Oscillatory and sign-alternating behaviors of the Seebeck coefficients in carbon monatomic junctions

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In the framework of density functional theory combined with the Lippmann-Schwinger formalism in scattering approaches, we calculate the Seebeck coefficients for carbon atom chains sandwiched between aluminum electrodes from first principles. The most striking feature is that the Seebeck coefficients are length dependent, and can be negative (n type) or positive (p type) for odd- or even-numbered carbon atom chains. Alternating n-type and p-type material properties of carbon atom chains are due to the full- and half-filled π^*-orbital states near the chemical potential.

I. INTRODUCTION

Carbon is an element capable of forming astoundingly versatile forms with multiple dimensionality ranging from three to zero. The allotropes of carbon include three-dimensional diamond, two-dimensional graphene, quasi-one-dimensional nanotubes, and zero-dimensional fullerenes as a quantum dot. The variability of the structural formations of carbon show varied and unusual material properties. For example, phase transition may happen in the temperature profile of Seebeck coefficients when the interface reconstruction occurs in C60 single-molecule junctions.[1] Low-dimensional carbon allotropes such as carbon nanotubes and graphene are among the few most promising candidates for the miniaturization of devices. The peculiar material properties associated with low dimensionality have continuously motivated a tremendous wave of scientific interest in the exploration of useful applications in nanoscale systems. Recently, researchers have materialized stable and rigid linear carbon atomic chains formed by removing carbon atoms in graphene using transmission electron microscopy.[2] *Ab initio* quantum transport calculations for carbon monatomic junctions show that patterned electronic structures with regard to the number of carbon atoms result in oscillatory conductance and shot noise in carbon atomic wires.[3–5] First–principles calculations show that the oscillatory conductance and shot noise arise from the detailed electronic structures related to the full- and half-filled π^* orbital for odd- or even-numbered carbon atom chains. Recent theoretical study suggests the carbyne chain be connected to gold electrodes via the sulfur atoms. The study shows that an even number of carbon chains are dimerized and dimerization causes plateaus in the I-V curves in the even-numbered carbyne chains.[6]

Recently, progress in the experimental measurements and theoretical calculations of the Seebeck coefficient (or thermopower) in molecular junctions has significantly advanced the fundamental understanding of thermoelectric properties at the nanoscale.[7–13] Thermoelectric atomistic junctions for use in the development of new forms of energy-conversion devices at the nanoscale have attracted rapidly growing attention.[14–16] We have investigated the dependence of the Seebeck coefficient and dimensionless thermoelectric figure of merit (ZT) on lengths.[17] The Seebeck coefficient is related not only to the magnitude but also to the slope of the transmission function in the vicinity of Fermi levels. Thus the Seebeck coefficient can provide more information on electronic structures than the usual conductance measurements. Consequently, the comparison of the Seebeck coefficients between first-principles calculation and experimental measurements are important to understand thermoelectric properties at the atomic level. We have theoretically observed that ZT of metallic Al atomic junctions and insulating alkanethiol molecular junctions have an opposite trend of length dependence. In other words, with increased length, ZT increases for aluminum atomic junctions but decreases for alkanethiol molecular junctions. Electrons coupled to atomic/molecular vibrations can also induce interesting many-body effects (e.g., normal modes causing small structure at biases with eV_B equals the energy of normal modes) on the Seebeck coefficients.[18]

The formation of carbon monatomic chains offers an unprecedented nanoscale system where peculiar material properties may be obtained owing to the unique atomistic electronic structures. This phenomenon motivates us to investigate the unknown thermoelectric properties of carbon atomic chains that bridge junctions from first-principles approaches. In this paper we investigate the the length-dependent Seebeck coefficients for carbon monatomic junctions. We observe that the Seebeck coefficients not only display odd-even oscillations, but also change signs due to the patterned electronic structures with regard to even- or odd-numbered carbon atoms. Thus, the length of the carbon atom chain can alter the carriers from n to p type in the language of semiconductors. Such length-dependent and sign-alternating thermoelectric material properties are quite unexpected and never before seen in other typical thermoelectric materials. Therefore, the thermopower is particularly interesting and important in understanding the peculiar properties of one-dimensional carbon allotropes. We restrict our attention to behaviors of Seebeck coefficients at zero bias at low temperatures, neglecting effects of electron-vibration interactions for simplicity.

