Atomic-scale Field-effect Transistor as a Thermoelectric Power Generator and Self-powered Device.

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Using first-principles approaches, we have investigated the thermoelectric properties and the energy conversion efficiency of the paired metal-Br-Al junction. Owing to the narrow states in the vicinity of the chemical potential, the nanojunction has large Seebeck coefficients such that it can be considered an efficient thermoelectric power generator. We also consider the nanojunction in a three-terminal geometry, where the current, voltage, power, and efficiency can be efficiently modulated by the gate voltages. Such current-voltage characteristics could be useful in the design of nano-scale electronic devices such as a transistor or switch. Notably, the nanojunction as a transistor with a fixed finite temperature difference between electrodes can power itself using the Seebeck effect.

I. INTRODUCTION

In the past decade, considerable concern has arisen regarding the transport properties of atomic-scale junctions, which are the basic building blocks for molecular electronics. This concern is motivated by the aspiration to develop new forms of electronic devices based on subminiature structures and by the desire to understand the fundamental properties of electron transport under non-equilibrium conditions. A growing number of research studies are now available to diversify the scope of electron transport properties in molecular/atomic junctions, including current-voltage characteristics, shot noise, local heating, and gate-controlled effects. Substantial progress in experiment and theory has been achieved.

Recently, growing attention has been paid to the thermopower of nanojunctions. Pioneering experiments have been conducted to measure the Seebeck coefficients at the atomic and molecular level. The Seebeck coefficient is related not only to the magnitude, but also to the slope of the transmission function in the vicinity of chemical potentials. Thus, it can provide richer information than the current-voltage characteristics regarding the electronic structures of the molecule bridging the electrodes. The thermoelectric effect hybridizes the electron and energy transport, which complicates the fundamental understanding for quantum transport of electron and energy under non-equilibrium conditions. This has spurred rapid developments in the fundamental thermoelectric theory in nanojunctions, including the effects of electron-vibration interactions and gate-controlled effects. The Seebeck coefficient is typically measured under equilibrium condition, non-equilibrium current and inelastic effects potentially offer new possibilities of engineering systems leading to enhanced the thermopower. The emergence of thermoelectric nanojunctions may also have profound implications on the design of subminiature energy-conversion devices, such as nano-refrigerators.

Thermoelectric power generators in bulk systems employ electron gas as a working fluid. It directly converts thermal energy into electric energy using the Seebeck effect. Provided a temperature difference is maintained across the device, it can generate electric power converted from the thermal energy. In this paper, we explore the energy conversion mechanism of nanojunctions. We present a parameter-free first-principles calculations for a thermoelectric power generator in a truly atomic-scale system. To gain further insight into the mechanism of energy conversion, we also developed an analytical theory for it. As a specific example, we consider an atomic junction depicted in Fig. 1a, where the left and right electrodes serve as independent cold- and hot-temperature reservoirs, respectively. This is not just an academic example since recent studies have demonstrated the capability to assemble one magnetic atom on a thin layer of atoms on the surface of STM. A similar technique might be applicable to a single Al atom adsorbed onto a layer of Br atoms on the metal surface. In this regard, the atomic junction could be formed by bringing two identical pieces of metal-Br-Al surfaces close together before the reconstruction of Br and Al atoms occurs.

As it was found in Ref. 57, the paired metal-Br-Al junction shows interesting device properties, such as negative differential resistance, that utilize the relatively narrow density of states (DOSs) near the chemical potentials. The narrow DOSs are due to the weak coupling between the Al atoms and the electrodes via the “spacer” Br atoms. This junction also serves as an efficient field-effect transistor because the narrow DOSs near chemical potentials can be easily shifted by the gate voltages. As the Seebeck coefficients are relevant to the slope of DOSs, the sharp DOSs result in a large magnitude in the Seebeck coefficient. When a temperature difference is maintained between electrodes in a closed circuit, the Seebeck effect generates an electromotive force (emf), which drives a current flowing through the junction, hence the nanojunction can also be considered as an efficient thermoelectric power generator.

We investigate further the possibility of powering an atomic-scale device as a field-effect transistor using heat instead of electricity. To illustrate this point, we consider the paired metal-Br-Al junction in a three-terminal geometry. When a finite temperature difference is maintained between electrodes, the Seebeck effect converts the
FIG. 1: (color online) (a) Schematics of the thermoelectric junction. The Br-jellium, Al-Br, and Al-Al distance is 1.8, 4.9, and 8.6 a.u., respectively. The Al-Al distance has been significantly enlarged. (b) The directions of electric current I and thermal current J for $S < 0$. Inside the power generator, current travels from the lower to the higher potential, which is opposite of what occurs when the nanojunction is a passive element in a circuit.

electron’s thermal current into the electric current flowing through the nanojunction. We observe that the current’s magnitude, polarity, and power on-off are controllable by the gate field. Such current-voltage characteristics could be useful in the design of nanoscale electronic devices, such as a transistor or switch. The nanojunction, therefore, can be considered a transistor that employs the Seebeck effect to power itself by converting the thermal energy into electric energy. The results of this study may be of interest to researchers attempting to develop new styles of thermoelectric nano-devices.

