

Current-induced rotation of helical molecular wires

Petr Král^{a)}*Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60607*

Tamar Seideman

Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113

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We show that electric current running through a nanojunction with a biased helical molecule can induce unidirectional rotation of the molecular component. In an electric field, conduction electrons injected into the molecule are accelerated along the helical path going through its body, thereby gaining directed angular momentum. Conservation laws require that an angular momentum of the same size but opposite sense is imparted to the rigid-body rotation of the helix. We describe the angular momentum exchange processes that underlie the operation of the nanorotor, discuss factors limiting its efficiency, and propose potential applications. © 2005 American Institute of Physics. [DOI: 10.1063/1.2107527]

I. INTRODUCTION

The past few years have witnessed a tremendous progress in the modeling and fabrication of molecular machines¹ such as shuttles,² switches,³ turnstiles,⁴ ratchets,⁵ and rotors.⁶ Inspired by natural supramolecular machines, which convert various natural forms of energy into coordinated motion,⁷ these machines are triggered by light,^{8–10} chemical or electrochemical energy,¹ or periodic electrical fields.¹¹ Novel assembly that merge artificial and biological features in their design have also been reported.¹²

In recent work, we suggested and investigated theoretically the possibility of driving molecular machines by electric currents passing through nanoscale junctions.^{13–15} This type of driving can have a number of advantages: the machines operate in the dry state, they can be constructed such that the motion is restricted to a chosen mode of the molecular moiety, and they can be individually triggered, hence circumventing the ensemble averaging of conventional environments. Moreover, if these currents are injected through scanning tunnel microscope (STM) tips they can induce surface nanochemistry,¹⁶ leading to a number of possible applications.¹⁷

It is of interest and potential use to realize that the driven molecular systems provide a variety of motions. For example, the molecule can get distorted¹⁸ or fully reorganized¹ by an applied bias voltage. Similarly, passing a spin-polarized current through a nanomagnet can lead to its torsional oscillations.¹⁹ On the other hand, one could take advantage of the fact that radicals attached to molecular wires can spontaneously rotate at elevated temperatures, and thus influence the electron transport.¹⁸

II. MODEL

In this work, we study such a motion and demonstrate that contacted and biased *helical* (spiral) molecules, such as

short helicines,²⁰ phenylacetylines,²¹ or polyanilins,²² can be driven into sustained unidirectional rotation by a dc electric current. The mechanism underlying the operation of the nanorotor resembles that which is responsible for the operation of a wind mill or a piston rod (found in cars), as illustrated schematically in Fig. 1. The electrons, injected from one contact and absorbed by the other, are accelerated by the bias voltage. Since through-bond tunneling dominates the transport,^{23,24} the electrons take a helical path through the molecular bridge, hence gaining directed angular momentum. An angular momentum of the same magnitude but opposite sense is imparted to the rigid body and sets it into unidirectional rotation. The sense of rotation is determined by the sense of the bias voltage and the molecular handedness.

We first briefly describe the character of the electronic states and the origin of angular momentum transfer in helical molecules. An “open” linear atomic chain of length l supports Bloch-type $|k_n\rangle$ states with wave vectors $k_n = \pm(2\pi/l)n$ and corresponding linear momenta $p_n = \hbar k_n$. A “closed” chain (quantum well) supports “standing-wave” states $||k_n|$, $|k_n| = (2\pi/l)n$, which do not carry linear momentum. Therefore, in a closed chain twisted into a cut ring of radius $r = l/2\pi$, the states $||k_n|$ do not carry angular momentum with a nonzero projection orthogonal to the ring. On the other hand, a closed ring supports conduction states $|k_n\rangle$, where electrons unidirectionally move around the ring and thus carry angular momenta $\mathbf{M}_n = \hbar \mathbf{r} \times \mathbf{k}_n = \pm \hbar n$ orthogonal to the ring.

