

Effects of phase-breaking scattering on the thermopower of molecular systems

Adrian Popescu^{1,2} and Paul M. Haney¹

¹*Center for Nanoscale Science and Technology, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-6202, USA*

²*Maryland NanoCenter, University of Maryland, College Park, Maryland 20742, USA*

Abstract

We study the effects of elastic and inelastic scattering on the thermoelectric transport properties of molecular systems. These systems can exhibit high thermopower due to resonant transmission through molecular orbitals. We focus on systems which exhibit suppressed conductance near transmission *anti*-resonances due to quantum interference. For coherent electronic transport, these anti-resonances also lead to very high thermopower. We find that elastic and inelastic scattering reduces the thermopower, and that this reduction is more severe for larger molecules, and for molecules which are more weakly coupled to the leads.

Introduction

The thermoelectric effect enables the conversion of heat flux to electrical power, and has the potential to be a renewable energy source through applications such as waste heat recovery. The efficiency of this conversion is related to the dimensionless figure of merit $ZT = S^2 \sigma T / \kappa$, where S is the thermopower, σ is the electrical conductivity, and κ is the thermal conductivity. Current values of ZT are around 1, and the conflicting materials requirements for high values of ZT inhibit the pace of further progress. There is hope, however, that nanostructured materials may offer a route to more efficient thermoelectrics [1]. For example, the electrical conductivity of systems with reduced dimensionality can vary rapidly with energy, resulting in a larger thermopower S . Additionally, such systems can scatter phonons more effectively, reducing κ [2]. Transport through molecular systems serves as an example of this general proposition: resonant transport through localized orbitals results in high thermopower [3-11], and the large mismatch between the phonon modes of bulk and molecular systems results in low κ [12,13].

Transport in molecular systems has been an active area of research since Aviram and Ratner proposed that a molecule could function as the building block of a circuit [14]. The miniaturization of electronics finds its natural endpoint in the transport through a single molecule. However, there are many challenges associated with the characterization and control of transport in molecular systems. In particular, the strong dependence of the conductance on the molecule-lead coupling and the molecular orientation/conformational shape complicate the interpretation of current-voltage curves. Recent experimental work has shown that thermopower in molecular systems is more immediately relevant as a diagnostic tool than as an energy-harvester [11]. For example, the sign of the Seebeck coefficient is used to distinguish between HOMO or LUMO-dominated transport [15], and ensemble studies of S can help determine the main sources of variability in transport measurements [16].

Thermoelectric transport in molecular systems may also exhibit specific features which are of fundamental interest. For example, it has also been predicted that quantum interference effects in molecular transport leads to high values of thermopower and large deviations from the Wiedemann-Franz law [6]. This prediction takes on added relevance in light of recent

experiments which demonstrate quantum interference effects in transport studies of conjugated molecules [17]. These interference effects are manifested in the suppression of charge transport at specific energies, which are geometry and molecule-dependent.

In this work we show that transmission anti-resonances due to quantum interference in atomic junctions indeed lead to thermopower enhancement for phase coherent transport. We additionally explore the effects of transport decoherence due to inherent phase breaking and dissipative processes. We present numerical results, develop an analytical expression for the effect of phase-breaking scattering on the transmission, and present the physical picture which underlies this phase-breaking transmission. It is shown that these processes have an adverse effect on the thermopower near anti-resonances, and that these effects are more severe for larger molecules and/or molecules that are weakly coupled to the leads.

Model.

