Electron transport through a single-molecule device with center-of-mass motion: A numerical renormalization group study

Chinmoy Bhattacharjee

*Columbia University*

Abstract

We study the conductance of a molecular conductor with center-of-mass motion using the numerical renormalization group method. For spinless fermions, the zero-temperature, zero-bias conductance as a function of gate voltage is always peaked at the particle-hole symmetric point. However, in the spinful case, when the coupling between the molecule’s position and the hopping of electrons to/from the leads is sufficiently large, the conductance peak is replaced by a dip. This result appears to settle a controversy in the literature.
I. INTRODUCTION

In some materials, known as strongly correlated electron systems, the Coulomb repulsion between electrons leads to some remarkable physical properties, including high-temperature superconductivity, “heavy fermion” behavior and the Kondo effect. This research project falls within the area of strongly correlated electrons that focuses on so-called quantum impurity models. These models consider a localized degree of freedom having only a few internal states coupled to a large system (a macroscopic host or environment) having many degrees of freedom.

The classic example of a quantum impurity model is the Kondo model, which considers a simple magnetic impurity in a nonmagnetic impurity. This model was first proposed in the 1960’s to explain a low-temperature upturn in the resistance of metals containing dilute magnetic impurities. This phenomenon occurs due to the strong interactions between an unpaired electron spin in the impurity atom and the spins of conduction electrons nearby in the metal. Under the laws of quantum mechanics, the conduction electrons can lower their energy by orienting themselves antiparallel to the impurity spin. This causes the spin of the impurity to become screened from other electrons. As the temperature goes down, this effect becomes stronger, and the screening cloud grows around the impurity. Since many electrons need to be involved in this process, the Kondo effect is a many-body phenomenon.

Nowadays, interest in quantum impurity problems has shifted from the context of magnetic impurities in bulk metals to nanoscale applications such as quantum dots. A quantum dot is a small region—a tiny semiconductor device or a carbon nanotube—that can hold only a few electrons. Quantum dots are often called artificial atoms because their properties resemble those of real atoms. The advantage of quantum dots is that the parameters of
these artificial atoms can be controlled experimentally.

Recently scientists have been able to engineer a molecule (the “impurity”) trapped between two electrodes. Using external knobs (gate voltages), it is possible to vary the discrete energy levels of the molecule. Instead of considering many levels, the idea of this quantum impurity system is to focus on one electron level that can hold zero, one, or two electrons. (Occupancies greater than two are forbidden by the Pauli exclusion principle.) The level has its lowest energy when occupied by one electron, which gives the level a net spin $\pm \frac{1}{2}$. However, quantum mechanics allows the system to briefly occupy a “virtual state” in which an electron hops between impurity level and the lead, causing the impurity to temporarily have occupancy zero or two. Then another hop causes the impurity to return to occupancy one. This process may result in a change in the direction of the impurity spin. This happens, for instance, if an “up” ($S_z = +\frac{1}{2}$) electron hops off the impurity, but a “down” ($S_z = -\frac{1}{2}$) electron hops back on. A succession of many such “spin flips” produces the Kondo effect, which can be observed via a dramatic change in the electrical conductance between the electrodes connected to the molecule.

We aim to study the conductance versus gate voltage characteristics of a molecular conductor, taking into account that the molecule can also vibrate between the leads. We do so using an enhanced version of Anderson’s single impurity model initially proposed in 1961 to understand magnetic impurities in nonmagnetic metals [1]. We employ the numerical renormalization group technique to solve the model, and we aim to resolve a controversy arising from two earlier theoretical studies that solved the same model using different methods.
II. MODEL

A. Hamiltonian

We study the conductance of a device consisting of a molecule that can oscillate between source and drain electrodes, as depicted schematically in Fig. 1. Here, we include not only the physics of a localized electronic level hybridizing with conduction bands or leads—the regular Anderson model [1]—but also terms coupling center-of-mass (CM) vibrations of the molecule to tunneling processes to and from the leads. Thus, following Al-Hassanieh et al. [2], we write the Hamiltonian, in standard second-quantized notation, as

\[ H = H_M + H_L + H_{M-L}. \] (1)