The electronic states of a helical chain are analogous. We can assume that the molecule forms N loops of radius r , with a pitch d per loop, and a pitch angle $\alpha = \arcsin(d/4r)$. On geometrical grounds, we can estimate that the $|k_n\rangle$ states carry electronic angular momentum \mathbf{J}_{el} , with projection $J_{\text{el},z} \approx \hbar n \cos(\alpha)$ onto the symmetry (z) axis. To a first approximation, $J_{\text{el},z}$ is *independent* of the number of loops (N), since the nodal pattern of the electron wave functions is invariant with N . When the helical molecule is contacted to conduct-

^{a)}Electronic mail: pkrál@uic.edu

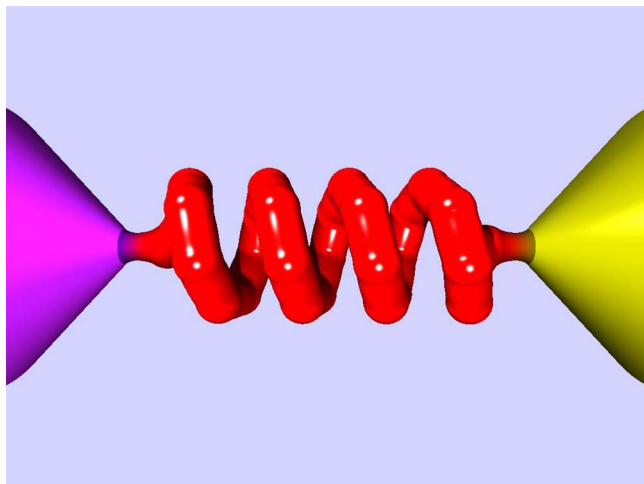


FIG. 1. Schematic illustration of a biased helical molecule, coupled by single bonds to two contacts. Free electrons injected into the molecule through the left contact are accelerated by the electric field and gain angular momentum ΔM before leaving through the right contact. In the process, torque is exerted on the molecule, which thus gains angular momentum $-\Delta M$. As a result the molecule undergoes unidirectional rotation at a speed controlled by the balance between the driving rate and the rate of relaxation processes.

ing electrodes and an electric field E is applied along the helix axis, the electrons are asymmetrically injected from the two contacts and, due to the bias potential, undergo asymmetric transitions between $|k_n\rangle$ and $|k_{n\pm 1}\rangle$ states of different $\mathbf{J}_{el,z}$ projections. Similar angular momentum transfer is induced by electron transport through bent mesoscopic conductors.²⁵

III. ANGULAR MOMENTUM EXCHANGE DYNAMICS

In general, the states of isolated molecules, $|\mathbf{J}_{el}, \mathbf{J}_{rot}, \mathbf{J}_{vib}; J_{el,z}, J_{rot,z}, J_{vib,z}\rangle$, can be characterized by a set of angular momentum vectors \mathbf{J}_i and their projections onto the symmetry axis $J_{i,z}$ in the relevant subspaces. Here, \mathbf{J}_{el} is the electronic, \mathbf{J}_{rot} the rotational, and \mathbf{J}_{vib} the vibrational angular momentum,²⁶ whereas the spin angular momentum is neglected. The total angular momentum of the molecule, $\mathbf{J} = \mathbf{J}_{el} + \mathbf{J}_{rot} + \mathbf{J}_{vib}$, and its z projection, $J_z = J_{el,z} + J_{rot,z} + J_{vib,z}$, are constants of the motion.

When the molecule is contacted to electrodes and subjected to a bias voltage, electrons are injected into the system and their scattering induces exchange of angular momentum among the individual subsystems. The E -field accelerated electrons gain angular momentum z projection in sequential transitions,

$$|J_{el,z}, J_{rot,z}, \dots\rangle \rightarrow |J_{el,z} \pm 1, J_{rot,z} \mp 1, \dots\rangle, \quad (1)$$

while an angular momentum of the opposite sense is passed on to the rotational subspace of the molecule, providing a mechanism for spinning of the helical backbone. In short molecules, relaxation can be neglected and the electrons carry away most of the gained angular momentum, $\Delta J_{el,z}$, as they leave the molecule through the contacts. In longer molecules, the transfer,

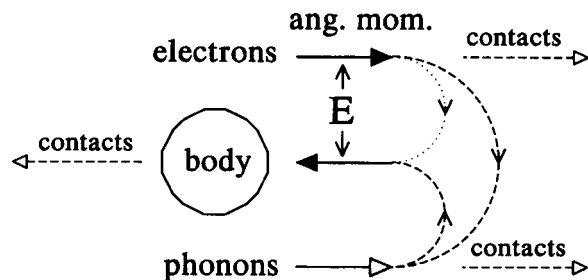


FIG. 2. Scheme of the storage and flow of angular momentum in a biased helical molecule. The electric field E accelerating the electrons causes the exchange of angular momentum between the electronic and rotational subspaces (two horizontal full arrows). In short molecules, electrons can largely carry away the gained angular momentum via the contacts and hence the angular momentum retained in the molecular body induces its rotation. In long molecules, the electrons transfer their angular momentum slowly back to the molecule via Coriolis and electron-electron umklapp coupling, but much of it is transferred to phonons (third horizontal open arrow). These transfer the angular momentum to the molecular moiety by scattering at the contacts and phonon-phonon umklapp processes. The contacts provide another mechanism of dissipation of the angular momentum.