The flow of the discussion in this paper is as follows. In Sec. II, we describe density functional theory, theory of thermoelectricity, and theory of thermoelectric power generator as a self-powered electronic device. In Sec. III, we discuss the thermoelectric properties of nanojunctions and the thermoelectric power generator as a self-powered device. Finally, we conclude our findings in Sec. IV.

II. THEORETICAL METHODS

We briefly present an introduction of the Lippmann-Schwinger (LS) equation and density-functional theory (DFT) in subsection A. In subsection B, we present the theory of the Seebeck coefficient, electric conductance and thermal conductance. In subsection C, we present the theory to calculate the Seebeck-induced electric current, voltage, power, and efficiency of energy conversion. These quantities are calculated in the truly atomic scale junction in terms of the nonequilibrium scattering wave-functions obtained self-consistently in the framework of DFT+LS calculations. Both DFT+LS and DFT+Keldysh nonequilibrium Green’s function (NEGF) have been applied extensively to a wide range of problems of nonequilibrium quantum transport of device physics problems under finite biases from first-principles approaches. The formal connection between DFT+LS and DFT+NEGF can be found in Ref. [61].

A. Density Functional Theory and Lippmann-Schwinger Equation

We model a nanoscale junction as a passive element formed by two semi-infinite metal with planar surfaces held a fixed distance apart connecting to an external battery of bias $V_B$, with a nano-structured object bridging the gap between them. The full Hamiltonian of the system is $H = H_0 + V$, where $H_0$ is the Hamiltonian due to the biased bimetallic electrodes that we model as ideal metal (jellium model), and $V$ is the scattering potential of a group of atoms bridging the gap. We assume that the left electrode is positively biased such that $V_B = (\mu_R - \mu_L)/e$, where $\mu_L = \mu$ and $\mu_R = \mu + eV_B$ are the chemical potential deep in the left and right electrodes, respectively.

The unperturbed wave functions of the biased bimetallic electrodes have the form, $\Psi_{E\mathbf{K}}^{L(R)}(\mathbf{r}) = e^{i\mathbf{K}\cdot\mathbf{r}_L} u_{E\mathbf{K}}^{L(R)}(z)$, where $\mathbf{r}_L$ is the coordinate parallel to the $z$ direction, and $\mathbf{K}_L$ is the momentum of electron in the plane parallel to the electrode surfaces. We assume that $V_B$ is small and neglect the zeroth-order term in $v_F eV_B$.

The charge density distribution and effective single-particle wave functions $u_{E\mathbf{K}}^{L(R)}(z)$ are calculated in the framework of the density functional formalism by solving the coupled Shrödinger and Poisson equations iteratively until self-consistency is obtained. The wave function describes the electrons incident from the right electrode, satisfying the following boundary condition:

$$u_{E\mathbf{K}}^R(z) = (2\pi)^{-\frac{3}{2}} \times \left\{ \begin{array}{ll}
\frac{1}{\sqrt{k_R}} (e^{-ik_Rz} + R e^{ik_Rz}), & z \rightarrow \infty, \\
\frac{1}{\sqrt{k_L}} e^{-ik_Lz}, & z \rightarrow -\infty.
\end{array} \right.$$  

The group of atoms is considered in the scattering approaches. Corresponding to each of the unperturbed wave functions, a Lippmann-Schwinger equation involving a Green’s function for the biased bimetallic junction is solved in the plane wave basis, where a basis of approximately 2300 plane waves has been chosen for this study.  

\[47\]
where \( \Psi_{E K_{i}}^{L(R)}(r) \) represents the nonequilibrium scattering wave function of the electrons with energy \( E \) incident from the left (right) electrode. The quantity \( G_{E}^{0} \) is the exchange-correlation potential calculated at the level of the left and right electrodes are independent electron density for the total system; and \( \delta n(r) \) is their difference. The wave functions of the entire system are calculated iteratively until self-consistency is obtained\(^{63,64} \).

These right- and left-moving wave functions, weighed with the Fermi-Dirac distribution function according to their energies and temperatures, are applied to calculate the electric current as:

\[
I(\mu_{L}, T_{L}; \mu_{R}, T_{R}) = \frac{e \hbar}{m_{i}} \int dE \int d\mathbf{r}_{\perp} \int d\mathbf{K}_{\parallel} \left[ f_{E}(\mu_{R}, T_{R}) \Gamma_{E,E, K_{\parallel}}^{R R}(\mathbf{r}) - f_{E}(\mu_{L}, T_{L}) \Gamma_{E,E, K_{\parallel}}^{L L}(\mathbf{r}) \right],
\]

where \( \Gamma_{E,E, K_{\parallel}}^{R R}(\mathbf{r}) = \left[ \Psi_{E,K_{\parallel}}^{R}(\mathbf{r}) \right]^{*} \nabla \Psi_{E,K_{\parallel}}^{R}(\mathbf{r}) - \nabla \left[ \Psi_{E,K_{\parallel}}^{R}(\mathbf{r}) \right]^{*} \Psi_{E,K_{\parallel}}^{R}(\mathbf{r}) \) and \( d\mathbf{r}_{\perp} \) represents an element of the electrode surface. Here, we assume that the left and right electrodes are independent electron reservoirs, with the electron population described by the Fermi-Dirac distribution function, \( f_{E}(\mu_{L(R)}, T_{L(R)}) = 1/\{\exp[(E - \mu_{L(R)})/(k_{B}T_{L(R)})] + 1\} \), where \( \mu_{L(R)} \) and \( T_{L(R)} \) are the chemical potential and the temperature in the left (right) electrode, respectively. More detailed descriptions of theory can be found in Refs. 63, 64.

