Quantum transport through nanostructures in the singular-coupling limit

Maximilian G. Schultz and Felix von Oppen
Institut für Theoretische Physik, Fachbereich Physik, Freie Universität Berlin, 14195 Berlin, Germany
(Received 12 May 2009; published 10 July 2009)

Geometric symmetries cause orbital degeneracies in a molecule's spectrum. In a single-molecule junction, these degeneracies are lifted by various symmetry-breaking effects. We study quantum transport through such nanostructures with an almost degenerate spectrum. We show that the master equation for the reduced density matrix must be derived within the singular-coupling limit as opposed to the conventional weak-coupling limit. This results in strong signatures of the density matrix's off-diagonal elements in the transport characteristics.

DOI: 10.1103/PhysRevB.80.033302 PACS number(s): 73.23.Hk, 05.60.Gg, 81.07.Nb

I. INTRODUCTION

The Anderson model of localized interacting electronic states coupled to two Fermi-gas electrodes is the archetypical model for studying electronic transport through quantum nanostructures. The model accurately describes a wide range of experimentally accessible transport regimes of quantum dots including the Coulomb blockade and the Kondo regime. It has been successfully extended to describe single-molecule junctions by coupling the electrons to the vibrational degrees of freedom of the molecule. The study of molecular electronics using this model has received enormous attention in recent years.[1]

An important issue that in contrast to the vibrational structure has been studied much less arises from the orbital degeneracies due to the geometric symmetries of molecules. The transport properties due to orbital degeneracies differ from those due to spin degeneracy, which are being studied extensively in the quantum-dot literature. Since there, the underlying SU(2) symmetry is respected both by the electrons in the reservoirs and by the tunnel couplings to the localized system, the low-temperature phenomenology is characterized by Kondo physics.[2]

The symmetry-induced orbital degeneracies of a molecule are in general lifted by binding it to metallic electrodes or the interaction with an underlying substrate. Asymmetries in the coupling of the orbitals to the leads cause a tunneling-induced splitting of the degenerate levels as the result of perturbation theory. The problem with orbital degeneracies, therefore, naturally extends to studying the role of near degeneracies in quantum transport theory.

The importance of coherent superpositions of degenerate localized levels for quantum transport has already been mentioned in the literature.[3,11] In this Brief Report, we generalize the discussion from the nongeneric case of exact degeneracy and show how the breaking of symmetries and the lifting of molecular degeneracies can be consistently accounted for in a master-equation formalism by employing the "singular-coupling limit" [4] in the derivation of the kinetic equation for sequential tunneling. Contrary to the weak-coupling limit, the singular-coupling limit can properly describe the coherent dynamics in the near-degenerate orbital subspace of the reduced density matrix and its competition with the transport dynamics due to electron tunneling. Our approach shows that this competition causes rich and interesting physics in the transport characteristics.

The singular-coupling limit also remedies the shortcomings of the Bloch–Redfield equation, which is a master equation that explicitly keeps the coherences between nondegenerate states in the density matrix[5] but is known to produce negative probabilities.[6] The master equation in the singular-coupling limit is included in the general theoretical framework of master equations and rate equations. It closes the gap between the description by rate equations and degenerate master equations enabling us to study high-temperature sequential tunneling for all possible energy regimes.

We illustrate the physics of an orbital near degeneracy within a minimal model; a two-level interacting but spinless Anderson impurity coupled to two electrodes

$$H = eV_g(n_\uparrow + n_\downarrow) + \frac{\Omega}{2}(n_\uparrow - n_\downarrow) + Un_\uparrow n_\downarrow + \sum_{\boldsymbol{k}\alpha} \varepsilon_{\boldsymbol{k}} c^\dagger_{\boldsymbol{k}\alpha} c_{\boldsymbol{k}\alpha} + \sum_{\boldsymbol{k}\alpha\sigma} t_{\alpha\sigma} c^\dagger_{\boldsymbol{k}\alpha} d_\sigma + \text{H.c.} \quad (1)$$

The on-site electronic orbitals are labeled by a pseudospin $\sigma = \uparrow, \downarrow$ and are separated in energy by Ω. This splitting is assumed to be due to symmetry-breaking mechanisms other than electronic tunneling. Double occupation of the system is suppressed by Coulomb repulsion of strength U and both orbitals are coupled to Fermi-gas electrodes $\alpha = L, R$, held in thermal equilibrium at temperature $k_B T$, via lead- and orbital-dependent amplitudes $t_{\alpha\sigma}$.

