Non-equilibrium charge susceptibility and dynamical conductance: Identification of scattering processes in quantum transport

H. Ness\textsuperscript{1,2} and L. K. Dash\textsuperscript{1,2}

\textsuperscript{1}Department of Physics, University of York, Heslington, York YO10 5DD, UK
\textsuperscript{2}European Theoretical Spectroscopy Facility (ETSF)

(Dated: February 9, 2012)

We calculate the non-equilibrium charge transport properties of nanoscale junctions in the steady state and extend the concept of charge susceptibility to the non-equilibrium conditions. We show that the non-equilibrium charge susceptibility is related to the non-linear dynamical conductance. In spectroscopic terms, both contain the same features versus applied bias when charge fluctuation occurs in the corresponding electronic resonances. However, we show that while the conductance exhibits features at biases corresponding to inelastic scattering with no charge fluctuations, the non-equilibrium charge susceptibility does not. We suggest that measuring both the non-equilibrium conductance and charge susceptibility in the same experiment will permit us to differentiate between different scattering processes in quantum transport.

PACS numbers: 71.38.-k, 73.40.Gk, 85.65.+h, 73.63.-b

Recent developments in modern techniques of microscopic manipulation and nanotechnologies enable us to build functional nanoscale systems, for example, electronic nanodevices or molecular motors [1–5]. In such systems, classical equilibrium thermodynamics is not suited to describe the quantization of the charge or heat flow. The properties of such devices differ from their equilibrium counter parts since non-equilibrium quantum and non-linear effects dominate. The concepts of conventional statistical mechanics and linear-response theory for these small systems need to be substituted with those of non-equilibrium quantum statistical mechanics [6–8]. This is the appropriate framework for dealing with nanoscale systems driven out of equilibrium, especially when one wants to design or control these systems as heat engines or electro-mechanical devices.

Extending the concept of equilibrium statistical mechanics (linear-response theory and response functions, fluctuation theorems) to the non-equilibrium (NE) conditions has seen a recent growing interest [9–11]. It is known from linear-response theory that there exists some relationship between different response functions, like for example, the density-density, current-density, or current-current correlation functions at equilibrium [12]. However there is no reason why these relationships should hold at NE. Motivated by understanding these NE properties and their use in practical nanoscale devices, we focus in this paper on a specific physical property: the electronic transport. In particular, we consider the relationship between the electrical conductance and the charge susceptibility in nanoscale junctions. We provide a definition for the NE charge susceptibility, which can be measured in experiments, and examine in detail its relationship with the full non-linear dynamical conductance.

We show that the non-equilibrium charge susceptibility and the dynamical conductance of such a system are related to each other, though in a different manner than at equilibrium. At finite bias, they both contain information about the charge fluctuation (induced by the bias) in the electronic resonances. However the NE charge susceptibility does not contain information about purely inelastic scattering processes which do not involve charge fluctuations. By measuring both the conductance and the NE charge susceptibility in the same experiment, one can identify the nature of scattering processes involved in transport through nanoscale junctions.

We illustrate this property with numerical calculations for a model of a single-molecule nanojunction in the presence of electron-phonon coupling. Our results are relevant, but not limited only, for electron-phonon scattering processes. Other examples could be electron-plasmon, electron-electron, electron-spin excitations scattering events. In the following, we first briefly recall the relationship between linear conductance and charge susceptibility at equilibrium. Then we derive the corresponding relationship in the NE conditions, and present numerical calculations.

Equilibrium response functions: Within the linear-response theory of a system at equilibrium [12, 14–15], the current $I$ is related to a frequency-dependent applied bias $V$ via the linear conductance $g$ as $I(\omega) = g(\omega)V(\omega)$. The linear conductance is a response function obtained from the current-density correlation function $g(t) = (ie/\hbar)\langle [\hat{I}(t), \hat{N}(0)]\rangle\theta(t)$, where $\hat{N}$ is the total occupancy operator and $\hat{I}$ is the current operator $\dot{I} = e\dot{N}/dt$. The linear conductance $g$ is directly related to the density-density correlation function $\chi_c(t) = -i\langle [\hat{N}(t), \hat{N}(0)]\rangle\theta(t)$ by the relation $g(\omega) = i\omega\frac{\chi_c}{\chi_c(\omega)}$. $\chi_c$ is also known as the charge susceptibility and represents the response function of the charge density modifications $\delta n$ due to variation of the electrostatic potential $\delta v$: $\delta n = \int \chi_c \delta v$ [16]. In the DC limit, one gets a finite linear conductance $g(\omega \to 0)$ when the charge sus-
ceptibility goes as \( \chi_c(\omega) = f(\omega)/\omega \) with \( f(0) \neq 0 \). At equilibrium, there is a clear and well-defined relationship between the charge susceptibility and the linear conductance. However there is no a priori reason why such a relation should still hold at non-equilibrium when an applied bias drives the system in a non-linear regime.