We consider a 1-d tight-binding model (illustrated in Fig. 1), with the overall system Hamiltonian given by:

$$H = \sum_{ij} (t'_{ij} + U_i \delta_{ij}) \hat{d}_i^\dagger \hat{d}_j + \sum_{\ell=L,R} \varepsilon_k^\ell \hat{c}_k^{\ell\dagger} \hat{c}_k^\ell + \sum_{i,k,\ell} (V_{ik} \hat{c}_k^{\ell\dagger} \hat{d}_i + \text{h.c.}) \\ + \sum_{\alpha} (\hbar\omega_{\alpha} + 1) \hat{b}_{\alpha}^\dagger \hat{b}_{\alpha} + \sum_{i,j,\alpha} M_{ij}^{\alpha} (\hat{b}_{\alpha}^\dagger + \hat{b}_{\alpha}) \hat{d}_j^\dagger \hat{d}_i \quad (1)$$

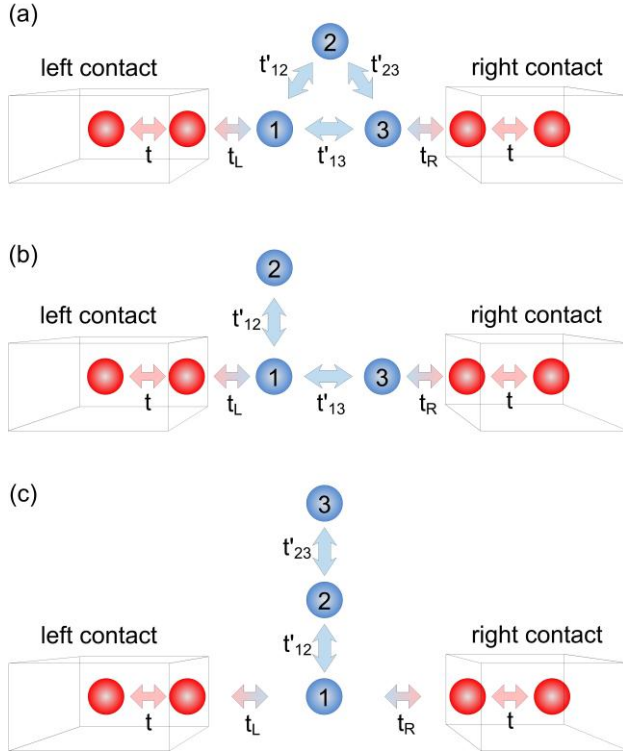


Fig. 1. Schematic drawing of the different atomic junctions connected to two contacts.

The first three terms describe the electronic system: \hat{d}_i^\dagger is the creation operator for a localized orbital i in the molecule, $\hat{c}_k^{L(R)\dagger}$ is the creation operator for propagating states with energy ε_k in the left (right) lead, and V_{ik} is the molecule-lead coupling. The molecular orbitals have a nearest neighbor hopping matrix element t'_{ij} and an onsite energy U_i . The last two terms in Eq. (1) result from the presence of phonons: \hat{b}_{α}^\dagger creates a phonon with energy $\hbar\omega_{\alpha}$, and M_{ij}^{α} is the coupling between the mode labeled by α , and orbitals i, j on the molecule:

$$M_{ij}^{\alpha} = \sum_n \sqrt{\frac{\hbar}{2M_n \omega_{\alpha}}} C_{n\alpha} \langle i | \nabla_{\mathbf{R}_n} H(\mathbf{R}) | j \rangle,$$

where the sum is over nuclei with coordinates \mathbf{R} , M is the ionic mass, and $C_{n\alpha}$ is the expansion of the α mode in real space coordinates.

The thermoelectric transport is described within the Landauer formalism in the linear response regime. The thermopower is expressed as:

$$S = \left(-\frac{k_B}{e} \right) \frac{I_1}{I_0}, \quad (2)$$

where

$$I_j = \int \left(\frac{E - E_F}{k_B T} \right)^j T(E) \left(-\frac{\partial f_0}{\partial E} \right) dE, \quad (3)$$

with f_0 being the Fermi-Dirac distribution function, E_F the Fermi energy, k_B the Boltzmann constant and T the absolute temperature. The transmission function $T(E)$ is expressed using the non-equilibrium Green function technique [18] as

$$T(E) = \text{Tr} \left[\Gamma_L G \Gamma_R G^\dagger \right], \quad (4)$$

where G is the retarded Green function matrix of the atomic junction and $\Gamma_{L,R} = i(\Sigma_{L,R} - \Sigma_{L,R}^\dagger)$ are the broadening matrices due to the left and right leads. The Green function is expressed as

$$G = (E - H - \Sigma_L - \Sigma_R - \Sigma_S)^{-1}, \quad (5)$$

where $\Sigma_{L,R}$ are the self-energy matrices due to the left and right leads, H is the Hamiltonian for