In Fig. 1(a), we show the stationary current through the model system for $eV_g = 0$. It is evaluated both for vanishing Ω using a master equation that includes the off-diagonal elements of the reduced density matrix ρ and for finite Ω, which is small compared with $k_B T$, using a rate equation for the diagonal elements of ρ. The *qualitative* difference between the two results is striking. While the rate equation yields a simple steplike increase in the current, the master equation produces additional structure; a suppression of the current and pronounced negative differential conductance. The phenomenological discrepancy between the two curves of Fig. 1(a) illustrates that there can be interesting and nonintuitive physics in the crossover regime, where Ω is of the order of the tunneling-induced broadening Γ of the electronic orbitals.

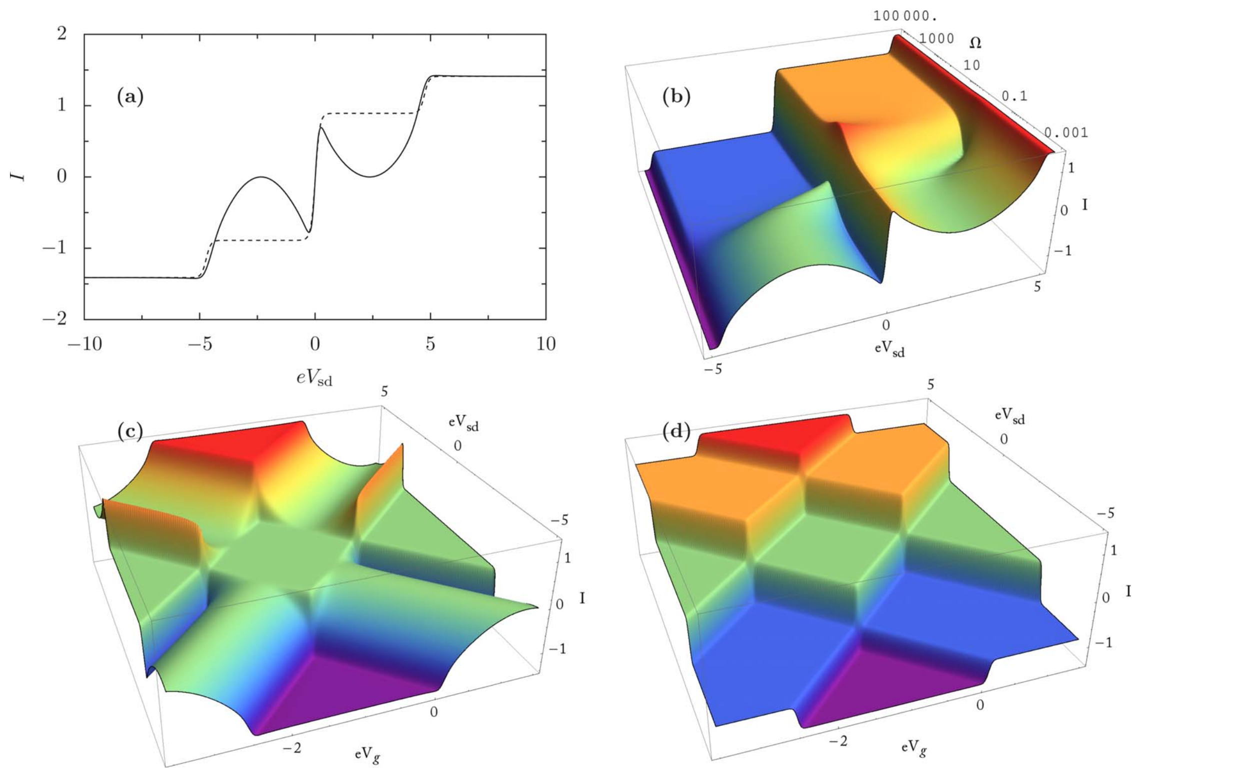

FIG. 1. (Color online) Numerical evaluation of the stationary current Eq. (9) through an interacting two-level Anderson model, $t_{\mathrm{L}\uparrow}=t_{\mathrm{R}\downarrow}=1$, $t_{\mathrm{L}\downarrow}=t_{\mathrm{R}\uparrow}=1.5$, $U=2.35$, and $k_{\mathrm{B}}T=0.02$. The tunnel amplitudes $t_{\alpha\sigma}$ and the splitting Ω are measured in units of $\frac{2\pi}{\hbar}\nu_0$. (a) illustrates the difference between the description by the degenerate master equation [Eqs. (7) and (8)] (solid) and the $\Omega=0$ rate equation, which is obtained from the master equation by setting $\rho_{\uparrow\downarrow}=0$ (dashed). Both models are evaluated at $eV_{\mathrm{g}}=0$ in order to highlight the quantitative as well as qualitative discrepancy. In (c) and (d), we show a full scan of the $(eV_{\mathrm{g}},eV_{\mathrm{sd}})$ plane for both equations illustrating the fundamental difference of the dynamics due to the two equations in the parameter space. While the rate-equation result is the familiar sequence