The above expression can be cast in a Landauer-Büttiker formalism:

\[
I(\mu_{L}, T_{L}; \mu_{R}, T_{R}) = \frac{2e}{\hbar} \int dE \tau(E) \left[ f_{E}(\mu_{R}, T_{R}) - f_{E}(\mu_{L}, T_{L}) \right],
\]

where \( \tau(E) = \tau^{R}(E) = \tau^{L}(E) \) is a direct consequence of the time-reversal symmetry, and \( \tau^{R(L)}(E) \) is the transmission function of the electron with energy \( E \) incident from the right (left) electrode,

\[
\tau^{R(L)}(E) = \frac{\pi \hbar^{2}}{m_{i}} \int d\mathbf{r}_{\perp} \int d\mathbf{K}_{\parallel} \Gamma_{E,E, K_{\parallel}}^{R R(L)}(\mathbf{r}).
\]

Note that \( e \) is positive in the definition of Eq. (5).

The electron’s thermal current, defined as the rate at which thermal energy flows from the right (into the left) electrode, is

\[
J_{el}^{R(L)}(\mu_{L}, T_{L}; \mu_{R}, T_{R}) = \frac{2e}{\hbar} \int dE (E - \mu_{R(L)}) \tau(E) \left[ f_{E}(\mu_{R}, T_{R}) - f_{E}(\mu_{L}, T_{L}) \right],
\]

respectively.

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**B. Theory of the Thermoelectric Properties in the Nanoscale Junctions**

We assume that the nanojunction is not connected to external circuit such that \( \mu_{R} = \mu_{L} = \mu \) and \( T_{R} = T_{L} = \)
$T$, and then we consider an infinitesimal current $[dI]_T = I(\mu, T; \mu, T + dT)$ induced by an infinitesimal temperature difference $dT$ in the right electrode [i.e., $T_R = T_L + dT$]. The Seebeck effect generates a voltage difference $dV$ in the right electrode [i.e., $\mu_R = \mu_L + d\mu$] which drives current $[dI]_V = I(\mu, T; \mu + e dV, T)$]. The current cannot actually flow, thus, $(dI)_T$ counterbalances $(dI)_V$ [i.e., $dI = (dI)_T + (dI)_V = 0$]. The Seebeck coefficient (defined as $S = \frac{dV}{dT}$) can be obtained by expanding the Fermi-Dirac distribution functions in $(dI)_T$ and $(dI)_V$ to the first order in $dT$ and $dV$:

$$S = -\frac{1}{eT} \frac{K_1(\mu, T)}{K_0(\mu, T)},$$

where

$$K_n(\mu, T) = -\int dE \tau(E) (E - \mu)^n \frac{\partial f(E, \mu, T)}{\partial E}.$$ (9)

The Seebeck coefficient up to the lowest order in temperatures is,

$$S \approx \alpha T,$$ (10)

where $\alpha = -\pi^2 k_B^2 \frac{\partial \tau(\mu)}{\partial E} / (3e^2 \tau(\mu) \Delta \mathcal{E}).$ Here, we have expanded $K_n(\mu, T)$ to the lowest order in temperatures by using Sommerfeld expansion: $K_0 \approx \tau(\mu)$, $K_1 \approx \frac{\pi^2 k_B^2 \tau(\mu)}{3} T^2$, and $K_2 \approx \frac{\pi^2 k_B^2 \tau(\mu)}{3} T^2$. The Seebeck coefficient is positive (negative) when the slope of transmission function is negative (positive) near the chemical potential.

When a finite temperature difference $\Delta T = T_R - T_L > 0$ is raised in the right electrode, the Seebeck effect generates a finite electromotive force, $emf = [\Delta V(T_L, T_R)]$, raising the potential energy of the charge. We assume that the voltage difference $\Delta V(T_L, T_R)$ is applied to the right electrode such that $\mu = \mu_L$ and $\mu_R = \mu_L + e \Delta V(T_L, T_R)$. The voltage difference $\Delta V(T_L, T_R)$ generated by the temperature difference $\Delta T$ is approximately given by,

$$\Delta V(T_L, T_R) \approx \int_{T_L}^{T_R} S(\mu, T) dT,$$ (11)

where the Seebeck coefficient $S(\mu, T)$ is given by Eq. (8) with $\mu = \mu_L$. Equation (11) becomes exact when $\Delta T \to 0$. The sign of $\Delta V(T_L, T_R)$ depends on the sign of the Seebeck coefficient $S(\mu, T)$. For example, $\Delta V(T_L, T_R) < 0$ for $S < 0$, as shown in Fig. (II.b).

