Noise-assisted charge pump in elastically deformable molecular junctions

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Abstract

We study a charge pump realized with an elastically deformable quantum dot whose center of mass follows a nonlinear stochastic dynamics. The interplay of noise, nonlinear effects, dissipation and interaction with an external time-dependent driving on the pumped charge is fully analyzed. The results show that the quantum pumping mechanism not only is not destroyed by the force fluctuations, but it becomes stronger when the forcing signal frequency is tuned close to the resonance of the vibrational mode. The robustness of the quantum pump with temperature is also investigated and an exponential decay of the pumped charge is found when the coupling to the vibrational mode is present. Implications of our results for nanoelectromechanical systems are also discussed.

Keywords: electronic transport in mesoscopic systems, adiabatic pumping, electron-vibration coupling

(Some figures may appear in colour only in the online journal)

1. Introduction

Modern nanoelectronic technologies open the possibility to test several transport regimes and quantum protocols at the boundary of the quantum and classical realm. In this intermediate regime the reduced device dimensions (smaller than the electronic mean free path) allow the preservation of the quantum coherence of the particles flux evidencing an emergent mesoscopic behavior. In mesoscopic systems, man-made nanocircuits can interact coherently with organic molecules giving origin to hybrid structures. A subclass of these organic-inorganic hybrids is represented by the heteroelastic nanodevices in which an elastic response is observed [1]. In these systems the charge density interacts with internal degrees of freedom that determine the elastic response of the device giving rise to new functionalities [2]. The simplest system belonging to this class of nanodevices is realized by an organic molecule (elastically soft part) connected to two external inorganic leads (elastically hard part). A minimal description for the above system is given in terms of the center of mass dynamics of the soft part (considered as classical) and its coupling to the charge state activated during the transport (requiring a quantum description) [3–5].

An interesting situation is the one of a charge pump realized by using a heteroelastic system [6]. Experimentally, organic materials like carbon nanotubes [7, 8] and graphene nanoribbons [9, 10] have been recently employed in the realization of pumping nanodevices exploiting their mechanical properties. In conventional quantum pumping, the adiabatic time modulation of two external parameters \( X_{1,2}(t) = X_{1,2}^0 + \delta X_{1,2} \sin(\omega t + \phi_{1,2}) \) parametrically affects the system Hamiltonian \( \hat{H}(X_1(t), X_2(t)) \) and produces a d.c. particle current proportional to the quantity \( \omega \delta X_1 \delta X_2 \sin(\Delta \phi) \), \( \omega \) being the pumping frequency and \( \Delta \phi = \phi_1 - \phi_2 \) the phase difference between the driving signals [11–13]. In recent years, many theoretical proposals appeared for free [11] and interacting [12] electron systems, while few experimental implementations of the pumping schemes appeared in [13]. The sinusoidal current-phase relation (CPR) is substantially modified when...
the scattering region reacts to the modifications of the internal charge state by adjusting its spatial configuration [14]. The latter situation has been studied in [15] where an elastically deformable quantum dot (DQD) has been studied. Assuming a linear deterministic dynamics for the mechanical deformation of the scattering region (harmonic oscillator paradigm), it has been demonstrated that the CPR is modified by the presence of a dynamical phase shift \( \phi_D \) of the response function of the harmonic oscillator. Furthermore, when the DQD model is generalized to include a weak nonlinearity in the oscillator dynamics [16], interesting memory effects take place. In general, as also observed in [17], the pumping current is fed by all the phase differences characterizing the scattering region and thus the presence of a hidden classical dynamics coupled to the transport determines a strong deviation from the conventional CPR of the charge pumping.

In this work, we study a charge pump realized with an elastically DQD whose dynamics is affected by stochastic forces induced by quantum and thermal fluctuations due to the electron charging of the quantum dot. Exploiting a non-equilibrium Green’s function approach that leads to a Langevin dynamics for the elastic part of the system, as formulated in [18–21], the pump response has been fully analyzed. The attention has been mainly focused on how the pumped charge depends on temperature and on the driving frequency. We show that, although pumping is strongly reduced with temperature, despite the moderate electron-phonon coupling. Finally, we observe nonlinear features in the resonator dynamics close to the resonance.

The paper is organized as follows: in section 2 the Anderson-Holstein model is introduced; in section 3 the adiabatic regime for quantum pumping is considered in the framework of a non-equilibrium Green’s functions approach and the Langevin dynamics is derived; in section 4 we discuss the results for the pumped charge and then give the conclusions. There are three appendices: appendix A on the numerical procedure, appendix B on the zero temperature behavior of the system, appendix C on the dynamical phase shift model.

2. The Anderson–Holstein (AH) model

The spinless Anderson–Holstein model is the simplest model of a molecular junction including the effect of electron-oscillator interaction (see figure 1 for a scheme of the device). The molecule is modeled as an electronic level interacting locally with a single vibrational mode and whose Hamiltonian

\[
\hat{H} = \hat{H}_{el} + \hat{H}_{osc} + \hat{H}_{int},
\]

where the electronic system is described by the standard junction Hamiltonian \( \hat{H}_d \):

\[
\hat{H}_d = V_G \hat{d} \hat{d} + \sum_{q,\alpha} \left[ Q_{q,\alpha}(t) \hat{c}_{q,\alpha} \hat{c}_{q,\alpha}^\dagger + h.c. \right] + \sum_{q,\alpha} \xi_{q,\alpha} \hat{c}_{q,\alpha} \hat{c}_{q,\alpha}^\dagger.
\]