Non-equilibrium charge susceptibility and transport: We consider a generic system consisting of a interacting central region \( C \), the scatterer of interest (e.g. a molecule or a quantum dot), connected to two electrodes, acting as source and drain. The electrodes are non-interacting Fermi seas at their own equilibrium and there is no direct contact between them. We use non-equilibrium Green’s functions (NEGF) to calculate the electric current and charge of the system in NE conditions [13]. The system is under a finite, but not small, applied bias and is assumed to have reached NE conditions [13]. The system is under a finite, but not small, applied bias and is assumed to have reached NE conditions [13]. The system is under a finite, but not small, applied bias and is assumed to have reached NE conditions [13]. The system is under a finite, but not small, applied bias and is assumed to have reached NE conditions [13].

The dynamical conductance \( G \) is given by the Meir-Wingreen expression [13]:

\[
G(V) = \frac{i e}{\hbar} \int \frac{d\omega}{2\pi} \text{Tr} \left[ \left( 1 - f_L(f_C^\text{NE})^{-1} \right) \partial V G_C^\text{NE} \Gamma_L \right. \\
- \partial V \left. \left( f_L(f_C^\text{NE})^{-1} \right) G_C^\text{NE} \Gamma_L \right],
\]

(3)

which shows a relation between the dynamical conductance and the derivative of the lesser Green’s function versus the applied bias \( \partial V G_C^\text{NE} \). To show more clearly how \( G(V) \) and \( \chi_c^\text{NE}(V) \) are related to each other, we consider the following simpler system.

A model system: The model consists of a single electron level in the region \( C \), in the presence of some arbitrary kind of interaction. For the moment, we consider the wideband limit where \( \Gamma_L(\omega) = \Gamma \), and that all the potential drop occurs at the left contact. Only the Fermi distribution \( f_L \) of the left lead depends explicitly on the bias \( V \) via the Fermi level \( \mu_L \). Within these conditions, we find a relation between the dynamical conductance \( G \) and the non-equilibrium charge susceptibility \( \chi_c^\text{NE} \):

\[
G(V) \left( \frac{e}{\hbar} \Gamma \right)^{-1} + \chi_c^\text{NE}(V) = \int d\omega \partial V (f_L A_C(\omega)),
\]

(4)

where \( A_C(\omega) = (G_C^\text{LE}(\omega) - G_C^\text{RE}(\omega))/2\pi i \).

For non-interacting systems, the spectral function \( A_C \) is independent of the bias, then \( \partial V A_C(\omega) = 0 \). By using the definitions of \( G \) and \( \chi_c^\text{NE} \) for symmetric contacts and the corresponding non-equilibrium distribution function \( f_C^\text{NE} = (\Gamma_L f_L + \Gamma_R f_R)/(\Gamma_L + \Gamma_R) = (f_L + f_R)/2 \), we find a direct proportionality between \( G \) and \( \chi_c^\text{NE} \):

\[
G(V) = \frac{e^2}{\pi} \Gamma \chi_c^\text{NE}(V)/\epsilon [21].
\]

Beyond the wideband approximation (with symmetric contacts), we obtain the relation: \( G(V) = \frac{e^2}{\pi} \Gamma (\mu_L) \chi_c^\text{NE}(V)/\epsilon \). Hence the compatibility between the equilibrium and NE approaches implies that \( \lim_{\omega \to 0} \omega \chi_c(\omega) \equiv \Gamma \chi_c^\text{NE}(V) \) (within the DC limit of linear-response).

For interacting systems, \( A_C \) depends on \( V \) through the interaction self-energy \( \Sigma_{\text{int}}(\omega, V) \). An analytical expression relating \( G \) and \( \chi_c^\text{NE} \) is more difficult to obtain [22]. However we show next, from numerical calculations beyond the wideband limit, that there is a clear relationship between \( G(V) \) and \( \chi_c^\text{NE}(V) \) for a model of interaction self-energy.