Equation (11) is an approximation when $\Delta T$ is finite. We have to remind ourselves of the fact that the left chemical potential $\mu_L$ differs from the right chemical potential $\mu_R$ when the temperature difference $\Delta T$ is large. In this case, the Seebeck coefficient becomes relevant to both $\mu_L$ and $\mu_R$ with a more complicated form.

$$S(\mu_L, T_L; \mu_R, T_R) = -\frac{1}{e} \frac{K_1(\mu_L, T_L)/T_L + K_1(\mu_R, T_R)/T_R}{K_0(\mu_L, T_L) + K_0(\mu_R, T_R)},$$ (12)

where $K_0(\mu_L, T_L)$ and $K_1(\mu_L, T_L)$ are given by Eq. (9). A more elaborate evaluation of the voltage difference $\Delta V(T_L, T_R)$ can be performed using

$$\Delta V(T_L, T_R) \approx \int_0^{T_R/2} S(\mu - \frac{e \Delta V(T - T, T + T)}{2}, T - T; \mu + \frac{e \Delta V(T - T, T + T)}{2}, T + T) dT,$$ (13)

where $T = (T_L + T_R)/2$, $\Delta T = T_R - T_L$ and $\mu = E_F$.

The induced voltage by the Seebeck effect using Eq. (11) and (13) have been numerically verified, showing that Eq. (11) is a good approximation when the transmission function $\tau(E)$ does not change rapidly around the chemical potentials and when $\Delta T$ is not too large. Accordingly, we evaluate $\Delta V(T_L, T_R)$ throughout this study using Eq. (11) instead of Eq. (13) for simplicity.

Corresponding to the electric current, the extra electron’s thermal current induced by an infinitesimal temperature ($dT$) and voltage ($dV$) across the junctions is,

$$dJ_{el} = (dJ_{el})_T + (dJ_{el})_V,$$ (14)

where $(dJ_{el})_T = J_{el}(\mu, T, \mu, T + dT)$ and $(dJ_{el})_V = J_{el}(\mu, T, \mu + e dV, T)$ can be calculated by Eq. (9). The electron’s thermal conductance (defined as $k_{el} = dJ_{el}/dT$) can be decomposed into two components:

$$\kappa_{el}(\mu, T) = \kappa_{el}^T(\mu, T) + \kappa_{el}^V(\mu, T),$$ (15)

where $\kappa_{el}^T = (dJ_{el})_T/dT$ and $\kappa_{el}^V = (dJ_{el})_V/dT$. Using Sommerfeld expansion, they can be can be written as,

$$\kappa_{el}^T(\mu, T) = \frac{2K_2(\mu, T)}{h},$$ (16)

and

$$\kappa_{el}^V(\mu, T) = \frac{2e}{h} K_1(\mu, T) S(\mu, T),$$ (17)

where $K_1(\mu, T)$ and $K_2(\mu, T)$ are given by Eq. (9). One should note that $\kappa_{el}^V = 0$ if the Seebeck coefficient of the system is zero.
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\[ \text{emf} = V_{AB} = |AV(T_L, T_R)| \]

FIG. 2: (color online) The circuit diagram of the thermoelectric power generator depicted in Fig. (b) as a self-powered electronic device. The thermoelectric nanojunction can be represented as an ideal battery of emf \( V_{AB} \) generated by the Seebeck effect and an internal resistance \( r \) for the nanojunction as an electronic device. We assume that the external resistor \( R \to 0 \) in this study for simplicity.

By expanding \( K_n(\mu, T) \) and \( S(\mu, T) \) to the lowest order in temperatures, Eqs. (10) and (17) become

\[ \kappa_{el}^V \approx \beta_V T^3 \quad \text{and} \quad \kappa_{el}^T \approx \beta_T T, \]

where \( \beta_V = -2\pi^4 k_B^2 \beta(\mu)^2 / (9 h \beta(\mu)) \) and \( \beta_T = 2\pi^2 k_B^2 \beta(\mu) / (3 h) \). In the above expansions, we have applied the Sommerfeld expansions: \( K_1(\mu, T) \approx [\pi^2 k_B^2 \beta(\mu) / 3] T^2 \), \( K_2(\mu, T) \approx [\pi^2 k_B^2 \beta(\mu) / 3] T^2 \), and Eq. (10).

In the limit of zero bias, Eq. (5) yields the electric conductance (defined as \( \sigma(T) = dI/dV \)),

\[ \sigma(T) = \frac{2e^2}{h} \int dE f_E(\mu, T) [1 - f_E(\mu, T)] \tau(E) / (k_B T), \]

which is relatively insensitive to temperatures if tunneling is the major transport mechanism.

