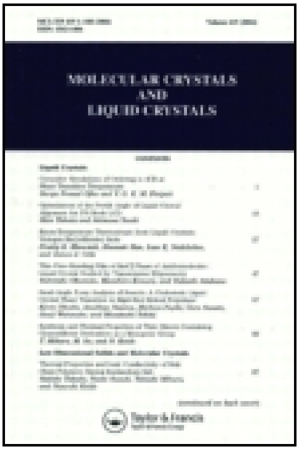

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V. May [a] [b] & M. Schreiber [a]

[a] Institut für Physikalische Chemie, Johannes-Gutenberg-Universität, Jakob-Welder-Weg 11, W-6500, Mainz, Federal Republic of Germany

[b] WIP, Max-Planck-Arbeitsgruppe “Halbleitertheorie”, Hausvogteiplatz 5-7, 0-1086, Berlin, Federal Republic of Germany

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DYNAMIC ASPECTS OF QUASI-PARTICLE TRANSFER IN MOLECULAR ELECTRONIC DEVICES

V. MAY* and M. SCHREIBER

Institut für Physikalische Chemie, Johannes-Gutenberg-Universität,
Jakob-Welder-Weg 11, W-6500 Mainz, Federal Republic of Germany

* permanent address: WIP, Max-Planck-Arbeitsgruppe "Halbleitertheorie",
Hausvogteiplatz 5-7, O-1086 Berlin, Federal Republic of Germany

Abstract The importance of the dissipative quantum dynamics of molecular systems for possible future device applications is emphasized. The necessity to study in detail the respective quasi-particle transfer phenomena is discussed. As a specific example charge transfer in a molecular dimer and a molecular chain is investigated in order to demonstrate how the quantum dynamical features can be controlled by different intrinsic nonlinearities.

INTRODUCTION

In view of the limitations of common semiconductor technology in the late seventies the idea became popular to realize information processing and information storage by using single molecules.[1] This dream has been labeled "molecular electronics", and it may be characterized as a concept for information storage and processing which is based on assemblies of nanometer-scale objects like single atoms and molecules as basic structural components. State changes related to single or few microscopic particles or respective excitations should act as information carriers. Hence the dynamic laws for information processing are essentially quantum mechanical in character. These low-level dynamics must therefore be considered as most relevant in molecular electronics (in contrast to present-day electronic devices) without, of course, excluding the emergence of significant higher-level dynamic features.

Besides the basic problems of the structuration on a nanometer scale and the development of an appropriate system architecture from the atomic and molecular level up to macroscopic (device) length-scales, the specification and especially the control of the dynamics on a nanometer scale is therefore of central interest. Although the dynamics of molecular structures are understood in principle the desire to deal with quantum objects (probably sometimes only a single quantum particle) in a definite and controllable manner requires further theoretical investigations and simulations.

In a first step we can carry out such studies without any regard to molecular electronic device conceptions. General models and the consideration of the dynamics in simple molecular systems as dimers or molecular chains are sufficient. However, such general models should contain all important interactions inherent in molecular systems and relevant to the "dream" of molecular electronics. As a specific example we consider in the following the motion of excess electrons. This situation has been frequently studied in various circumstances.[2,3] The similarities with the dynamics of excitons are obvious and shall not be discussed here.

The particular form of the different types of interactions is, of course, determined by the structure of the molecular system under consideration. The most important interaction is usually the coupling between electronic and internal vibrational degrees of freedom. The type of this coupling and its strength determine the structure of the time-dependent wave function and thus the velocity of the particle motion and the occurence of such phenomena as self-localization. The interaction with environmental degrees of freedom introduces different dissipation channels into the molecular system. The strength of the dissipation determines whether the dynamics are wave-like (coherent) or hopping-like (incoherent). The consideration of the simultaneous motion of two or more electrons introduces the Coulomb forces as an additional interaction mechanism.

All the mentioned interaction processes determine the characteristics of the particle dynamics. Since the type and strength of the interaction itself depends on the molecular structure and the given environmental conditions we can in principle exercise the control of the particle motion by appropriately choosing this structure and by adjusting the environmental conditions. In this way the time scale of the particle motion and the temperature regime in which transfer is effective can be determined, and the significance of the nonlinearities in the model which will be important, e.g., for switching purposes in device applications can be controlled.

