Pair Tunneling through Single Molecules

Jens Koch,[1] M. E. Raikh,[2] and Felix von Oppen[1]
[1]*Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany*
[2]*Department of Physics, University of Utah, Salt Lake City, Utah 84112, USA*

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By a polaronic energy shift, the effective charging energy of molecules can become negative, favoring ground states with even numbers of electrons. Here we show that charge transport through such molecules near ground-state degeneracies is dominated by tunneling of electron pairs which coexists with (featureless) single-electron cotunneling. Because of the restricted phase space for pair tunneling, the current-voltage characteristics exhibit striking differences from the conventional Coulomb blockade. In asymmetric junctions, pair tunneling can be used for gate-controlled current rectification and switching.

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Introduction.—Electronic transport through single molecules is distinguished from transport through quantum dots by the coupling to well-defined vibrational degrees of freedom. This coupling has two principal consequences: First, it leads to the emergence of vibrational sidebands in the current-voltage (IV) characteristics. This phenomenon occurs at large voltages which exceed the vibrational frequency ω. Its theoretical description was pioneered in Refs. [1,2] and extended in, e.g., Refs. [3–5], following experiments [6–9] on transport through molecular junctions.

Second, the coupling to molecular vibrations induces a polaron shift and can lead to a *negative* effective charging energy U. In physics, the concept of negative-U centers was first pointed out more than three decades ago [10] and is realized in many amorphous semiconductors. In chemistry, the scenario of negative U is known as “potential inversion” [11]. An important ingredient in realizing this scenario in molecular junctions may be a reduction of the true molecular charging energy by screening due to metallic electrodes [12] or an electrolytic environment [13]. Unlike vibrational sidebands, negative U manifests itself in transport through molecules already at low voltages. The prime manifestation of negative U studied to date [14–17] concerns the Kondo transport at very low temperatures.

In general, finite on-site interaction (of any sign) opens a new transport channel between molecule and leads. Namely, at finite U, *two* electrons can hop onto the molecule *simultaneously*. But it is only for negative U that this process can dominate the transport. Indeed, negative U favors even electron occupation numbers of the molecule. A Kondo resonance occurs when two states, whose occupation numbers differ by two, are degenerate. Then a virtual pair transition assumes the role of the spin-flip [18], leading to the formation of Kondo correlations in the ground state. However, the fact that the relevant pseudospin degree of freedom is associated with charge makes this Kondo state rather fragile. The underlying reason for this was elucidated by Haldane [19], who pointed out that for the charge Kondo effect, any deviation from degeneracy acts as a Zeeman field on the pseudospin and, thus, suppresses the Kondo correlations. This observation has a drastic consequence for transport. For the conventional (spin) Kondo effect, the low-temperature conductance eventually reaches the unitary value over a wide range of gate voltages. By contrast, for the charge Kondo effect the unitary value is only achieved *precisely* at the resonance gate voltage. This fragility of the charge Kondo effect in transport through molecules with negative U was illustrated by several recent numerical simulations [15–17]. The main message of the present Letter is that negative U strongly affects the transport through a molecule even in the rate-equation regime at high temperatures, where Kondo correlations are irrelevant. We show that in this regime, a negative U leads to a unique scenario for the passage of current through the molecule, which we study analytically at all gate voltages and biases.

Effective Hamiltonian.—Consider a molecule with a single spin-degenerate single-particle orbital ε_d dominating the transport between two metallic electrodes. As ε_d is swept by a gate voltage, the electron occupation n_d of the molecule switches from empty ($n_d = 0$) to doubly occupied ($n_d = 2$) at the resonant gate voltage defined by the condition $2\varepsilon_d + U = 0$ [20]. (We measure all energies from the Fermi energy.) Because of the negative U, single occupation ($n_d = 1$) of the molecule is unfavorable at any gate voltage. A schematic of the corresponding configuration of one-particle energies near resonance is shown in Fig. 1(a). Sequential tunneling of single electrons is clearly exponentially suppressed at bias voltages $|eV| \ll |U|$. Instead, the dominant sequential transport processes near resonance involve the coherent transfer of *electron pairs* [21]. Representative pair-tunneling processes are illustrated in Figs. 1(c) and 1(d). It is important to realize that in addition to processes in which the two electrons enter the molecule from the same lead, the electron pair on the molecule can be created (or annihilated) by two electrons tunneling in from (or out to) opposite leads. In parallel with these sequential pair-tunneling processes, single-particle cotunneling processes [see Fig. 1(b)] also take place. We find that while both processes are of the same order, they can be easily distinguished since the single-particle cotunneling contribution does not exhibit any structure near the resonance gate voltage.