C. Theory of the Thermoelectric Power Generator as a Self-powered Electronic Device

In this subsection, we present a closed-circuit theory of the thermoelectric nanojunction as a power generator and a self-powered electronic device by itself. We consider the nanojunction with the Seebeck coefficient \( S < 0 \) and \( \Delta T = T_R - T_L > 0 \) such that the open-circuit Seebeck-effect induced emf is \( |AV(T_L, T_R)| \), as depicted in Fig. (b). Figure (b) can be represented as a circuit diagram shown in Fig. (c) where the thermoelectric junction is considered to consist of an ideal battery of \( V_{AB} \) plus an internal resistance \( r \). The thermoelectric junction employs the Seebeck effect to generate an \( \text{emf} \) and converts thermal energy into electric energy. Concurrently, the nanojunction itself serves as a passive element with resistance \( r \) which consumes electric energy.

We choose clockwise as positive such that the induced current \( I > 0 \) for \( S < 0 \). Beginning at point \( A \) as the current traverses the circuit in the positive direction, we obtain from Kirchhoff’s loop rule,

\[ V_{AB} - Ir - IR = 0, \]

where the open-circuit \( \text{emf} \) is \( V_{AB} = -\Delta V(T_L, T_R) > 0 \) for \( S < 0 \), \( r \) is the internal resistance of the nanojunction, and \( R \) is the resistance of the external resistor, as depicted in Fig. (c). Note that the current \( I \) encounters a potential increase due to the source of \( \text{emf} \) between points \( A \) and \( B \), a potential drop [\( V_{BC} = Ir \)] due to the internal resistance between points \( B \) and \( C \), and a potential drop [\( V_{CA} = IR \)] as the current traverses the external resistor with resistance \( R \) between points \( C \) and \( A \), respectively.

In particular, we carry out this research considering \( R \to 0 \) such that the voltage drop between points \( C \) and \( A \) is \( V_{CA} = IR = 0 \). It yields

\[ V_{AB} = Ir. \]

It implies that external circuit does not consume electric energy because the potential difference across two terminals of the thermoelectric power generators (i.e., the terminal voltage) is zero due to \( R \to 0 \). This simplified scenario helps us to analyze the detailed mechanism of energy conversion between the thermal current and electric current. Such analysis will provide us an insight into the device physics of the thermoelectric junctions as self-powered electronic devices.

The current \( I = \sigma V_{AB} \) can be evaluated by Eq. (21), where \( V_{AB} \) is the Seebeck-effect induced \( \text{emf} = |\Delta V(T_L, T_R)| \) which is evaluated by Eq. (18) and \( \sigma \approx 1/r \) is the conductance of nanojunction [which is evaluated by Eq. (19)]. We have numerically verified and confirmed that \( I = (I)_{\Delta V} = (I)_{\Delta T} \), where

\[ (I)_{\Delta V} = -2e \int dE \tau(E) [f_E(\mu_L + e\Delta V(T_L, T_R), T_L) - f_E(\mu_L, T_L)], \]

and

\[ (I)_{\Delta T} = \frac{2e}{h} \int dE \tau(E) [f_E(\mu_L, T_L + \Delta T) - f_E(\mu_L, T_L)]. \]
Fig. 3 for $S < 0$. We may interpret $(I)_{\Delta T}$ as the current which traverses the thermoelectric nanojunction as a "pure" source of emf generated by the temperature difference $\Delta T$ using the Seebeck effect. Similarly, $(I)_{\Delta V}$ is the current which traverses the nanojunction as an internal resistor. Equations (22) and (23) describe the flow of electrons associated with the probability flux.

\[
(J_{el}^{R(L)})_{\Delta V} = -\frac{2}{h} \int dE (E - \mu_{R(L)}) \tau(E) [f_E(\mu_L + e\Delta V(T_L, T_R), T_L) - f_E(\mu_L, T_L)],
\]

where $\mu_R = \mu_L + e\Delta V(T_L, T_R)$ and $\Delta V(T_L, T_R)$ is given by Eq. (11). Similarly, the $\Delta T$-induced electron’s thermal current carried by the probability current flowing out of the right electrode (into to the left electrode) is,

\[
(J_{el})_{\Delta T} = \frac{2}{h} \int dE (E - \mu_L) \tau(E) [f_E(\mu_L, T_R + \Delta T) - f_E(\mu_L, T_L)],
\]

Note that $(J_{el}^{R})_{\Delta V}$ and $(J_{el}^{L})_{\Delta V}$ are positive and $(J_{el}^{R})_{\Delta V} > (J_{el}^{L})_{\Delta V}$ for $S < 0$. The sign convention defined in Eqs. (22)–(24) comply with the direction depicted in Fig. 1(b) and Fig. 2 for $S < 0$.