The first term,

\[ H_M = V_g \hat{n}_d + U \hat{n}_{d\uparrow} \hat{n}_{d\downarrow} + \omega_0 a^\dagger a + \lambda (1 - \hat{n}_d) (a + a^\dagger), \] (2)

describes the isolated molecule. As in the regular Anderson impurity model [1], we consider a single electronic level of energy \( V_g \). The level can hold at most two electrons, which must be of opposite spin due to Pauli’s exclusion principle. The operator \( \hat{n}_{d\sigma} \) gives the number of electrons of spin \( \sigma = \uparrow \) or \( \downarrow \) in the impurity level. Coulomb interactions between electrons enter the model only in the molecular level, where the energy cost associated with double occupancy is \( U \). Such a level, hybridizing with a noninteracting band of conduction electrons is Anderson’s original Hamiltonian introduced over four decades ago to understand local moment formation in metals with magnetic impurities. In the present context, the level
energy \( V_g \) is controlled by the gate voltage. The remaining terms in \( \hat{H}_M \) concern the CM vibrations of the molecule, modeled as a quantum-mechanical oscillator of frequency \( \omega_0 \). The operator \( a (a^\dagger) \) destroys (creates) one quantum of vibrational excitation or one phonon. The combination \( a^\dagger a \) measures the number of phonons in the system, while the final term in \( \hat{H}_M \) couples the vibrational excitations to the net charge on the molecule \( \hat{n}_d - 1 \).

The left and right leads of the device are described by \( \hat{H}_L \). Each lead is taken to be a noninteracting band of electrons, modeled as a tight-binding chain where only the end site (labeled \( i = 0 \)) connects to the molecule. Thus,

\[
\hat{H}_L = -t \sum_{l=L,R} \sum_{i=0}^{\infty} \sum_{\sigma=\uparrow,\downarrow} (c_{i+1,\sigma}^\dagger c_{i,\sigma} + \text{H.c.}).
\]  

The third term in Eq. (1) describes the molecule-lead connection:

\[
\hat{H}_{M-L} = t' [1 - \alpha(a + a^\dagger)] \sum_\sigma (d_{\sigma}^\dagger c_{L0\sigma} + \text{H.c.}) + t'[1 + \alpha(a + a^\dagger)] \sum_\sigma (d_{\sigma}^\dagger c_{R0\sigma} + \text{H.c.}).
\]  

Here, \( d_{\sigma}^\dagger c_{\sigma} \) describes the hopping of an electron of spin \( \sigma \) from the end site of the chain representing lead \( l \) onto the impurity level; \( t' \) is the quantum-mechanical amplitude for this hopping when the molecule is half-way between the two leads; and \( \alpha \) parametrizes the change in this amplitude due to displacement of the vibrating molecule from its average position.
When the displacement $\hat{x} = (a + a^\dagger)$ is positive, hopping to the left lead is reduced while the right lead is enhanced; thus, the signs in front of the $\alpha$ term are opposite for the two leads. We will find it convenient to define $\Gamma_0 = 2\pi \rho(\varepsilon_F) t'^2$ and $\Gamma' = \alpha^2 \Gamma_0$, where $\rho(\varepsilon_F)$ is the density of lead states at the Fermi level.

We are interested in calculating the conductance $G$ through the molecule as a function of gate voltage $V_g$ for fixed values of the other model parameters $U$, $t$, $t'$, $\lambda$, and $\alpha$. The conductance $G$ at zero temperature and zero bias can be written [2] $G = (2e^2/h)|t^2 G_{LR}(\varepsilon_F)|^2 \rho(\varepsilon_F)^2$, where $G_{LR}$ is the Green function that propagates electrons from the left to the right lead.

**B. Solution: Numerical Renormalization Group**

Solution of quantum impurity problems is very challenging because of the very large number of degrees of freedom involved. (In fact, we idealize the leads as being infinitely long.) In our studied system, the impurity interacts not only with two conduction bands but also with a set of bosons describing the CM motion. This complicated quantum-mechanical problem requires a nonperturbative approach to understand the physics underlying the system. We have turned to the numerical renormalization group (NRG), which has provided comprehensive numerical solutions to many-body problems such as the Kondo model and the Anderson-Holstein model. We now discuss the essential elements of the NRG method.

First, the continuum of conduction band energies $-D \leq \varepsilon \leq D$ (where $D$ is the half-bandwidth) is replaced by a discrete set of energies $\varepsilon = \pm \Lambda^{-n}$, $n = 0, 1, 2, \ldots$ where $\Lambda > 1$ (typical values lie in the range $1.5 \leq \Lambda \leq 3$). Second, this discretized band is mapped exactly onto a semi-infinite chain.

The discretization leads to the exponential decay of tight binding coefficients along the chain; in Fig. 2, $t_n \simeq D\Lambda^{-n/2}$. This allows one to solve the Hamiltonian iteratively by
FIG. 2: Three important steps in the NRG transformation of the Anderson impurity model in which the impurity (filled circle) hybridizes with a continuous conduction band: (a) The conduction band is divided logarithmically using the NRG discretization parameter $\Lambda$. (b) The continuum of conduction band states within each interval is replaced by a single state. (c) The discretized model is mapped onto a semi-infinite chain where the impurity couples only to the first chain site via a hybridization (hopping) $V$. (Figure reproduced from [3].)