The more important type of control concerns the modification of the particle motion or the switching between different asymptotic states of the particle dynamics in a given molecular structure. Such a control of the time development of the particle motion can be realized by the application of external fields. In the following we present some simple examples showing why the particle motion changes and thus demonstrating various possibilities for the control of the particle motion.

THEORETICAL MODEL

According to our general considerations we use minimal models for the considered molecular systems. Since we are interested in the dynamics of externally injected electrons (excess electrons) we adopt the standard model[4,5] for electron transfering molecular systems with some non-standard extensions. In view of local concepts of information processing (which means that such processes occur inside single molecular complexes) it is useful to consider the time-dependence of the occupation probabilities $P_m(t)$ of the electronic sites m for the description of the dynamic behavior of the molecular system. (The investigation of the dynamics in a representation of extended states of the system may be, of course, an alternative approach.) The quantity P_m has to be deduced from an appropriately defined reduced density matrix. The numerical solution of the corresponding equations of motion allows to discuss the different transfer scenarios and to study the influence of internal nonlinearities as well as the action of external fields.

COUPLED ELECTRON VIBRATION DYNAMICS

At first, we consider the minimal model of a two-center system (a molecular dimer) with electronic inter-center transfer coupling V and a single vibrational mode Q with frequency ω_v. This simple system has the advantage to comprise the electron-vibration coupling and the quantum dynamics of the vibrations in a correct manner. We use a representation of the vibronic states in the Born-Oppenheimer states $|\mu>$ of the single monomer (diabatic representation) where μ comprises the electronic site index m and the vibrational quantum number M $(= 0, 1, \ldots)$. The density matrix defined with respect to these diabatic states follows as

$$\rho_{\mu\nu}(t) = \mathrm{tr}\left(\hat{W}(t)\, |\mu><\nu|\right) \tag{1}$$

where $\hat{W}(t)$ is the time-dependent statistical operator. In such a representation the harmonic approximation for the vibrational dynamics is justified. However, the numerical solution of the density matrix equations takes into account the anharmonic vibrational motion in the corresponding adiabatic double-well potential.[5]
The corresponding equations of motion read

$$\frac{\partial}{\partial t}\rho_{\mu\nu}(t) = i\,\tilde{\omega}_{\mu\nu}\,\rho_{\mu\nu} - \frac{i}{\hbar}\sum_{\kappa}\left(V_{\nu\kappa}\,\rho_{\mu\kappa} - V_{\kappa\mu}\,\rho_{\kappa\nu}\right) + \left[\frac{\partial}{\partial t}\rho_{\mu\nu}(t)\right]_{\mathrm{diss.}} \tag{2}$$

where $V_{\mu\nu}$ denotes the inter-center transfer coupling multiplied by the Franck-

Condon factor. In Eq. 2 the transition frequencies $\tilde{\omega}_{\mu\nu}$ between the vibronic states $E_\mu = U_m(0) + \hbar\omega_\nu(M+½)$ of the diabatic potential surfaces $U_m(Q)$

$$\tilde{\omega}_{\mu\nu} = (E_\mu - E_\nu)/\hbar + i\left[\frac{1}{2}(M+N)\left(\gamma(\omega_\nu) + \gamma(-\omega_\nu)\right) + \gamma(-\omega_\nu)\right] \tag{3}$$

contain dephasing contributions. These and the further dissipative terms indicated on the r.h.s. of Eq. 2 follow from the linear coupling between the single vibrational coordinate Q and a continuum of environmental coordinates. Details of the derivation are published elsewhere.[5] The corresponding vibrational level broadening

$$\gamma(\omega) = 2\pi\, a(\omega)\, \left[1 + n(\omega)\right] \tag{4}$$

contains the density of states of the environmental coordinates $a(\omega)$ and the corresponding thermal distribution $n(\omega)$.