The molecular electronic level has energy \( V_G \), determined by the gate voltage and \( \hat{d} \) is creation (annihilation) operators. The operators \( \hat{c}_{q,\alpha} \) create (annihilate) electrons with momentum \( q \) and energy \( \xi_{q,\alpha} = \xi_{q,\alpha} - \mu_\alpha \) in the left (\( \alpha = L \)) or right (\( \alpha = R \)) free metallic leads. The chemical potentials in the leads, \( \mu_L \) and \( \mu_R \), are assumed to be equal: \( \mu_L = \mu_R = 0 \) (absence of external voltage bias). The leads will be considered as thermostats in equilibrium at temperature \( T \). The electronic tunnelling between the molecular dot and a state \( k \) in the lead \( \alpha \) has the time-dependent amplitude \( V_G \). For the sake of simplicity, we will suppose that the density of states \( \rho_{q,\alpha} \) for the leads is flat within the wide-band approximation: \( \rho_{q,\alpha} \to \rho_0 \), \( V_G \to V_G \mu_\alpha \), with \( \mu_\alpha \) a periodic function of time governing the strength of the pumping (see figure 1). Therefore, the time-dependent full hybridization width of the molecular orbital is \( \Gamma(t, t') = \sum_\alpha \hbar \Gamma_\alpha(t, t') = \sum_\alpha \hbar \Gamma_\alpha \mu_\alpha(t) \mu_\alpha(t') \), with \( \hbar \) Planck constant and the tunnelling rate \( \Gamma_\alpha = 2\pi \rho_0 |V_G|^2 / \hbar \). In the following, we consider the symmetric configuration: \( \Gamma_L = \Gamma_R = \Gamma_0 \).

In equation (1), the Hamiltonian of the oscillator (or vibrational mode) is given by

\[
\hat{H}_\text{osc} = \frac{\hat{p}^2}{2m} + \frac{1}{2} k \hat{x}^2,
\]

with \( \hat{p} \) and \( \hat{x} \) momentum and position operator, respectively, while \( m \) is the effective mass, \( k \) the spring constant and the oscillator frequency is \( \omega_0 = \sqrt{k/m} \).

The interaction term \( \hat{H}_{int} \) (typically of electrostatic origin [21]) is provided by a simple linear coupling between the electron occupation on the molecule, \( \hat{n} \), and the displacement \( \hat{x} \) of the oscillator:

\[
\hat{H}_{int} = \lambda \hat{x} \hat{n},
\]

where \( \lambda \) is the electron-oscillator coupling strength and \( \hat{n} = \hat{d} \hat{d}^\dagger \) is the density operator. In the following, the coupling between the electron system and the vibrational mode will be often described in terms of the electron-oscillator coupling energy \( E_{ep} = \lambda^2 / (2k) \).
3. Adiabatic regime

In the following we will study the system under generic pumping strength and arbitrary electron-oscillator coupling in the experimentally relevant limit $\hbar \omega_0 \ll K_B T$, with $K_B$ Boltzmann constant. In this regime, the dynamics of the oscillator is classical. Therefore, the electronic dynamics is equivalent to a time-dependent single level problem with energy $E_0(t) = V_0 + \lambda x(t)$. Using the Keldysh formalism [22–24] we can solve the Dyson and Keldysh equations for the molecular Green’s functions. Actually, the retarded molecular Green’s function can be easily obtained as

$$G_r(t, t') = -\frac{i}{\hbar} \theta(t - t') e^{-\frac{1}{\hbar} \int_{t'}^t dt_1 E_0(t_1) - \frac{i}{2} \Gamma(t_1)},$$

(5) with $\theta(t)$ Heaviside function and $\Gamma(t) = \Gamma(t, t)$. The lesser Green’s function at equal time can be evaluated exactly:

$$G_<(t, t') = i \sum_{\alpha} \int_{-\infty}^{\infty} \frac{d(\hbar \omega)}{2\pi} f(\omega)|B_\alpha(\omega, t)|^2,$$

(6) with $f(\omega)$ Fermi function for both the leads $\alpha = R, L$ and the function $B_\alpha(\omega, t)$ defined as

$$B_\alpha(\omega, t) = \int_{-\infty}^{\infty} dt_1 u_\alpha(t_1) G_r(t, t_1) e^{i\omega(t-t_1)}.$$ (7)

It can be interpreted as the retarded Green’s function dressed with the pumping term $u_\alpha(t)$.

We analyze the electron system in the adiabatic regime for the electronic dynamics, which is in the limit of slow temporal perturbations: $\omega_0 \ll \Gamma_0$ and $d\Gamma/dt \ll \Gamma_0$. Within this regime, one uses the following expansion for the pumping parameter: $u_\alpha(t) \simeq u_\alpha(t) + \dot{u}_\alpha(t)(t-t_0)$, with the dot indicating the time derivative. Therefore, one can calculate the adiabatic expansion of the Green’s function considering the explicit dependence of the electronic quantities on the oscillator variables $x, v$ and its intrinsic dependence on time $t$ governed by the pumping terms $u_\alpha(t)$.