Subtracting $(J_{el}^{R})_{\Delta V}$ from $(J_{el}^{L})_{\Delta V}$, we obtain

\[
\Delta P = (J_{el}^{R})_{\Delta V} - (J_{el}^{L})_{\Delta V} > 0,
\]

where $\Delta P$ is the electric power delivered by the thermoelectric junction served as a "pure" battery which employs the Seebeck effect to convert the electron’s thermal current into electric energy. If the external resistor with resistance $R \to 0$, then the external circuit does not consume electric energy. In this case, the nanojunction simultaneously serves as an electronic device which consumes the entire electric power generated by itself,

\[
\Delta P \approx \sigma(\Delta V)^2 \approx \int_{T_L}^{T_R} S dT \int_{T_L}^{T_R} \sigma dT.
\]

Note that Eq. (27) can alternatively be expressed as,

\[
\Delta P = -\Delta V(T_L, T_R) \cdot I(T_L, T_R) > 0.
\]

Eqs. (20)–(25) have been numerically verified to be consistent with each other. If the system is n-type (i.e., $S < 0$), then $\Delta V(T_L, T_R) < 0$ and $I(T_L, T_R) > 0$, as shown in Fig. 1(b). Similarly, if the system is p-type (i.e., $S > 0$), then $\Delta V(T_L, T_R) > 0$ and $I(T_L, T_R) < 0$. Both cases render $\Delta P > 0$.

III. RESULTS AND DISCUSSION

Provided that a finite temperature difference is raised between electrodes, the Seebeck effect will generate an electric current. It is observed that the nanojunction itself can be deemed a field-effect transistor, where gate field can control the current. Thus and so, the atomic junction in three-terminal geometry can be considered as an electronic device which can be self-powered by providing a temperature difference across the junction.

As an a specific example, we consider an atomic-scale junction in a three-terminal geometry as a thermoelectric power generator, depicted in Fig. 6(a). In the paired metal-Br-Al junction, we assume that the distance between two Al atoms is sufficiently large. The interaction between two pieces of metal-Br-Al is minimal, and in this fashion, no rearrangement of atom positions occurs. Accordingly, the phonon’s thermal current could be suppressed because of poor mechanical coupling between two pieces of metal-Br-Al is minimal. We neglect it for simplicity in this study.

A. Thermoelectric Properties of the Junction

In an open circuit, an infinitesimal temperature $dT$ raised in the right electrode induces $(dI)_{T}$ and $(dI)_{V}$, which counterbalance each other. This renders the Seebeck coefficient defined in Eq. (8), as described in subsection IIB.

Correspondingly, the electron’s thermal conductance is defined as $\kappa_{el} = dJ_{el}/dT$, as given by Eq. (15). The electron’s thermal conductance can be decomposed into two components, $\kappa_{el} = \kappa_{el}^{T} + \kappa_{el}^{V}$, where $\kappa_{el}^{T}$ and $\kappa_{el}^{V}$ are given by Eqs. (10) and (17), respectively.

Fig. 3(a) shows that the system is characterized by a sharp transmission function corresponding to a narrow DOSs near the chemical potential. As it was found in Ref. [5], the DOSs become narrower when the distance between two Al atoms increases. The narrow DOSs result in substantial Seebeck coefficients, as shown in Fig. 3(b). It shows that the thermoelectric junction is n-type ($S < 0$) since the narrow DOSs are slightly above the chemical potential and the slope of the transmission $\tau'(\mu)$ is positive. At low temperatures (about $T < 100$ K), the Seebeck coefficients remain linear $(S \approx aT)$, as described in Eq. (10). We present the absolute values of $\kappa_{el}^{T}$ and $\kappa_{el}^{V}$ as functions of temperatures in Fig. 3(c) and (d), respectively. At low temperatures, $\kappa_{el}^{V} \approx -\beta_{V} T^{3}$ and $\kappa_{el}^{T} \approx \beta_{T} T$, as shown in Eq. (18). The inset of Fig. 3(c)
B. The Junction as a Thermoelectric Power Generator and a Self-powered Electronic Device

Suppose that the junction is not connected to battery (i.e., \( \mu_R = \mu_L = \mu \)) and \( T_R = T_L = T \). Provided that a finite temperature difference \( \Delta T = T_R - T_L \) is raised in the right electrode (i.e., \( T_L = T \) and \( T_R = T + \Delta T \)), the Seebeck effect generates a finite electromotive force \( emf = |\Delta V(T_L, T_R)| \) where \( \Delta V(T_L, T_R) \) is given by Eq. (11). This voltage difference induces a net electric current \( I(T_L, T_R) \) which travels from lower to higher potential inside the power generator, as described in Eq. (22) and Fig. 1(b). Correspondingly, the electron’s thermal current \( (J_{el}^R)_{\Delta V} \) [Eq. (24)] absorbs energy in heat from the hot (right) electrode, produces electric power \( \Delta P \) [Eq. (20)] using the Seebeck effect, and then gives up energy in heat to the cold (left) electrode via \( (J_{el}^L)_{\Delta V} \) [Eq. (24)], as described in Fig. 1(b) for \( S < 0 \). To gain further insight into the mechanism of energy conversion, we theoretically analyze the electron’s thermal current. Applying Sommerfeld expansion to \( (J_{el}^R)_{\Delta V} \) and \( (J_{el}^L)_{\Delta V} \) in Eq. (23), we obtain