$$|J_{el,z}, J_{vib,z}, \dots\rangle \rightarrow |J_{el,z} \mp 1, J_{vib,z} \pm 1, \dots\rangle, \quad (2)$$

of electron angular momentum $\Delta J_{el,z}$ to the vibrational degrees of freedom may be significant on the time scale of electron travel through the molecule.²⁷ The generated phonons transfer angular momentum to the molecular rotational subspace either by phonon-phonon umklapp scattering processes¹⁰ or by phonon-scattering events at the contacts in a sequence of transitions,

$$|J_{rot,z}, J_{vib,z}, \dots\rangle \rightarrow |J_{rot,z} \pm 1, J_{vib,z} \mp 1, \dots\rangle. \quad (3)$$

In solids, umklapp scattering processes allow the relaxation of linear momenta of excited electron and phonon baths through coupling with the lattice.²⁸ In this way, their eventual nonzero average linear momentum (and hence velocity) is transferred to the rigid body, the lattice, which thus accelerates. In the present case, due to the helical geometry of the molecular system, the same umklapp processes are accompanied by an exchange of angular momenta between these subsystems. As a result of the “closed-loop” compensation described by Eqs. (1)–(3), one may expect the efficiency of the nanorotor to degrade as the chain length grows. Figure 2 summarizes schematically the angular momentum exchange dynamics envisioned.

IV. APPROXIMATIONS AND NUMERICAL RESULTS

Given the complexity of the dynamics involved, we develop in the present work a semiclassical model that entails substantial approximations but is capable of extracting the essential physics and point to future opportunities. We assume that a monochromatic beam of electrons is injected into the helical molecule through one contact. An electron injected at time $t=0$ with momentum p_0 and accelerated by an electric field E gains momentum from the rigid-body rotations at a rate $\dot{p}_e = eE_\alpha [E_\alpha = E \sin(\alpha)]$. Electron-phonon coupling gives rise to relaxation of the angular momentum on a time scale of $\tau_p \approx 0.5$ ps. The net rate of change of electronic linear momentum is, thus,

$$\dot{p}_e(t) = eE_\alpha - [p_e(t)/\tau_p]. \quad (4)$$

Integrating Eq. (4), we obtain the time evolution of p_e given as

$$\Delta p_e(t) = eE_\alpha \tau_p (1 - e^{-t/\tau_p}). \quad (5)$$

Within the classical approximation, this momentum corresponds to an electronic angular momentum gain $\mathbf{M} = \mathbf{p} \times \mathbf{r}$. The projection of \mathbf{M} onto the helix axis is, thus,

$$\Delta M_e(t) = \Delta p_e(t) r_\alpha, \quad (6)$$

where $r_\alpha = r \cos(\alpha)$. This angular momentum is directly but very slowly transferred back to the molecular body by Coriolis scattering²⁶ and umklapp electron-electron scattering (weak for small electron densities).²⁸ Typically, it is transferred to the phonons on a much shorter time scale, τ_p .

The field-driven acceleration of the injected electrons imparts to the rigid body an angular momentum of the same rate but of the opposite sense to that imparted to the electrons,

$$\dot{M}_{e \rightarrow m}(t) = -eE_\alpha r_\alpha. \quad (7)$$

Similarly, from Eq. (4), we find that the angular momentum transferred from the electronic subspace to the phonons is described through

$$\dot{M}_{e \rightarrow p}(t) = p_e(t) r_\alpha / \tau_p = eE_\alpha r_\alpha (1 - e^{-t/\tau_p}). \quad (8)$$

