In recent years it has become possible to fabricate devices in which the active element is a very small organic molecule. Such a device may be thought of as a 'quantum dot': a structure weakly coupled to the macroscopic charge reservoirs ('leads') and small enough that the quantization of the energy levels on the dot is important. Quantum dots fabricated using conventional semiconductor technology have been extensively studied experimentally and theoretically. However, the use of small molecules may lead to new physics. In particular, as electrons are added or removed from a small molecule the shape of the molecule is altered. The energies associated with this shape change are not small, and the time scales may be comparable to those related to the flow of electrons into and out of the molecule. Interesting recent data indicate that these effects may lead to interesting structures in the conductance spectra of the dot.

The shape change may be thought of as a coupling of electrons on the molecule to phonon modes of the molecule. The subject of electron-phonon coupling in quantum dots has received some theoretical attention, however the existing literature appears contradictory, and many papers omit important physics or make apparently incorrect statements. For example, the phonon-induced renormalization of the coupling between the molecule and the leads is often neglected. Further, some papers assert (incorrectly, we believe) that phonon sidebands may be observed even in the linear-response conductance. There is apparently no comprehensive discussion of the relation between model parameters and the phonon-induced features of the conductance. Further, a coupling of the dot to leads implies a mechanical coupling between the dot and the external world which may allow the phonons on the dot to relax to an equilibrium determined by the leads, instead of following the electrons. The effect of this physics on the conductance has apparently not been examined.

In this paper we present a theoretical treatment of a simple model of electron-phonon effects in a molecular quantum dot which addresses these issues. Our treatment is valid in the limit (likely of greatest immediate experimental relevance) in which the temperature is higher than the level broadening induced by coupling the molecule to the leads, and is based on a rate equation approach with coefficients derived via a golden-rule analysis. We present results for average current as functions of gate and source-drain voltage for two limiting cases: phonons uncoupled from the external world and responding only to on-dot electrons (phonon equilibration slow compared to dwell time of electron on dot), and phonons equilibrated to the external world independent of the electron occupation (phonon equilibration fast compared to dwell time of electron on molecule). Subsequent papers will analyze the low-$T$ limit and the equilibrium/nonequilibrium crossover.

For simplicity we consider here the case of a molecule with a single relevant level, coupled to a single (Einstein) phonon mode and to two leads, which we label as 'left' and 'right', described by the Hamiltonian

\[
H = H_{\text{dot}} + H_{\text{phonon}} + H_{\text{mix}}
\]

with

\[
H_{\text{dot}} = \varepsilon_n d_n + U n_d (n_d - 1) + \lambda \omega_{ph} (b^\dagger b + b^\dagger b^\dagger) n_d
\]

\[
H_{\text{phonon}} = \omega_{ph} b^\dagger b
\]

\[
H_{\text{mix,el}} = \sum_{a=L,R} \sum_{\sigma} V_a \left( \epsilon_{a\sigma} d^\dagger_{a\sigma} d_{a\sigma} + H.c. \right)
\]

Here the number of electrons on the molecule, $n_d$, is given by

\[
n_d = \sum_{\sigma} d^\dagger_{\sigma} d_{\sigma}.
\]

![FIG. 1: Energy level diagram. $\mu_{L,R}$ represent the chemical potential in the left and right leads respectively, while $\epsilon'$ represents the ground state of the singly occupied dot and the dashed lines indicate phonon excitations of the singly occupied dot. The solid line indicates the energy $\epsilon'' + U$ of the doubly occupied dot. In this paper we take the $U \rightarrow \infty$ limit.](image-url)
the parameter $U$ is the charging energy of the molecule, the parameter $e$ gives the energy of putting one electron into the dot, the $V$ represent the hybridization of the molecule and the leads, while the left and right leads are characterized by chemical potentials $\mu_L$ and $\mu_R$ and densities of states $N_{L,R}$. We have defined the zero-phonon state to be the ground state when $n_d = 0$, and we neglect anharmonicity in the lattice part of the Hamiltonian (such anharmonicity is of course induced by the electron-phonon coupling and an intrinsic anharmonicity could easily be added).