of steps in the stationary current, the master-equation result shows a strong current suppression for voltages below the double-charging threshold. Using the master equation in the singular-coupling limit as it is derived in the text, we interpolate the two different curves of (a) by letting $\Omega\to\infty$ in (b).

II. THE SINGULAR-COUPLING LIMIT

The emergence of additional physics in the crossover regime $\Omega\sim\Gamma$ can already be understood with the help of the noninteracting, $U=0$, version of the two-level Anderson model, Eq. (1). Due to the absence of interactions, the retarded propagator of the model can be computed exactly, and a straightforward calculation yields for the off-diagonal element of the spectral function

$$\mathcal{A}_{\uparrow\downarrow}(\omega)=\frac{\gamma\left[\left(\omega-\frac{\Omega}{2}\right)\left(\omega+\frac{\Omega}{2}\right)-\frac{\Delta}{4}\right]}{\left|\left(\omega-\frac{\Omega}{2}+\imath\frac{\Gamma_\uparrow}{2}\right)\left(\omega+\frac{\Omega}{2}+\imath\frac{\Gamma_\downarrow}{2}\right)+\frac{\gamma^2}{4}\right|^2}. \qquad (2)$$

The self-energy $\Sigma=\imath\frac{\pi}{\hbar}\nu_0W^\dagger W$, where $(W)_{\alpha\sigma}:=t_{\alpha\sigma}$, gives rise to the broadenings $\Gamma_{\alpha\sigma}:=\frac{2\pi}{\hbar}\nu_0t_{\alpha\sigma}^2$ and $\gamma_\alpha:=\frac{2\pi}{\hbar}\nu_0t_{\alpha\uparrow}t_{\alpha\downarrow}$, with a missing index indicating that it has been summed over; the density of states ν_0 in the electrodes is assumed to be uniform. We also set $\delta\Gamma:=\Gamma_\uparrow-\Gamma_\downarrow$. The parameter $\Delta:=\Gamma_\uparrow\Gamma_\downarrow-\gamma^2$ is proportional to $\det(\Sigma)$. A vanishing Δ allows for a complete decoupling of one electronic level from both electrodes by a unitary transformation of the Hamiltonian.[7,8] We therefore focus on the generic situation $\Delta\neq0$ in the following.