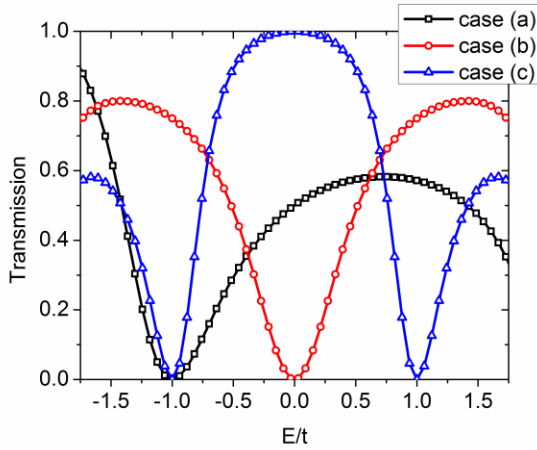


Fig. 2. Energy dependence of the transmission function for all types of junctions shown in Fig. 1. The energy is normalized by the overlap energy of the reservoirs. We take $U_i = 0$ and $t' = t$.

the isolated molecule, and Σ_S describes the effects of carrier scattering. The nonzero matrix elements of the lead self-energies are $\Sigma_{L,R} = t_{L,R} \exp(ik_{L,R}a)$, where $t_{L,R}$ are the hopping matrix elements between the left and right lead and the molecule (see Fig. 1). The energy dependence $k_{L,R}(E)$ is determined by the dispersion relation $E = 2t \cos(k_{L,R}a)$.

We follow the procedure described in Ref. [18] to calculate $\Sigma_S(E)$ in terms of the electronic Green's function and phonon properties. We assume that the phonons remain in equilibrium, and employ a self-consistent Born approximation for the electrons. Within this approximation, the electron-phonon interaction is essentially viewed as an inflow and outflow of electronic carriers through an additional scattering terminal described by its

self-energy $\Sigma_S(E) = -i\Gamma_S(E)/2$ [19]. If the scattering process is elastic the broadening is given by

$$\Gamma_{S,\text{el}}(E) = D_{\text{el}} A(E), \quad (6)$$

where $A(E) = i(G(E) - G^\dagger(E))$ is the spectral function and D_{el} is the elastic deformation potential [20]. For inelastic scattering, we assume a single phonon mode with energy $\hbar\omega_0$ and occupation N_{ω_0} given by the Bose-Einstein factor. This leads to a broadening term given by:

$$\begin{aligned} \Gamma_{S,\text{inel}}(E) = & D_{\text{inel}}(N_{\omega_0} + 1) [G^p(E - \hbar\omega_0) + G^n(E + \hbar\omega_0)] \\ & + D_{\text{inel}}N_{\omega_0} [G^n(E - \hbar\omega_0) + G^p(E + \hbar\omega_0)] \end{aligned} \quad (7)$$

Here G^n and G^p are the electron (hole) correlation functions [18], related by $A(E) = G^n(E) + G^p(E)$. In this work, we assume the electron-phonon matrix element M_{ij}^α is

