The Relation between the Electric Conductance of Nanostructure Bridge and Friedel Sum Rule

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Abstract. We analyze the electric conductance through nanostructure bridges in terms of phase-shifts, which satisfy the Friedel sum rule. The phase-shifts are given by solving the eigenvalue equation obtained by extending the method applied to a single impurity problem in a metal. The local charge neutrality condition is introduced through the Friedel sum rule. It is analytically shown that the electric conductance can increase as the two electrodes separate with the condition in which the phase-shifts satisfy the Friedel sum rule. The increment of the distance between two electrodes is obtained by gradually separating interatomic distance.

1. Introduction

Recently, the electron transport through a nanostructure bridging two electrodes has been a subject of considerable investigation. In the experiments involving Al and Pt, the increment of the electric conductance has been observed as the two electrodes separate and this phenomena has theoretically investigated.1,2 Most of theoretical studies have been based on the electronic states calculations. Among them, there has been a theory based on the phase-shifts analysis with the Friedel sum rule (FSR).3 Datta and Tian have discussed the single orbital case with the inversion symmetry of the whole system based on the phase-shifts analysis.4 Moreover Makoshi, Shima and Otsuka have extended their study to general case.5

In an atomic contact, the charge neutrality is very important to understand the behavior of the electric conductance.7,8 In the tight-binding approximation, this effect can be self-consistently corrected imposing local charge neutrality.7,8 It is considered that the charge relates electric conductance, because some experiments is reproduced by imposing the charge neutrality condition on the models. However the electric conductance described by general calculation does not involve the information about local charge.

On the other hand, the electric conductance described by the phase-shift is directly related to charge through the FSR. Moreover the phase-shift analysis can analytically introduce the charge neutrality condition. Consequently, we consider that phase-shift analysis gives more understanding of the electron transport property through a nanostructure bridges.

In this paper, we analyze the electric conductance through nanostructure bridges in terms of phase-shifts and construct the theory directly relating to the charge through the FSR. The phase-shifts are given by solving the eigenvalue equation obtained by extending the method applied
to a single impurity problem in a metal. It is analytically shown that the electric conductances through nanostructure bridges consisting of an atom such as Al and Pt can increase when the distance between two electrodes is larger when the phase-shifts satisfy the FSR. We suppose that increment of the distance between two electrodes is obtained by gradually separating interatomic distance. This workshop was supported in part by the Grant-in-Aid for the Global COE Program “The Next Generation of Physics, Spun from Universality and Emergence” from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan.

2. Formalism

The Green’s function theory applicable to the nonequilibrium system is employed to formulate the electric conductance. We calculate the conductance at 0 bias limit. The relation between Green’s functions and phase-shifts are obtained by the extending method applied to a single impurity problem in a metal. It is analytically shown that the electric conductances with electron correlation, as long as the electric conductance is represented by the phase-shifts, can be obtained as

$$ G(\omega) = (\omega - H + i0)^{-1}. $$

The expression of the electric conductance at 0 bias limit, i.e., in the linear response regime, $\sigma = (2e^2/h)\bar{\sigma}$, can be obtained as

$$ \bar{\sigma} = 4\text{Tr}^C[\Delta^L(\epsilon_F)G^C(\epsilon_F)\Delta^R(\epsilon_F)G^C\dagger(\epsilon_F)], $$

where $\epsilon_F$ is the Fermi energy at electrodes. $\text{Tr}^C$ is taken over the states in bridging part. Here, $G^C(\omega)$ is the bridging part of the full retarded Green’s function $G(\omega)$. This is given by

$$ G^C(\omega) = (\omega - H^C_0 + i0 - \Sigma)^{-1}, $$

$$ \Sigma(\omega) = \Lambda(\omega) - i\Delta(\omega) $$

with the retarded free Green’s function of the bridging part $g$. The self-energy part $\Sigma(\omega) = \Lambda(\omega) - i\Delta(\omega)$ is given by