An application: For this we have to make a choice for the interactions in the central region \( C \). The NE charge susceptibility has been briefly studied for a model of electron-electron interaction in the Anderson impurity model at non-equilibrium in [23]. In the following we consider a model electron-phonon interaction in the central region \( C \) [23][25]. Considering such a model permits us to get several different physical effects: the renormalization of the electron level but also all the phonon replica (the phonon side-band peaks). So effectively we are dealing with a richer model of multi-electronic resonances. Such a model includes different inelastic scattering events: those related to charge fluctuations in...
the electronic resonances (resonant elastic and inelastic transmission) and those involving off-resonant inelastic scattering by tunneling electrons. However the relationship derived previously for $G(V)$ and $\chi_{c}^{\text{NE}}(V)$ is independent of the nature of the interaction (electron-phonon or electron-electron) in the central region $C$.

In our model, the Hamiltonian for the region $C$ is

$$H_C = \varepsilon_0 d^\dagger d + \omega_0 a^\dagger a + \gamma_0 (a^\dagger + a) d^\dagger d,$$

where $d^\dagger$ ($d$) creates (annihilates) an electron in the level $\varepsilon_0$, which is coupled to the vibration mode of energy $\omega_0$ via the coupling constant $\gamma_0$. The central region $C$ is connected to two (left and right) one-dimensional tight-binding chains via the hopping integral $t_{0L}$ and $t_{0R}$. The corresponding lead $\alpha = L, R$ self-energy is $\Sigma_{\alpha}^{\varepsilon}(\omega) = t_{0\alpha}^2 / \beta_{\alpha} \exp[i k_{\alpha}(\omega)]$ with the dispersion relation $\omega = \varepsilon_{\alpha} + 2\beta_{\alpha} \cos(k_{\alpha}(\omega))$. Here, the imaginary part $\Gamma_{\alpha} = -2\Im\Sigma_{\alpha}^{\varepsilon}$ is energy dependent and goes beyond the wideband limit, unless $\beta_{\alpha}$ is much larger than any other parameters. At equilibrium, the whole system has a well-defined unique Fermi level $\mu^{eq}$. A finite bias $V$, applied across the junction, lifts the Fermi levels as $\mu_{L,R} = \mu^{eq} + \eta_{L,R} eV$. The fraction of potential drop at the left contact is $\eta_L$, and $\eta_R = \eta_L - 1$ at the right contact [26], with $\mu_L - \mu_R = eV$ and $\eta_L \in [0, 1]$.

Finally the electron-phonon interaction is treated at the Hartree-Fock level (first order diagrams in terms of the interaction) and is incorporated as self-energies $\Sigma_{\text{eph}}^{L,R}/a(\omega)$ in the NEGF. Self-consistent calculations provide a partial resummation of the diagrams to all orders [21, 25].

Within this model, we calculate the dynamical conductance $G(V)$ from Eq. (2) and the NE charge susceptibility $\chi_{c}^{\text{NE}}(V)$ from Eq. (1) for different sets of parameters. We consider symmetric ($t_{0L} = t_{0R}$) and asymmetric ($t_{0L} \neq t_{0R}$) coupling to the leads, different strength of coupling to the leads, symmetric and asymmetric potential drops at the contacts, and different transport regimes (off-resonant $\varepsilon_0 \ll \mu^{eq}$, and resonant $\varepsilon_0 \sim \mu^{eq}$). We restrict ourselves here to the medium electron-phonon coupling $(0.5 < \gamma_0/\omega_0 < 1)$ regime which corresponds to realistic coupling in organic molecules. The strong coupling regime requires higher-order diagrams and more time consuming calculations [21, 24].

Figure 1 shows the NE charge susceptibility $\chi_{c}^{\text{NE}}(V)$ and the dynamical conductance $G(V)$. We consider a symmetric coupling to the leads ($t_{0L} = t_{0R}$ and an asymmetric potential drop ($\eta_1 = 1$). On this scale, both the conductance and the NE charge susceptibility present peaks at an applied bias corresponding to an electronic resonance: a main resonance peak close to full polaron shift renormalised level $\varepsilon_0 = \varepsilon_0 - \gamma_0/\omega_0$, and phonon sideband peaks around $V \sim \varepsilon_0 + n\omega_0$ [27]. In the NE conditions, the charge fluctuates in these electronic resonances whenever the bias window includes $\varepsilon_0 + n\omega_0$. Hence peaks are obtained in the charge susceptibility $\chi_{c}^{\text{NE}}(V)$ for these biases. The peaks correspond to elastic ($V \sim \varepsilon_0$) and inelastic ($V \sim \varepsilon_0 + n\omega_0$) resonant scattering processes. For the non-interacting case Fig. 1(a), there is only one resonance at $\varepsilon_0$, and, as demonstrated, $\chi_{c}^{\text{NE}}$ and $G$ are related via $\Gamma(\mu_L)$ beyond the wideband limit.

