

Effects of lattice fluctuations on electronic transmission in metal/conjugated-oligomer/metal structures

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The electronic transmission across metal/conjugated-oligomer/metal structures in the presence of lattice fluctuations is studied for short oligomer chains. The lattice fluctuations are approximated by static white noise disorder. Resonant transmission occurs when the energy of an incoming electron coincides with a discrete electronic level of the oligomer. The corresponding transmission peak diminishes in intensity with increasing disorder strength. Because of disorder there is an enhancement of the electronic transmission for energies that lie within the electronic gap of the oligomer. If fluctuations are sufficiently strong, a transmission peak within the gap is found at the midgap energy $E=0$ for degenerate conjugated oligomers (e.g., *trans*-polyacetylene) and $E \neq 0$ for *AB*-type degenerate oligomers. These results can be interpreted in terms of soliton-antisoliton states created by lattice fluctuations. [S0163-1829(97)00135-5]

Inorganic tunneling devices such as metal/semiconductor/metal and metal/superconductor/metal structures are important both because of a rich variety of physics and of technological applications. It has recently become possible to fabricate organic counterparts of tunneling devices, e.g., metal/conjugated-oligomer/metal structures. Several experimental groups have observed electronic transmission through ‘‘molecular wires’’ attached to two metallic contacts,¹⁻⁴ and organic self-assembled-monolayers have been used to modify the injection properties of contacts in organic light-emitting diodes.^{5,6} Conjugated polymers are quite different from conventional semiconductors in that conjugated polymers are flexible and thus lattice effects, including polaron formation and lattice fluctuations, are critical for understanding optical and transport properties of these materials.⁷⁻⁹ In the existing calculations of organic tunneling structures, the role of lattice fluctuations has not been taken into account.¹⁰⁻¹² Here we study the transmission properties of metal/conjugated-oligomer/metal structures, emphasizing the importance of lattice fluctuations (approximated as static intrinsic disorder). We find that the transmission properties in these structures are significantly changed by both thermal and quantum lattice fluctuations.

We study an oligomer chain with $2N$ atoms sandwiched between two semi-infinite metal leads (Fig. 1). The Hamiltonian of the system consists of three parts:

$$H = H_{\text{metal}} + H_{\text{oligomer}} + H_{\text{interface}}. \quad (1)$$

We describe the metal by a one-dimensional, noninteracting tight-binding model

$$H_{\text{metal}} = \sum_{l=-\infty}^{-1} (-t_0 c_l^\dagger c_{l+1} + \text{H.c.}) + \sum_{l=2N+1}^{\infty} (-t_0 c_l^\dagger c_{l+1} + \text{H.c.}), \quad (2)$$

where $c_l^\dagger (c_l)$ is the electron creation (annihilation) operator at site l , t_0 is the electronic hopping integral between the

neighboring metal sites, and the spin indices are implicit in l . For this structure the energy spectrum is given by $E_k = -2t_0 \cos k$.

In general, the hopping integral at the contacts between metal and conjugated oligomer is different from that in the metal,

$$H_{\text{interface}} = -t_1 (c_0^\dagger c_1 + c_{2N}^\dagger c_{2N+1} + \text{H.c.}). \quad (3)$$

The oligomer is modeled by a Su-Schrieffer-Heeger Hamiltonian⁷ used for degenerate polymers. To describe *AB*-type degenerate oligomers,¹³ we include the difference in the on-site energies of the *A* and *B* monomer units, $2\alpha = \epsilon_A - \epsilon_B$,

$$H_{\text{oligomer}} = \sum_{l=1}^{2N} \{h_{l,l+1} (c_l^\dagger c_{l+1} + \text{H.c.}) + (-1)^l \alpha c_l^\dagger c_l\}, \quad (4)$$

where $h_{l,l+1} = -t[1 - (-1)^l \delta_l]$, and δ_l is the lattice distortion at site l of the oligomer.

In the oligomer the lattice is dimerized (alternating long and short bonds) and the lattice sites fluctuate around their equilibrium positions. As a consequence, the bond lengths also fluctuate: $\delta_l = \delta_0 + \xi_l$. Here δ_0 is the lattice dimerization, and ξ_l the lattice fluctuation. The lattice fluctuations can be approximated as static white-noise disorder with a Gaussian distribution⁸ $\langle \xi_l \xi_{l'} \rangle = 2D \delta_{l,l'}$. Here D measures the strength of the fluctuations, and can be written as $D = \lambda \coth(\omega/2T)$, where ω is the optical-phonon frequency of the oligomer, T is the temperature, and λ is a parameter. Thus both quantum and thermal fluctuations are considered. The fluctuation strength can be extracted from experiments, e.g., the width of the intragap ‘‘tail’’ states in the luminescence spectra of polymers,¹⁴ and for polyacetylenelike polymers $\lambda \sim 0.02$.