To capture all eight pair-tunneling processes systematically, we perform a Schrieffer-Wolff transformation [22]. We start from the Hamiltonian $H = H_{\rm mol} + H_{\rm vib} + H_{\rm leads} + H_i$ [1,4], where the separate contributions correspond to the electronic molecular orbital $H_{\rm mol} = \varepsilon_d n_d + U n_{d\uparrow} n_{d\downarrow}$, to the molecular vibrations $H_{\rm vib} = \hbar\omega b^\dagger b + \lambda\hbar\omega(b^\dagger + b)n_d$, to the noninteracting leads $H_{\rm leads} = \sum_{a=L,R}\sum_{\mathbf{p},\sigma}\epsilon_{\mathbf{p}} c^\dagger_{a\mathbf{p}\sigma}c_{a\mathbf{p}\sigma}$, and to the tunneling between leads and molecule $H_i = \sum_{a=L,R}\sum_{\mathbf{p},\sigma}(t_a c^\dagger_{a\mathbf{p}\sigma}d_\sigma + \text{H.c.})$. Here the operator d_σ annihilates an electron with spin σ on the molecule, $c_{a\mathbf{p}\sigma}$ annihilates an electron in lead a ($a = L, R$) with momentum $\mathbf{p}$ and spin σ, vibrational excitations are annihilated by b, and $t_{L,R}$ denotes the tunneling matrix elements. The electron-phonon coupling (with coupling constant λ) can be eliminated as usual by a canonical transformation [1,4], which implies renormalizations of the tunneling Hamiltonian $t_a \rightarrow t_a e^{-\lambda(b^\dagger - b)}$, of the orbital energy $\varepsilon_d \rightarrow \varepsilon_d - \lambda^2\hbar\omega$, and of the charging energy $U \rightarrow U - 2\lambda^2\hbar\omega$. It is this last renormalization which opens the possibility of a negative effective charging energy. The underlying reason for this renormalization is that the energetic polaron shift is proportional to the excess charge of the molecule *squared* which is of the same form as the Coulomb charging energy. To be specific, we focus on temperatures and biases where only the vibrational ground state is populated. In this case, we obtain an effective Hamiltonian $H_{\rm eff} = H_{\rm mol} + H_{\rm leads} + H_i$ with negative effective charging energy U and Franck-Condon suppressed tunneling matrix elements $t_a \rightarrow t_a e^{-\lambda^2/2}$ (absorbed into the definition of t_a in the following).

Performing the Schrieffer-Wolff transformation on $H_{\rm eff}$ in the usual way [23], we eliminate H_i to lowest order and obtain a transformed Hamiltonian

$$H_{\rm SW} = H_{\rm mol} + H_{\rm leads} + H_{\rm dir,ex} + H_{\rm pair}, \tag{1}$$

where we ignore a term which merely renormalizes ε_d. For positive U, one retains only

$$H_{\rm dir,ex} = \frac{1}{2}\sum_{aa'\mathbf{p}\mathbf{p}'\sigma}\bigg[\frac{t_a t^*_{a'}}{\epsilon_{a\mathbf{p}} - \varepsilon_d} c^\dagger_{a\mathbf{p}\sigma}c_{a'\mathbf{p}'\sigma} + t_a t^*_{a'} M(\epsilon_{a\mathbf{p}}) \times (d^\dagger_{\bar\sigma} d_\sigma c^\dagger_{a\mathbf{p}\sigma} c_{a'\mathbf{p}'\bar\sigma} - c^\dagger_{a\mathbf{p}\sigma} c_{a'\mathbf{p}'\sigma} n_{d\bar\sigma}) + \text{H.c.}\bigg], \tag{2}$$

which describes the direct and exchange interactions between molecule and lead. Here we have introduced the abbreviations $M(\epsilon) = [\epsilon - \varepsilon_d]^{-1} - [\epsilon - (\varepsilon_d + U)]^{-1}$ and $\bar\uparrow, \bar\downarrow = \downarrow, \uparrow$. With $U > 0$ and in the absence of charge fluctuations, transport predominantly proceeds via single-electron cotunneling described by $H_{\rm dir,ex}$. By contrast, for negative U it is crucial to retain the pair-tunneling terms

$$H_{\rm pair} = \sum_{aa'\mathbf{p}\mathbf{p}'} t_a t_{a'} M(\epsilon_{a\mathbf{p}}) d_\uparrow d_\downarrow c^\dagger_{a'\mathbf{p}'\downarrow} c^\dagger_{a\mathbf{p}\uparrow} + \text{H.c.} \tag{3}$$

Obviously, $H_{\rm pair}$ contributes only for *nonzero* effective charging energy U.