Figure 1 shows the time dependence of the occupation probability P_1 for an excess electron which is introduced into the dimer on the first site at time $t=0$ for different values of the scaled spectral density $a(\omega_\nu)/\omega_\nu$ in Eq. 4. The time range up to $t = 50/\omega_\nu$ allows us to distinguish the change of the transfer from the coherent type via the incoherent, hopping-like type up to the overdamped case. This change is caused by an increase of the coupling to the environment. In the weak-dephasing limit the electron remains localized at the first site, if no vibrational quanta are initially excited (see the full line in Fig. 1a). In this case the Franck-Condon factor is small for the employed values of the electron-vibration coupling. If there are three vibrational quanta initially excited, we are in the region of activated transfer. Now the Franck-Condon factor is so large that the occupation probability oscillates markedly between the two sites as displayed by the full line in Fig. 1b. If the coupling to the environment is increased, the localization or, respectively, the oscillations are considerably dampened, as demonstrated by the dashed lines in Figs. 1a and 1b. For very large coupling (compare the dash-dotted lines in Figs. 1a and 1b) the electron transfer between the sites is impeded so that a time much larger than shown here is necessary in order to reach the equidistribution of the occupation probability.

The results can be used to propose a control mechanism of the charge transfer by an externally applied electromagnetic field: In the case of a high frequency infrared-active vibrational mode and an electronic inter-center coupling which is comparable to the energy of a vibrational quantum one can initiate electron transfer by the absorption of a sufficient number of infrared photons, because this means switching from nuclear tunneling to the region of activated transfer.

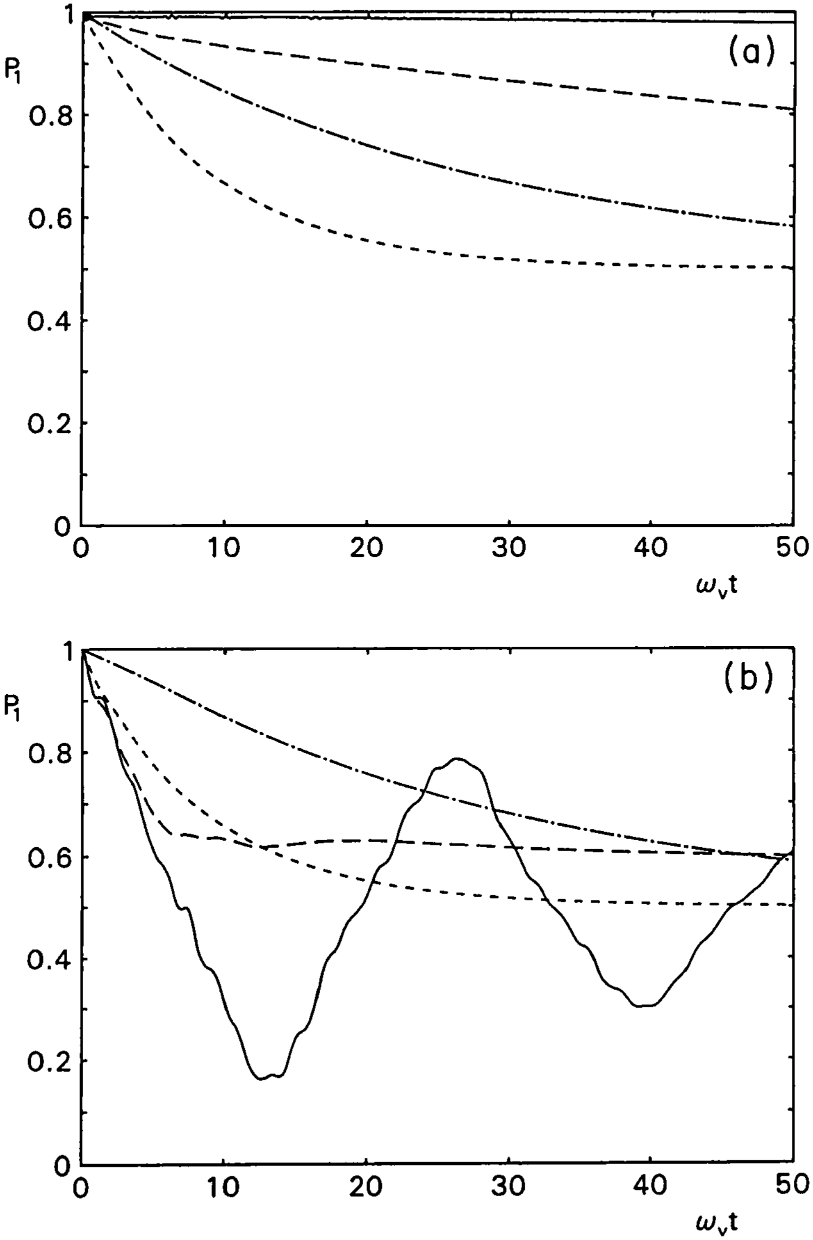


FIGURE 1 Electronic occupation probability $P_1(t)$ of the first site of a molecular dimer for $V = \hbar\omega_v$ and $k_BT = 0.1\,\hbar\omega_v$. The coupling to the environmental degrees of freedom is characterized by $a/\omega_v = 10^{-3}$ (full lines), 10^{-2} (long-dashed lines), 10^{-1} (dashed lines), and 1 (dash-dotted lines). The number of initially excited vibrational quanta was zero in (a) and three in (b).