For an incoming electron with energy E_k , we compute the transmission coefficient by solving the Schrödinger equation $H|\Psi\rangle = E_k|\Psi\rangle$. The wave function can be represented by the Wannier basis $|\Psi\rangle = \sum_{l=-\infty}^{\infty} c_l |l\rangle$. In the left metal

lead, the wave function includes two parts, the incident and reflected waves, $c_l = e^{ikl} + R e^{-ikl}$ for $-\infty < l \leq 0$. Similarly, in the right metal lead, the wave function is an outgoing wave, $c_l = T e^{ikl}$ for $2N+1 \leq l < \infty$.

$$\begin{pmatrix} E_k + \alpha & -h_{12} & 0 & 0 & \dots & 0 \\ -h_{12} & E_k - \alpha & -h_{23} & 0 & \dots & 0 \\ \cdot & \cdot & \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \cdot & \cdot & \dots & \cdot \\ 0 & \dots & 0 & -h_{2N-2,2N-1} & E_k + \alpha & -h_{2N-1,2N} \\ 0 & \dots & 0 & 0 & -h_{2N-1,2N} & E_k - \alpha \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \cdot \\ \cdot \\ \cdot \\ c_{2N} \end{pmatrix} = \begin{pmatrix} -t_1 c_0 \\ 0 \\ \cdot \\ \cdot \\ 0 \\ -t_1 c_{2N+1} \end{pmatrix}. \quad (5)$$

If we denote the above $2N \times 2N$ symmetric matrix as M , we have

$$c_1 = (M^{-1})_{1,1}(-t_1 c_0) + (M^{-1})_{1,2N}(-t_1 c_{2N+1}), \quad (6)$$

$$c_{2N} = (M^{-1})_{2N,1}(-t_1 c_0) + (M^{-1})_{2N,2N}(-t_1 c_{2N+1}).$$

Substituting Eq. (6) into the tight-binding equations for the two interfaces gives

$$E_k c_0 = -t_0 c_{-1} - t_1 c_1, \quad (7)$$

$$E_k c_{2N+1} = -t_1 c_{2N} - t_0 c_{2N+2},$$

and we obtain two equations for R and T . The reflection and transmission coefficients are obtained by ensemble averaging over 10 000 configurations: $r = \langle |R|^2 \rangle$, $t = \langle |T|^2 \rangle$.

Figure 2 shows the transmission coefficient for a $2N=8$ oligomer chain versus the energy of the incoming electron for different disorder strengths. Here $\alpha=0$, so the oligomer is of *trans*-polyacetylene-type, and the edges of the energy gap are approximately at $\pm 2t\delta_0 = \pm 0.4t$. When the fluctuations are absent (no disorder), four resonant tunneling peaks are observed, and their energies correspond to the four discrete levels above the gap in the oligomer. As the disorder strength increases, the transmission above the gap is greatly reduced and the peaks diminish in intensity. This is easily understood, since the incoming electron loses its coherence due to scattering resulting from the disorder. When the energy of the incoming electron lies within the gap, the tunneling is enhanced. This enhancement becomes more pronounced as we increase the fluctuations. For sufficiently strong fluctuations we find a peak in the middle of the gap, i.e., $E=0$. This enhancement arises from the lattice-assisted tunneling.

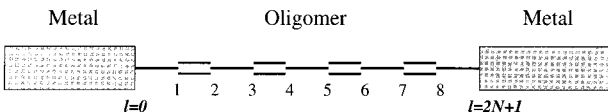


FIG. 1. Schematic diagram showing metal and oligomer sites in a chain.

The wave function of the oligomer is determined by matching the wave function at the interfaces between the metal and the oligomer. Thus we have a set of equations for the oligomer,

The enhancement of transmission within the energy gap of the oligomer can be better understood from the electronic density of states of the oligomer. We calculate the density of states of the oligomer with free boundary conditions by averaging the distribution of the discrete electronic levels over different lattice configurations. In Fig. 3, we present the ensemble-averaged density of states of a $2N=8$ oligomer for different disorder strengths. We observe that, when the fluctuations are strong enough, the density of states has a maximum in the middle of the gap. This result is consistent with the theoretical prediction of the density of states in an infinite chain with disorder,¹⁵ where it was shown that the density of states at the middle of the gap diverges if the disorder strength is larger than some critical value. We interpret the state at the middle of the gap to be a virtual soliton-antisoliton state due to lattice fluctuations. When fluctuations are strong, the bond alternation has some probability to ac-