The stationary coherences of the nondegenerate system are described by the equal-time correlator $\int_{\mathbb{R}}\mathcal{A}_{\uparrow\downarrow}(\omega)d\omega$. In the weak-coupling limit, when $\Gamma\to0$, these are expected to vanish for every finite Ω. To confirm this explicitly, we rescale $t_{\alpha\sigma}\mapsto\lambda t_{\alpha\sigma}$ and shift the energy $\xi:=\omega-\frac{\Omega}{2}$. As λ tends to zero, the rescaled spectral function $\mathcal{A}^\lambda_{\uparrow\downarrow}(\xi)$ converges to zero almost everywhere except at the four roots of its denominator

$$\xi_{1,2}=\frac{\lambda^2}{4}\left[\delta\Gamma-2\frac{\Omega}{\lambda^2}-\imath\Gamma\pm2\sqrt{\left(\frac{\Omega}{\lambda^2}\right)^2-\gamma^2}\right] \qquad (3)$$

and $\xi_{3,4}=\xi^*_{1,2}$. By use of the residue theorem, we find that also the contribution of these poles to the integral converges to zero such that $\int_{\mathbb{R}}A^\lambda_{\uparrow\downarrow}(\xi)d\xi\to0$ as $\lambda\to0$. When, on the contrary, both Γ and Ω are of the same order, we have to rescale not only $t_{\alpha\sigma}$ but also $\Omega\mapsto\lambda^2\Omega$, such that $\Gamma_{\alpha\sigma}/\Omega$ and γ_α/Ω remain fixed in the limit process. This simultaneous scaling is known as singular-coupling limit in contrast to the weak-coupling limit, in which Ω is kept constant.[4] Repeating the above calculation, the roots of the spectral function's denominator are now proportional to λ^2 and the integral

$$\int_{\mathbb{R}} \mathcal{A}^{\lambda}_{\uparrow\downarrow}(\xi)d\xi = 2\pi \frac{2\gamma\delta\Gamma^2}{\Gamma[\Gamma^2+4(\Omega^2-\gamma^2)]} \tag{4}$$

is independent of the scaling parameter and finite. Although the system is nondegenerate, some coherences between the electronic levels are retained. As we let $\Omega\to\infty$, these converge to zero. In this limit, our approach reproduces the weak-coupling result.

III. MASTER EQUATION

We now derive the master equation for the near-degenerate *interacting* two-level Anderson model in the singular-coupling limit. The underlying challenge of the regime $\Omega\sim\Gamma$ is that the tunneling dynamics takes place on the very same time scale as the coherent on-site dynamics due to the almost degenerate electronic levels. We consider the Hamiltonian, rescaled according to the previous observation, $H^{\lambda}=\lambda^2 H_S+H_E+\lambda H_{S-E}$. The term $\lambda^2 H_S$ describes the system, that is the near-degenerate electronic orbitals. We set $eV_g=0$ for convenience—it can easily be restored later on. H_E is the bath, in our case the Fermi-gas electrodes, and λH_{S-E} is the system-bath interaction, the tunnel Hamiltonian. We rewrite the von Neumann equation as an integral equation for the reduced density matrix $\rho_S=\mathrm{Tr}_E(\rho)$. The limit $\lambda\to 0$ then generates the markovian dynamics.[9] The reduced density matrix itself is obtained by a projection $\mathcal{P}\rho := \mathrm{Tr}_E(\rho)\otimes\rho_E$ with ρ_E being the equilibrium distribution of the bath. With the complementary projection $\mathcal{Q}:=1-\mathcal{P}$, the von Neumann equation $\dot{\rho}=-\imath[H^{\lambda},\rho]=-\imath\mathcal{L}^{\lambda}\rho=-\imath(\lambda^2\mathcal{L}_S+\mathcal{L}_E+\lambda\mathcal{L}_{S-E})\rho$ reads in the interaction picture[6,9]

$$\rho_S^I(t)=\rho_S^I(0)-\lambda^2\int_0^t e^{\imath\lambda^2\mathcal{L}_S v} \times\left\{\int_0^{t-v} e^{\imath\lambda^2\mathcal{L}_S s}\,\mathrm{Tr}_E(\mathcal{L}_{S-E}\mathcal{Q}e^{-\imath\mathcal{L}^{\lambda}s}\mathcal{Q}\mathcal{L}_{S-E}\rho_E)ds\right\} \times e^{-\imath\lambda^2\mathcal{L}_S v}\rho_S^I(v)dv. \tag{5}$$

