# Towards a Chemically Driven Molecular Electron Pump

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Charge can be pumped through a tiny gated portal from a reservoir at low electrochemical potential to one at the same or higher electrochemical potential by cyclically modulating the portal and gate energies. A theoretically and experimentally well established mechanism is Thouless adiabatic pumping, achieved by a precisely timed out-of-phase modulation of at least two parameters of the system. Here we show that stochastic modulation between two configurations of gate and portal energies can drive efficient pumping by a different, nonadiabatic, mechanism that may provide a basis for chemically driven electron pumping through a molecular wire.

A charge pump is a device that drives net transport of electrical charge from a reservoir at low electrochemical potential to one at the same or higher electrochemical potential by a cyclic modulation of some internal parameters. Recently, Switkes *et al.* [1] demonstrated an experimental realization of an adiabatic electron pump [2] where the modulation is so slow that almost no energy is lost in the process. Their approach, suggested theoretically by Thouless [3], relies on precisely timed out-of-phase modulation of two parameters that control the equilibrium charge on the dot and the ease of transmission of charge through gates between the dot and the external charge reservoirs. Here we discuss a similar but fundamentally different approach involving stochastic modulation of a single parameter [4]. We show that randomly switching between two configurations of well and gate energies, with exponentially distributed lifetimes in each configuration, can also support efficient pumping and provide a mechanism for chemically driven electron pumping through a molecular wire. Aside from being of tremendous intellectual interest and possibly shedding light on the function of biological electron transport proteins, a chemically driven electron pump could play a role in the design of molecular computers [5–7], acting as a molecular device [8] that uses a chemical reaction to power gain and prevent dissipation of an input signal traveling through the molecular computational circuit. In principle, the nonequilibrium chemical reaction that provides the power could be entropically driven and even endothermic, allowing the system to be self-cooling.

Consider the diagram in Fig. 1 where we compare the transfer of charge through a *quantum dot* (Fig. 1a) to the passage of an electron along a *molecular wire* with an energy well created by interposition of $\sigma$ bonds along the $\pi$ bonded backbone [7] (Fig. 1b). In the case of the quantum dot the energy barriers between the well and the left and right reservoirs are governed by the voltages on the left and right gates, $V_L$ and $V_R$ respectively, the number of electrons in the dot at equilibrium is governed by the voltage

$V_D$ and the chemical potential of the reservoirs, and the overall bias voltage $V_{bias}$ sets the direction of the steady state current. For the molecular wire (Fig. 1b) the gate and well energies are set by the electron donating/withdrawing strength of the substituents $R$ and $R'$. The ends of the wire can be connected to external electrodes by thiol linkages functioning as molecular alligator clips [9]. The overall direction of the current is governed by $\Delta\mu = \mu_R - \mu_L$ where $\mu_R$ and $\mu_L$ are the chemical potentials of electrons on the right and left, respectively. The energy levels in the well are discrete, and we have shown the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). An electron can tunnel into the LUMO from the left or right, and so the wire can
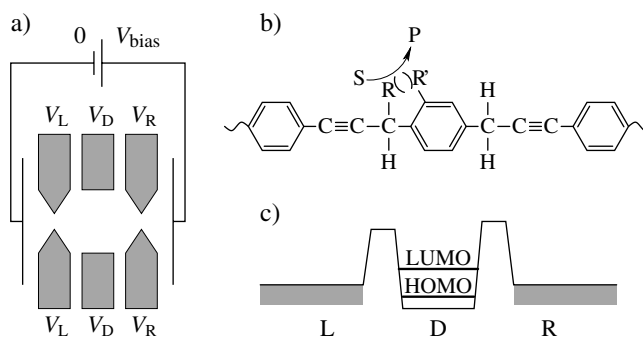


FIG. 1. (a) Illustration of a quantum dotlike device for pumping charged particles from a left reservoir to a right reservoir against a bias $V_{bias}$ by modulating the gate ($V_L$ and $V_R$) and dot ($V_D$) voltages. (b) A wire molecule that gives rise to a similar well structure as the quantum dot, but at a scale of a few angstroms rather than a micron. The well is formed because of the interposition of the $\sigma$ bonds in the $\pi$ bonded backbone of the wire. The functional groups $R$ and $R'$ can influence the left gate height and well energy level depending on how strongly electron withdrawing or donating they are. We have illustrated a hypothetical but plausible possibility that these substituents can form an active site for catalysis of some reaction $S \rightleftharpoons P$. (c) The well structure for the molecular wire showing the Fermi levels of the right and left reservoirs and the frontier LUMO and HOMO orbitals of the well.

conduct. If the barrier structure is asymmetric because of the properties of the substituents $R$ and $R'$, the molecule will also display rectification. Because of Coulomb interactions, the number of electrons in the LUMO is for all practical purposes restricted to 0 or 1.