CHARGE MOTION IN A SOFT MOLECULAR CHAIN

Next we discuss the motion of an electron in a molecular chain controlled by an internal chain nonlinearity and influenced by environmental degrees of freedom. The applied model is similar to the standard model of the motion of self-localized excitation energy in soft molecular chains, the so-called Davydov solitons.[6-10] The longitudinal chain vibrations are explicitly taken into account in a harmonic approximation. Other vibrational modes of the chain as well as of the environment are considered to produce dephasing effects with characteristic dephasing time τ. The coupling of the electron at site m to the local longitudinal chain distortion u_m is taken in a non-symmetric form proportional to $u_{m+1} - u_m$. Due to the large extension of the investigated system we can apply the so-called self-trapping approximation. It takes the chain distortion due to the presence of an electron into account via a quadratic non-linearity in the density matrix equations (with coupling constant Δ).[11] The equations of motion for the density matrix ρ_{mn} in site-representation read

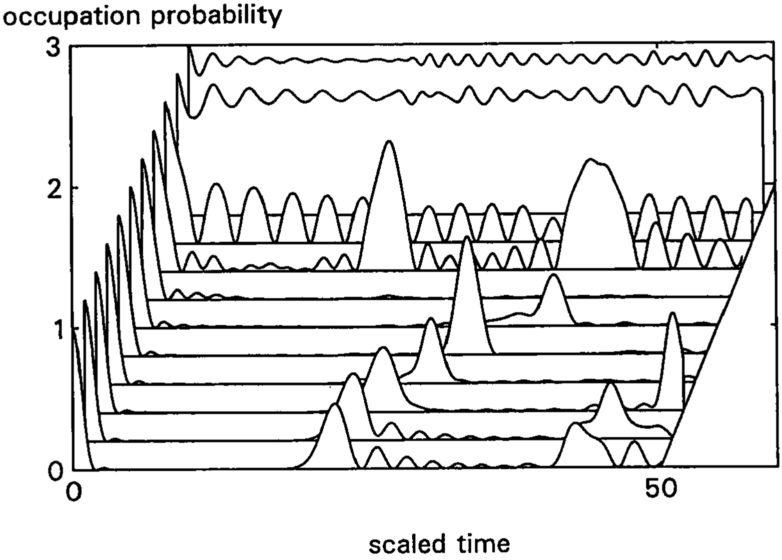


FIGURE 2 Electronic occupation probability $P_1(t)$ of the first site of a chain of 20 molecules with the excess electron introduced on the first site at t=0. The scaled time is given by t/t_c, with a coherent transfer time $t_c = \hbar/V$. The scaled self-trapping constant $\hbar\Delta/V$ increases from 0 (front panel) to 5 (back panel) in steps of 0.5. The dephasing time τ is infinite.

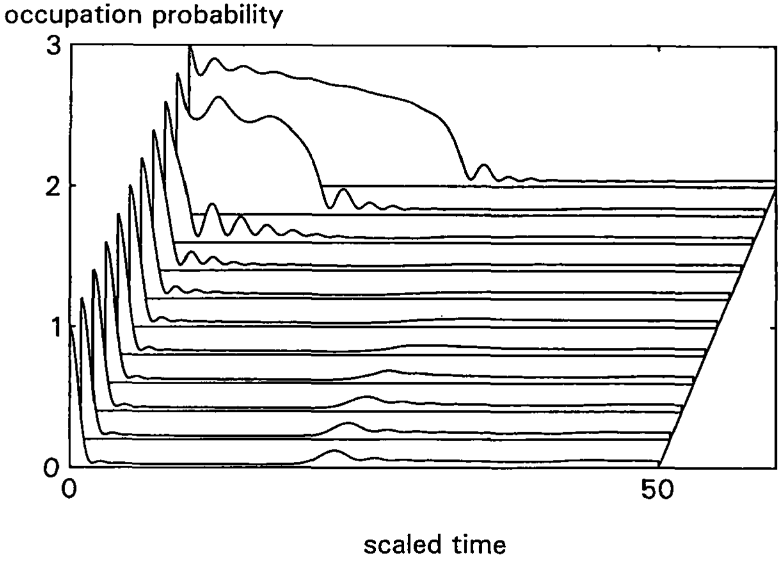


FIGURE 3 Same as Fig. 2, but for dephasing time $\tau = 10 t_c$.