$$ \Delta_{cc'}(\omega) = \Delta_{cc'}^L(\omega) + \Delta_{cc'}^R(\omega) $$

$$ = \pi \sum_l V_{cl}V_{lc'}\delta(\omega - \epsilon_l) + \pi \sum_r V_{cr}V_{rc'}\delta(\omega - \epsilon_r). $$
We define the phase-shifts $\phi_\alpha(\omega)$ which satisfy the FSR, by the extending Langreth’s method given by Makoshi, Shima and Otsuka as

$$G^C(\omega)G^C(\omega) = e^{2i\phi_\alpha(\omega)} \bar{u}^\alpha,$$

where $\bar{u}^\alpha$ is an eigenvector. The phase-shifts take a value from 0 to $\pi$. We obtain the excess electron number due to the contact $N_{el}(\epsilon_F)$ by the phase-shifts defined in eq.(10) as

$$N_{el}(\epsilon_F) = -\frac{1}{\pi} \int_{-\infty}^{\epsilon_F} d\omega \text{ImTr}[G(\omega) - G_0(\omega)]$$

$$= \frac{2}{\pi} \sum_\alpha \phi_\alpha(\epsilon_F).$$

Here, $G_0(\omega)$ is defined as

$$G_0(\omega) = \begin{pmatrix} G_{01}^L(\omega) & 0 & 0 \\ 0 & G_{02}^R(\omega) & 0 \\ 0 & 0 & G_{03}^R(\omega) \end{pmatrix},$$

$$G_{01}^{L(R)}(\omega) = (\omega - H_{01}^{L(R)} + i0)^{-1}.$$

In our calculation, we introduce the charge neutrality condition through the FSR as

$$Z = N_{el}(\epsilon_F),$$

where $Z$ is the total number of valence electrons.

The simple expression of the electric conductance at 0 bias limit, i.e., in the linear response regime, $\sigma = G_0\bar{\sigma}$, is obtained as follows:

$$\bar{\sigma} = 4 \sum_\alpha \sin^2 \phi_\alpha [\hat{P}^\dagger \Delta_L \hat{P}^\dagger \Delta_R \hat{P}] + \sum_{\alpha > \beta} \sin^2 (\phi_\alpha - \phi_\beta) [\hat{P}^\dagger (\Delta_L - \Delta_R) \hat{P}]^2_{\alpha \beta}. $$

Here the matrix $\hat{P}$ ($N \times M$) is given by

$$\hat{P} = (\bar{u}^1, \ldots, \bar{u}^M),$$

where $N$ is the total number of sites and atomic orbitals in the bridging part, and $M$ is the number of the phase-shifts contributing to the electric conductance.

3. Examples

We investigate two concrete examples. In these models, we suppose that increment of the distance between two electrodes is obtained by gradually separating interatomic distance. We impose the charge neutrality condition on the phase-shifts through the FSR.

3.1. Single atom bridge with Al-like character

First example is a contact consisting of an atom with $sp$-orbitals such as Al atomic contact shown in Fig.1. We can write $H_0^C$ and $\Delta$ as

$$H_0^C = \begin{pmatrix} \epsilon_s & 0 & 0 & 0 \\ 0 & \epsilon_s & 0 & 0 \\ 0 & 0 & \epsilon_x & 0 \\ 0 & 0 & 0 & \epsilon_y \end{pmatrix},$$

and
\[ \Delta = \begin{pmatrix} \Delta_{spz}^L + \Delta_{spz}^R & 0 \\ 0 & \Delta_{xy}^L + \Delta_{xy}^R \end{pmatrix}, \] (19)

\[ \Delta_{spz}^L = \begin{pmatrix} a_1 & a_3 \\ a_3 & a_2 \end{pmatrix}, \quad \Delta_{spz}^R = \begin{pmatrix} a_1 & -a_3 \\ -a_3 & a_2 \end{pmatrix}, \quad \Delta_{xy}^L = \Delta_{xy}^R = \begin{pmatrix} b_1 & 0 \\ 0 & b_2 \end{pmatrix}. \] (20)