Rates.—Using Fermi's golden rule, the pair Hamiltonian $H_{\rm pair}$ leads to the rate

$$W^{aa'}_{0\rightarrow 2} = \frac{\Gamma_a\Gamma_{a'}}{h}\int d\epsilon\, M^2(\epsilon) f_a(\epsilon) f_{a'}(2\varepsilon_d + U - \epsilon) \tag{4}$$

for pairs of electrons tunneling onto the molecule. Here $\Gamma_a = 2\pi\nu_a|t_a|^2$ is the energy scale of single-particle tunneling in junction a for a constant density of states ν_a. The superscripts (aa') denote the leads from where the spin-up electron (a) and the spin-down electron (a') originate. The analogous rates $W^{aa'}_{2\rightarrow 0}$ for pairs leaving the molecule are obtained from Eq. (4) by replacing each lead Fermi function f_a with a factor $(1 - f_a)$.

In the regime where single-particle occupation of the molecule is negligible, i.e., $|2\varepsilon_d + U|$, $|eV|$, $k_BT \ll \varepsilon_d$, $|\varepsilon_d + U|$, the integral in Eq. (4) approximately reduces to an integral over the Fermi functions alone and can be expressed in terms of the function $F(\epsilon) = \epsilon/[\exp(\beta\epsilon) - 1]$. For symmetric voltage splitting, i.e., $f_a(\epsilon) = f(\epsilon - eV_a)$ with $V_{L,R} = \pm V/2$, the explicit result for pair tunneling reads

$$W^{aa'}_x = \frac{\Gamma_a\Gamma_{a'}}{h} M^2(0) F[\pm(2\varepsilon_d + U + eV_a + eV_{a'})], \tag{5}$$

where the upper (lower) sign refers to $x = 0 \rightarrow 2$ ($x = 2 \rightarrow 0$).

The pair-tunneling rates, Eq. (5), have several remarkable features. (i) Pair tunneling with electrons originating from the same lead [$a = a'$, Fig. 1(c)] leads to bias-dependent rates. By contrast, pair tunneling with electrons from different leads [$a \neq a'$, Fig. 1(d)] is bias independent, as the energy missing in the lead with lower Fermi energy is exactly compensated for by the additional energy available in the lead with higher Fermi energy. (ii) When pair tunneling is energetically allowed, its rate is *proportional to the detuning* of the pair state $2\varepsilon_d + U$ from the relevant Fermi energy. This is in sharp contrast with rates for single-electron sequential tunneling, which are *independent* of the energy of the single-particle state. This unusual behavior of the pair-tunneling rates arises from the fact that only the

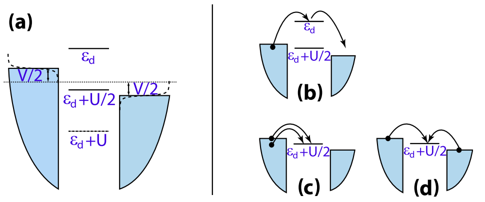

FIG. 1 (color online). (a) Level configuration of the negative-U model. Shown are the one-particle energies for the singly occupied dot (ε_d), the doubly occupied dot ($\varepsilon_d + U/2$), and the energy for which holes can propagate through the doubly occupied dot ($\varepsilon_d + U$). The right panel illustrates the relevant types of processes: (b) cotunneling, (c),(d) pair tunneling.

sum of the energies of the two tunneling electrons is fixed by energy conservation, making the *phase space* for pair tunneling proportional to the detuning [24]. We will see below that this leads to characteristic features of pair tunneling in both the gate-voltage and bias dependence of the conductance.

Similarly, the rates for cotunneling from lead a to a' can be obtained from $H_{\mathrm{dir,ex}}$ as $W_{0\to 0}^{aa'} = 2\Gamma_a\Gamma_{a'}F(eV_a)/h\varepsilon_d^2$, including an explicit factor of 2 for spin. The corresponding rates $W_{2\to 2}^{aa'}$ are obtained by the replacement $\varepsilon_d^2 \to (\varepsilon_d + U)^2$.