The substituents $R$ and $R'$ can be designed to form an active site [10] for the catalytic conversion between some substrate $S$ and product $P$. The binding of $S$ and $P$ will raise or lower the height of the left barrier and the energy levels of the LUMO depending on whether substrate and product are electron donating or withdrawing. Thus, in the presence of $S$ and/or $P$, the energy level of the LUMO will fluctuate, with an exponentially distributed lifetime in each configuration. If the chemical reaction $S \rightleftharpoons P$ is far from equilibrium, the resulting nonequilibrium fluctuations of the energy levels can drive electron pumping. It is important to note that for chemically driven pumping, the molecular wire must be chemically asymmetric. This is achieved here by having the catalytic active site at the left-hand sigma bond. Thus in order to observe macroscopic current in an ensemble of such molecules it is necessary that they be oriented on a surface or across a phase boundary.

A standard scenario for *adiabatic pumping* [11] shown in Fig. 2a is to modulate the gate heights and well energy level in the following sequence of basically four steps which are repeated cyclically. For simplicity, we take the case that the well is never open to more than one reservoir at a time (because a high energy barrier isolates it from the other reservoir), and both gates are modulated in addition to the well energy. As we will see later the modulation of only one gate (as in our system discussed above) is enough to achieve adiabatic pumping. The energies $\varepsilon_1$ and $\varepsilon_2$ are given relative to the reservoir to which the well is open.



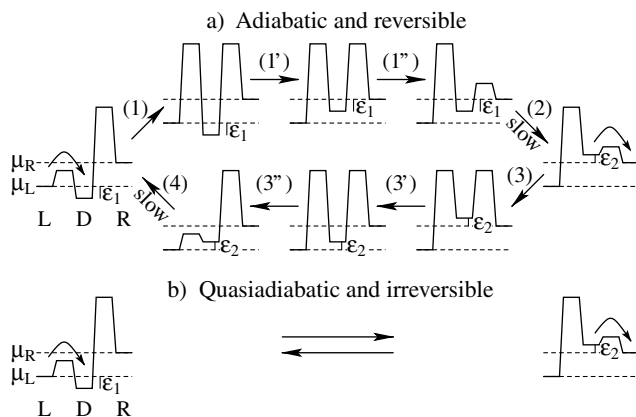a) Adiabatic and reversible

b) Quasiadiabatic and irreversible

FIG. 2. Schematic illustration of (a) adiabatic pumping, which is time reversible and where no energy is dissipated in the limit that the well is never open to more than one reservoir at a time and the energy level of the well is changed infinitesimally slowly in steps (2) and (4); and (b) quasiadiabatic pumping which is intrinsically irreversible, and which dissipates $(\varepsilon_1 + \varepsilon_2)(P_L - P_R)$ energy per cycle. Pumping can be achieved by stochastically switching between the two configurations.

Then, starting with the well open to and in equilibrium with the left reservoir and isolated from the right: (1) raise the left gate, (1') raise the well (LUMO) energy level from $\mu_L - \varepsilon_1$ to $\mu_R - \varepsilon_1$, and (1'') lower the right gate. Now the dot is in equilibrium with the right reservoir. Then (2) very slowly (adiabatically) increase the well energy level to $\mu_R + \varepsilon_2$ letting the electron flow to the right reservoir; (3) lower the left gate, (3') lower the well energy level to $\mu_L + \varepsilon_2$, and (3'') raise the right gate. Now the dot is in equilibrium with the left reservoir again. As the last step of the cycle (4) very slowly decrease the well energy level to $\mu_L - \varepsilon_1$. During these steps the dot is always at equilibrium with the reservoir to which it is open, so the entire cycle can be called adiabatic. After steps (2) and (4) the probability that the dot is occupied is given by the Fermi distribution $P_R = (e^{\varepsilon_2} + 1)^{-1}$ and $P_L = (e^{-\varepsilon_1} + 1)^{-1}$, respectively. Throughout this paper we measure the energies in units of $k_B T$. During every complete cycle the number of electrons transferred from the left to the right reservoir is $P_L - P_R$ on average.

This adiabatic pumping cycle is time reversible. If the sequence of steps is reversed, the same number of electrons are pumped from right to left as are pumped from left to right by the forward sequence. If the isolation from one or the other reservoirs is absolute and steps (2) and (4) are very slow, the cycle approaches thermodynamic reversibility and the amount of energy dissipated per cycle approaches zero.