$$\frac{\partial}{\partial t}\rho_{mn}(t) = -(1-\delta_{mn})\,\frac{1}{\tau}\,\rho_{mn} + i\Delta\,(\rho_{mm}-\rho_{nn})\,\rho_{mn} - \frac{i}{\hbar}\sum_k\,(V_{nk}\rho_{mk} - V_{km}\rho_{kn}) \qquad (5)$$

where V_{mn} denotes the nearest-neighbor transfer coupling.

Figures 2 and 3 display $P_1(t)$ for an excess electron in a chain of 20 molecules. Figure 2 shows that for infinite dephasing time and small or intermediate nonlinearities the particle moves as a solitonic wave packet forward and backward in the chain. At $\hbar\Delta/V = 3.5$ pinning can be observed. Taking a value of $10 t_c$ for the dephasing time (see Fig. 3) the self-localized motion is destroyed and the pinned state possesses a finite life time.

SIMULTANEOUS MOTION OF FEW ELECTRONS

The case of the simultaneous motion of two or more excess electrons along the molecular chain is of special interest.[12] In such a case a further intrinsic nonlinearity appears which results from the mutual Coulomb interaction between the excess electrons. Controlling the number of electrons inside the chain allows to control the nonlinear motion of the charge through the system.

If two or more electrons are initially localized, e.g., at the beginning of the chain, they may remain together and move as a localized charged wave packet. Such a clustering of excess electrons appears, if the potential energy of the Coulomb interaction W between the electrons overcomes their kinetic energy, which is limited from above in the chain by $2V$. This charge localization is removed, if dissipative channels are introduced. Dephasing of the electronic wave function which extends over different molecules of the chain diminishes the exchange contributions to the Coulomb interaction. As a result the electronic occupation probability is redistributed nonexponentially over the whole chain.[12]

According to the above mentioned mechanism a nonlinear input-output characteristic can be proposed for a molecular chain that is attached at its ends to a particle source and a particle sink, respectively: A switching from a large particle output to a small particle output happens, if the mean time that an electron needs to enter the chain is about one-tenth of the coherent transfer time.

The equations of motion for the density matrix in site-representation appropriate to describe this mechanism are

$$\begin{aligned}\frac{\partial}{\partial t}\rho_{mn}(t) = {} & R_g\left(\delta_{m1}\delta_{1n} - \frac{1}{2}(\delta_{m1}+\delta_{1n})\rho_{mn}\right) \\ & - \frac{1}{2}R_o(\delta_{mN}+\delta_{Nn})\rho_{mn} - (1-\delta_{mn})\frac{1}{\tau}\rho_{mn} \\ & - \frac{i}{\hbar}\sum_k\left(V_{nk}\rho_{mk} - V_{km}\rho_{kn} + (W_{nk}-W_{km})(P_k\rho_{mn}-\rho_{mk}\rho_{kn})\right) . \end{aligned} \tag{6}$$

Here R_g is the electron generation rate at the first center of the chain and R_o is the output rate at the last center N. The nearest-neighbor Coulomb interaction W_{mn} between an electron at site m and one at site $n = m \pm 1$ has been taken into account by a Hartree-Fock approximation factorizing the two-electron density matrix.[12]