Within the adiabatic approximation one can derive the following expansion of the dot occupation $N(x, v, t)$:

$$N(x, v, t) = \langle \hat{n}(t) \rangle(t) \simeq N^{(0)}(x, t) + N^{(1)}(x, v, t),$$

(8) where the zero order ‘static’ term $N^{(0)}_{el}(x, t)$ is

$$N^{(0)}(x, t) = \int_{-\infty}^{\infty} \frac{d(\hbar \omega)}{2\pi} \left( \frac{\hbar \Gamma(t)}{\hbar \omega - \lambda x} \right)^2,$$

(9) and the first order ‘dynamic’ term $N^{(1)}_{el}(x, v, t)$ is

$$N^{(1)}(x, v, t) = \frac{\hbar}{2} [\lambda v [\hbar \Gamma(t)] R(x, t) + [\hbar \dot{\Gamma}(t)] R_1(x, t)],$$

(10) with

$$R(x, t) = \int_{-\infty}^{\infty} \frac{d(\hbar \omega)}{2\pi} \left( \frac{\hbar \omega}{\hbar \omega - \lambda x} \right)^2,$$

(11)

$$R_1(x, t) = \int_{-\infty}^{\infty} \frac{d(\hbar \omega)}{2\pi} \left( \frac{\hbar \omega}{\hbar \omega - \lambda x} \right)^2 \frac{g(\omega)}{\left( \hbar \omega - \lambda x \right)^2 + \frac{\hbar \Gamma(t) \Gamma}{4}}.$$ (12)

where $\hbar g(\omega) = -\partial_\omega f(\omega)$.

We note that while $N^{(0)}$ depends on the Fermi distribution $f(\omega)$, $N^{(1)}$ depends on its derivative.

One can calculate the adiabatic expansion for the current $J_\alpha(x, v, t)$ from the lead $\alpha$ to the dot. We emphasize that the zeroth order expansion for the current vanishes (due to absence of voltage bias) and then $J^{(0)}(x, v, t) \simeq J_{\alpha}(x, v, t)$, where

$$J_{\alpha}(x, v, t) \simeq -e \left( \lambda v [\hbar \Gamma_\alpha(t)] V(x, t) + [\hbar \dot{\Gamma}_\alpha(t)] V_1(x, t) \right),$$

(13) with $e$ the modulus of electron charge,

$$V(x, t) = \int_{-\infty}^{\infty} \frac{d(\hbar \omega)}{2\pi} \left( \frac{\hbar \omega}{\hbar \omega - \lambda x} \right)^2$$

(14) and

$$V_1(x, t) = \int_{-\infty}^{\infty} \frac{d(\hbar \omega)}{2\pi} \frac{g(\omega) [\hbar \omega - \lambda x]}{\left( \hbar \omega - \lambda x \right)^2 + \frac{\hbar \Gamma(t) \Gamma}{4}}.$$ (15)

Within the adiabatic expansion, the charge conservation is valid at the zeroth order of the dot occupation: $eN^{(0)}(x, t) = J_L(x, v, t) + J_R(x, v, t)$.

3.1. Langevin equation for the oscillator

In this subsection, we analyze the dynamics of the oscillator within the adiabatic regime. The effect of the electron bath and the electron-oscillator coupling gives rise to a stochastic Langevin equation for the vibrational mode. This equation is characterized by a position and a time-dependent dissipation term and a multiplicative noise.

Within the adiabatic limit, the force can be decomposed as:

$$F(x, v, t) = F^{(0)}(x, v, t) + F^{(1)}(x, v, t).$$

(16) The zero order force $F^{(0)}(x, v, t)$ represents the ‘static’ part sensitive to the average charge occupation

$$F^{(0)}(x, t) = -kx - \lambda N^{(0)}(x, t),$$

(17) with $N^{(0)}(x, t)$ given in equation (9). The first order ‘dynamic’ term $F^{(1)}(x, v, t)$ is sensitive to charge fluctuations but also a very complex nonlinear term due to the effects of the pumping:

$$F^{(1)}(x, v, t) = -\lambda N^{(1)}(x, v, t) = -A(x, t) v + B(x, t) \dot{\Gamma}(t),$$

(18) with the damping coefficient $A(x, t)$ (positive definite) and $B(x, t)$ taken from equation (10):

$$A(x, t) = \frac{\hbar \lambda^2}{2} [\hbar \Gamma(t)] R(x, t),$$

(19)
and
\[ B(x, t) = -\frac{\hbar^2}{2} R_1(x, t). \] (20)

We point out that the pumping term introduces a complex forcing contribution dependent on the position \( x \) through \( B(x, t) \).

In the adiabatic limit, exploiting the effect of the fast electronic environment on the oscillator motion, one derives the following fluctuating term
\[ \langle \delta \hat{F}(t) \delta \hat{F}(t') \rangle = D(x, t) \delta(t-t'), \] (21)
where, due to the absence of electron voltage bias, \( D(x, t) = 2k_B T A(x, t) \), that is the fluctuation-dissipation condition is verified for each fixed position \( x \) and time \( t \).

The resulting Langevin equation for the oscillator dynamics becomes
\[ \dot{x} = v, \]
\[ \dot{v} = -A(x, t)v + F_{\text{col}}(x, t) + \sqrt{D(x, t)} \xi(t), \] (22)
where \( F_{\text{col}}(x, t) \) is the deterministic part of the force
\[ F_{\text{col}}(x, t) = F^{(0)}(x, t) + B(x, t) \bar{\dot{f}}(t), \] (23)
and \( \xi(t) \) is a standard white noise term. In the limit of zero temperature \( D(x, t) = 0 \), so that we have a deterministic equation.

In the following, we will use these equations to investigate the role of the deformable quantum dot on the pumped current. Specifically, we will study how the quantum dot softness affects the dependence of the pumped current on the generic pumping strength and arbitrary electron-oscillator coupling (the calculation procedure for \( P(x, v, t) \) is explained in appendix A). Hence, one can determine the properties of the oscillator and the time behavior of an electronic observable \( O_{\text{el}}(x, v, t) \):
\[ \langle O_{\text{el}}(t) \rangle = \int \int dx dv P(x, v, t) O_{\text{el}}(x, v, t). \] (24)

If the pumping terms \( u_\alpha(t) \) are periodic over \( T_P \), then the coefficient \( A(x, t) \) and the force \( F_{\text{col}}(x, t) \) exhibit the same periodic behavior. Consequently, we have found that the solutions of the Langevin equation reproduce themselves after one period, apart from a constant factor. In appendix A, we will discuss the numerical convergence of the results obtained from the solution of the Langevin equation (22). Most numerical results reported in this work will be shown with symbols whose size will provide an estimate of the numerical error involved.