A key feature of adiabatic pumping is the out-of-phase modulation of the gate and dot voltages. We can take advantage, however, of the fact that the relaxation time [12] of the charge distribution within the well is much faster (typically psec) than the relaxation between the well and reservoirs to accomplish pumping with in-phase modulation of the dot and gate voltages requiring only two steps [4] as shown in Fig. 2b. First we simultaneously raise the left gate, increase the well energy level to $\varepsilon_2$ relative to the chemical potential on the right, and lower the right gate. During the switching process almost no energy is lost since the local equilibrium within the well is not disturbed and no charge transfer between the dot and reservoirs occurs. Now, we wait until equilibrium between the dot and the right reservoir is established; and then simultaneously lower the left gate, decrease the well energy level to $-\varepsilon_1$ relative to the chemical potential on the left, raise the right gate; and wait again. After equilibrium is established between the dot and the left reservoir the average number of electrons transferred from left to right is $P_L - P_R$, exactly the same as in the case of adiabatic pumping.

This in-phase modulation is *quasiadiabatic*–local equilibrium in the well is maintained at every instant so energy is not lost when the energy level is raised and lowered without a change in the number of electrons in the well, but global equilibrium between the reservoirs and well does not hold at every instant. Thus this pumping mechanism is clearly not time reversible. There are only two steps

and there is no difference between carrying them out in the forward or reverse sequence. The amount of energy dissipated per cycle is $(\varepsilon_1 + \varepsilon_2)(P_L - P_R)$ even if the period is very long. The efficiency $\frac{\Delta\mu}{\Delta\mu+\varepsilon_1 1+\varepsilon_2}$ can, nevertheless, approach unity as $\Delta\mu$ becomes large [4]. It makes little difference whether the modulation is periodically or stochastically switched between the two configurations [13]. Switching between the two configurations with an exponentially distributed waiting time in each configuration, much like a chemical reaction, also supports pumping [14].

Altshuler and Glazman [15], and Switkes et al. [1] claimed that pumping through a quantum dot requires modulation of at least two parameters out-of-phase with one another, arguing that if the two parameters are modulated in-phase with each other, any charge transported during the first half period of modulation flows back in the second half period. This holds only for very slow (adiabatic) processes during which the system is always in global thermodynamic equilibrium, and so is not in contradiction to our results for quasiadiabatic pumping which uses in-phase modulation of the well and gate energies and is not in global equilibrium at every instant. To see how this is true and obtain better insight into the relationship between adiabatic and quasiadiabatic pumping, and to illustrate that pumping can be accomplished with only a small modulation of only one gate and the dot energy, we consider small amplitude sinusoidal modulation where the dot is not totally isolated from either reservoir at any time, and where the chemical potentials of the left and right reservoirs are the same, i.e. $\Delta\mu = 0$ (see the inset of Fig. 3). If the modulation of the gate or well energy is slow enough that the charge distribution within the well is always in local equilibrium, the transfer of charge between the dot and the reservoirs can be described by rate theory

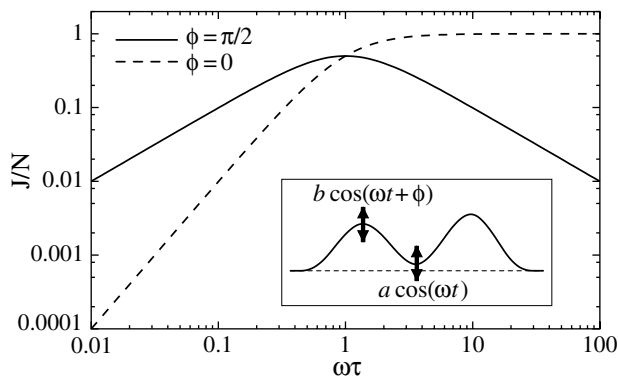$$\frac{dP}{dt} = -(k_{DL} + k_{DR})P + (k_{LD} + k_{RD})(1 - P), \quad (1)$$



FIG. 3. Log-log plot of the pumped flux (normalized by $N = abP^{(0)}(1 - P^{(0)})/[\tau 2(s + s^{-1})^2]$) vs frequency for out-of-phase (solid line) and in-phase (dashed line) modulation of the system shown in the inset. The left gate height and the dot voltage are modulated with small amplitudes $a$ and $b$.

where $P$ is the instantaneous probability that the well LUMO contains an electron and $k_{DL}$ and $k_{DR}$ are the rate constants for an electron to exit the dot to the left or right reservoir, respectively. The rates for an electron to enter the dot from the left and right reservoirs are $k_{LD}$ and $k_{RD}$. Because $\Delta\mu = 0$ the relation $k_{LD}/k_{DL} = k_{RD}/k_{DR}$ for the rate constants.

