(\mathbf{h}) \approx -\frac{\mathcal{J}}{\mathcal{Q}} (\mathbf{k} \cdot \mathbf{g}) \rho_{\mathbf{0}}(\mathbf{h}) .
\]

From \( (3\cdot21) \), we obtain the following equation in the mixed representation:

\[
\frac{\partial \rho_{\mathbf{0}}(\mathbf{h})}{\partial t} + i \mathcal{J} \sum_{\mathbf{g} \neq \mathbf{0}} \rho_{\mathbf{g}} [e^{i \mathbf{k} \cdot \mathbf{g}' - 1}] = -i \mathcal{Q} \rho_{\mathbf{0}}(\mathbf{h}) .
\]

By inserting \( (3\cdot26) \) into \( (3\cdot27) \), we obtain the following equation for \( \rho_{\mathbf{0}}(\mathbf{h}) \):

\[
\frac{\partial \rho_{\mathbf{0}}(\mathbf{h})}{\partial t} = -k^2 (D_c + \Gamma) \rho_{\mathbf{0}}(\mathbf{h}) ,
\]

\[
D_c = \frac{za^2}{3} \frac{\mathcal{J}^2}{\mathcal{Q}} ,
\]

where \( z \) is the number of nearest neighbor sites for tunneling motion of the particle. The result \( (3\cdot28) \) can be applied not only to band-like diffusion but also to hopping-like diffusion, as stressed by Kagan et al.\(^{10,11} \) For the latter case, we can solve \( (3\cdot20) \) and \( (3\cdot21) \) also in the site-representation. We assume that we find a particle at site \( \mathbf{l} \) at the time \( t = 0 \). Then \( \rho_\mathbf{u} \) can be determined by the equation,

\[
\frac{\partial \rho_\mathbf{u}}{\partial t} = -(z \mathcal{J}^2 a^2 / \mathcal{Q} + \Gamma) \rho_\mathbf{u} .
\]

Equations \( (3\cdot28) \) and \( (3\cdot30) \) give the same diffusion rate except a numerical factor. Thus we obtain the diffusion rate as

\[
\nu \approx \frac{\mathcal{J}^2}{\mathcal{Q} + \Gamma a^2} .
\]

Now, we confine ourselves to the low temperature region, compared with the Debye temperature. At low temperatures, non-adiabatic electron scattering on a particle gives main contributions to the damping factor \( \mathcal{Q} \), which is given by

\[
\mathcal{Q} = \pi \sum_{\mathbf{k}, \mathbf{k}'\neq 0} f(\epsilon_{\mathbf{k}}) (1 - f(\epsilon_{\mathbf{k}'}) \delta(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}'}) \{ |V_{\mathbf{m} h, \mathbf{h}'}|^2 + |V_{\mathbf{m} h, \mathbf{h}'}|^2 - 2 V_{\mathbf{m} h, \mathbf{h}'} V_{\mathbf{m} h, \mathbf{h}'} \} .
\]

If it is assumed that \( \tilde{V}_{\mathbf{m} e} \) has a spherical symmetry around site \( \mathbf{m} \) and only the s-wave part gives main contributions, \( \mathcal{Q} \) is given by

\[
\mathcal{Q} = 4\pi (\rho V_0)^2 (1 - j_0^2(k_F a)) T .
\]

In more general case, \( \mathcal{Q} \) is given by

\[
\mathcal{Q} = 4\pi \sum_{\mathbf{i}, \mathbf{m}} (\rho V_0)^2 (1 - x_i a^2) + \sum_{\mathbf{i}, \mathbf{i}', \mathbf{m}} \rho V_0 V_{\mathbf{i} \mathbf{i}' \mathbf{m}} \} T ,
\]
where \( x_i^m \) and \( y_i^n \) are given by (2.16) and (2.20), respectively, \( V_i \) being the \( l \)-wave part of \( V^{kk'} \) in the partial wave expansion. If we include higher order terms of \( \rho V_i \), we would obtain the general result,

\[
Q = 2\pi KT,
\]

where \( K \) is given by (1.2). By combining (3.18), (3.31) and (3.35), we obtain the following diffusion rate at low temperatures:

\[
\nu = \frac{J_0^2 e^{-2S (T/D)^2K}}{2\pi KT} = \frac{J_0^2 e^{-2S}}{2\pi KD (T/D)^{2K-1}}.
\]

This result coincides with that obtained before \(^2,4,6\) and explains the experimental results. \(^2\) Here it should be noted that we cannot determine a numerical pre-factor of (3.36), since the overlap integral (1.1) is given within the logarithmic accuracy \(^5,7\) though it includes all the logarithmic terms. An approach beyond the logarithmic accuracy for the overlap integral is developed by Ohtaka and Tanabe. \(^15\)

\section*{§ 4. Conclusion and discussion}

According to the Kagan-Klinger theory, diffusion rate \( \nu \) for the coherent diffusion is given by

\[
\nu = \frac{J_0^2}{Q}.
\]

This result holds also for the hopping-like diffusion as well as for the band-like diffusion. In the previous section we have confined ourselves to the case where temperature \( T \) is the largest cutoff parameter for the overlap integral of electron clouds screening the charges of heavy particles. However, we must consider other cutoff parameters to be compared with thermal energy \( T \) at very low temperatures.