Now we neglect the effect of \( \Lambda \) for simplicity. In this model, we can show that four phase-shifts \( \varphi_s, \varphi_z, \varphi_x \) and \( \varphi_y \) contribute to the conductance as

\[ \bar{\sigma} = \sin^2 \varphi_s + \sin^2 \varphi_z + \sin^2 \varphi_x + \sin^2 \varphi_y - 2 \frac{a_3^2}{a_1 a_2} \sin \varphi_s \sin \varphi_z \cos(\varphi_s - \varphi_z). \] (21)

The electric conductance of eq.(21) takes a value between 0 and \( 4G_0 \). The phase-shifts are defined as

\[ \cot \varphi_s = -\frac{\epsilon_m F - \epsilon_s}{a_1}, \quad \cot \varphi_z = -\frac{\epsilon_m F - \epsilon_z}{a_2}, \quad \cot \varphi_x = -\frac{\epsilon_m F - \epsilon_x}{b_1}, \quad \cot \varphi_y = -\frac{\epsilon_m F - \epsilon_y}{b_2}. \] (22)

In this model, we impose the charge neutrality condition through the FSR as

\[ 3 = \frac{2}{\pi}(\varphi_s + \varphi_z + \varphi_x + \varphi_y). \] (23)

Here the change of the site energy from isolated system corresponding to \( p_x \) is smaller than the ones of \( s- \) and \( p_z- \)orbitals and the matrix element corresponding to the \( \pi \)-bond \( (b_1) \) is smaller than the ones corresponding to the \( \sigma \) bonds, because the broadening of the wave function of \( p_x \)-orbitals in the direction of electrodes is smaller than the ones of \( s- \) and \( p_z- \)orbitals. The same is true of \( p_y \)-orbital. Therefore it is considered that \( \varphi_x \) and \( \varphi_y \) are nearly equal to 0 and the contributions of the phase-shifts corresponding to \( \pi \)-bond is very little under the condition that the phase-shifts satisfy the FSR. Thus \( \varphi_s \) and \( \varphi_z \) mainly contribute to the electric conductance and the electric conductance becomes

\[ \bar{\sigma} = \sin^2 \varphi_s + \sin^2 \varphi_z - 2 \frac{a_3^2}{a_1 a_2} \sin \varphi_s \sin \varphi_z \cos(\varphi_s - \varphi_z), \] (24)

and the FSR is represented as

\[ 3 = \frac{2}{\pi}(\varphi_s + \varphi_z). \] (25)

The relationship between \( \varphi_s \) and \( \varphi_z \) is given by eq.(25) as

\[ \cot \varphi_s = \tan \varphi_z, \] (26)

\[ \varphi_s, \varphi_z, \varphi_x \text{ and } \varphi_y \text{ are nearly equal to 0 and the contributions of the phase-shifts corresponding to } \pi \text{-bond is very little under the condition that the phase-shifts satisfy the FSR. Thus } \varphi_s \text{ and } \varphi_z \text{ mainly contribute to the electric conductance and the electric conductance becomes} \]

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\[ \cot \varphi_s = \tan \varphi_z, \] (26)

Figure 1. Sketch of system considered here. The bridge is the contact consisting of an atom with \( sp \)-like character. We consider four orbitals in this model, however we draw only three orbitals \( s- \), \( p_z- \) and \( p_x- \) orbital in this figure.
or equivalently,
\[ \frac{a_1}{\epsilon_F - \epsilon_s} = \frac{\epsilon_F - \epsilon_z}{a_2}. \]  

Finally, the electric conductance is represented as
\[ \bar{\sigma} = 1 - \frac{a_3^2}{a_1a_2} \sin^2 2\varphi_z. \]  