Having established the relevant processes and their rates, we now describe transport outside the Kondo regime by the corresponding rate equations [25,26]. Since the occupation probability for the singly occupied molecule is negligible for $|eV| \ll |U|$, the stationary rate equations reduce to $0 = P_2W_{2\to 0} - P_0W_{0\to 2}$, with the solution $P_0 = W_{2\to 0}/[W_{2\to 0} + W_{0\to 2}]$, $P_2 = 1 - P_0$. Here $W_{i\to f}$ denotes the total rate for transitions from initial state i to final state f, i.e., $W_x = \sum_{a,a'} W_x^{aa'}$. The stationary current $I = I^{\mathrm{pairs}} + I^{\mathrm{cot}}$, evaluated in the left junction, involves contributions from pair tunneling and cotunneling,

$$I^{\mathrm{pairs}}/e = P_0 w_{0\to 2} - P_2 w_{2\to 0}, \tag{6}$$

$$I^{\mathrm{cot}}/e = P_0 v_{0\to 0} + P_2 v_{2\to 2}. \tag{7}$$

Here the coefficients v and w are given by

$$\begin{aligned} v_{0\to 0} &= W_{0\to 0}^{LR} - W_{0\to 0}^{RL}, \\ w_{0\to 2} &= 2W_{0\to 2}^{LL} + W_{0\to 2}^{LR} + W_{0\to 2}^{RL}. \end{aligned} \tag{8}$$

The factor of 2 in the last equation originates from the coherent transfer of *two* electrons in this pair-tunneling process. [All remaining coefficients are obtained from Eq. (8) by interchanging "2 ↔ 0" in the subindices.]

Results.—The rate equations provide a complete *analytical* description of the nonlinear current-voltage characteristics through negative-U molecules. Specifically, we find for the linear conductance

$$G = \frac{2e^2\Gamma_L\Gamma_R}{h}\left[\frac{U^2}{\varepsilon_d^2(\varepsilon_d + U)^2}\frac{\beta(2\varepsilon_d + U)}{2\sinh[\beta(2\varepsilon_d + U)]} + f(-2\varepsilon_d - U)\frac{1}{\varepsilon_d^2} + f(2\varepsilon_d + U)\frac{1}{(\varepsilon_d + U)^2}\right]. \tag{9}$$

Here the last two terms in brackets, which arise from cotunneling, give a slowly varying background. By contrast, pair tunneling, described by the first term in brackets, leads to a remarkable conductance peak. As illustrated in Fig. 2(a), its height $G_0 = 24e^2\Gamma_L\Gamma_R/U^2h$ exceeds twice the cotunneling background and is temperature independent, while its width is proportional to T. This feature, which is a direct consequence of the phase space for pair tunneling, should provide an unambiguous experimental signature of pair tunneling as opposed to ordinary Coulomb-blockade conductance peaks, whose integral strength is temperature independent.

While the linear conductance is identical for symmetric and asymmetric devices, their finite-bias behavior differs considerably. For large voltages $|eV| \gg k_BT$, we find for the pair-tunneling current

$$I^{\mathrm{pairs}} = \frac{e}{\hbar}\frac{16U^2}{(U^2 - \delta^2)^2}\frac{2\Gamma_L\Gamma_R}{\Gamma_L^2|\delta_+| + \Gamma_R^2|\delta_-| + 2\Gamma_L\Gamma_R|\delta|} \times [\Theta_+\Gamma_L|\delta_+|(\Gamma_R|\delta_-| + \Gamma_L|\delta|) + (L \leftrightarrow R, + \leftrightarrow -)], \tag{10}$$

where $\delta = 2\varepsilon_d + U$, $\delta_\pm = \delta \pm eV$, and $\Theta_\pm = \theta(-\delta) \times \theta(\mp\delta_\pm) - \theta(\delta)\theta(\pm\delta_\pm)$. For symmetric devices, Eq. (10) implies that the width of the conductance curve is fixed by the bias voltage, as illustrated in Fig. 2(b). This behavior is in stark contrast to the conventional Coulomb blockade, where one finds two symmetric sharp peaks at detunings $\pm V/2$ from resonance. This difference which also arises from the phase space for pair tunneling, is further emphasized in Fig. 3(a) for all bias and gate voltages.