Figure 2 shows the relationship between $\chi_{c}^{\text{NE}}$ and $G$ is robust against our model parameters. It holds for asymmetric coupling to the leads ($t_{0L} \neq t_{0R}$) and different fractions of potential drops at the contacts - see Fig 2(d). It holds for strong coupling to the leads $t_{0\alpha} \sim \omega_0 > \gamma_0$ - see Fig 2(c); and beyond the wideband limit - see Fig. 2(b). It also holds when the interaction is modelled only with the Fock diagram - see Fig. 2(a). Therefore the relation between $\chi_{c}^{\text{NE}}$ and $G$ is not due to the fact that the Hartree self-energy $\Sigma_{\text{eph}}$ is proportional to $(n_{L}^{eq})$ (hence $\partial \Sigma_{\text{eph}} / \partial n_L \propto \chi_{c}^{\text{NE}}$).

Note that with potential drops at both contacts, $\mu_L$ and $\mu_R$ support a fraction of the bias, and the relationship between $\chi_{c}^{\text{NE}}$ and $G$ includes terms in $\partial \Sigma_{\text{eph}} / \partial n_L$. However both quantities still present the same features versus applied bias - see Fig. 2(d).

On a smaller energy scale, the conductance also contains physical information for biases around excitation energies which goes beyond resonant transmission.
deed, the conductance also varies at bias thresholds corresponding to other inelastic scattering processes (for example inelastic electron tunneling). At the bias threshold $V \sim \omega_0$, the conductance increases in the off-resonance transport regime (opening of new conduction channels) or decreases in the resonant transport regime (electron-phonon backscattering). These effects are better seen in the inelastic electron tunneling spectroscopy (IETS) as peaks or dips for the off-resonance or resonant transport regime respectively [25,28]. The IETS is obtained from the second derivative of the current versus applied bias $d^2I/dV^2 = dG/dV \equiv \partial V G(V)$. In experiments, the IETS signal is usually given normalised by the conductance itself or by the current itself. Figure 3 shows the IETS signal as well as the corresponding variation of the non-equilibrium charge susceptibility versus applied bias $\partial V \chi^\text{NE}$. One can clearly see a peak feature at $V \sim \omega_0$ in the IETS signal, while $\chi^\text{NE}$ is virtually featureless at the corresponding bias for both the off-resonant and resonant transport regimes. This means that these inelastic tunneling electron-phonon scattering processes (at $V \sim \omega_0$) are not related to charge fluctuations. Instead the phonon population fluctuates because of phonon emission induced by the tunneling electron. Note that the tiny features pointed by the arrows in Figure 3 correspond to tiny peak features in both $\chi^\text{NE}$ and $G$. They are related to charge fluctuations in the electron resonances at $V = \tilde{\varepsilon}_0 - \omega_0$ (phonon emission by a hole).

**Discussion:** We have hence shown that the non-equilibrium charge susceptibility and the dynamical conductance are directly related to each other, though in a different manner than for the equilibrium case. They both present features (peaks) versus the applied bias whenever there are charge fluctuations in the corresponding electronic resonances of the nanojunction.

Therefore we suggest that measuring both the conductance and the NE charge susceptibility simultaneously in the same experiment is essential in quantum transport. It permits one to identify the nature of the scattering processes involved in the transport, i.e. processes involving charge fluctuation or not. This result is very important for the analysis of the transport properties in complex systems such as large single-molecule junction and does not involve the presence of a third gate electrode. Although our result is mostly relevant for electron-phonon scattering processes, it is not limited only to these processes. The measurement of the NE charge susceptibility could be performed by measuring the potential drop around a capacitor placed in series with the nanojunction ($V_{\text{cap}} = e/nC/C_{\text{cap}}$). One can then obtain $\chi^\text{NE}(V)$ in a similar way as the dynamical conductance $G(V)$ is obtained from the current by using a lock-in set up.