Let the modulation of the level of the dot and left height of the gate be $a(t) = a\cos(\omega t)$ and $b(t) = b\cos(\omega t + \phi)$ with a phase lag $\phi$ between them, as shown in Fig. 3. $a(t)$ and $b(t)$ enter the rate equation via the multiplication of $k_{LD}$, $k_{DR}$, and $k_{DL}$ by $e^{-b(t)}$, $e^{a(t)}$, and $e^{a(t)-b(t)}$, respectively. For small $a$ and $b$ the theory for pumping by systems described by rate equations [16] yields

$$J = \omega ab \frac{P^{(0)}(1 - P^{(0)})}{2(s + s^{-1})^2} \frac{\sin(\phi) + \omega\tau\cos(\phi)}{1 + \omega^2\tau^2} \quad (2)$$

for the flux of the electrons, where $\tau = (k_{LD} + k_{DL} + k_{RD} + k_{DR})^{-1}$ is a characteristic time, $P^{(0)} = (k_{LD} + k_{RD})\tau = (1 + k_{DR}/k_{RD})^{-1}$ is the stationary Fermi probability for an electron to occupy the LUMO in the absence of the modulation, and we defined an anisotropy or "shape" factor $s = \sqrt{k_{DL}/k_{DR}}$ that reflects the symmetry of the dot. A plot of the pumped current for out-of-phase and in-phase modulation is seen in Fig. 3. If the modulation of the gate and the dot are out-of-phase the current increases linearly with frequency for slow modulation but decreases rapidly at frequencies greater than the inverse relaxation time of the system. If the modulation is in phase the current increases quadratically at low frequency and remains constant at high frequency. The time reversal properties mentioned for the traveling wave and standing wave pumping in Fig. 3 are apparent here—changing the sign of "$t$" changes the sign of $\phi$ and hence the sign of $\sin(\phi)$ but leaves the sign of $\cos(\phi)$ unchanged. The coefficient $\omega abP^{(0)}(1 - P^{(0)})/[2(s + s^{-1})^2]$ is identical to that obtained using scattering approach for adiabatic pumping in the bilinear regime [17,18]. The regime $\omega \ll \tau^{-1}$ can be called adiabatic, because the modulation is much slower than any characteristic time scale of the system, and consequently, the in-phase modulation produces vanishingly small flux compared to the out-of-phase modulation. Similarly, $\omega \gg \tau^{-1}$ can be identified as the quasiadiabatic regime. Here the in-phase modulation wins out as seen in Fig. 3. This out-of-phase modulation is similar to the photovoltaic current caused by microwave electric fields [19], which as here results from relaxation of a nonequilibrium electron distribution via inelastic processes. At low frequency the ratio of the in-phase ($\phi = 0$) quasiadiabatic current to the out-of-phase ($\phi = \pi/2$) adiabatic current is the ratio of the frequency to the relaxation rate $\omega\tau$ [18].

There has been much recent attention paid to pumping by "ratchets" [20] (for a quantum mechanical treatment of ratchets, see Refs. [21]), as a mechanism for chemically driven transport, where most often the potentials considered are periodic and infinitely extended in space, or

equivalently, defined on a circle. Instead of the infinitely extended potentials the physics of mesoscopics deals typically with a small system separating two or several reservoirs and localized potentials having nonzero gradients only in a finite region of space as illustrated by the quantum dot structure of Fig. 1a. The quasiadiabatic pumping mechanism discussed here is the localized analog to a "flashing" ratchet [22] and is in many ways similar to that used by *biomolecular pumps* for driving ions up an electrochemical gradient [23]. The basic principle of a flashing ratchet was recently used in the design of synthetic molecular motors that use light [24] or chemical [25] energy to cyclically modulate the heights of energy barriers along a reaction coordinate and thereby induce unidirectional rotation of one chemical group relative to another about a bond.

We have shown that coupling a catalyzed chemical reaction to electrical current through a molecular wire can lead to a very rich behavior, and provide a means of powering an electric circuit with a nonequilibrium chemical reaction. One drawback is that the current is limited by the catalytic rate. This is compensated by the tremendous density of molecular wires that can be achieved, and suggests that the future of this approach lies in the design of massively parallel molecular computers.

The systems on which we focused were chosen to be as simple as possible to best illustrate the fundamental principles. More complex chemistry (such as a catalyst that cycles through more than two states during a catalytic cycle) should lead to even more interesting possibilities, especially when combined with a very rich circuit architecture [5]. The experimental challenges to implementation of such devices are of course enormous. The molecular wire structure that we used in our discussion has been synthesized and shown to conduct [5], and the inclusion of an energy well by incorporation of sigma bonds should present few problems. However, the principles for designing a catalytic active site where the binding and release of substrate will couple to the electronic levels of the energy well are far from clear. We gave one specific hypothetical possibility, but doubtless that will not be the ultimate solution. Fortunately, there are many approaches to the design of molecular electronic devices [6,8], and the idea of incorporating a catalytic reaction can in principle be adopted in any of them.

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