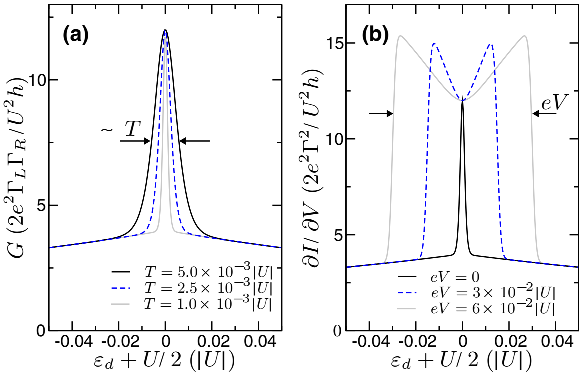

FIG. 2 (color online). Conductance as a function of gate voltage, based on our analytical results. (a) Linear conductance G for several temperatures. The conductance curve exhibits a featureless background due to cotunneling and a distinct peak of constant height and width $\sim T$ due to pair tunneling. (b) Conductance for several bias voltages at $T = 1.0 \times 10^{-3}|U|$ for a symmetric junction. With bias voltages $eV \gg k_BT$, the width of the double peak is given by eV.

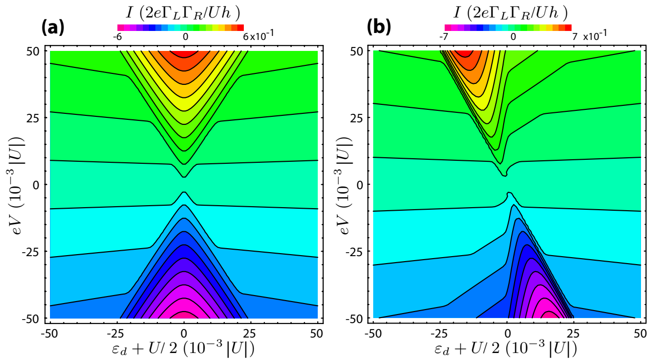

FIG. 3 (color online). Current as a function of bias and gate voltage for (a) a symmetric junction with $\Gamma_L = \Gamma_R = k_BT$, (b) an asymmetric junction with $\Gamma_L = 0.1k_BT$, $\Gamma_R = 10k_BT$, and with $k_BT = 0.5 \times 10^{-3}|U|$. For asymmetric junctions, one observes the rectification effect due to pair tunneling.

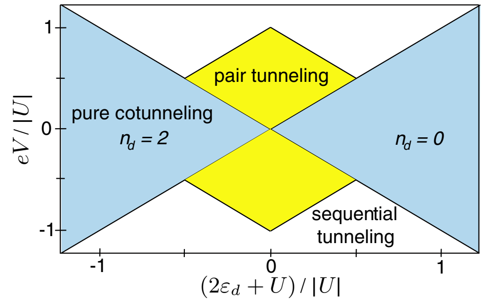

FIG. 4 (color online). Stability diagram for the ground-state occupation n_d and dominant transport modes as a function of gate and bias voltages for a symmetric device with negative U.

Devices with a significant asymmetry in the molecule-lead couplings exhibit a striking asymmetry with respect to voltage inversion; see Fig. 3(b). We find in this case that pair tunneling causes strong current rectification, whose transmission direction can be switched by a gate voltage. To understand this rectification effect, consider an asymmetric device with $\Gamma_R \gg \Gamma_L$ and suppose that the Fermi level is higher in the left lead. Then the pair-tunneling current proceeds as follows: (i) A pair with electrons from opposite leads jumps onto the molecule; (ii) the electron pair on the molecule is transferred to the right lead. While (ii) is a fast process ($\sim\Gamma_R^2$), the current is limited by process (i) with rate $\sim\Gamma_L\Gamma_R$. Then the switching by a gate voltage immediately follows from the rate for process (i), which is exponentially suppressed only for $2\varepsilon_d + U > 0$. By a similar analysis for the opposite bias, one finds an exponential suppression of the pair current for $2\varepsilon_d + U < 0$, thus also explaining the rectification. These features render molecules with negative U interesting candidates for devices with transistorlike characteristics.

Conclusions.—Near the degeneracy point, transport through a molecular junction with negative U differs drastically from the conventional Coulomb-blockade scenario at positive U. For negative U, current flow makes the molecule alternate in time between even occupation numbers, which is accomplished by pair tunneling. This is the dominant transport mode in the gate-voltage–bias-voltage domain shown in Fig. 4.