II. THEORY

From first-principles approaches, we investigate the Seebeck coefficients for various lengths of carbon atom chains sandwiched between aluminum electrodes. The geometries of carbon atom junctions are optimized using the Vienna *ab initio* simulation package (VASP). The structural
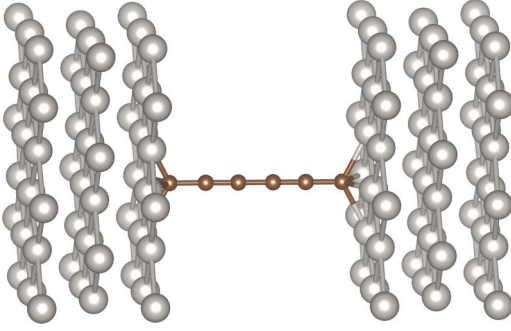
FIG. 1. (Color online) Schematic of a monatomic chain with six-carbon atoms bridging the aluminum electrodes.

relaxations show that even-numbered carbon atom chains are dimerized while odd-numbered carbon atom chains have uniform C–C bond lengths, in agreement with the observation in Ref. 6. The uniform C–C bond lengths are around 2.43 a.u., while the alternating C–C bond lengths are around 2.5 and 2.346 a.u., respectively. Figure 1 shows a prototypical nanojunction consisting of a six-carbon chain connecting two aluminum metallic electrodes that we model as the electron jellium with $r_s \approx 2$. To simplify notation, the number of carbon atoms in the nanojunctions are denoted by C_N. We successively vary the number of carbon atoms N from three to nine in the monatomic carbon junctions, where the end carbon atoms are placed at 1.4 a.u. from the jellium edge.

We perform parameter-free first-principles calculations to calculate the Seebeck coefficients of the carbon monatomic junctions with different numbers of carbon atoms connected to two semi-infinite Al metal electrodes. The calculations are performed in the framework of density-functional theory in scattering approaches.[19] The full Hamiltonian of the system is

$$H = H_0 + V(\mathbf{r}_1, \mathbf{r}_2), \qquad (1)$$

$$V(\mathbf{r}_1, \mathbf{r}_2) = V_{ps}(\mathbf{r}_1, \mathbf{r}_2) + (\{V_{xc}[n(\mathbf{r}_1)] - V_{xc}[n_0(\mathbf{r}_1)]\}$$

$$+ \int d\mathbf{r}_3 \frac{\delta n(\mathbf{r}_3)}{|\mathbf{r}_1 - \mathbf{r}_3|}) \delta(\mathbf{r}_1 - \mathbf{r}_2), \qquad (2)$$

where H_0 is the Hamiltonian of the bare electrodes, $V_{ps}(\mathbf{r}_1, \mathbf{r}_2)$ refers to the electron-ion interaction at the norm conserving pseudopotential level, and V_{xc} is the exchange-correlation energy in the local density approximation (LDA). The unperturbed wave functions have the form $\Psi_{E\mathbf{K}}^{0,L(R)}(\mathbf{r}) = (2\pi)^{-1} e^{i\mathbf{K} \cdot \mathbf{R}} \cdot u_{E\mathbf{K}}^{L(R)}(z)$, where $u_{E\mathbf{K}}^{L(R)}(z)$ is the wave function of the bare electrodes along the z direction before the inclusion of a nanostructured object between electrodes. The equation $u_{E\mathbf{K}}^{L(R)}(z)$ is calculated by solving the coupled Schrödinger and Poisson equations iteratively until self-consistency is reached. Deep inside the electrodes ($z \to \pm\infty$), the right- and left-moving waves satisfy the scattering boundary conditions,

$$u_{E\mathbf{K}}^L(z) = \sqrt{\frac{m}{2\pi\hbar^2 k_L}} \times \begin{cases} e^{ik_L z} + R_L e^{-ik_L z} & z < -\infty \\ T_L e^{ik_R z} & z > \infty \end{cases} \quad (3)$$