This equation incorporates the Born approximation by choosing $\rho(0)=\rho_S(0)\otimes\rho_E$ as the initial condition. On the slow markovian time scale $\tau=\lambda^2 t$, the term in curly brackets converges to a time-independent quantity[9] and the master equation assumes the markovian form

$$\dot{\rho}_S=-\imath\mathcal{L}_S\rho_S-\int_0^{\infty}\mathrm{Tr}_E(\mathcal{L}_{S-E}e^{-\imath\mathcal{L}_E s}\mathcal{L}_{S-E}\rho_E)ds\,\rho_S. \tag{6}$$

If H_S had not been rescaled by λ^2, the exponential factors enclosing the curly bracket in Eq. (5) due to the interaction picture would have taken the form $\exp(\pm\imath\mathcal{L}_S\tau/\lambda^2)$ on the markovian time scale τ. In this case, letting $\lambda\to 0$ would have caused faster and faster oscillations for coherences belonging to nondegenerate states. In the limit, those terms would have been averaged to zero, commonly known as the secular approximation.[10]

As it is plausible from Eq. (6), the master equation in the singular-coupling limit is formally obtained by setting $\Omega=0$ in the dissipative term but retaining the nonzero Ω in the free-evolution Hamiltonian.[3] The splitting Ω must not appear in the Fermi functions coming from the trace over the bath degrees of freedom because due to the limit $\lambda\to 0$, the temperature of the bath is too large to resolve the splitting. The Bloch–Redfield equation would, however, have such a dependence on Ω.

We now evaluate the master equation (6) for the Anderson model Eq. (1) and recast it as a Bloch equation for the pseudospin $\vec{S}:=(2\,\mathrm{Re}\,\rho_{\uparrow\downarrow}, 2\,\mathrm{Im}\,\rho_{\uparrow\downarrow}, \rho_{\uparrow\uparrow}-\rho_{\downarrow\downarrow})$, which is defined by the electronic two-level system coupled to an equation for the populations p_i, i being the number of electrons on the device,

$$\dot{\vec{S}}=\sum_{\alpha}\left[f_{\alpha}p_0+\frac{1}{2}(f_{\alpha 2}-(1-f_{\alpha}))p_1-(1-f_{\alpha 2})p_2\right]\vec{n}_{\alpha} -\frac{1}{2}\sum_{\alpha}[f_{\alpha 2}+(1-f_{\alpha})]\Gamma_{\alpha}\vec{S}-(\vec{B}+\Omega\hat{e}_z)\times\vec{S}, \tag{7}$$

$$\frac{d}{dt}\begin{pmatrix}p_0\\p_1\\p_2\end{pmatrix}=\frac{1}{2}\sum_{\alpha}\Gamma_{\alpha}\begin{pmatrix}-2f_{\alpha} & (1-f_{\alpha}) & 0\\ 2f_{\alpha} & -f_{\alpha 2}-(1-f_{\alpha}) & 2(1-f_{\alpha 2})\\ 0 & f_{\alpha 2} & -2(1-f_{\alpha 2})\end{pmatrix} \times\begin{pmatrix}p_0\\p_1\\p_2\end{pmatrix}+\frac{1}{2}\sum_{\alpha}\begin{pmatrix}1-f_{\alpha}\\ f_{\alpha 2}-(1-f_{\alpha})\\ -f_{\alpha 2}\end{pmatrix}\vec{n}_{\alpha}\cdot\vec{S}, \tag{8}$$

$$I_{\alpha}=\Gamma_{\alpha}[f_{\alpha}p_0-((1-f_{\alpha})-f_{\alpha 2})p_1-(1-f_{\alpha 2})p_2] -\frac{1}{2}((1-f_{\alpha})+f_{\alpha 2})\vec{n}_{\alpha}\cdot\vec{S}. \tag{9}$$