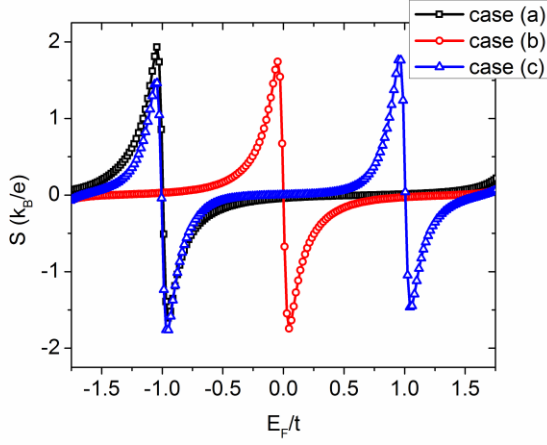


Fig. 3. Thermopower as a function of the Fermi level for the three atomic junctions. The energy is normalized by the contacts bandwidth.

diagonal in orbital space with a uniform value, so that $D_{\text{inel}} = \sum_i |M_{ii}^0|^2$ [18]. Of

relevance to the current work is the observation that the effective electron-phonon coupling parameter D_{inel} is expected to vary with the number of atoms in the molecule N as $D_{\text{inel}} \propto 1/N$ [22]. This is understood by noting that the matrix element in Eq. (1) M_{ii}^α should vary as $1/N$ from the normalization of the atomic wavefunctions over a molecule with N delocalized π -orbitals. The same reasoning is used in Ref. [22], which additionally verifies the relation with first principles calculations. We separate out the N dependence by letting $D_{\text{inel}} = D_{0,\text{inel}}/N$, where $D_{0,\text{inel}}$ is independent of N . Finally,

we note that the broadening associated with the non-coherent processes (Eqs. (6) and (7)) depends on the correlation functions $G^{n,p}$, requiring an iterative self-consistent solution. Given the above assumptions, the Green's function of the system can be found to any desired accuracy (the threshold we use for numerical convergence is a maximum change of $10^{-5} t^{-1}$ in the Green's function between iterations).

Results.

We begin by considering an atomic junction consisting of three atoms in different geometrical configurations connected to two leads, as shown in Fig. 1. The energy dependence of the calculated transmission across the different atomic junctions for fully coherent transport ($\Sigma_S = 0$) is shown in Fig. 2. There are transmission anti-resonances for all the considered cases. This is purely a quantum interference effect due to the specific geometrical configuration considered. Transmission anti-resonances occur when the phases acquired by electrons along different pathways of the molecule cancel each other leading to destructive interference. Fig. 2 illustrates that in addition to the usual “molecule-like” configuration in Fig. 1(a), where electrons

would acquire different phases along the different pathways, a simple chain-like configuration (as in Fig. 1(b)) can also cause a suppression of the transport.

The thermopower is shown in Fig. 3 as a function of the Fermi level at room temperature. There is a strong enhancement in the thermopower when the Fermi level is tuned across a

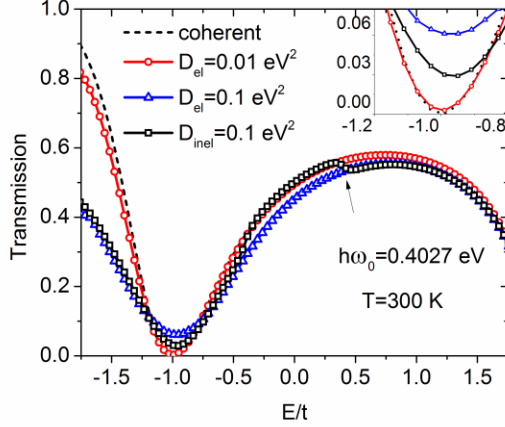


Fig. 4. Energy dependence of the transmission function for different values of the elastic/inelastic scattering deformation potential.

resonances and anti-resonances.

Next the effects of phase-breaking and dissipative processes on the thermoelectric transport are explored. The energy dependence of the transmission calculated for configuration (a) in Fig. 1 is shown in Fig. 4 with elastic or inelastic scattering processes taken into account. The case of coherent transport is also shown in Fig. 4 for reference. With inelastic scattering, there is a decrease in the transmission at the energy value corresponding to the phonon energy $\hbar\omega_0$. When elastic carrier scattering is included the transmission nodes are lifted and the transmission zeros become finite values (see inset of Fig. 4). As more carrier scattering is present, the values of the transmission minima become larger. Both elastic and inelastic scattering have a similar effect of reducing the effect of destructive quantum interference. We discuss the physical picture behind this below.