At $t > \tau_p$ the rates of Eqs. (7) and (8) are practically equal in magnitude and opposite in sense. Therefore, the angular momentum of each passing electron that is gained from the molecular body is practically completely passed on to the phonons. Angular momentum conservation requires that these three terms cancel, $\dot{M}_e(t) + \dot{M}_{e \rightarrow m}(t) + \dot{M}_{e \rightarrow p}(t) = 0$, where we neglect the phonon-rotational coupling in Eq. (3). Within the above framework, the average transfer time t_m of an electron through the molecule is given as $l = \int_0^{t_m} dt v(t)$, where l is the length of the (helical) electron path, $v(t) = p(t)/m_e$ is its average velocity, and m_e is its effective mass. Therefore, the total angular momentum transfer per electron passing the helix are $\Delta M_{e \rightarrow m} = -eE_\alpha r_\alpha t_m$ and $\Delta M_{e \rightarrow p} = eE_\alpha r_\alpha (t_m + \tau_p (e^{-t_m/\tau_p} - 1))$. In long molecules, phonons may transfer the gained angular momentum back to the molecular body before being able to carry it away from the molecule.

Perhaps the most significant change to the above picture might be caused by contacts which can partially reflect the electrons and phonons and thus redistribute their angular momenta before they leave the molecule. To account for this effect on a qualitative level, we assume that such processes result in angular momentum transfer from the electron and phonon subspaces into the helix rotations with probabilities P_e and P_m , respectively. One then finds that during the passage of a single electron through the helix the angular momentum,

$$\Delta M_m = (1 - P_e) \Delta M_{e \rightarrow m} + P_m \Delta M_{e \rightarrow p}, \quad (9)$$

is transferred to the rigid-body rotation. Therefore, the larger the P_e , the less angular momentum is transferred from the electron to the molecular rotation. This rotation is also inhibited

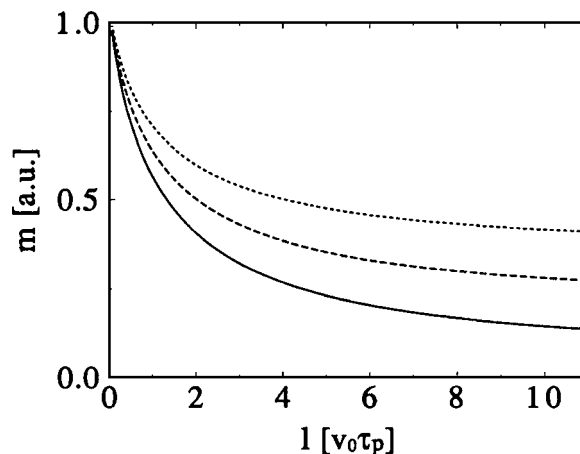


FIG. 3. The steady-state normalized angular momentum $m = \Delta M_m / l$ transferred into rotation of a helical molecule as a function of the length l of the electronic path through the molecule. The three curves (top to bottom) correspond to $P_m = 0.3, 0.6, 0.9$ and $P_e = 0$.

when P_m grows, since $\Delta M_{e \rightarrow m}$ and $\Delta M_{e \rightarrow p}$ enhance each other in Eq. (9) by having opposite signs.

In Fig. 3, we show the steady-state normalized angular momentum, $m = \Delta M_m / l$, imparted to the molecular rotation by an injected electron accelerated along a helical path of length l . We choose $p_0 = eE_\alpha \tau_p$ and $t = 0 - 6\tau_p$, and consider the cases $P_m = 0.3, 0.6, 0.9$ and $P_e = 0$. As is evident from Fig. 3, the most efficient driving is in the ballistic transport regime, realized in molecules with electronic path l shorter than the electron mean free path $\lambda_e \approx v\tau_p$, where electron relaxation is negligible. In the opposite limit of diffusive transport in long molecules m saturates, since the velocity of the transported electrons saturates when their acceleration and scattering balance each other [see Eqs. (5) and (6)]. As a result, each transported electron transfers in average a constant angular momentum into a unit length of the molecule, and the same but opposite angular momentum is transferred to the phonons, leading to dissipation of the angular momentum. As the probability P_m grows, phonons carry away a decreasing fraction of the gained angular momentum, due to scattering at the contacts, and the saturated value of m decreases. In realistic nanoscale molecular devices the contacts-molecule coupling strength varies in a broad range and may be, to some extent, controllable.