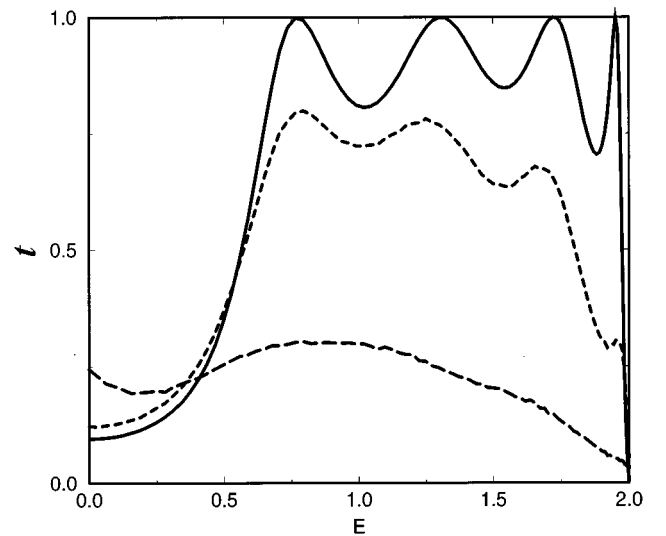


FIG. 2. Electronic transmission for an eight-atom oligomer device structure as a function of the energy of the incoming electron E . The parameters are $\alpha=0$, $t_0=t=1$, $t_1=0.8$, and $\delta_0=0.2$. The solid, dashed, and long-dashed lines correspond to disorder strengths $D=0$, $D=0.05$, and $D=0.15$, respectively.

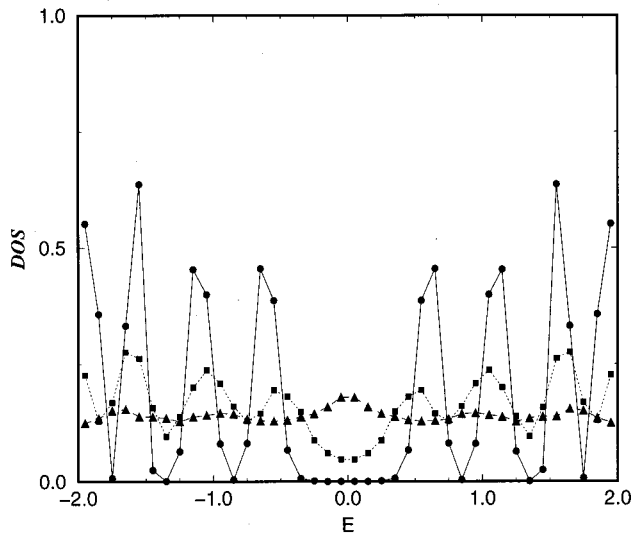


FIG. 3. Density of states for an eight-atom oligomer device structure. The parameters are the same as those in Fig. 2. The circles, squares, and triangles correspond to $D=0.05$, 0.15 , and 0.3 , respectively.

quire the “opposite” sign with respect to the regular long-short bond sequence, which results in a kink. The soliton level in a degenerate system (e.g., *trans*-polyacetylene) is at $E=0$, the middle of the gap.

We have also carried out the calculation of transmission for longer oligomers. For example, the results for a $2N=18$ oligomer chain are summarized in Fig. 4. Resonant transmission occurs when the energy of the incoming electron coincides with an electron level of the oligomer. When the energy of the incoming electron lies within the gap, the transmission is much smaller as compared to the $2N=8$

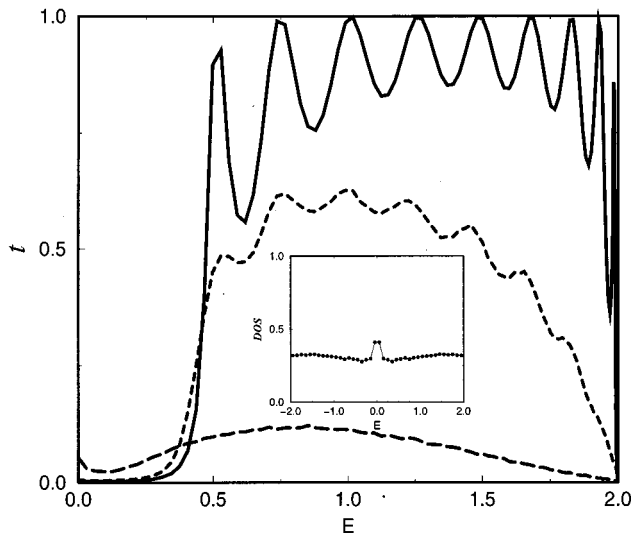


FIG. 4. Electronic transmission for an 18-atom oligomer device structure as a function of the energy of the incoming electron. The parameters are the same as in Fig. 2. The solid, dashed, and long-dashed lines correspond to disorder strengths $D=0$, 0.05 , and 0.15 , respectively. The inset shows the density of states of this oligomer for $D=0.3$.