In the calculation, we study the pumping with a very simple perturbation periodic over a period \( T_P \): \( u_\alpha(t) = 1 + S \cos((\omega_P t + \phi_\alpha), \) with \( \omega_P = 2\pi/T_P \) the pumping frequency

\[ \phi_\alpha \] the phase of the lead \( \alpha \). Therefore, we define \( \Delta \phi = \phi_\alpha - \phi_R \) as the phase shift between the two pumping parameters. We calculate the average \( \bar{O}_{\text{el}} \) of a time-dependent electron quantity \( \langle O_{\text{el}}(t) \rangle \), such as the dot occupation or the current, on a period \( T_P \) as
\[ \bar{O}_{\text{el}} = \frac{1}{T_P} \int_{0}^{T_P} dt \langle O_{\text{el}}(t) \rangle. \] (25)

In the regime of adiabatic pumping, one has \( \omega_P \ll \Gamma_0 \) and \( \omega_0 \ll \Gamma_0 \), so that the dimensionless ratio \( r_P = \omega_P/\omega_0 \) is of the order of unity. The regime of weak pumping is defined by the condition \( S \ll 1 \). Through the paper, we will assume \( \omega_0 = 0.1 \Gamma_0 \). We will measure lengths in units of \( \lambda/k \), times in units of \( 1/\Gamma_0 \) and energies in units of \( \hbar \Gamma_0 \).

4. Results

4.1. Distribution probabilities of the vibrational mode in the presence of pumping

In order to understand the role of a deformable quantum dot on a charge pump, it is useful to analyze preliminarily the distribution probabilities in the configuration space of the vibrational (center of mass) mode. As elucidated in the previous section, these are calculated self-consistently under generic pumping strength and arbitrary electron-oscillator coupling (the calculation procedure for \( P(x, v, t) \) is discussed in appendix A). In figure 2 (upper panel) we plot the reduced position probability distribution as a function of \( x \) for different times away from the mechanical resonance. For comparison, the equilibrium stationary distribution for the harmonic oscillator is shown as a dotted line. The effect of the pumping-assisted mechanical deformation causes a shift of \( \langle x \rangle \) and a redefinition of the probability distribution variance \( \sigma_x^2(t) \). However, we note that the bell-shaped character of the unperturbed distribution is maintained. Very close to the mechanical resonance, figure 2 (lower panel), a relevant temporal variation of the position probability distribution appears and a bimodal distribution is produced (black line) when \( P(x, v, t) \) is integrated over time. The features described above can be understood by analyzing the oscillation amplitude \( R_c \) of an effective forced Duffing oscillator (DO) [16] taken as an oversimplified version of equation (22). For a DO \( R_c \approx S \times \Pi(\omega_P - \omega_0) \times C(\Delta \phi) \), where the function \( \Pi(\omega_P - \omega_0) \) is peaked on resonance and it is related to the modulus of the response function of the vibrational mode, while \( C(\Delta \phi) \) contains information related to the oscillator response to the phase shift \( \Delta \phi \) of the driving signals. In the upper panel of figure 2 the oscillation amplitude \( R_c \) is lowered by the off-resonant value of the response function \( \Pi \) despite the moderate value of the pumping strength \( S = 0.5 \); on the other hand (lower panel), on-resonance, the oscillation amplitude \( R_c \) is strongly amplified despite the smaller value of \( S \). The above arguments suggest that the effective pumping cycle seen by the electrons is completely dominated by the vibrational response to the driving signals. The correctness of the above arguments can be qualitatively validated by neglecting the nonlinear part of the problem and working with a simple harmonic oscillator.
Figure 2. Upper panel: reduced position probability distribution as a function of $x$ for different times in the regime far from the mechanical resonance. For comparison, the equilibrium stationary distribution for the harmonic oscillator is shown as a dotted line. Lower panel: reduced position probability distribution as a function of $x$ for different times in the regime very close to the mechanical resonance. The time average of the distribution is shown as a black line and indicated as ‘total’.

In the following, we will investigate the dependence of the magnitude of the leading contribution to the total charge pumped per cycle $Q = T P \langle \bar{J}_L \rangle$ on several model parameters. In particular, we will focus on the pumped charge dependence on temperature and driving frequency $\omega_P$. Moreover, we discuss the dependence of the pumped charge on the phase difference between the pumping perturbations $\Delta \phi$, the pumping strength $S$, the gate voltage $V_G/e$ and the electron-oscillator coupling $E_{ep}$ in order to optimize the amount of pumped charge and to characterize possible nonlinear effects. We will analyze the features of pumped charge as a function of the external frequency and temperature in the next subsection, as a function of the phase difference in the third subsection and as a function of the gate voltage and electron-oscillator coupling in the fourth subsection.

4.2. Pumped charge as a function of the external frequency and temperature

As we will show in the following, the resonance condition is met for $\omega_P$ smaller than $\omega_0$, since the dot occupation induces a strong softening of the bare frequency [21]. Therefore, the resonance takes place when the pumping frequency coincides with an effective oscillator frequency $\omega_{eff} < \omega_0$. At the resonance, the distance between the maxima in the bimodal reduced position probability distribution (shown for example in the lower panel of figure 2) is the largest. In this subsection, we will show that the pumped charge vanishes at the mechanical resonance. Moreover, the amplitude of the pumped charge close to the resonance decreases with increasing the temperature.

