Recent progress in molecular electronics has led to many interesting experiments on single-molecule junctions [1]. In particular, current-voltage (I-V) curves for a number of molecules have been measured in lithographically fabricated break junctions [2] and using scanning tunneling microscopy (STM) [3]. Several different theoretical approaches have been suggested for modeling charge-transport across single molecules [1], in conjugation with molecular modeling at various different levels of sophistication, ranging from the simple Hückel model [3] to density functional theories [4]. The nonequilibrium Green’s Function (NEGF) formalism [5], which allows self-consistent calculations of the electrostatic potential along the junction and transmission probabilities, offers a very promising method of calculating I-V characteristics of single molecule junctions.

Existing calculations of transport in organic molecular junctions have mostly been limited to determinations of I-V characteristics. It is well known, however, that thermal and quantum fluctuations play important roles in the nanometer scale. For future device applications, it therefore is essential to investigate current fluctuations in these systems. In order to design molecular junctions with the lowest possible current fluctuations, an efficient algorithm to calculate the noise power in molecular junctions is needed. To the best of our knowledge, there exists currently only one such calculation of the shot noise, in Si atomic wires, using a field-theoretic approach [3]. In the present Letter we investigate polyene molecules sandwiched between two metallic contacts using the NEGF technique. We calculate both the current and the noise power as a function of the applied voltage. The latter is calculated using an an expression due to Blanter and Büttiker [6]. Our I-V curves shows the step-like behavior that has been observed in resonant tunneling junctions [2]. We show that the current and noise power decreases with increasing size of the polyene molecules. We also show that I-V characteristics can be asymmetric even with symmetric connections to the metal, provided that the molecule under investigation is asymmetric [2]. One of the most interesting results of our calculation is Poissonian to sub-Poissonian crossover in the shot noise as a function of the applied voltage, which we hope can be tested experimentally.

The expressions for the current $\langle I \rangle$ and the noise power $S$ for the general two-terminal device are given by [9]

$$\langle I \rangle = \frac{2e}{h} \int_{-\infty}^{\infty} dE \, T(E) \, (f_L - f_R),$$

$$S = \frac{1}{2} \int_{-\infty}^{\infty} dt (\Delta I(t) \Delta I(0) + \Delta I(0) \Delta I(t))$$

$$= \frac{4e^2}{h} \int_{-\infty}^{\infty} dE \{T(E)(f_L(1 - f_L) + f_R(1 - f_R)) + T(E)[1 - T(E)](f_L - f_R)^2\},$$

where $T(E)$ is the transmission probability, $f_L$ and $f_R$ are the Fermi distributions for left and right terminals, respectively, and $\Delta I(t) = I(t) - \langle I \rangle$. Note the additional factor of two due to the summation over spin degrees of freedom.

The principal problem in calculating transmission probabilities through a metal-molecule-metal system is incorporating the infinitely many degrees of freedom of the metallic contacts. The NEGF formalism allows tracking out these degrees of freedom, such that the dimension of the Green’s function for the metal-molecule-metal system is comparable to the degrees of freedom of the molecule [6]. According to the NEGF formalism the transmission probability is given by

$$T(E) = \text{trace}[\Gamma_L G T(\Sigma R) G^\dagger],$$

where $G = [(E + 0^+) I - H - \Sigma_L - \Sigma_R]^{-1}$ is the Green’s function, $\Gamma_{L/R} = i [\Sigma_{L/R} - \Sigma_{L/R}^\dagger]$ and $\Sigma_{L/R}$ is the self-energy of the left/right terminal.