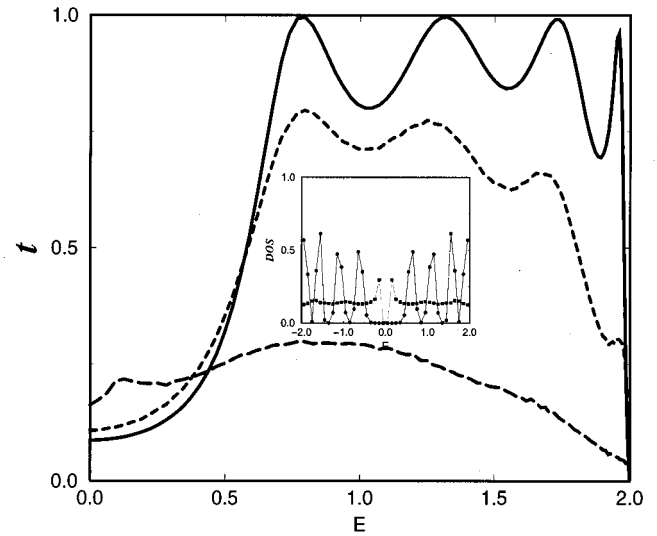


FIG. 5. Electronic transmission for an eight-atom oligomer device structure as a function of the energy of the incoming electron. The parameters are $\alpha=0.1$, $t_0=t=1$, $t_1=0.8$, and $\delta_0=0.2$. The solid, short dashed, and long-dashed lines correspond to disorder strengths $D=0$, 0.05 , and 0.15 , respectively. The inset shows the density of states of this oligomer for $D=0.05$ (circles) and 0.3 (squares).

chain. Qualitatively, within the gap the transmission decreases exponentially with an increase in the oligomer length.¹² There is again an enhancement of tunneling when the energy of the incoming electron lies within the gap, and a transmission maximum at $E=0$ when the fluctuations are sufficiently strong.

Next we study the *AB*-type polymer. In Fig. 5, we illustrate the transmission coefficient as a function of the electron energy for $\alpha=0.1$. When there are no lattice fluctuations, the transmission profile is very similar to that in Fig. 2. As we increase the fluctuation strength, the tunneling is enhanced in the low-energy region similar to the $\alpha=0$ case. However, unlike *trans*-polyacetylene-type oligomers, we observe a maximum of transmission within the gap at energy $E \neq 0$. We have also calculated the density of states for this *AB*-type polymer and found that two maxima of density of states occur at $E = \pm \alpha$. This is consistent with a virtual soliton-antisoliton states picture for lattice fluctuations, since, for an *AB*-type polymer, soliton levels are not at the middle of the gap but at $\pm \alpha$.¹³

We have not explicitly included electron correlation effects in our calculations. It is known that these effects are important in determining several material properties such as exciton states.¹⁶ Nevertheless, we note that for the single-electron tunneling considered here, correlations merely renormalize the parameters (t, α) in Eq. (4). The latter would change the discrete electronic levels and therefore shift the energy of resonance peaks. We have also neglected other effects such as the presence of a Coulomb blockade at the metal-oligomer contact which might be important when the coupling between the metal and oligomer is very weak or for a small tunneling device like a quantum dot. However, for the long oligomer chains considered here, we expect this effect to be unimportant.

In conclusion, we have shown that lattice fluctuations fundamentally change the electronic transmission properties of conjugated oligomers. They reduce the electronic transmission at energies corresponding to electronic levels of the ordered oligomer, and enhance the electronic transmission at energies in the gap of the ordered oligomer. This is consistent with a recent quantum-mechanical simulation¹⁷ and experimental measurements of the photoelectron kinetic-energy distribution and transmission function in thin organic films.¹⁸ These studies showed that the efficiency of scattering processes is enhanced by microscopic disorder. The electronic

transmission peaks in the gap of degenerate oligomers can be associated with virtual soliton-antisoliton states. These effects become more pronounced as the length of the oligomer is increased. Apart from a basic understanding of disorder, our results are potentially important for improving the efficiency of organic electronic devices.¹⁻⁶

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