In the band-like diffusion, mean free path \( l \) is larger than site-distance \( a \) and charged particles change the sites in the time interval of \( J^{-1} \). In this case electron-hole pair excitations with energy smaller than \( J \) cannot follow the motion of charged particles. Therefore, \( J \) is a cutoff parameter of the overlap integral. For the temperatures lower than \( J \), cutoff parameter \( \Delta_c \) should be given by \( J \) instead of \( T \). Thus, we obtain the following results for the band-like diffusion \((l/a = J/Q = \nu/J > 1)\),

\[
\nu = \frac{J_0^2 (T/D)^{2K}/Q}{Q} \quad \text{for} \quad T > J,
\]

\[
\nu = \frac{J_0^2 (J_0/D)^{2K(1-K)}/Q}{Q} \quad \text{for} \quad T < J.
\]

On the other hand, for the hopping-like diffusion with \( l \leq a \) charged particles change the trapping sites in the time interval of \( \nu^{-1} \). In this case electron-hole pair excitations within the energy region smaller than \( \nu \) cannot follow the charged particles. If \( T \) is smaller than \( \nu \) in this case, \( \nu \) should be put as the cutoff parameter of the overlap integral. Thus, we obtain the following hopping rate for the hopping-like diffusion:

\[
\nu = \frac{J_0^2 (T/D)^{2K}/Q}{Q} \quad \text{for} \quad T > \nu,
\]

\[
\nu = D \left( \frac{J_0^2}{D} \frac{J_0}{Q} \right)^{1/(1-2K)} \quad \text{for} \quad J_0 < T < \nu.
\]
The above discussion is general. Now we consider the case where damping factor \( Q \) is given by \( 2\pi KT \) due to the electron scattering. In this case \( Q \) itself depends on temperature. Since \( 2K \) is always smaller than unity for a heavy particle having a unit charge,\(^{5,6}\) we have the inequality:

\[
Q \leq \pi T \quad (2K \leq 1)
\]

At very low temperatures, if \( \nu > \tilde{J} > \pi T \geq Q \), band-like diffusion is realized. The diffusion rate is given by

\[
\nu = J_0^2 (\tilde{J}_0/D)^{2K(1-K)} / 2\pi KT \quad \text{for} \quad \pi T \leq \tilde{J}.
\]

When we increase the temperature, \( \pi T \) becomes larger than \( \tilde{J} \). For this case, \( \nu \) is given by

\[
\nu = J_0^2 (\pi T/D)^{2K} / 2\pi KT
\]

for

\[
\pi T > \tilde{J} > Q.
\]

This situation is realized for the case with \( K \ll 1 \) and may be possible in systems such as \( \mu^+ \) in Al metal.\(^6\) If we increase further the temperature, \( Q \) proportional to \( T \) becomes larger than \( \tilde{J} \) proportional to \( T^{2K} \).

If

\[
\pi T > Q > \tilde{J} > \nu,
\]

\[
\nu = J_0^2 (\pi T/D)^{2K} / 2\pi KT \quad \text{(4.11)}
\]

Here, both the cases of (4.8) for band-like diffusion and (4.11) for hopping-like one give the same temperature dependence proportional to \( T^{2K-1} \). Thus, band-like diffusion changes continuously to hopping-like one at \( \tilde{J}/Q = \nu/\tilde{J} = 1 \) with increasing temperature, in contrast to the statement by Kondo.\(^9\)

In Ref. 4), Yamada obtained \( Q = 4\pi \rho^2 V_0^2 T \) by calculating the scattering probability of muons on electrons. In that case the mass of muons was assumed to be infinity and the dispersion of muon band was neglected. Therefore, value \( \tau^{-1} = 4\pi \rho^2 V_0^2 T \) can be regarded as the decay rate of Bloch state in the case of band motion as well as level width of the trapping state in the case of the hopping motion.\(^{16}\) In this paper, we found \( Q = 2\pi KT \) by applying Kagan-Klinger method to the tight-binding model of the charge density located in the region \( k^{-1} = L \gg l = \tilde{J}_0/\tilde{Q} \). In the hopping case, \( 2\pi KT \) is rigorous.\(^{5,6}\) In the band-like motion, there are other cases not given by (4.8). If \( l \), mean free path of Bloch states is larger than \( L \), or if muons make a continuous motion, mean free time \( \tau_o = (4\pi \rho^2 V_0^2 T)^{-1} \) determines the diffusion of the particle. Thus, the difference in \( Q \) comes from the type of diffusion process. Moreover, the constant factor of the diffusion coefficient is also related to the non-singular terms of the overlap integral, which cannot be determined within the present theory.