Equation (9) gives the stationary current through lead α by $I_{\alpha}=\mathrm{Tr}_S(\rho\hat{I}_{\alpha})$.The pseudomagnetic fields are determined by the principal-value integrals

$$\vec{B}:=\frac{1}{2\pi}\sum_{\alpha}\mathcal{P}\int f_{\alpha}(\varepsilon)\left(\frac{1}{U-\varepsilon}+\frac{1}{\varepsilon}\right)d\varepsilon\,\vec{n}_{\alpha}, \tag{10}$$

with $\vec{n}_{\alpha}:=(2\gamma_{\alpha},0,\Gamma_{\alpha\uparrow}-\Gamma_{\alpha\downarrow})$. The Fermi functions are abbreviated by $f_{\alpha}:=f(eV_g-\mu_{\alpha})$ and $f_{\alpha 2}:=f(eV_g+U-\mu_{\alpha})$. For $\Omega=0$, Eqs. (7)–(9) are reminiscent of the ones derived in.[11]

In Eqs. (7) and (8), the electronic splitting term $-\imath\mathcal{L}_S\rho_S$ appears as a contribution to the pseudomagnetic field directed along $\hat{e}_z$. Due to this interpretation, the pseudomagnetic fields describe the tunneling-induced energy renormalizations of the electronic levels in exactly the same way as any other term in the Hamiltonian of this order would have to be treated, namely, in the singular-coupling limit. The singular-coupling limit provides a nondiscriminating description for both, the tunneling-induced renormalization of the on-site levels as the *result* of perturbation theory and any other splitting of the same order, which has to be included in the model *explicitly*.

IV. RESULTS

Based on our theoretical considerations, we understand the qualitative behavior of the stationary current-voltage characteristics of the two-level Anderson model and its remarkable sensitivity to Ω. The rate-equation results of Figs. 1(a) and 1(d) show the familiar steps in the stationary current whenever the voltage is large enough to add another electron to the device. Since $\Omega \ll k_B T$, the near degeneracy remains unresolved.

The $\Omega=0$ master equation also yields a finite linear conductance at zero bias, but below the double-charging threshold, in Figs. 1(a) and 1(c), the stationary current is strongly suppressed. Since the equation is one for the full reduced density matrix of the system's on-site levels, the underlying mechanism is explained by choosing a particular electronic basis. The key idea is: for general tunneling amplitudes $t_{\alpha\sigma}$, there always exists a unitary transformation to eliminate at least one of them and hence decouple one of the levels from one electrode. Let this level be $|\uparrow\rangle$ and let the electrode it is decoupled from be the drain electrode, $\Gamma_{d\uparrow}=0$. Then $\gamma_d=0$. If we neglect the pseudomagnetic fields for the time being, the degenerate master equation is actually only a rate equation, whose physics is easily understood. The tunneling dynamics will eventually populate the decoupled state $|\uparrow\rangle$, which due to $\Gamma_{d\uparrow}=0$ cannot be left again. Below the double-charging threshold, Coulomb repulsion then obstructs any current through the device.

The pseudomagnetic fields, which describe virtual switching processes between the degenerate levels, soften this picture. They induce a precession of the pseudospin that corresponds to moving the electron from the decoupled state $|\uparrow\rangle$ via virtual intermediate states on the source electrode into the conducting state $|\downarrow\rangle$.[11] Except for those voltages, for which $|\vec{B}|=0$ and the above argument for complete current suppression applies, the device carries the highly voltage-dependent stationary current shown in Figs. 1(a) and 1(d).