\[
(J_{el}^R)_{\Delta V} \approx \sigma (\Delta V)^2 T / \Delta T + \sigma (\Delta V)^2 / 2,
\]

and

\[
(J_{el}^L)_{\Delta V} \approx \sigma (\Delta V)^2 T / \Delta T - \sigma (\Delta V)^2 / 2,
\]

where we have simplified Eqs. (29) and (30) using the following approximations: \( \tau(\mu + \epsilon \Delta V) \approx \tau(\mu) \), \( \tau'(\mu + \epsilon \Delta V) \approx \tau'(\mu) \), \( \sigma \approx 2e^2\tau(\mu)/h \), \( S \approx -\pi^2 k_B^2 \sigma(\mu) T / (3e\tau(\mu)) \), and \( \Delta V \approx S \Delta T \).

Equations. (29) and (30) immediately provides the law of energy conservation as further described below. The thermoelectric junction serves as an ideal source of \( emf \) which delivers electric power \( \Delta P = (J_{el}^R)_{\Delta V} - (J_{el}^L)_{\Delta V} \) converted from the electron’s thermal currents using the Seebeck effect. Concurrently, the nanojunction itself serves as a passive element which consumes electric power dissipated by the internal resistor at a rate of \( \sigma (\Delta V)^2 \).

Equations (29) and (30) imply that each electrode approximately provides one half of the electric power using the Seebeck effect and the electric power is mainly converted from \( (J_{el})_{\Delta V} \). No energy conversion is possible when the Seebeck coefficients is vanishing because \( (J_{el})_{\Delta V} = 0 \). We note that \( J_{el}^R = (J_{el}^R)_{\Delta V} + (J_{el}^L)_{\Delta V} \) removes heat energy from the hot electrode, converts heat energy into electric energy, and rejects waste heat to the cold electrode by \( J_{el}^L \). Both \( (J_{el})_{\Delta V} \) and \( J_{ph}^R \) do not play active role in the energy conversion. The above discussions are summarized in Fig. 4(a).

The energy current \( (J_{el}^L)_{\Delta V} \) flowing into the cold electrode could be negative when \( \Delta T \) is sufficiently large, as shown in Fig. 4(b). To show this, we integrate Eq. (11) using Eq. (10). \( K_1(\mu, T) \approx \pi^2 k_B^2 T^2 / 3 \), \( K_2(\mu, T) \approx \pi^2 k_B^2 T^2 / 3 \). We obtain \( \Delta V \approx \alpha T^2 (\Delta T/T)^2 + \)

\[
\Delta P = (J_{el}^R)_{\Delta V} - (J_{el}^L)_{\Delta V}
\]
\[ 2(\Delta T/T)/2, \text{ where } \alpha = -[\pi^2 k_B^2 \beta_r(\mu)/(3e\tau(\mu))]. \] Together with Eq. (30), we arrive at
\[ (J_{cl}^L)_{\Delta T} \approx \sigma ST\Delta V\{1 - [(\Delta T/T) + (\Delta T/T)^2]/4\}, \quad (31) \]
from which we observe that \((J_{cl}^L)_{\Delta T}\) changes sign at \(\Delta T \approx 1.236 T\) (which is universal), and \((J_{cl}^L)_{\Delta T} < 0\) when \(\Delta T \gtrapprox 1.236 T\). Fig. 4(a) and 4(b) illustrate the schematic representation of energy conversion for positive and negative \((J_{cl}^L)_{\Delta T}\), respectively. Fig. 4(a) and 4(b) illustrate the schematic representation of energy conversion for positive and negative \((J_{cl}^L)_{\Delta T}\), respectively.

Let us focus on the energy conversion efficiency \(\eta_{el}\) defined as the ratio of the electric power \(\Delta P\) generated by the Seebeck effect to the electron’s thermal current \(J_{el}^R\) which removes thermal energy from the high temperature reservoir:
\[ \eta_{el} = \frac{\Delta P}{J_{el}^R}, \quad (32) \]
where \(\Delta P\), \((J_{el}^R)_{\Delta V}\), and \((J_{el})_{\Delta T}\) are given by Eq. (28), (24), and (25), respectively. In the above definition, we have neglected other effects [e.g., the phonon’s thermal current \(J_{ph}^R\) and possible photon radiation] which transfer energy from the hot to cold electrodes. From this viewpoint, the energy conversion efficiency presented in this study may be overestimated. We note that the size of the paired metal-Br-Al system is small. This may lead to suppression of the photon radiation because photon radiation is proportional to the surface area. Moreover, the paired metal-Br-Al system has a poor mechanical link between electrodes when the distance of two Al atoms is sufficiently far apart. The poor mechanical coupling between two phonon reservoir could lead to suppression of the phonon’s thermal current. These two features are helpful to increase the energy conversion efficiency. Note that the phonon’s thermal current and photon radiation do not affect the magnitudes of the current and electric power generated by the Seebeck effect.