---

* Electronic address: herve.ness@york.ac.uk

[1] M. A. Ratner and D. Ratner, *Nanotechnology: A Gentle Introduction to the Next Big Idea* (Prentice Hall, New Jersey, 2002).
[2] M. A. Reed and T. Lee, *Molecular nanoelectronics* (American Scientific Publishers, California, 2003)
[3] *Introducing Molecular Electronics*, edited by G. Cuniberti, G. Fagas, and K. Richter, Lecture Notes in Physics
[4] M. Di Ventra, Electrical Transport in Nanoscale Systems (Cambridge University Press, UK, 2008).
[5] C. Joachim and L. Plevert, Nanosciences: The Invisible Revolution (World Scientific Publishing Company, Singapore, 2009).
[6] J. A. McLennan, Physical Review 115, 1405 (1959).
[7] D. N. Zubarev, Condensed Matter Physics 4, 7 (1994).
[8] S. Hershfield, Physical Review Letters 70, 2134 (1993).
[9] M. Esposito, U. Harbola and S. Mukamel, Rev. Mod. Phys. 81, 1665 (2009).
[10] A. Shimizu and T. Yuge, J. Phys. Soc. Jpn 79, 013002 (2010).
[11] M. Campisi, P. Hänggi and P. Talkner, Rev. Mod. Phys. 83, 771 (2011).
[12] J. Rammer, Quantum Transport Theory (Perseus Books, 1998).
[13] Y. Meir and N. S. Wingreen, Physical Review Letters 68, 2512 (1992).
[14] A. L. Fetter and J. D. Walecka, Quantum Theory of Many-Particle Systems (McGraw-Hill, New York, 1971).
[15] M. Lee, R. López, M.-S. Choi, T. Jonckheere, and T. Martin, Physical Review B 83, 201304 (2011).
[16] The charge susceptibility is also sometimes defined as the response of the occupancy of an electronic level upon variation of the energy of that level: \( \delta n = -\chi_c \delta \epsilon \) as in T. Brunner and D. C. Langreth, Phys. Rev. B 55, 2578 (1997).
[17] P. Dutt, J. Koch, J. Han, and K. L. Hur, Annals of Physics 326, 2963 (2011).
[18] In Ref. [24], we have found that the Hartree self-energy (proportional to the occupancy of the region \( C \)) and the non-equilibrium current behave similarly when varying the bias (see Figure 6 and footnote [76] therein). Eq. (1) shares the same concept of the generalized susceptibilities for nonlinear systems developed in I. Safi and P. Joyez, Phys. Rev. B 84, 205129 (2011).
[19] H. Ness, L. Dash, and R. W. Godby, Physical Review B 82, 085426 (2010).
[20] In the most general cases, \( f^\text{NE}_C \) is also a functional of the interaction self-energies in the central region [19].
[21] \( \chi^\text{NE}_C(V) / e \) has the dimension of inverse energy and \( \Gamma \) of energy, so \( G(V) \) is given in quantum of conductance \( G_0 = e^2 / h \).
[22] For the single electron level, we find the general expression:

\[
\chi^\text{NE}_C(V) = \int d\omega \partial V (F(\omega) A_C(\omega))
\]

where \( F(\omega) = \Gamma(\omega)(f_L - f_R) + \bar{\gamma}(\mu_L,R) f^\text{NE}_C \) and \( \Gamma = \Gamma_L \Gamma_R / (\Gamma_L + \Gamma_R) \) and \( \bar{\gamma} \) is a function which ideally depends only on \( \mu_L,R \) and \( \Gamma_L,R \). This result can be generalized to the many-electron levels case by introducing traces over the electron states.
[23] S.-P. Chao and G. Palacios, Physical Review B 83, 195314 (2011).
[24] L. K. Dash, H. Ness, and R. W. Godby, Journal of Chemical Physics 132, 104113 (2010).
[25] L. K. Dash, H. Ness, and R. W. Godby, Physical Review B 84, 085433 (2011).
[26] S. Datta, W. D. Tian, S. H. Hong, R. Reifenberger, J. I. Henderson, and C. P. Kubiak, Physical Review Letters 79, 2530 (1997).
[27] The reasons why the resonances are not exactly at \( V \approx \tilde{\epsilon}_0 + n\omega_0 \) have been explained in detail in [24, 25]. This does not change the physics of the relationship between \( \chi^\text{NE}_C \) and \( G \).
[28] M. Galperin, M. A. Ratner, and A. Nitzan, Journal of Physics: Condensed Matter 19, 103201 (2007).