In the singular-coupling limit, the splitting Ω generates an additional pseudomagnetic field of the same order as the tunneling-induced one. Its orientation along $\hat{e}_z$ distinguishes this direction in the system's Hilbert space. As Ω is being increased, the precession frequency of $\vec{S}$ about the z axis will dominate the virtual tunneling dynamics, which are on the order of the electronic dwell time on the device. In the limit $\Omega \to \infty$, the residual precession dynamics is too fast compared with the average tunneling time, such that only the projection of $\vec{S}$ onto the z axis is relevant for the tunneling dynamics. For very large Ω, the pseudospin is effectively oriented along $\hat{e}_z$. Since then $S_x + \imath S_y = 2\rho_{\uparrow\downarrow} \approx 0$, the master equation is rendered a rate equation for the electronic occupations. As still $\Omega \ll k_B T$, the Fermi functions cannot resolve the physics due to Ω and the system is effectively described by the $\Omega=0$ rate equation.

The numerical results shown in Fig. 1(b) support this reasoning; as the splitting Ω is numerically increased, the current-suppression curve is shifted toward positive bias. The suppression of the stationary current is lifted and eventually lost in the flat current profile of the $\Omega=0$ rate-equation result.

V. CONCLUSIONS

The omnipresence of orbital degeneracies in molecular physics and their lifting due to various symmetry-breaking effects in single-molecule junctions requires the modeling of degenerate and near-degenerate systems in quantum transport theory.

We have shown that within the framework of master equations for sequential tunneling, such near-degenerate systems fall into a descriptive gap between the energy regimes that are discussed in the theoretical literature: whereas for degenerate systems a master equation for the full reduced density matrix is used, systems with energy differences larger than the tunneling-induced broadening Γ have to be described by rate equations. In the interesting crossover regime, the tunneling of electrons, the tunneling-induced splitting, and the coherent on-site dynamics are both of order Γ. By using the notion of the singular-coupling limit, we have derived a master equation for this regime. We have, thereby, also given meaning to the rate-equation treatment of degenerate systems as being the proper description when $\Gamma \ll \Omega \ll k_B T$. Since for the high-temperature regime $\Gamma \ll k_B T$ is always implied, we have actually presented a method to describe all possible energy regimes for sequential tunneling through multilevel quantum nanostructures.

Aside from the simple model that we have used to illustrate and explain its physics, our approach has a wide range of applications in molecular electronics. It provides a means to generically account for symmetry-breaking mechanisms in single-molecule junctions. And it allows the study of complex molecular models such as Jahn–Teller active systems, pseudo-Jahn–Teller structures, the valley degeneracy in carbon nanotubes, or the interaction of orbital symmetries and vibrational degrees of freedom, which is a leitmotif in the theory of molecular electronics.

This work was supported by SPP 1243 of the Deutsche Forschungsgemeinschaft.

[1] M. Galperin, M. A. Ratner, and A. Nitzan, J. Phys.: Condens. Matter **19**, 103201 (2007).
[2] L. Glazman and M. Pustilnik, *Nanophysics: Coherence and Transport*, edited by H. Bouchiat *et al.* (Elsevier, 2005), pp. 427–478; arXiv:cond-mat/0501007.
[3] For the special case of benzene molecules, similar observations to ours have been made independently by D. Darau, G. Begemann, A. Donarini, and M. Grifoni, Phys. Rev. B **79**, 235404 (2009).
[4] H. Spohn, Rev. Mod. Phys. **52**, 569 (1980), Sec. V C.
[5] C. Timm, Phys. Rev. B **77**, 195416 (2008).
[6] R. Dümcke and H. Spohn, Z. Phys. B **34**, 419 (1979).
[7] T. V. Shahbazyan and M. E. Raikh, Phys. Rev. B **49**, 17123 (1994).
[8] R. Berkovits, F. von Oppen, and J. W. Kantelhardt, Europhys. Lett. **68**, 699 (2004).
[9] E. B. Davies, Commun. Math. Phys. **39**, 91 (1974).
[10] H.-P. Breuer and F. Petruccione, *The Theory of Open Quantum Systems* (Oxford University Press, Oxford, 2002), Chap. 3.3.
[11] M. Braun, J. Konig, and J. Martinek, Phys. Rev. B **70**, 195345 (2004); S. Braig and P. W. Brouwer, *ibid.* **71**, 195324 (2005).