After many iterations, these solutions describe the physics at a sequence of exponentially decreasing temperatures, $T_N \sim D\Lambda^{-N/2}$. Consecutive solutions diagonalizing in turn chains of length $N + 1$, where $N = 0, 1, 2, \ldots$. After many iterations, these solutions reach a scale-invariant fixed point, which can be used to calculate the low-temperature properties of the quantum impurity system.
In practice, it is not possible to solve exactly even the discretized version of Eq. (1). At iteration 0, the number of phonons can take any non-negative value, making the number of quantum mechanical states of the system infinite. However, since each phonon carries an energy $\omega_0$, the low-energy many-body states—those that determine the low-energy and low-temperature properties—contain small numbers of phonons. It is therefore a good approximation to restrict the number of phonons considered to a maximum value $N_B$. As will be shown below, values of $N_B$ in the range 6 to 12 gave similar results in our calculations.

Even with a finite $N_B$, the total number of quantum-mechanical states increases by a factor of four at each subsequent iteration. In order to keep the memory and computational time finite, it is necessary to keep at most $N_S$ states at the end of one iteration to form the starting point for the next iteration. In our runs, we used $N_S$ in the range 300 to 2000.

III. RESULTS

A. Anderson-Holstein Model

Before delving into the problem involving center-of-mass motion, we validated our NRG method by reproducing some results for another closely related quantum impurity model. The Anderson-Holstein model describes a magnetic impurity atom interacting with both a conduction band and with lattice vibrations represented by a phonon mode. The Hamiltonian for this model is identical to Eq. (1) with $\alpha = 0$, and $V_g = \epsilon_d$, the energy of the singly-occupied impurity level. The Anderson-Holstein model has been successfully studied using NRG by Hewson and Meyer [4] and by others.

We have focused on the case $V_g = -0.05D$, $U = 0.1D$, $\Gamma_0 = 0.016D$ and $\omega_0 = 0.05D$ and first calculated the spectral density $A(\omega)$ for different values of $\lambda$. $A(\omega)d\omega$, which represents
FIG. 3: Spectral density $A$ vs frequency $\omega$ for the Anderson-Holstein model with $V_g = -0.05D$, $U = 0.1D$, $\Gamma_0 = 0.016D$, $\omega_0 = 0.05D$, and the values of $\lambda$ shown in the legend.

the probability that an electron in the impurity level has an energy between $\omega$ and $\omega + d\omega$, exhibits a peak centered on the most probable energy, $\omega = 0$. Figs. 3 and 4 show that when the electron-phonon coupling $\lambda$ is increased from zero, the peak initially broadens, but it then rapidly narrows. By $\lambda = 0.1D$, the central resonance peak has collapsed to be replaced by two broad peaks centered at the finite energies above and below $\omega = 0$. These trends reproduce the behavior reported by Hewson and Meyer [4].

Now, we use the same $\alpha = 0$ model to calculate the conductance of a molecular device. Following the method of Cornaglia et al. [5], we calculate conductance $G$ of the molecular junction at zero bias as

$$G = \left. \frac{dI}{dV} \right|_{V=0} = G_0 \pi \Gamma_0 \int_{-\infty}^{\infty} d\omega \left( \frac{-\partial f(\omega)}{\partial \omega} \right) A(\omega), \quad (5)$$

where $f(\omega)$ is the Fermi-Dirac distribution, and $G_0 = 2e^2/h$ is the quantum of conduc-
At absolute temperature $T = 0$, $\partial f(\omega)/\partial \omega = \delta(\omega)$ (a Dirac delta function), so $G = G_0 \Gamma_0 A(0)$.

Fig. 5 shows the linear conductance $G$ as a function of gate voltage for $T = 0$ and for three values of the coupling $\lambda$. We see a peak centered at the symmetric point $V_g = U/2$ becomes narrower as $\lambda$ increases from zero. This trend, which reproduces the results of Cornaglia et al. [5], shows that increasing electron-phonon coupling makes it harder to change the charge on the impurity and thereby pass an electron through the level.

**B. Molecular Conductor with Center-of-Mass Motion**

Having checked the validity of our NRG method, we move onto the original problem incorporating CM motion. Al-Hassanieh et al. [2] have found that the key signature of the term $\alpha$ in $\hat{H}_{M-L}$ is a dip in the zero-temperature conductance to $G = 0$ at $V_g = -U/2$. 
FIG. 5: Conductance $G$ vs gate voltage $V_g$ for the Anderson-Holstein model with $U = 0.1D$, $\Gamma_0 = 0.016D$, $\omega_0 = 0.05D$, and the values of $\lambda$ shown in the legend.