In the following, we will denote $r_{eff} = \omega_{eff} / \omega_0$. The renormalization of the bare resonator frequency is due to an effective potential of the oscillator and depends on the parameters of the system, which includes the electron-oscillator coupling $E_{ep}$, the energy $V_G$ and the temperature $T$. In particular, at increasing temperature, the anharmonic contributions of the effective potential tend to become less important. This clearly induces a modification of the resonance frequency which approaches $\omega_0$ at high temperature.

In figure 3 (upper panel) we plot the pumped charge $Q$ as a function of the pumping frequency $\omega_P$, hence as a function of $r_P$ ($r_P = \omega_P / \omega_0$) for different temperatures. The $Q$ versus $r_P$ curves show a resonance peak close to $\omega_P \approx \omega_0$. The...
point where the pumped charge vanishes can be correctly assumed as the position of the renormalized effective frequency $r_{\text{eff}}$. For example, one finds $r_{\text{eff}} \approx 0.953$ at $T = 0.3$. A similar behavior is obtained by describing the vibrational mode in terms of a simple harmonic oscillator (see figure 4 of [15]). In the following, we will focus our analysis on the region close to the resonance. In the lower panel of figure 3 the maximum pumped charge (in logarithmic scale) versus the temperature is shown. At increasing temperatures the pumped charge decreases even though it remains always higher than the value obtained in the absence of the electron-oscillator coupling $E_{\text{cp}}$. While in the presence of the electron-oscillator coupling $E_{\text{cp}} = 0.2$ an exponential decay with temperature is observed, for $E_{\text{cp}} = 0$ the pumped charge decays more rapidly than a simple exponential. The above result indicates that the presence of a vibrational mode provides an amplifying mechanism of the external driving signals assisting the pumping. From the experimental point of view the slower decay of the pumped charge with temperature would favour the observation of the pumped current at temperatures higher than $mK$, overcoming the problem of measurements at cryogenic temperature. Finally, we point out that, on resonance, the pumped charge $Q$ at finite $E_{\text{cp}}$ is amplified compared to the value at $E_{\text{cp}} = 0$, while the situation is inverted out of resonance.

### 4.3. Pumped charge as a function of the phase difference

Up to now, we have discussed the features of the pumped charge at a fixed value of the phase difference $\Delta \phi = \pi/4$. This value has been chosen since the pumped charge close to the mechanical resonance has the largest values. In this subsection, we will study the behavior of the pumped charge as a function of the phase difference $\Delta \phi$ in the weak and intermediate pumping regime. In the latter regime, the pumped charge exhibits nonlinear features close to the resonance.

In figure 4 we plot the pumped charge $Q$ as a function of the phase difference $\Delta \phi$ for different values of the external frequency, hence for different ratios $r_p = \omega_p/\omega_0$.

![Figure 4](image.png)

**Figure 4.** The pumped charge $Q$ as a function of the phase difference $\Delta \phi$ for different values of the external frequency, hence for different ratios $r_p = \omega_p/\omega_0$.

$$Q \propto E_{\text{cp}} \Pi(\omega_p - \omega_{\text{eff}}) \cos(\phi_D) \sin(\Delta \phi),$$

(26)

where $\Pi(\omega_p - \omega_{\text{eff}})$ is the modulus of the response function of the oscillator, while $\phi_D \sim \arctan(Q^{-1}_f \omega_p/(2\omega_{\text{eff}}^2 - \omega_p^2))$ is a dynamical phase shift which depends on the effective quality factor $Q_f$ of the resonator. The phase shift of $\phi$ taking place on resonance, is fully explained by the functional dependence of the $\phi_D$ on $\omega_p$ (in appendix C we report the excellent fit of the numerical results shown in figure 4 with equation (26)). We also note that, since we are in a symmetric case ($\Gamma_L = \Gamma_R$), the pumped charge is zero when $\Delta \phi = 0$ and no rectification terms appear in the pumped charge. The analytical expression of the phase shift model given in equation (26) is inspired by the result given in equation (11) of [15], where the weak pumping regime and the zero temperature limit are assumed. In order to analytically validate equation (26) in the presence of force fluctuations at finite temperature, the linear response theory for a stochastic system is required. This analysis, however, goes beyond the purposes of this work. It is worth mentioning that the sinusoidal form of the charge-phase relation expressed in equation (26) is originated by the finite temperature effects which are able to weaken high harmonics contributions that are instead present in the zero temperature limit (see the appendix B for details).

While for weak pumping strength (the case $S = 0.05$ has been shown in figure 4), a sinusoidal charge-phase relation is expected, further harmonics can develop in the moderate pumping regime ($S > 0.20$). In the latter condition, the oscillation amplitude of the vibrational mode increases and explores the nonlinear region of the oscillator potential. In figure 5, where the $Q$ versus $\Delta \phi$ curves are computed in the moderate pumping regime ($S = 0.5$), the deviation from the sine function becomes dramatic when approaching the resonance at $r_p = 0.950$. As shown, the pumped charge increases in the strong coupling regime but its value does not reach a quantized value for the considered parameters range. The lack of quantization of the pumped charge per cycle can be ascribed to the difficulty in achieving sufficient modulation amplitude of the tunnelling rates compared to the static part. Indeed, apart from the time dependence induced by the vibrational mode, the pumping signals produce a lifetime modulation of the form $\Gamma_a(t) \equiv \Gamma^0_a + \Gamma^\omega_a \cos(\omega_p t + \phi_a)^6$. Due to the form of $u_a(t)$ the pumping ratio $\rho(S) \equiv \Gamma^0_a/\Gamma^\omega_a = \frac{4S}{\Gamma^\omega_a S^2}$.