and

$$u_{E\mathbf{K}}^R(z) = \sqrt{\frac{m}{2\pi\hbar^2 k_R}} \times \begin{cases} T_R e^{-ik_L z} & z < -\infty \\ e^{-ik_R z} + R_R e^{ik_R z} & z > \infty, \end{cases} \quad (4)$$

where $\mathbf{K}$ is the electron momentum in the plane parallel to the electrode surfaces, and z is the coordinate parallel to the direction of the current. The condition of energy conservation gives $\frac{\hbar^2 k_R^2}{2m} = E - \frac{\hbar^2 \mathbf{K}^2}{2m} - v_{\text{eff}}(\infty)$ and $\frac{\hbar^2 k_L^2}{2m} = E - \frac{\hbar^2 \mathbf{K}^2}{2m} - v_{\text{eff}}(-\infty)$, where $v_{\text{eff}}(z)$ is the effective potential comprising the electrostatic potential and exchange correlation energy. The inclusion of the carbon chain is considered in the scattering approach. After obtaining $\Psi_{E\mathbf{K}}^{0,L(R)}(\mathbf{r})$, the wave functions of the total system are calculated by solving the Lippmann-Schwinger equation iteratively until self-consistency is reached,

$$\Psi_{E\mathbf{K}}^{L(R)}(\mathbf{r}) = \Psi_{E\mathbf{K}}^{0,L(R)}(\mathbf{r})$$

$$+ \int d^3 \mathbf{r}_1 \int d^3 \mathbf{r}_2 G_E^0(\mathbf{r}, \mathbf{r}_1) V(\mathbf{r}_1, \mathbf{r}_2) \Psi_{E\mathbf{K}}^{L(R)}(\mathbf{r}_2). \quad (5)$$

A basis of 2300–3500 plane waves has been chosen for the different carbon atom chain lengths. Localized electron states are considered and solved by the diagonalization of the full Hamiltonian.

The effective single-particle wave functions are then applied to calculate the Seebeck coefficients[12]

$$S = -\frac{1}{e} \frac{\frac{K_1^L}{T_L} + \frac{K_1^R}{T_R}}{K_0^L + K_0^R}, \qquad (6)$$

where

$$K_n^{L(R)} = -\int dE (E - \mu_{L(R)})^n \frac{\partial f_E^{L(R)}}{\partial E} \tau(E), \qquad (7)$$

where $f_E^{L(R)} = 1/\exp[(E - \mu_{L(R)})/k_B T_{L(R)}] + 1$ is the Fermi-Dirac distribution describing the electron statistics in the deep left (right) electrodes; the left (right) electrode temperature is kept at $T_{L(R)}$; and the transmission function $\tau(E) = \frac{\pi\hbar^2}{mi} \int d\mathbf{R} \int d\mathbf{K} (\Psi_{E\mathbf{K}}^{R*} \nabla \Psi_{E\mathbf{K}}^R - \nabla \Psi_{E\mathbf{K}}^{R*} \Psi_{E\mathbf{K}}^R)$ is calculated from the probability density using the wave functions obtained self-consistently in the DFT framework in scattering approaches.

In the linear response and low-temperature regime, the plot of the Seebeck coefficient vs the temperature is linear. The magnitude of the Seebeck coefficient is proportional to the slope of the transmission function, and inversely proportional to the magnitude of the transmission function at the chemical potential

$$S \approx -\frac{\pi^2 k_B^2}{3e\tau(\mu)} \frac{\partial \tau(\mu)}{\partial E} T. \qquad (8)$$

Equation (8) indicates that the Seebeck coefficient is positive (negative) when the slope of the transmission function is negative (positive).