It is intriguing that the on-site attraction of two electrons makes pair tunneling through molecules qualitatively similar to tunneling through a superconducting grain, considered in Ref. [27]. However, in the case of molecules, the physical picture of transport is more complex. This is because a pair can be created on the molecule by electrons tunneling from *different* leads, as illustrated in Fig. 1(d). By contrast, for a grain with size larger than the superconducting correlation length, electron pairs enter and exit the grain only from the *same* lead; i.e., only the processes in Fig. 1(c) are responsible for the passage of current [28]. As an important consequence of this difference, negative-U molecules act as gate-controlled rectifiers.

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[1] L. I. Glazman and R. I. Shekhter, Sov. Phys. JETP **67**, 163 (1988).
[2] N. S. Wingreen, K. W. Jacobsen, and J. W. Wilkins, Phys. Rev. Lett. **61**, 1396 (1988).
[3] S. Braig and K. Flensberg, Phys. Rev. B **68**, 205324 (2003).
[4] A. Mitra, I. Aleiner, and A. J. Millis, Phys. Rev. B **69**, 245302 (2004).
[5] J. Koch, M. E. Raikh, and F. von Oppen, Phys. Rev. Lett. **95**, 056801 (2005).
[6] H. Park *et al.*, Nature (London) **407**, 57 (2000).
[7] X. H. Qiu, G. V. Nazin, and W. Ho, Phys. Rev. Lett. **92**, 206102 (2004).
[8] L. Yu *et al.*, Phys. Rev. Lett. **93**, 266802 (2004).
[9] A. N. Pasupathy *et al.*, Nano Lett. **5**, 203 (2005).
[10] P. W. Anderson, Phys. Rev. Lett. **34**, 953 (1975).
[11] C. Kraiya and D. H. Evans, J. Electroanal. Chem. **565**, 29 (2004), and references therein.
[12] S. Kubatkin *et al.*, Nature (London) **425**, 698 (2003).
[13] L. Grüter *et al.*, Nanotechnology **16**, 2143 (2005).
[14] A. S. Alexandrov, A. M. Bratkovsky, and R. S. Williams, Phys. Rev. B **67**, 075301 (2003); A. S. Alexandrov and A. M. Bratkovsky, Phys. Rev. B **67**, 235312 (2003).
[15] P. S. Cornaglia, H. Ness, and D. R. Grempel, Phys. Rev. Lett. **93**, 147201 (2004); P. S. Cornaglia, D. R. Grempel, and H. Ness, Phys. Rev. B **71**, 075320 (2005); P. S. Cornaglia and D. R. Grempel, Phys. Rev. B **71**, 245326 (2005).
[16] L. Arrachea and M. J. Rozenberg, Phys. Rev. B **72**, 041301(R) (2005).
[17] J. Mravlje, A. Ramšak, and T. Rejec, Phys. Rev. B **72**, 121403(R) (2005).
[18] A. Taraphder and P. Coleman, Phys. Rev. Lett. **66**, 2814 (1991).
[19] F. D. M. Haldane, Phys. Rev. B **15**, 281 (1977).
[20] In the presence of additional orbitals, this remains true as long as $|U|$ is smaller than the level spacing.
[21] We define sequential-tunneling processes as involving real occupation of the molecule as opposed to cotunneling during which the molecule is only virtually occupied.
[22] J. R. Schrieffer and P. A. Wolff, Phys. Rev. **149**, 491 (1966).
[23] H.-B. Schüttler and A. J. Fedro, Phys. Rev. B **38**, 9063 (1988).
[24] Similar phase-space arguments apply to pair tunneling between superconductors; see J. W. Wilkins, in *Tunneling Phenomena in Solids*, edited by E. Burstein and S. Lundqvist (Plenum, New York, 1969), Chap. 24.
[25] C. W. J. Beenakker, Phys. Rev. B **44**, 1646 (1991).
[26] D. V. Averin, A. N. Korotkov, and K. K. Likharev, Phys. Rev. B **44**, 6199 (1991).
[27] F. W. J. Hekking *et al.*, Phys. Rev. Lett. **70**, 4138 (1993).
[28] Another difference between transport through negative-U molecules and superconducting grains lies in the absence of BCS coherence factors in the former.