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5 The fitting curve of $Q$ versus $T$ for $E_{\text{cp}} = 0$ is of the form $Q = \exp(a + b T + c T^2)$ with $a = -2.21602$, $b = -1.46152$, $c = 0.27523$ for the values of the parameters considered in figure 2.

6 See footnote 4.
is a bounded function of $S$, i.e. $0 < \rho(S) \leq 2$ and its value determines the weak or strong pumping regime. The strong pumping regime, defined by $\rho(S) > 1$, is obtained in the interval $S\epsilon[2 - \sqrt{3}, 2 + \sqrt{3}] \approx [0.268, 3.732]$, while the maximum pumping ratio $\rho_M = 2$ is reached for $S = 1$. Thus the value of $\rho_M$ could be not sufficiently strong to reach the charge quantization condition. Alternatively, the noise-induced transformation of the pumping cycle into a complex trajectory contained within a circular crown in the driving space ($I_I(t), I_K(t)$) can reduce the phase coherence required to maximize the transferred charge.

4.4. Pumped charge as a function of the gate voltage and electron-oscillator coupling

In this subsection, we analyze the pumped charge as a function of the gate voltage and electron-oscillator coupling. Usually, in the absence of electron-oscillator coupling, when the resonant tunnelling condition through the quantum dot level is met by varying the voltage gate, one expects a rapid sign change of the pumped charge and a vanishing current. This happens because the electron-hole symmetry holds at resonance. In the presence of coupling to a mechanical degree of freedom, the molecular level is renormalized and this could cause multiple sign changes of the pumped charge. The specific form of the pumped charge around the sign change voltages depends on $r_{\text{eff}}(V_G)$, the mechanical resonance frequency renormalized by the gate voltage $V_G/\epsilon$.

In the upper panel of figure 6, the pumped charge $Q$ is plotted as a function of $V_G$ for different values of $r_P$. The charge behaves symmetrically for positive and negative values of $V_G$ and, for fixed $r_P$, a change of sign of $Q$ versus $V_G$ is observed. As expected, we find a sharp sign change of the pumped charge as a function of $V_G$. The distance of the inversion points from $V_G - E_{\text{ep}} = 0$ is an increasing function of $r_P$. In particular the gate values $V_G^*$ where the sign changes occur are determined by the resonance condition which is found by solving the equation $r_P = r_{\text{eff}}(V_G^*)$. The function $r_{\text{eff}}(V_G)$ versus $V_G^*$ asymptotically ($|V_G^*| \to \infty$) saturates to the bare resonance frequency of the oscillator (1 in dimensionless units), while it presents a single minimum close to $V_G^* = 1$. The value of $\rho_M$ could be not sufficiently strong to reach the charge quantization condition. Alternatively, the noise-induced transformation of the pumping cycle into a complex trajectory contained within a circular crown in the driving space ($I_I(t), I_K(t)$) can reduce the phase coherence required to maximize the transferred charge.

Figure 5. The pumped charge $Q$ as a function of the phase difference $\Delta \phi$ for different values of $r_P$ for an intermediate value of pumping strength $S$. Going

Figure 6. Upper panel: the pumped charge $Q$ as a function of $V_G - E_{\text{ep}}$ for different values of $r_P$. Lower panel: the pumped charge $Q$ as a function of the electron-oscillator coupling $E_{\text{ep}}$ for different values of the pumping strength $S$. Notice that the pumping strength $S = 0.6$ corresponds to the driving ratio $\Gamma_{\text{ep}}/\Gamma_{\text{mp}} = 1.765$, which is very close to the maximal value of 2.
from small to moderate values of the pumping strength $S$, an amplifying behavior at $E_p = 0.2$ before the sign change is visible. Moreover, one also notices that the force fluctuations induced by the charging effects of the molecular energy level do not destroy the quantum pumping mechanism.

5. Conclusions and discussions

We have employed a non-equilibrium Green’s function approach to study the quantum pumping through a molecular level coupled to a classical vibrational mode governed by a stochastic dynamics. We have shown that the presence of dissipation and noise doesn’t destroy the quantum pumping mechanism and, even, reinforces it when the pumping frequency is tuned close to the resonance. Actually, a wide parameter range has been identified where the vibrational mode provides an amplifying mechanism that cooperatively assists the quantum pumping and the simulation results can be often understood in term of an effective frequency which renormalizes the bare resonator frequency $\omega_0$. When looking at the pumped charge as a function of $\Delta \phi$ a non-sinusoidal CPR is found. The behavior is clearly different from a $\sin(\Delta \phi)$ and the contributions of more harmonics are already clear at $T = 0$ (see appendix B) as a result of the nonlinear dynamics. The robustness of the noise-assisted quantum pumping has also been investigated as a function of the temperature and an exponential decay of the pumped charge in the presence of the electron-oscillator coupling has been found.