Fig. 1 shows the energy level diagram corresponding to the problem we consider. We choose as zero of energy the value $\epsilon'$ corresponding to the ground state of one electron on an isolated dot, and we consider the behaviour as the chemical potentials of the left and right leads are varied. We specialize here to the large U limit most likely to be relevant for small molecules, so restrict the dot occupancy to zero or 1. In conventional language the source-drain voltage $V_{sd} = \frac{\mu_L - \mu_R}{e}$, while the gate voltage $V_g = \frac{\mu_L + \mu_R}{2e}$. One should include in the model a coupling between the phonons on the molecule and phonons in the leads or elsewhere in the device. Such coupling would provide a mechanism for the molecular phonons to equilibrate to the leads, and should be included in a fully general treatment. Here we study only the limit of uncoupled phonons (described by $H$ above) and the limit of fully equilibrated phonons, which we obtain as described below.

We shall be interested in the current $I$ flowing between the leads,

$$I = \frac{2e}{h} \sum_{\sigma} \left( \langle c^\dagger_{L\sigma} c_{L\sigma} \rangle - \langle c^\dagger_{R\sigma} c_{R\sigma} \rangle \right)$$

as a function of the two chemical potentials.

The term $H_{mix}$ leads to broadening of the electron levels. The resulting widths due to coupling to the left and right leads are $\Gamma_{L,R} = N_{L,R} V_{L,R}^2$. We specialize here to the case in which temperature is large compared to the level broadening: $\Gamma_{L,R} << T$. In this case, the behavior may be described by rate equations describing transitions between different states of the system.

A state of the system is specified by a number of electrons on the dot, and a number of excited phonons, and transitions involve changing the number of electrons or phonons or both. Before writing the rate equations, it is convenient to perform a standard canonical transformation to eliminate the explicit electron-phonon coupling in Eq. 11. Defining $S = \lambda \sum_{\sigma} d_{\sigma}^d d_{\sigma}$) $| \lambda | > 0$ and transforming all operators $O$ via $e^{S O e^{-S}}$ leads to a transformed Hamiltonian $H' = H'_{dot} + H'_{mix}$ with

$$H'_{dot} = \epsilon' n_d + \omega_{ph} a^\dagger a + \hat{U} n_d (n_d - 1)$$

$$H'_{mix} = \sum_{\alpha = L,R} V_{\alpha} \sum_{\sigma} \left( \tilde{X} c^\dagger_{q\sigma} d_{\sigma} + H.c. \right)$$

where the transformed phonon operator $\alpha = b - \lambda \sum_{\sigma} d_{\sigma}^d d_{\sigma}$, so the phonon ground state depends on the dot occupancy. $\epsilon' = \epsilon - \frac{2\omega_{ph}}{\omega_{ph}}$ is the ‘polaron shift’ in the energy for adding one electron to the molecule and the interaction parameter $U$ is also renormalized, but as we shall focus here on $U \to \infty$ we do not write the renormalization explicitly here. The crucial phonon renormalization of the electron-lead coupling is given by

$$\tilde{X} = \exp \left[ -\lambda (a^\dagger - a) \right]$$

After the transformation the state of the system is specified by the dot occupancy $n$ and the number of phonons $q$ excited above the ground state corresponding to the given occupancy $n$ and we shall be concerned with the probability $P^n_q$ that the system has $n$ electrons and $q$ excited phonons. Transitions between states are determined by applying the golden rule to $H'_{mix}$. The resulting transition rate depends on the change in phonon occupation number (it also depends on the electron distribution in the leads but we write this dependence separately).

The transition rate involving hopping an electron from the dot to lead $a$ and changing the phonon occupancy from $q$ (measured relative to the ground state of $H'_{dot}$ with occupancy $n$) to $q'$ (measured relative to the ground state of $H'_{dot}$ with occupancy $n - 1$) is equal to the transition rate involving hopping an electron from the lead $a$ to the dot and changing the phonon occupancy from $q$ (measured relative to the ground state of $H'_{dot}$ with occupancy $n - 1$) to $q'$ (measured relative to the ground state of $H'_{dot}$ with occupancy $n$) and is

$$\Gamma_{n \to q} = \Gamma_a |< q'| X |q >|^2$$

The matrix element can be computed by standard methods its absolute value $|< q'| X |q >|^2 \equiv X^2_{qq'}$ is symmetric under interchange of $q$ and $q'$ and is

$$X^2_{q<q'} = \sum_{k=0,q} (-\lambda^2)^k \frac{(q!k!)^{1/2}}{(k!)^{q-k}!(k+|q'-q|)!}$$