The thermopower in the presence of elastic/inelastic carrier scattering is shown in

Fig. 5 as a function of the Fermi level. The effect of non-coherent processes is to reduce the thermopower of the atomic junction. For large values of the deformation potential, the reduction

Since the integrands of the quantities I_j in Eq. (3) contain the thermal averaging factor $-\partial f/\partial E$, the thermopower has maxima when this factor is centered near the transmission minima. The absolute value of the maximum thermopower has similar values for all of the configurations considered. This is consistent with the analysis of Ref. [6], which shows that the maximum thermopower S_{\max} is temperature independent and insensitive to model details near an anti-resonance, and that S_{\max} takes the simple form

$S_{\max} = \mp \pi k_B / \sqrt{3} e$. Quite generally, a large thermopower follows from a strong energy dependence of the transmission function near the Fermi level, and in this sense there is no qualitative difference between transmission

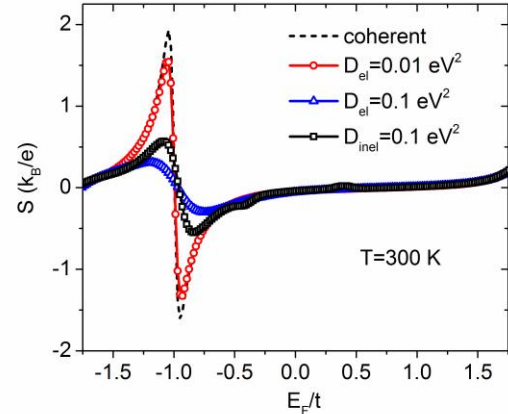


Fig. 5. Thermopower as a function of the Fermi level with the elastic/inelastic scattering processes taken into account.

can be quite drastic. For example, a small shift in transmission corresponding to $D_{\text{el}} = 0.01 \text{ eV}^2$ relative to the coherent case (see the inset of Fig. 4) reduces the thermopower by about 20 %.

The evolution of the maximum value of the thermopower with the deformation potential is shown in Fig. 6(a) for all of the configurations considered in Fig. 1. When phase decoherence due to elastic scattering is present, the maximum thermoelectric performance decreases with increasing deformation potential regardless of the geometrical configuration. The same qualitative behavior is observed when inelastic scattering processes are taken into account

(shown for simplicity in Fig. 6(a) for case (a) only). This shows that both elastic and inelastic processes suppress the transmission nodes in a similar fashion. At larger D_{el} the maximum thermopower saturates and becomes less sensitive to the carrier scattering.

To develop an intuitive picture of how phase-breaking scattering affects transport near anti-resonance conditions, it is instructive to consider the simplest system which exhibits complete destructive interference in its transmission spectrum. Such a system is depicted in the inset of Fig. (6b). In the absence of phase breaking scattering, there is complete destructive interference when the phase acquired by the electron in going up and back down the chain cancels that of the incoming electron. This cancellation occurs for wave vectors k^* that satisfy $\exp(2ik^*N) = -1$; accordingly, anti-resonances in the transmission occur at energies $E^* = 2t' \cos k^*$.

We can understand the effects of phase breaking scattering by performing an expansion of the transmission coefficient at the $E=0$ resonance (present in chains with an even number of atoms N) to lowest order

in D_{el} . We omit details of this expansion, and show the final result:

$$T(E=0) = N^4 D_{\text{el}}^2 \left(\frac{t}{t'^2} \right)^4. \quad (8)$$

This expression can be intuitively understood by recognizing the broadening Γ_s in Eq. (5) as a spread in an electron's energy ΔE (see Eq. (6)). This leads in turn to a spread in its wave vector Δk , with the relation $\Delta k = (2t' \sin k)^{-1} \Delta E$ (since we focus here on $E=0$, we have