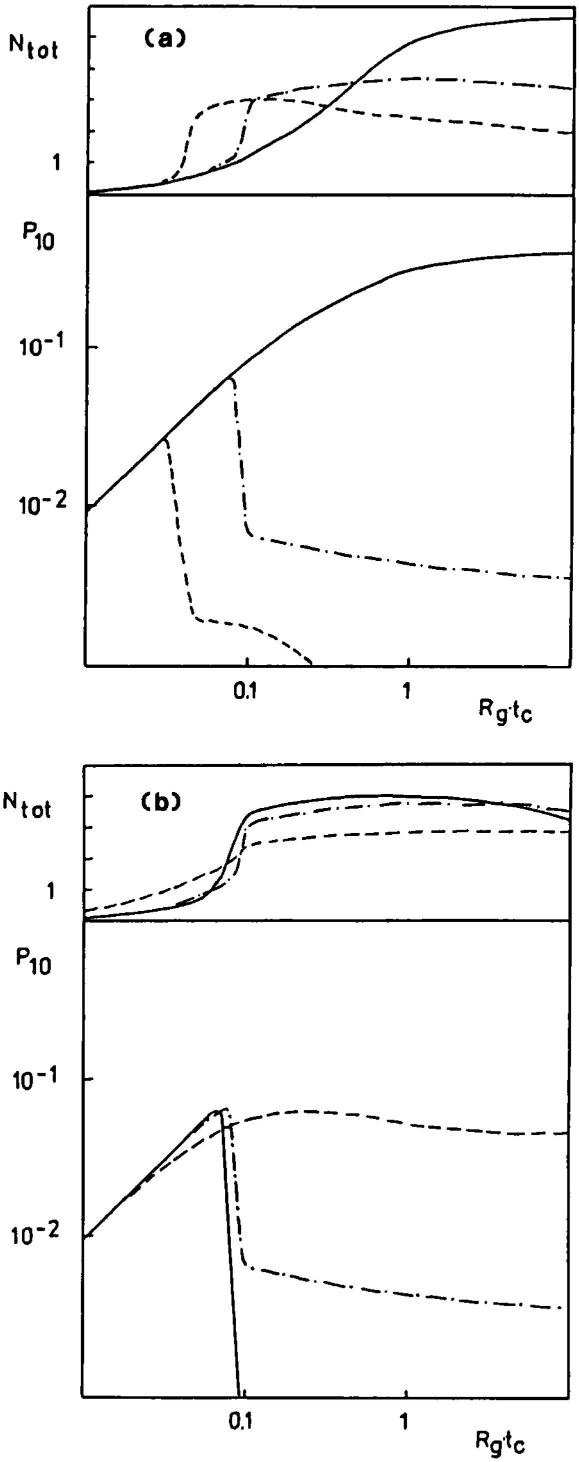
Figure 4 reflects the stationary characteristics by showing the occupation probability of the last center of a chain of 10 molecules in dependence on the generation rate. If this rate becomes sufficiently high, the Coulomb interaction leads to a sudden drastic reduction of the particle output, accompanied by a sudden increase of the total number of electrons in the system (see Fig. 4a). This switching occurs, because two or more electrons remain localized at the beginning of the chain reducing the further input and thus the stationary charge flow. Figure 4b shows that the switch becomes less effective, i.e., the change of the total output rate is smaller, if the dephasing time decreases. This is due to the reduced localization for short dephasing time.

FIGURE 4 Total number of electrons N_{tot} summed over all centers (top) and electronic occupation probability P_{10} of the last site (bottom) of a chain of 10 identical molecules versus the generation rate R_g in the stationary case. An electron can leave the chain via the last site with a constant rate of $1/t_c$, so that the total output per unit of time is given by P_{10}/t_c.

The ratio of the nearest-neighbor Coulomb interaction W and the transfer coupling V, and the dephasing time τ are chosen as:

(a) $\tau = 10t_c$ and $W/V=0$ (full line), 5 (dash-dotted line), 10 (dashed line).

(b) $W/V=5$ and $\tau=\infty$ (full line), $10t_c$ (dash-dotted line), t_c (dashed line).



CONCLUSIONS

The presented examples of charge motion in simple molecular systems demonstrate the possibility to control the corresponding dynamics. However, we notice the destructive influence of environmental effects. All specific features of the dynamics are destroyed for times comparable to characteristic dephasing times. Equidistribution of the electronic occupation probability over the whole system appears and no (quasi-)deterministic behavior can be expected any more for longer times. This observation may serve as a motivation to employ molecular mechanisms which take effect faster than this particular time limit. In contrast one can of course take the orthodox position, namely to design systems in which only those states are of interest which are occupied in the asymptotic limit of long times.

In any case, however, one has to notice that the density matrix description yields the mean time dependence with respect to an ensemble average. The dynamics of the single molecular system are stochastic. Therefore design principles should become productive for molecular electronics which govern information processing systems with stochastic state variables.

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