We notice that the electric conductance cannot exceed \( 1G_0 \). Here we discuss the increment of the electric conductance when the distance between two electrodes increases. The increment of the distance is obtained by gradually increasing interatomic distance in our work. In other words, this effect is expressed by taking limit value of parameters \((a_1 \text{ and } a_2 \text{ tend to } 0)\). In a simple treatment, the phase-shifts in eqs.(22) take values 0 or \( \pi \) when the parameters tend to 0. We notice that the phase-shifts do not satisfy the FSR in this treatment. However when the numerator in the right-hand side takes a value 0 (for example \( \epsilon_F - \epsilon_z = 0 \)), the phase-shift is allowed to take a value \( \pi/2 \) as the limit value. Considering these results, there is the only allowable solution that \( \varphi_z \) tends to \( \pi/2 \) and \( \varphi_s \) tends to \( \pi \). Actually in eq. (27), the matrix element corresponding to \( s \)-orbital \((a_1)\) converges to 0 faster than that corresponding to \( p_z \)-orbital \((a_2)\), because the wave function of \( p_z \)-orbital is broader than that of \( s \)-orbital. It is shown the solution that the phase-shift takes a value \( \pi/2 \) is reasonable.

Therefore the phase-shift \( \varphi_z \) tends to \( \pi/2 \) and the electric conductance approaches to \( 1G_0 \) leading to the increment, when the matrix elements \((a_1 \text{ and } a_2 \text{ tend to } 0)\) under the condition that the phase-shifts satisfy the FSR. This phenomenon is interpreted by the FSR and this result is consistent with the experiments.\(^{1,2}\)

3.2. Single atom bridge with Pt-like character

Second example is a contact consisting of Pt atom with \( sd \)-orbital shown in Fig.2. We can write \( H_0^C \) as

\[ H_0^C = \begin{pmatrix} \epsilon_s & 0 & 0 & 0 & 0 & 0 \\ 0 & \epsilon_{3z^2-r^2} & 0 & 0 & 0 & 0 \\ 0 & 0 & \epsilon_{yz} & 0 & 0 & 0 \\ 0 & 0 & 0 & \epsilon_{zx} & 0 & 0 \\ 0 & 0 & 0 & 0 & \epsilon_{xy} & 0 \\ 0 & 0 & 0 & 0 & 0 & \epsilon_{x^2-y^2} \end{pmatrix}. \]  

**Figure 2.** Sketch of system considered here. The bridge is the contact consisting of an atom with \( sd \)-like character. We consider the six orbitals in this model, however we draw only three orbitals \( s^- \), \( d_{xy} \) and \( d_{yz} \)-orbital in this figure.
Then $\Delta$ is written as

$$\Delta = \begin{pmatrix} \Delta_\sigma & 0 & 0 \\ 0 & \Delta_\pi & 0 \\ 0 & 0 & \Delta_\delta \end{pmatrix},$$

$$\Delta_\sigma = \begin{pmatrix} a_1 \\ a_3 \\ a_2 \end{pmatrix}, \quad \Delta_\pi = \begin{pmatrix} b \\ 0 \\ b \end{pmatrix}, \quad \Delta_\delta = \begin{pmatrix} c \\ 0 \\ c \end{pmatrix},$$

where $\Delta_\sigma$, $\Delta_\pi$ and $\Delta_\delta$ correspond to $\sigma$-, $\pi$- and $\delta$-bond between electrodes and bridging part respectively. Again we neglect the effect of $\Lambda$ for simplicity. Because of the symmetry of this model, one can consider that the site energies corresponding to $\pi$-bond degenerate (i.e. $\epsilon_{yz}=\epsilon_{zx}=\epsilon_\pi$). Also those corresponding to $\delta$-bond degenerate (i.e. $\epsilon_{xy}=\epsilon_{x^2-y^2}=\epsilon_\delta$). Moreover because of the strength of the interaction between each atomic orbital and electrodes, Fermi energy and the site energies have the relationship as follows:

$$\epsilon_\pi > \epsilon_\delta > \epsilon_s > \epsilon_{3z^2-r^2}. \quad (32)$$

We can show that only four phase-shifts $\varphi_8$, $\varphi_{3z^2-r^2}$, $\varphi_\pi$ and $\varphi_\delta$ contribute to the conductance as

$$\bar{\sigma} = \sin^2 \varphi_8 + \sin^2 \varphi_{3z^2-r^2} + 2 \sin^2 \varphi_\pi + 2 \sin^2 \varphi_\delta. \quad (33)$$