To show that the atomic junction can be considered as a field-effect transistor which can be self-powered, we consider the nanojunction in a three-terminal geometry with a finite temperature \(\Delta T = 100 \text{ K}\) between electrodes (where \(T_L = 200 \text{ K}\) and \(T_R = 300 \text{ K}\)). The gate field is introduced as a capacitor composed of two parallel circular charged disks separated at a certain distance from each other. The axis of the capacitor is perpendicular to the transport direction. One plate is placed close to the nano-object while the other plate, placed far away from the nano-object, is set to be the zero reference field.\[ \eta_{el} \approx \frac{\Delta P}{J_{el}^R} \]
given by Eq. (22) for \(T_L = 200 \text{ K}\) and \(T_R = 300 \text{ K}\) as functions of gate voltages. We observe that the extremal of \(\Delta V(T_L, T_R)\) and \(I(T_L, T_R)\) do not occurs at the same value of \(V_G\) because the gate voltage also modulates the conductance of the junction [note that \(\sigma = I(T_L, T_R)/\Delta V(T_L, T_R)\)]. Figure 4 demonstrates that the gate field can efficiently control the magnitude, polarity, and power on-off of the voltage and current induced by the Seebeck effect. Such current-voltage characteristics could be useful in the design of nanoscale electronic devices such as a transistor or switch. Note that the induced voltage and induced current described in Fig. 4 comply with the sign convention described in Fig. 1(b).

Figure 7 shows the electric power \(\Delta P\) [upper panel; given by Eq. (20) delivered by the battery and the energy conversion efficiency \(\eta_{el}\) [lower panel; given by Eq. (22)] as functions of the gate voltages. It illustrates that the gate field is capable of controlling and optimizing the electric power and energy conversion efficiency \(\eta_{el}\). The energy conversion efficiency \(\eta_{el} \approx 0.09\) if optimized by the gate field. The optimized power is about 3.5 nW at \(V_G \approx -2 \text{ V}\). We also observe that the maximum values of electric power and energy conversion efficiency occur at different voltages, similar to the case of induced voltage and current. If a macroscopic system can be formed by two identical pieces of surfaces, each of which is formed by a layer of Al atoms adsorbing onto metal surface coated with a layer of Br atoms as spacer. The macroscopic system could be equivalent to more than \(10^{12}\) single paired metal-Br-Al-Al-Br-M junctions which are connected in
FIG. 6: (color online) (a) Schematic of the three-terminal junction. The Seebeck-effect induced (b) voltage \( V(T_L, T_R) \) and (c) current \( I(T_L, T_R) \) as functions of gate voltages via the temperature difference \( \Delta T = T_R - T_L \), where \( T_L = 200 \) K and \( T_R = 300 \) K.

parallel on 1 cm\(^2\) surface. We conjecture that the power could be substantial in such a macroscopic system.

Finally, we investigate the efficiency of energy conversion \( \eta_{el} \) as a function of \( T_C (= T_L) \) and \( \Delta T = T_R - T_L \) for \( V_G = 0 \), as shown in Fig. 7. The paired metal-Br-Al junction shows sufficiently large efficiency around 0.05 when \( T_C = 300 \) K and \( \Delta T = 60 \) K. Such a high efficiency is attributed to the enhanced the Seebeck coefficients.

IV. CONCLUSIONS

In summary, we developed a theory for thermoelectric power generator in the truly atomic scale system. The theory is general to any atomic/molecular junction where electron tunneling is the major transport mechanism. As an example, we investigated the thermoelectric properties and the efficiency of energy conversion of the paired metal-Br-Al junction from first-principles approaches. Owing to the narrow states near the chemical potentials, the nanojunction has large Seebeck coefficients; thus, it can be considered as an efficient thermoelectric power generator. Provided that a finite temperature difference is maintained between electrodes, the thermoelectric power generator converts thermal energy into electric energy. The optimized electric power generated by the Seebeck effect is about 3.5 nW at \( T_L(R) = 200 \) (300) K at \( V_G \approx -2 \) V. To gain further insight into the mechanism of energy conversion, we investigate the electron’s thermal currents analytically. The electron’s thermal current which removes heat from the hot temperature reservoir can be decomposed into two components, \( J_{el}^R = (J_{el}^R)_{\Delta V} + (J_{el}^R)_{\Delta T} \). Only \( (J_{el}^R)_{\Delta V} \) is capable of
converting energies. The electron’s thermal current removes heat from the hot reservoir via \( J^\text{e}_{\text{th}} \) and rejects waste heat into the cold reservoir via \( J^\text{e}_{\text{w}} \). No energy conversion is possible when the Seebeck coefficients is vanishing.

We also consider the nanojunction in a three-terminal geometry, where the current, voltage, and electric power can be modulated by the gate voltages, which shift the states of the junction. We observe that the gate field can control the magnitude, power on-off, and polarity of the induced current and voltages generated by the Seebeck effect. Such current-voltage characteristics could be useful in the design of nanoscale electronic devices such as a transistor or switch. Notably, the nanojunction as a transistor with a fixed finite temperature difference between electrodes can power itself using the Seebeck effect. The results of this study may be of interest to researchers attempting to develop new forms of thermoelectric devices.

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