The molecular systems we consider are linear polyenes, described within the simple Hückel Hamiltonian,

$$H = \sum_{i,\sigma} \epsilon_i c_{i,\sigma}^\dagger c_{i,\sigma} - \sum_{i,\sigma} t_{i,i+1} (c_{i,\sigma}^\dagger c_{i+1,\sigma} + h.c.)$$

where $c_{i,\sigma}^\dagger$ creates an electron with spin $\sigma$ on site $i$ of a linear chain and $\epsilon_i$ is the site energy. The nearest neighbor
electron hopping integrals $t_{i,i+1}$ correspond to the alternate double and single bonds in the polyene molecules, and are taken to be $-2.6$ eV and $-2.2$ eV, respectively. The site energies are equal for the simple polyene (and hence may be taken to be zero). We will simulate asymmetry effects (see below) by considering unequal site energies, which can be achieved experimentally by chemical substitution. Self-energies that account for the semi-infinite leads with outgoing plane waves are now calculated using the procedure described in Reference [7]. We set the hopping integral within the lead $-5$ eV, the Fermi energy to $5.5$ eV and temperature $300$ K. This value of the Fermi energy corresponds to that of gold electrodes. While we report the results of calculations done with this one set of parameters only, we emphasize that our calculations were done with the lead hopping integral ranging from $-3.5$ eV to $-5.5$ eV, Fermi energy ranging from $3.5$ eV - $5.5$ eV and temperature $1$ K - $350$ K. In all cases our results were qualitatively the same.

Assuming that the voltage drops linearly along the polyene molecule, which is a good approximation for molecules with small cross section [10], we have calculated the current and noise power for polyenes with 4 and 10 carbon atoms (butadiene and decapentaene). In Fig. 1(a) we plot current and noise power as a function of the bias voltage ($V_b$) for butadiene.

The step-like behavior for the current has been observed in a number of mesoscopic conductors and is a result of resonant tunneling phenomenon [9]. Since electrons can travel from one terminal to another using molecular levels only, a sharp increase in current occurs whenever Fermi level of the metal aligns with the molecular level.

Our results for the noise power indicates Poissonian ($S = 2eI$) to sub-Poissonian ($S < 2eI$) shot noise crossover as a function of the applied voltage. We note that sub-Poissonian shot noise has also been observed in experiments on mesoscopic conductors [9].

We introduced asymmetry in the butadiene molecule by taking $\epsilon_1 = \epsilon_2 = -0.5$ eV and $\epsilon_3 = \epsilon_4 = 0.5$ eV. This resulted in asymmetric I-V and noise curves (see Figs. 1(b)). Note that for positive voltages, noise power exhibits a nonmonotonic behavior. It would be interesting to have experimental confirmations of this result.

In Reference [11], a different mechanism for asymmetric I-V curves, based on asymmetric metallic contacts, was proposed. A recent experiment has demonstrated asymmetric I-V curves for an asymmetric molecule [12]. Thus, our calculations confirm theoretical findings in Reference [11], that asymmetry in I-V curves can result from asymmetry of the molecule too.

Our results for the polyene with 10 carbon atoms (decapentaene) are shown in Fig. 2. Both the current and noise power are now smaller. In addition, many more steps now appear in the I-V curve. This can be easily explained based on a resonant tunneling phenomena.

Since decapentaene has more energy levels that butadiene, there are more values of the applied voltage when Fermi level of the metal aligns with the molecular levels.

In Reference [13], where similar I-V curves were calculated, it was suggested that low temperatures I-V curves can be used for predicting the electronic structure of molecules, based on the number of steps in I-V curve. Note that the plot of the noise power indicates Poissonian to sub-Poissonian shot noise crossover similar to one we have found for butadiene.

In summary, we have calculated current and noise power for symmetric and asymmetric polyene molecules sandwiched between two metallic contacts using the NEGF formalism. Our results indicate that the current and noise power decrease with increasing size of polyene molecules. We have shown that asymmetry in I-V and noise power curves can result from asymmetry
FIG. 2: Current and noise power for polyene with 10 carbon atoms.

of the molecule. We have also shown Poissonian to sub-Poissonian shot noise crossover as a function of the applied voltage. With constantly shrinking size of electrical circuits, the limit of single molecular junctions is being rapidly approached. For single-molecule junctions experimental results on the noise power are as important as I-V characteristics. We believe that the algorithm presented here for the noise power calculation can provide an efficient theoretical approach to designing molecules with the lowest possible noise.

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