The electric conductance eq.(33) obviously takes a value between 0 and $6G_0$. The phase-shifts are, respectively, defined as

$$\cot \varphi_{3z^2-r^2} = \frac{-(a_1E_{3z^2-r^2} + a_2E_s) \pm \sqrt{(a_1E_{3z^2-r^2} - a_2E_s)^2 + 4a_3^2E_{3z^2-r^2}E_s}}{a_1a_2 - a_3^2}, \quad (34)$$

$$E_{3z^2-r^2} = \epsilon_\pi - \epsilon_{3z^2-r^2}, \quad E_s = \epsilon_\pi - \epsilon_s, \quad (35)$$

$$\cot \varphi_\pi = \frac{\epsilon_\pi - \epsilon_\delta}{b}, \quad (36)$$

$$\cot \varphi_\delta = \frac{\epsilon_\pi - \epsilon_s}{c}. \quad (37)$$

In this model, we impose the charge neutrality condition through the FSR as

$$10 = \frac{2}{\pi} (\varphi_8 + \varphi_{3z^2-r^2} + 2\varphi_\pi + 2\varphi_\delta). \quad (38)$$

Considering eq.(32), the equations (34)-(37) take negative values. Therefore the phase-shifts have the following relationship.

$$\frac{\pi}{2} \leq \varphi_\delta < \varphi_\pi < \varphi_{3z^2-r^2} < \varphi_8 < \pi \quad (39)$$

To elucidate the behavior of the electric conductance just before the Pt atomic contact fractures by the increment of the distance between electrodes, we discuss the Pt system under the condition that the distance between electrodes is larger than the equilibrium distance. When the distance increases, each phase-shift tends to $\pi$ with the condition that they satisfy the relationship in eq.(39). Here we discuss the electric conductance in the range that three phase-shifts $\varphi_8$, $\varphi_{3z^2-r^2}$ and $\varphi_\pi$ are regarded as nearly equal. Therefore the electric conductance and the FSR become

$$\bar{\sigma} = 4 \sin^2 \varphi_\pi + 2 \sin^2 \varphi_\delta, \quad (40)$$
Finally, the electric conductance is represented as

\[ \bar{\sigma} = 2 \left( \sin \varphi_{\delta} - \frac{1}{2} \right)^2 + \frac{3}{2}. \]  

(42)

Therefore the electric conductance of an atomic contact consisting of sd-orbital does not exceed \(2G_0\) under the condition that the phase-shifts satisfy the FSR.

Furthermore we notice that when the matrix elements of \(\Delta\) tend to 0 under the condition that the phase-shifts satisfy the FSR, there is the only allowable solution that \(\varphi_{\delta}\) tends to \(\pi/2\) and the other phase-shifts tend to \(\pi\). This result is derived by a similar reason in the discussion about Al contact. Therefore the electric conductance increases towards \(2G_0\). This result agree with the experiment involving Pt.\(^2\)

4. Conclusion

We have analytically studied the electric conductance through nanostructure bridges consisting of an atom with sp-orbital and sd-orbital. We have analytically introduced the charge neutrality through the FSR. We have treated that increment of the distance between two electrodes is gradually separating interatomic distance. We suggest that the Friedel sum rule can leads to a guiding principle for interpretation of the phenomena in these contacts.

The electric conductance of an atomic contact consisting of atoms with sp-orbital such as Al can take a value from 0 to \(4G_0\). However, we have shown that the electric conductance does not exceed \(1G_0\) under the condition that the phase-shifts satisfy the FSR. Furthermore, when the matrix elements of \(\Delta\) tend to 0 under the condition that the phase-shifts satisfy the FSR, the electric conductance increases to \(1G_0\). In the same way, we have analytically shown the behavior of an atomic contact consisting of atoms with sd-orbital such as Pt. These results are consistent with the results of the experiments.\(^1,\(^2\)

We speculate that the expression given here can be applied even with the electron correlation effect, although we have not dealt with it. The effect would be involved in the actual calculation of the phase-shifts. This point must be studied in near future.

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