The interesting case with small \( K \) is realized in systems where many partial waves contribute to screening the charged particles.\(^{5,8}\) In this paper we have extended the expression for \( K \) to more general one with other partial waves added to the \( s \)-wave,
though it is given only up to the first order terms with respect to the smaller phase shifts in coupled terms, which give a negative contributions for $K$ (see (2·35)).

For $\mu^+$ in Al metal, $p$-waves as well as $s$-wave seem to screen the charged particles to give a small $K$ value. In the case of $d$-hole in transition metals, $\bar{J}$ is not so small compared with conduction band width $D$ and $(\bar{J}/D)^K$ is not very small. In this case the band-like motion can be easily realized with a certain mass correction due to screening. As shown in this paper, hopping-like diffusion continuously changes to band-like one. We expect that band-like diffusion will be found in many systems.

**Appendix**

Here we discuss the physical meaning of incoherent diffusion (3·23) by using the boson representation for both of electron and lattice systems. By this approximation $H'_{tt+g}^{\nu\bar{\nu}}$ is given by

\begin{equation}
H'_{tt+g} = \bar{J} - \bar{J}(T) = J_0\{\theta t^+\theta t+g - \langle \theta t^+\theta t+g \rangle \langle \xi t^+\xi t+g \rangle \}. \tag{A·1}
\end{equation}

$\zeta$ is given by

\begin{equation}
\zeta_n = \exp \left[ -\frac{1}{\sqrt{N}} \sum_{\mu} Y_{\mu n}(B_{\mu +} - B_{\mu -}) \right], \tag{A·2}
\end{equation}

where $Y_{\mu n}$ is the coupling constant between the particle and lattice distortion. The thermal average $\langle \theta t^+\theta t+g \rangle$ and $\langle \xi t^+\xi t+g \rangle$ are given by

\begin{align}
\langle \theta t^+\theta t+g \rangle &= (T/D)^K, \tag{A·3} \\
\langle \xi t^+\xi t+g \rangle &= e^{-S(t)}. \tag{A·4}
\end{align}

Equation (A·1) can be rewritten as

\begin{align}
(A·1) &= J_0\{\theta t^+\theta t+g - \langle \theta t^+\theta t+g \rangle \langle \xi t^+\xi t+g \rangle + J_0\langle \theta t^+\theta t+g \rangle \langle \xi t^+\xi t+g \rangle - \langle \xi t^+\xi t+g \rangle \}
\end{align}

\begin{align}
&+ J_0\langle \theta t^+\theta t+g - \langle \theta t^+\theta t+g \rangle \rangle \langle \xi t^+\xi t+g \rangle}
\end{align}

The first term of (A·5) represents the tunneling motion of the particle accompanying excitations in the electron system, the second term is that in phonon system and the last term is that accompanying excitations in both of electron and phonon systems. The first term gives the following contributions to the hopping rate:

\begin{align}
\Gamma_1 &= J_0^2 e^{-2S(t)} \int_{D-1}^{T-1} dt \left\{ \left( \frac{1}{D} \right)^{2K} - \left( \frac{T}{D} \right)^{2K} \right\} \\
&\approx J_0^2 e^{-2S(t)} \left( \frac{T}{D} \right)^{2K-1} \frac{1}{D} \frac{2K}{D - 2K}. \tag{A·6}
\end{align}

This incoherent term accompanying electron-hole pair excitations vanishes at $K=0$.

The second and third terms give the contributions to the hopping rate:

\begin{align}
\Gamma_2 + \Gamma_3 &= J_0^2 \int_{D-1}^{T-1} dt \left( \frac{1}{D} \right)^{2K} \{ \exp[\Psi(t)] - 1 \}, \tag{A·7}
\end{align}
Application of the Orthogonality Theorem

where energy conservation is satisfied in the sum of electron-hole and phonon excitations. \(\Psi(t)\) is given by \(^{(10)}\)

\[
\Psi(t) = \sum_{\mu} \frac{2|W_\mu|}{\sinh(\omega_\mu/2T)} \frac{(1 - \cos k \cdot a) \cos \omega_\mu t}{\sinh(\omega_\mu/2T)},
\]

where \(W_\mu\) is the dimensionless component of the distortion field near the particle for the \(\mu\)-th normal mode.

References

1) J. Kondo, Physica 84B (1976), 40, 207.