This has been disputed by Mravlje et al. [6], who report a peak in $G$ at $V_g = -U/2$. Since Al-Hassanieh et al. [2] have claimed that the dip appears even in the noninteracting limit $U = 0$, it would be interesting to consider first the case of spinless electrons where the Coulomb interaction plays no role in the $\hat{H}_M$. Fig. 6 shows the conductance vs. gate voltage for the spinless version of Eq. (1) with fixed Hamiltonian parameters but keeping different numbers of states after each NRG iteration. The curves lie on top of each other, showing that it suffices to keep 300 states for this problem.

In Fig. 7, we plot the conductance for the same parameters as in Fig. 6, except this time varying $N_B$, the maximum number of bosons allowed at each site of the chain. The results presented indicate that $N_B = 6$ yields well-converged results. We also test the change in the conductance curve as we vary $\Gamma'$, keeping $\Gamma_0$, $\omega_0$, and $\lambda$ fixed. In Fig. 8, we observe that the height of the central peak in $G$ vs $V_g$ does not change as $\Gamma'$ is increased from zero, but the
FIG. 6: Conductance $G$ vs gate voltage $V_g$ for the spinless model of a molecular conductor with $\Gamma_0 = 0.016D$, $\Gamma' = 0.004D$, $\omega_0 = 0.05D$, and $\lambda = 1.2\omega_0$. The conductance does not change significantly as the number of retained states is increased from $N_S = 300$ to $N_S = 1000$, holding fixed at $N_B = 8$ the maximum number of bosons per site of the NRG chain.

width of the peak decreases monotonically.

Even if the conductance curve does not change significantly for the spinless case, it is not safe to assume that this holds for the spinful case. To check this explicitly, we also consider the spinful case with $U \neq 0$. The spinful case has many degrees of freedom, so we must keep more NRG states to achieve the same accuracy. However, the NRG code also has to do much more computational work for this case, which makes it slower. We have fixed $U = 0.1D$, $\Gamma_0 = 0.016D$, $\omega_0 = 0.05D$, and $\lambda = 1.2\omega_0$. We have performed runs keeping between $N_s = 100$ and 1500 states for several combinations of $\Gamma'$ and $V_g$. Now we see a marked change in the conductance curve between $0.004D$, for which $G$ peaks at $V_g = -U/2$, $\Gamma' = 0.008D$, for which there is a dip to $G = 0$ for $V_g = -U/2$. This dip exists for all values
FIG. 7: Conductance $G$ vs gate voltage $V_g$ for the spinless model of a molecular conductor with $\Gamma_0 = 0.016D$, $\Gamma' = 0.004D$, $\omega_0 = 0.05D$, and $\lambda = 1.2\omega_0$. The conductance does not change significantly as the maximum number of bosons at each site of the NRG chain increases from $N_B = 6$ to $N_B = 12$, holding fixed as $N_S = 300$ the number of retained states.

IV. SUMMARY

We have studied the conductance of a molecular conductor with center-of-mass motion using the numerical renormalization group method to calculate spectral density for the physically most important molecular level. For spinless fermions, the zero-temperature, zero-bias conductance as a function of gate voltage is always peaked at the particle-hole symmetric point. In the spinful case, when the coupling between the molecule’s position and the hopping of electrons to/from the leads is sufficiently large, the conductance peak is
FIG. 8: Conductance $G$ vs gate voltage $V_g$ for the spinless model of a molecular conductor with $\Gamma_0 = 0.016, \omega_0 = 0.05$, and $\lambda = 1.2\omega_0$. Increasing $\Gamma'$ does not change the height of the central resonance peak.

FIG. 9: Conductance vs gate voltage for the spinful model of a molecular conductor with $U = 0.1D$, $\Gamma_0 = 0.016D$, and $\Gamma' = 0, \omega_0 = 0.05D$, and $\lambda = 1.2\omega_0$. Increasing $N_S$, the number of retained states, does not change the central resonance peak but slightly decreases the peak width.
FIG. 10: As for Fig. 9 except $\Gamma' = 0.004$. Changing number of states does not change the central resonance peak, however the width of the central resonance peak decreases as the number of states $N_s$ changes.

FIG. 11: Same as Fig. 8 except $\Gamma' = 0.008$. A dip is visible around the symmetric point $V_g = -0.05$. Changing number of states does not change the central resonance peak, however the width of the central resonance peak decreases as the number of states $N_s$ changes.

replaced by a dip. This result seems to support the picture presented by Al-Hassanieh et al. [2] and contradicts the results of Mravlje et al. [6].
V. ACKNOWLEDGEMENT

I thank Prof. Kevin Ingersent and Dr. Matthew Glossop for their guidance and support throughout this project, and acknowledge NSF funding for the REU program.