III. RESULTS

Figure 2 shows the Seebeck coefficients as a function of the electrode temperatures for various C_N junctions. The Seebeck coefficients of different chain lengths exhibit linear dependence with respect to the temperature of electrodes. The most striking feature is that the sign of the Seebeck coefficients are alternating with respect to the oddness or evenness of C_N
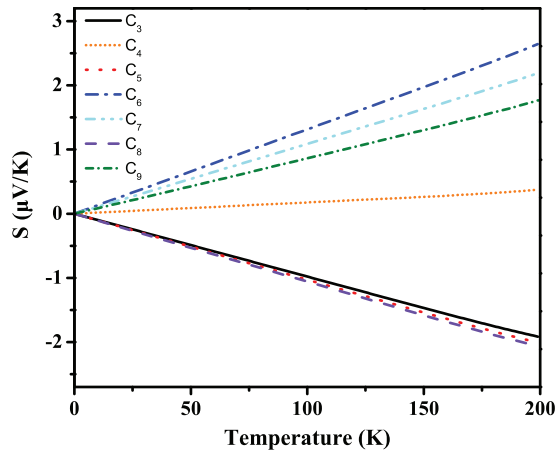
FIG. 2. (Color online) Seebeck coefficient S as a function of the electrode temperature T for various lengths of carbon monatomic junctions (denoted by C_N).

FIG. 3. (Color online) (a) Density of states and (b) the transmission function as a function of the electron energy E for various lengths of carbon monatomic junctions. The chemical potential is set to be zero energy.

junctions. We observe that the Seebeck coefficients are positive (p type) when N is even and negative (n type) when N is odd. The characteristics of the carrier type in the carbon monatomic can change according to odd- or even-numbered carbon atoms in the junction.

We explain the origin of such odd-even effects by the electronic structures peculiar to the carbon monatomic chains. The continuum states near the chemical potential show π^*-orbital characters that have twofold (p_x and p_y) degeneracy such that each π^* state can hold four electrons. When C_N is increased by one, the additional carbon atom with four valence electrons provides two electrons in the continuum states and the other two electrons in the localized states. Accordingly, each additional carbon atom can provide two more electrons contributing to the π^* orbital just below the Fermi level. This phenomenon leads to the fact that the π^* orbital below the Fermi level is full-filled in an odd-numbered atom chain and half-filled in an even-numbered atom chain. This peculiar electronic structures of carbon monatomic junctions can be seen in the density of states plotted in Fig. 3(a). As a result, the slope of the transmission function at the Fermi level can be positive or negative if the number of the carbon in the wires is even (odd), as shown in Fig. 3(b). Equation (8) shows the Seebeck coefficient is positive (negative) when the slope of the transmission function is negative (positive). The finding explains why the Seebeck coefficients undergo sign changes with respect to oddness or evenness of C_N.
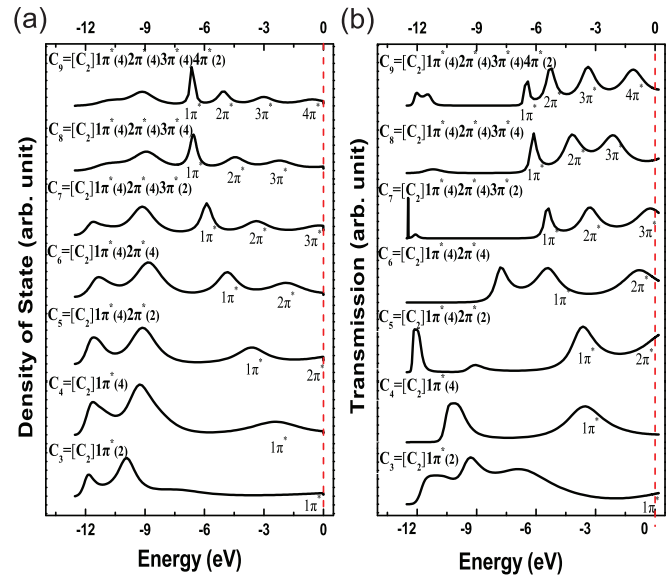
In conclusion, the Seebeck coefficient is an important tool that can enable the simultaneous determination of the magnitude and slope of the density of states. It provides insight into the fundamental properties of one-dimensional carbon allotropes. We have shown that Seebeck coefficients have length-dependent and sign-alternating behaviors in carbon monatomic junctions. Hence, the characteristics of carrier types in carbon monatomic junctions can be n or p type according to C_N. Such peculiar thermoelectric properties are features of the one-dimensional carbon allotropes and never seen in other materials. These unprecedented thermoelectric material properties arise from the unique atomistic electronic structures of carbon monatomic junctions related to full- and half-filled π^* orbital just below the Fermi level.

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