Our results clarify the effect of a classical perturbation (a single resonant harmonic oscillator) on the quantization of the charge pumped in a pumping cycle. We stress that the equations for the pumped charge considered in this work generalize those presented in P W Brouwer’s work (the first of [11]). In addition to the term due to the adiabatic variation of two parameters, we have a new term derived from the electron coupling to the oscillator dynamics. As reported in equation (13) of this paper, there is an additional term in the instantaneous current proportional to the velocity of the oscillator. When properly averaged in the presence of electron-oscillator coupling, this term provides a finite contribution to the current and ensures that the pumped charge vanishes for $\Delta \phi = 0$. Finally, we notice that our study is complementary to that reported in [25] where the coupling of a bosonic bath to a charge pump has been studied in the low temperature regime in a fully quantum mechanical approach. We point out that there is an analogy between our work and that of [25] regarding the equations of the charge pump. Actually, in [25], the pumped charge also consists of the sum of two terms: the non-interacting result (elastic channel) plus a correction due to the loss of unitarity of the elastic S-matrices (inelastic channel due to the presence of the bosonic bath). In [25], a proper account of inelastic scattering processes ensures the quantization of the total pumped charge at very low temperatures. We emphasize that, in our case, the temperature is larger than the oscillator frequency, while in [25] the typical cut-off frequency of the bosonic bath is much larger than the temperature. The difference between the two approaches comes out clearly in the temperature dependence of the pumped charge. In the case of a quantum bosonic bath, a power law decay of the pumped charge from the quantized value is observed, while, in the case of a single classic resonator, as mentioned, we find an exponential decay. From this point of view, the differences can be interpreted as the result of the quantum nature of the bosonic bath against the classical nature of the resonator present in our set-up.

Appendix A.- Numerical procedure

In this appendix we will discuss the numerical procedure followed in this work. We will focus on the numerical convergence of the physical quantities, in particular the pumped charge $Q$.

All the results discussed in the main text derive from the numerical solution of the Langevin equation (22). We solve this second order stochastic differential equation extending a fourth order stochastic Runge–Kutta algorithm [26, 27]. In order to solve the second order equation with multiplicative white noise, we decompose the problem into a set of three first order differential equations [28]. The third equation takes into account the effect of spatial dependence of the noise, involving a non-multiplicative noise term. For our simulations we have fixed a time step $t_e = 0.1/\omega_0$ and set long simulation times up to $10^9 t_e$. Within these settings, the algorithm shows an excellent stability and reaches the convergence for all the oscillator and electronic quantities. In order to average upon statistically independent events, we have sampled the values of $x(t)$ and $v(t)$ every 10 time steps.

The sampling procedure can be used for determining the full probability distribution $P(x,v,t)$ and the reduced position probability distribution $P(x,t)$. Actually, after a long transient (more than 20 periods $T_P$), one divides the resulting time steps of the dynamics in multiples of the period $T_P$. After fixing the bin for the velocity and the position, one collects statistically independent values of $x(t)$ and $v(t)$ at times $t = n t_e + M T_P$, with $M$ larger than 20 and $n t_e$ smaller than $T_P$. Therefore, due to the periodicity of the motion equations, the sampled values correspond to the equivalent time $t_e = n t_e$. At fixed $t_e$ in a period $T_P$, one builds up the corresponding distribution function for $x$ and $v$ which in general has to be normalized to provide the full probability distribution $P(x,v,t)$. If one wants to construct the reduced position probability distribution $P(x,t_e)$, the procedure is easier since only the values of $x$ at times $t_e = n t_e + M T_P$ have to be collected.

In the Langevin equation (22), the fluctuating term $D(x,t)$ gets smaller with decreasing the temperature $T$ and the electron-oscillator coupling $E_{ep}$. Therefore, the parameter regime with very small values of $T$ ($T < 0.1$) and $E_{ep}$ ($E_{ep} < 0.1$) is not easily accessible since it requires longer and longer dynamics. A hint about this regime comes from the analysis at $T = 0$ (see appendix B), where in the absence of the fluctuating term, the features of the model can be obtained for very weak electron-oscillator coupling $E_{ep}$. The pumped charge $Q$ is affected by the mechanical resonance and by the temperature increase. Indeed, accurate numerical convergence is needed for the estimation of the pumped charge particularly in the regime of weak pumping. For this reason, in this

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Actually, for $N$ charge number figure A1 tend to be always opposite. This is due to the relation $\Delta$ of the charge at pumped charge increasing the number of time steps in a parameter regime $\Delta \times 4$ time steps, the two charge values coincide within an error of the numerical procedure.

In the appendix, we discuss the features of the pumped charge within the numerical procedure.

In figure A1, we report the convergence of $Q$ with increasing the number of time steps in a parameter regime close to the mechanical resonance. In particular, we show the pumped charge $Q$ at values of the phase difference $\Delta \phi$ where the symmetry of the problem constrains the results. In the upper panel of figure A1, we consider the cases $\Delta \phi = 0$ and $\Delta \phi = \pi$, where, by symmetry considerations, one expects the vanishing of $Q$. We point out that the convergence is not fast. Actually, for $N = 5 \times 10^8$ time steps, the charges at $\Delta \phi = 0$ and $\Delta \phi = \pi$ still differ in terms of $5 \times 10^{-4}$. Only for $N = 10^9$ time steps, the two charge values coincide within an error of $4 \times 10^{-5}$, which is one order of magnitude smaller than the case $N = 5 \times 10^8$.

The values of the charges shown in the upper panel of figure A1 tend to be always opposite. This is due to the relation of the charge at $\Delta \phi$ and $2\pi - \Delta \phi$. Actually, these relations are also found for finite values of the charge. In the lower panel of figure A1, we report $Q$ at $\Delta \phi = \pi/2$ and $-Q$ at $\Delta \phi = 3\pi/2$. They tend to become equal with increasing $N$. We point out that the convergence for these values of $\Delta \phi$ improves quite sensitively. For $N = 5 \times 10^8$ time steps, the charges are different only in terms of $2 \times 10^{-5}$. Moreover, for $N = 10^9$ time steps, the error in the estimate of the charges is smaller than $10^{-5}$. From the comparison of the charges at several values of $\Delta \phi$, we have checked that the error at $\Delta \phi = 0$ and $\Delta \phi = \pi$ is the largest, therefore it sets an estimate of the numerical resolution within our procedure. In the main text, most results have been plotted with symbols whose size provides an estimate of the error. The error bars in the curves of $Q$ versus $\Delta \phi$, have been estimated by the maximal error of $Q$ obtained at $\Delta \phi = 0$. In all the results reported in the main text, the minimum number of steps has been $5 \times 10^8$.