As interesting special cases, let us write the several lowest operators:

$$X_0 = e^{-\lambda^2/2} \lambda^n \sqrt{n!}$$

$$X_1 = (1 - \lambda^2) e^{-\lambda^2/2}$$

$$X_2 = \sqrt{2} \lambda (1 - \frac{\lambda^2}{4}) e^{-\lambda^2/2}$$

$$X_3 = (1 - 2\lambda^2 + \frac{\lambda^4}{4}) e^{-\lambda^2/2}$$

Observe that for certain values of $\lambda$ some of the matrix elements vanish. This unusual behavior is an interference phenomenon, which is slightly obscured by the notation. A state which has $q$ phonons excited above the ground state of the system with $n = 0$ electrons is a superposition (with varying sign) of many multiphonon states, when viewed in the basis which diagonalizes the $n = 1$ electron problem, and therefore the transition described by $X_{qq'}$ is really a superposition of many different transitions, which for some values of $\lambda$ may destructively interfere. The phonon renormalization of the molecule-lead
coupling is apparently omitted, or treated in an average manner which neglects the \( q, q' \) dependent structure, in several recent papers\(^{10,11,12} \).

We are now in a position to write rate equations, following e.g.\(^{15} \). If the phonons are uncoupled from the leads we have (\( f_a \) is the fermi function for lead \( a \)).

\[
\dot{P}^a_q = \sum_{a,q,q'} f_a ((q - q') \omega_{ph} + U(n + 1)) \Gamma^a_{q,q'} P^{(n-1)}_{q'} + (1 - f_a ((q' - q) \omega_{ph} + U(n + 1))) \Gamma^a_{q,q'} P^{(n+1)}_{q',q} - (1 - f_a ((q - q') \omega_{ph} + U(n - 1))) \Gamma^a_{q',q} P^n_{q,q'}
\]

The net current flowing into the dot from lead \( a \) is

\[
I^a = \sum_{n,q,q'} P^n_{a,q} f_a ((q' - q) \omega_{ph} + U(n + 1)) \Gamma^a_{q,q'} (17)
\]

where the sum on \( n \) is from 0 to \( (d_{max} - 1) \), \( d_{max} \) being the maximum occupation of the dot. Note that in steady state it follows from the rate equation that \( I^L = -I^R \) which equals the total current across the dot.

The opposite limit, of phonons equilibrated to the leads (assumed here to be at the same temperature) may be treated in steady state by forcing the probability distributions on the right hand side of Eq.\(^{17} \) to have the phonon-equilibrium form \( P^n_{a,q} = P^n e^{-\omega_{ph}/T}(1 - e^{-\omega_{ph}/T}) \). In the \( U \to \infty \) limit this ansatz implies that the probability \( P^0 \) that the dot is empty is given by,

\[
P^0 = \frac{\sum_{a,q,q'} \Gamma^a_{q,q'} e^{-\omega_{ph}/T} f_{a,q,q'} - \sum_{a,q,q'} 2 \Gamma^a_{q,q'} e^{-\omega_{ph}/T} f_{a,q,q'} + \Gamma^a_{q,q'} e^{-\omega_{ph}/T} f_{a,q,q'}}{\sum_{a,q,q'} 2 \Gamma^a_{q,q'} e^{-\omega_{ph}/T} f_{a,q,q'}}
\]

where \( f_{a,q,q'} = 1 - f_a ((q' - q') \omega_{ph}) \), \( f_{a,q,q'} = 1 - f_a ((q - q') \omega_{ph}) \) while, \( P^1 = 1 - P^0 \).

In general for both equilibrated and unequilibrated cases the steady state rate equations \( \dot{P}^e_n = 0 \) constitute an eigensystem which we solve numerically. From these solutions we have computed the current. Representative results are shown in Fig. 2 which plots the low-T current as a function of \( V_{sd} \) for two gate voltages: \( V_g = 0 \) (\( \mu_L = -\mu_R \), upper panel) and \( V_g = \frac{eV_{sd}}{2} \) (\( \mu_R = 0 \), lower panel), for both equilibrated and unequilibrated phonons.