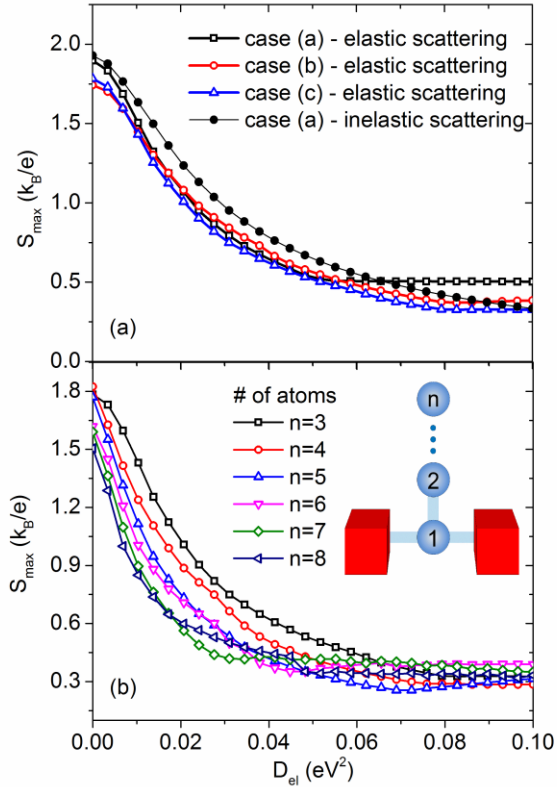


Fig. 6. The maximum thermopower as a function of the scattering deformation potential for (a) the different geometrical configurations in Fig. 1 and (b) the configuration in Fig. 1c with different number of atoms.

$\Delta k = \Delta E / 2t'$). The smearing of k results in a nonzero density at site (1) due to the suppression of exact phase cancellation. This density is given by:

$$n(0) = |1 - \exp(2iN\Delta k)|^2 = 2(1 - \cos(2iN\Delta k)) \approx \left(\frac{N\Delta E}{t'}\right)^2, \quad (9)$$

where in the last approximate expression, we assume $N\Delta k \ll 1$. Since we assume the elastic scattering D_{el} is confined to the molecular region, the energy scale is t' , and from Eq. (6), the relevant energy broadening is $\Delta E = \frac{t}{t'} D_{\text{el}} A(E)$. Importantly, $A(E)$ contains off-diagonal terms, so that electrons lose phase information during a hopping process. We find this leads to an

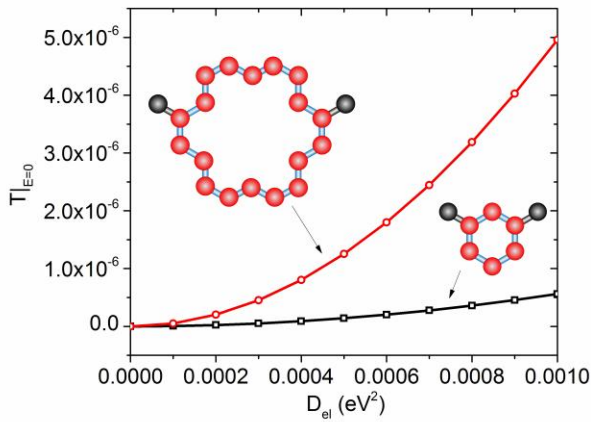


Fig. 7. Transmission at $E=0$ as a function of the scattering deformation potential for a smaller (1,3-benzenedithiol) and larger (18-annulene) molecule.

breaking scattering events increases.