**Appendix B. Results at $T = 0$**

The result of this appendix clarified some points explained in the main text. In particular, we analyze the system at $T = 0$ focusing on the parameter region close to the mechanical resonance. In this case, the Langevin equation reduces to a deterministic equation. We solve this second order differential equation with a fourth order Runge–Kutta algorithm. In analogy with the numerical procedure at finite temperature, we have fixed a time step $t_s = 0.1/\omega_0$ and considered long simulation times up to $10^9 t_s$. The numerical accuracy of the results is very good. Symbols are used in the plots to indicate an estimate of the error within the numerical procedure.

The analysis at $T = 0$ allows us to describe in more detail the response close to the mechanical resonance in the limit when the electron-oscillator coupling $\omega_P$ is small, even though some quantities, like the effective oscillator frequency $\omega_{\text{eff}}$, show a temperature-dependent renormalization not captured in this limit. Despite these limitations, the $T = 0$ case treated here clarifies the system behavior.

In comparison with the results obtained at $T = 0.3$ and reported in figure 4 (with $\omega_{\text{eff}}$ close to 0.952), in figure B1 we focus on the resonance at $T = 0$ maintaining the remaining parameters as fixed in figure 4. Figure B1 ($T = 0$ case) clearly shows that $\omega_{\text{eff}} \simeq 0.942$, while, crossing the resonance, a phase shift of $\pi$ is observed. Moreover, even if the amplitude of the pumped charge is small, we recognize additional nodes in the $Q$ versus $\Delta \phi$ curve, evidencing the contribution of a second harmonic term. We have checked that higher harmonics are
Figure B2. Upper panel: the effective oscillator frequency $r_{\text{eff}} = \omega_{\text{eff}} / \omega_0$ as a function of $V_G - E_{\text{ep}}$ for $T = 0$. The horizontal lines correspond to the values of $r_P$ considered in the lower panel. Lower panel: the pumped charge $Q$ as a function of $V_G - E_{\text{ep}}$ for different values of $r_P$ at $T = 0$.

Figure C1. Upper panel: $Q$ versus $\Delta \phi$ curves reproduced from figure 4 of the main text. The black labels close to the curves indicate the corresponding values of $r_P$. The black dashed lines indicate the fitting curves obtained by using the model given in equation (C.1). The fitting curves are obtained for the following choice of parameters: $A = 1.05 \times 10^{-4}$, $r_{\text{eff}} = 0.952$, while the values of $Q_f$ are reported in the lower panel. Lower panel: quality factor $Q_f$ versus $r_P$ as deduced by the fitting procedure of the curves given in the upper panel. The black dashed line is a guide for the eyes.

In the lower panel of figure B2, we show that $r_P = 0.980$ is smaller than the values in the grey area, therefore the pumped charge never approaches the resonance. However, $r_P = 0.990$ is well within the grey area, therefore, the resonance has already occurred and the pumped charge has a different sign. For $V_G - E_{\text{ep}}$ larger than 0.8, the system cannot approach the resonance, therefore the pumped charge has again a negative sign. For $V_G - E_{\text{ep}}$ around 0.8, the crossing of the resonance takes place with a rapid change of the pumped charge. Another point shown in the lower panel of figure B2 is the behavior far from the resonance. With increasing $r_P$, the pumped charge flattens ($r_P = 0.995$), then, for $r_P$ close to unity ($r_P = 0.998$), it reaches small negative values. Finally, for $r_P$ larger than one ($r_P = 1.050$), the pumped charge recovers a positive sign and the small values characteristic of the regime before the resonance.

Appendix C. Dynamical phase shift model

In this appendix, we compare the $Q$ versus $\Delta \phi$ curves given in figure 4 of the main text with the behavior predicted by equation (26). To this purpose, starting from equation (26) and using dimensionless units, we deduce the following fitting...
formula:

$$Q = \frac{A}{\sqrt{(r_{eff}^2 - r_P^2)^2 + (r_P/Q_f)^2}} \times \cos\left(\arctan\left(\frac{r_P/Q_f}{r_{eff}^2 - r_P^2}\right)\right)\sin(\Delta\phi),$$ (C.1)

which contains the free parameters $A$, $r_{eff}$, $Q_f$, while $r_P$ is constrained by the pumping frequency. The number of free parameters is further reduced by fixing the renormalized $Q_f$ from the pumping frequency, is fixed by fitting a single $Q$ versus $\Delta\phi$ curve (not shown, but presenting an analogous behavior of the one reported in the upper panel of figure 3). The value of $A$, which is assumed to be independent from the pumping frequency, is fixed by fitting a single $Q$ versus $\Delta\phi$ curve far from resonance. Once the value of $A = 1.05 \times 10^{-4}$ has been found for a single curve, it is fixed in the subsequent fitting procedures. The remaining curves are fitted by the single free parameter $Q_f$, the latter being the effective quality factor characterizing the dissipation mechanisms of the electromechanical system.

The results of this analysis are shown in figure C1. In the upper panel of that figure the fitting curves are shown as black dashed lines and present a good agreement with the numerical factors.

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