Steps (broadened by \( T \)) in the current associated with “phonon side-bands” are observed when the source-drain voltage passes through an integer multiple of the phonon frequency. However, in the opposite ‘linear response’ limit \( V_{sd} \to 0 \) (not shown), as \( V_g \) is varied we find just one main step in the \( I - V \)-curve, as \( V_g \) passes through 0, and only very tiny structures (vanishing as \( e^{-\omega_{ph}/T} \), which is the probability of the dot being empty with one phonon excited) when \( V_g \) is a non-zero multiple of the phonon frequency. This result appears to differ from that stated in Ref.\(^{12} \) who find phonon side bands as \( V_g \) is swept at \( V_{sd} \to 0 \). The difference occurs because Ref \(^{10} \) neglected the fact that the phonon side-bands “float” i.e., shift with the fermi level as \( V_g \) is changed.

Fig. 2 reveals on first sight an apparently surprising result: for symmetric bias (\( V_g = 0 \)) and for the coupling considered, the current is larger for equilibrated phonons than for the unequilibrated case, whereas for the strongly asymmetric case (\( \mu_R = 0 \)), the opposite is true. This is surprising because one expects that in the unequilibrated case the phonons arrange themselves so as to maximize the current. To gain more insight into this phenomenon we have calculated the dependence of the ratio of currents for unequilibrated and equilibrated phonons on the coupling \( \lambda \) for different degrees of bias asymmetry. We find that except for \( \mu_R = 0 \) (the most asymmetric case) a minimum in the ratio occurs for \( \lambda \sim 1 \). This behaviour may be traced back to Eq.\(^{15} \) which reveal that higher order “diagonal” (n phonon- n phonon) matrix elements vanish for \( \lambda \sim 1 \).

The steps in current may be conveniently parametrized by the height (or the area, as the width is simply proportional to \( T \)) of the corresponding peaks \( G_{max} \) in the differential conductance \( G = dI/dV \). Ratios of peak heights (or areas) provide a convenient experimental measure of whether the phonons are in equilibrium. At low \( T \), the equilibrium phonon distribution corresponds to occupancy only of the \( n = 0 \) phonon state, so the \( n \)-th side band involves a transition from the 0 phonon to the \( n \) phonon state. Therefore the ratios of the peak heights or areas are controlled by ratios of \( |X_n|^2 \). In particular Eqns.\(^{12,15} \) imply that if \( \mu_L = -\mu_R \) and \( T \ll \omega_{ph} \),

\[
\frac{G_{max}^{n}}{G_{max}^{0}} = \frac{|X_n|^2}{|X_0|^2} = \frac{\lambda^{2n}}{2(n!)}
\]

Note that if \( \mu_L \neq \mu_R \), then \( \mu \) dependent changes in the occupation probabilities lead to additional, and not simply characterized \( n \) dependence.

Deviations from this pattern imply non-equilibrium phonons. As illustration we display in Fig. 3 \( G_{max} \) values
ent electron-phonon coupling constants calculated for equilibrated phonons and two different coupling strengths and $\mu_L = -\mu_R$. The points for $\lambda = 0.5$ (open symbols) have been multiplied by 10.

FIG. 3: Ratio of peak heights for equilibrated and unequilibrated phonons and two different coupling strengths and $\mu_L = -\mu_R$. The points for $\lambda = 0.5$ (open symbols) have been multiplied by 10.

FIG. 4: Phonon probability distributions for two different electron-phonon coupling constants calculated for $\mu_L = -\mu_R = 2\omega_{ph}$.

(normalized to the zero frequency peak) for equilibrium and non-equilibrium phonons and a weak and strong electron phonon coupling. One sees that the non-equilibrium case the peak heights display a non-systematic dependence on electron-phonon coupling and peak index, but that in general measurements of the $n = 1$ and $n = 2$ peaks reveal the effect clearly.

It is also of interest to consider how far out of equilibrium the phonon distribution may be driven. Fig. 4 shows the phonon occupation probabilities for weak and strong electron-phonon coupling and $V_g = 0$. One sees immediately that the phonon distribution function is farther from equilibrium for weak couplings than for strong couplings. We associate this effect to the strong $\lambda$ dependence of operators $X_{\lambda n}$, Eq. (12) which allows the system at large $\lambda$ to “jump down” from a highly excited state to one of low phonon occupancy. The deviation from equilibrium is largest for $V_g = 0$ for similar reasons.

In summary we have investigated a rate equation model for quantum dots with strong electron-phonon coupling. We find important effects arising from the phonon renormalization of the dot-lead matrix element and from whether or not the phonons are able to equilibrate. Future papers will address bistability and also the low-T limit in which the rate equation approach is not valid.

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