This formula illustrates the strong dependence of the transmission on N and t' : bigger molecules that are more weakly coupled to the leads have a much higher transmission at the anti-resonance energy. This results in a reduced thermopower for such molecules, due to phase-breaking scattering. This analysis is verified by the numerics: Fig. 6(b) illustrates the sharper decrease of thermopower due to scattering as the number of atoms in the system increases. Finally, we can rewrite Eq. (8) to include the expected dependence of the electron-phonon coupling parameter D_{el} on the number of atoms in the molecule N : $D_{\text{el}} = D_{0,\text{el}} \times (1/N)$ (see discussion at the end of Section 2):

$$T(E=0) = N^2 D_{0,\text{el}}^2 \left(\frac{t}{t'^2}\right)^4 \quad (10)$$

As described in Ref. [6], an analytic expression for the thermopower near an anti-resonance can be established by assuming the transmission to be of the form $T(E) = (E - E_0)^2 + \varepsilon$, where E_0 is the location of the anti-resonance, and ε is a background term. We identify this background term with the phase-breaking transmission coefficient. For

an additional spread in phase that scales with N (or the number of hops present in the interfering paths) so that, effectively $\Delta E \propto N$. In addition, weaker molecule-lead coupling results in a more strongly peaked spectral function near the energies of the isolated molecule, so that $A(E=0) \propto t/t'^2$.

Hence the effective energy broadening is $\Delta E = \frac{t^2 N D_{\text{el}}}{t'^3}$. Plugging this ΔE into Eq. (9)

leads to directly to Eq. (8). As discussed in Refs. [21,23], the sensitivity of phase coherent effects on the molecule-lead coupling parameter t' can also be understood in terms of time scales: \hbar/t' represents the lifetime of a state on the molecule, and as this becomes greater, the opportunity for phase-

the particular case analyzed above, this leads to an expression of the maximum thermopower S_{\max} in terms of molecular parameters:

$$S_{\max} = \pm \frac{\pi k_B}{\sqrt{3}e} \left[1 + \frac{3}{\gamma} \left(\frac{ND_{0,\text{el}}}{\pi k_B T} \right)^2 \left(\frac{t}{t'} \right)^4 \right]^{-1/2}, \quad (11)$$

where γ depends on the details of the transmission spectrum near the anti-resonance. Although the above applies to the chain-like model shown in Fig. 6(b), we expect that different configurations will follow the same general dependencies on parameters N and t' .

To illustrate that these general considerations apply to more realistic scatterers, we again focus on the $E=0$ node in the transmission for a smaller (1,3-benzenedithiol) and larger (18-annulene) molecule. Fig. 7 shows the transmission at the $E=0$ node. As in previous cases, we find a $T(E=0) \propto D_{\text{el}}^2$ dependence, and a larger transmission for the larger molecule, as expected from the above considerations. We note however that the increase with molecule size is not as steep as predicted with the analytic treatment of the finite chain.

The above analysis shows that the effects of phase-breaking scattering can be mitigated by using small molecules which are not weakly coupled to the leads. However, in the absence of phase-breaking scattering, the thermopower is maximized for the opposite conditions: weak molecule-lead coupling leads to a transmission which is sharply energy-dependent near a transmission node - advantageous for high thermopower values. Moreover previous work has shown that small molecules exhibit conductance through σ -tunneling, which suppresses the thermopower enhancement due to quantum interference [24]. Hence the factors that lead to high thermopower in the absence of phase-breaking scattering are the very same that make the enhancement vulnerable to phase-breaking scattering. In order to balance these opposing considerations, the ideal molecule for observing thermopower enhancement from quantum interference should therefore be intermediate in size and molecule-lead coupling.

To summarize, the thermoelectric transport properties across atomic junctions are calculated using the Landauer formalism and the non-equilibrium Green function technique. The atomic junctions are described with a simple toy model capable of showing the characteristics of quantum interference. It is found that the thermopower is strongly enhanced near transmission anti-resonances due to quantum interference. However, the predicted thermopower enhancement is reduced by the presence of coherence breaking processes. Our analysis shows that this reduction is more severe for larger molecules that are weakly coupled to the leads. This indicates the need for the careful choice of molecule and geometry to observe thermopower enhancement from quantum interference effects.

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