So far, we have included in our analysis only processes described in Eqs. (6) and (7). Therefore, we have neglected the weak l dependence of P_e and P_m , originating from Coriolis scattering and umklapp electron and phonon processes, respectively, that are relevant in very long molecules. These processes should be included when one considers the limit of a long helix, with an electronic path of length $l > \lambda_p > \lambda_e$, where $\lambda_p \approx 50 - 100$ nm is the phonon mean free path.²⁹ In this regime, both P_e and P_m should increase with l and eventually approach unity, while m falls to zero. This is the result of angular momentum gained by electrons that is either directly or indirectly (via phonons) returned to the molecular body, leading to partial cancellation of the angular momentum gained by the rigid-body rotations.

V. SPINNING RATE

We proceed to estimate the rotation speed of the helical molecule corresponding to the angular momentum transfer determined above. We assume that a steady-state electric current $J=e\dot{n}$ runs through the system, where \dot{n} is the number of transferred electrons per unit time and e is the electron charge. With Eq. (9) we know that the rigid-body rotational subspace gains angular momentum at a rate $\dot{M}_i=\Delta M_m\dot{n}$, while losing angular momentum at a rate $\dot{M}_r=-M_T/\tau_{m-c}$, where M_T is the total angular momentum of the molecular body and τ_{m-c} is the molecular-rotation damping time, due to coupling with the contacts. In steady state, $\dot{M}_T=\dot{M}_i+\dot{M}_r=0$, which gives $M_T=\Delta M_m\dot{n}\tau_{m-c}$. The molecule-electrode coupling in realistic devices can give rise to a broad range of damping times τ_{m-c} , depending on the linking groups that connect the molecule to the electrodes. We note that while the parameters P_e , P_m , and τ_{m-c} are sensitive to this molecule-contact coupling, they are not directly linked to one another.

The molecular moment of inertia about the rotational axis is $A=\sum_i m_i r_i^2 \approx al$, where m_i are the masses of the individual atoms and r_i denote their radial distances from the helix axis. Therefore, the helical molecule rotates with an average frequency

$$\omega_{\text{rot}} = \frac{M_T}{A} = \frac{\tau_{m-c}}{ea} Jm, \quad (10)$$

which follows the l dependence of m , shown in Fig. 3. In the ballistic and diffusive electron-transport regime, where $J \propto El$ and $J \propto E$, respectively, ω_{rot} depends on the applied voltage $U=El$ as $\omega_{\text{rot}} \propto U^2/l$ and U^2/l^2 , respectively.

As an example, we consider a short helicine²⁰ with ballistic electron transport. For a *single loop* in a helicine the moment of inertia is $A \approx 5 \times 10^{-44}$ kg m² and the average electronic path length is $l=2\pi r \approx 1.6$ nm ($r \approx 0.25$ nm), yielding $a=3 \times 10^{-35}$ kg m and a pitch angle $\alpha \approx 0.2\pi$. In the ballistic regime, with a single open channel, the conductance is $g_0=2e^2/h$. Hence the application of voltage $U=0.13$ V between the contacts gives rise to a current $J=g_0U=10$ μ A.

In this voltage drop, the change of the electronic kinetic energy is $\Delta E_k=(p_f^2-p_0^2)/2me=eU$. Thus, if the initial electron velocity is $v_0=p_0/m_e=0.001c$, where c is the velocity of light, its momentum change is $\Delta p=p_f-p_0=6.2 \times 10^{-26}$ kg m/s. The corresponding change of the electron angular momentum is $\Delta M_m=r_\alpha\Delta p \approx 1.25 \times 10^{-35}$ kg m²/s. Given that $J/e=\dot{n}=62.5$ ps⁻¹ and assuming that $\tau_{m-c} \approx 1$ ps, we find $M_T=\Delta M_m\dot{n}\tau_{m-c} \approx 7.8 \times 10^{-34}$ kg m²/s. The associated rotational frequency is thus $\omega_{\text{rot}}=M_T/A \approx 16.6/N$ GHz, where N is the number of loops of the short helicine. We note that this rotation has a partly diffusive character at room temperatures, where $k_{\text{Bolt}}T > \hbar\omega_{\text{rot}}$.

VI. CONCLUSION

We have demonstrated that electrical current running through a helical molecule attached between contacts can induce its unidirectional rotary motion. In the analogous surface experiment, where the molecule is attached to the sur-

face through only one end, spin-polarized electrons can be emitted²² and the spinning molecules used, for example, to push nanosystems in liquids. Similar rotation of helical molecules might be induced by chemical, pressure, or temperature gradients. One may thus envision a variety of fundamentally interesting and potentially useful applications.

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