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Research paper

Peculiarities of migration and capture of a quantum particle in a chain with traps

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ABSTRACT

The presence of sinks-traps at the nodes of a 1D chain disturbs coherency of propagation of a quantum particle in the chain. This results in nontrivial dependences of the quantum yield of capture on the trap intensity and initial placement of the particle. We obtain these dependences in the cases of infinite, semi-infinite, and finite chains with one or two traps.

1. Introduction

The 1D chain of nodes interacting with nearest neighbours is a basic theoretical tool and proving ground for countless models of a huge variety of physical processes, especially transport ones. Their main features, either in classical or quantum cases, are well known. Nevertheless, some of them, being of both academic and practical importance, still have not received proper attention. Here we analyze one of the kind: peculiarities of the quantum yield of capture of a quantum particle migrating in a regular 1D chain with traps. The set of models considered below includes those containing one or two traps in an infinite, semi-infinite and finite chain. The latter, in particular, is closely related to the popular problem of donor-acceptor transfer via intermediate states and to the trade-off between so-called hopping/activation and superexchange/tunnel mechanisms of the transfer (see e.g. [1–3]). As shown in [4], under the condition of weak population of the chain-mediator the effective donor-acceptor transfer rate can be expressed precisely through such quantum yields.

Introducing even a single chain irregularity (here trap or chain edge) immediately makes the dynamics/kinetics of the particle migration complicated. On the contrary, the quantum yields can be exactly calculated in an elegant fashion, leading to sometimes not so obvious results. Below we describe them, starting from a demonstrative comparison between classic and quantum migration in an infinite chain.

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2. Polya's theorem and quantum migration (infinite chain)

Consider the standard skeleton of diffusion models, the drunkard's walk problem (Fig. 1, *top*).

According to Polya's recurrence theorem [5], the wandering particle always returns to the origin (this remains to be true for a 2D lattice, while the walk becomes transient in three or more dimensions).

There are many ways to prove Polya's theorem. In particular, Montroll [6] reduced the question of recurrence to the divergence of the following integral:

$$U_1(1) = \sum_{t=0}^{\infty} P_t(n=0) = \frac{1}{\pi}\int_0^{\pi}\frac{d\varphi}{1-\cos\varphi}, \tag{1}$$

where $P_t(n=0)$ is the probability of the particle to occur at the origin after t jumps. The obvious divergence of (1) means that the walk is recurrent [6]. Attaching now the meaning of continuous time to t, one arrives at the diffusion analog of the Polya's problem with the balance evolution equation $dp_n/dt = \kappa(p_{n-1} - 2p_n + p_{n+1})$, where $p_n(t)$'s (now playing the part of $P_t(n)$'s) are diagonal elements of the density matrix and κ is 'rate constant' of jumping. It's easy to show that $p_n^{(0)}(\tau) = \exp(-\tau)I_{|n|}(\tau)$, where $\tau = 2\kappa t$, $I_{|n|}(\tau)$ is modified Bessel function, and the upper index means the initial condition $p_n(0) = \delta_{n0}$. Of course, the recurrence requirement $\int_0^{\infty} p_n(t)dt = \infty$ holds in this case, too, and no escape to infinity takes place.

Now introduce a sink (trap) at node N (Fig. 1, *bottom*), so that the evolution equation reads $d\rho_n/dt = \kappa(\rho_{n-1} - 2\rho_n + \rho_{n+1}) - \chi\rho_n\delta_{nN}$. What is the quantum yield $W_N^{(0)} = \chi\int_0^{\infty}\rho_N^{(0)}(t)dt$ of such a trap?

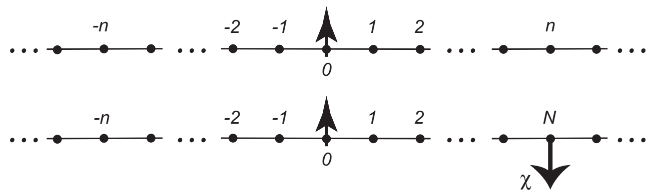

Fig. 1. *Top*: the particle starts jumping from the origin to one of the two neighbour nodes with equal probability ½. *Bottom*: at node *N* the particle could be irreversibly captured by the trap of intensity χ.

To calculate it, it is sufficient to find the Laplace transform $\tilde{\rho}_N(s) = \int_0^\infty e^{-st}\rho_N(t)\,dt$, as $W_N = \chi\tilde{\rho}_N(s)|_{s\to 0}$. One can easily show that $\tilde{\rho}_n(s) = \tilde{p}_n(s) - \chi\tilde{p}_n^{(N)}(s)\tilde{\rho}_N(s)$, and

$$W_N^{(0)} = \frac{\chi\tilde{p}_N^{(0)}(s)}{1+\chi\tilde{p}_N^{(N)}(s)}|_{s\to 0}. \tag{2}$$

Using the known Laplace transform $\tilde{I}_{|n|}(s)$ [7] in (2), we conclude that $W_N^{(0)} \equiv 1$. In other words, *irrespective of* χ or N, the particle *always leaves the chain*. Of course, it is a direct consequence of Polya's theorem. But what will happen in the quantum case?

Behind the latter, we mean that the schemes in Fig. 1 remain the same but the exchange between adjacent nodes is realized due to exchange matrix elements L's. As for sink χ, it can be represented by an imaginary addition to the energy at node N. This allows us to remain within the Schrödinger equation (albeit with non-hermithian Hamiltonian), avoiding bulkier density matrix formalism without any loss of correctness. Thus, the Hamiltonian to the scheme in Fig. 1, *bottom* reads

$$H = H_0 - (i\chi/2)|N\rangle\langle N|, \tag{3}$$

where $H_0 = L\sum_{-\infty}^{\infty}(|n\rangle\langle n+1| + |n+1\rangle\langle n|)$ corresponds to the scheme in Fig. 1, and the node energies ε_n's are assumed equal to zero. The wave function $|\Psi(t)\rangle = \sum_n C_n(t)|n\rangle$ has the initial condition $|\Psi(t=0)\rangle = |0\rangle$, or $C_n(0) = \delta_{n0}$, whereas the function $|\psi(t)\rangle = \sum_n c_n(t)|n\rangle$ satisfies the Schrödinger equation $\mathrm{d}|\psi\rangle/\mathrm{d}t = -iH_0|\psi\rangle$ ($\hbar = 1$). In terms of c_n's, the latter reads

$$\mathrm{d}c_n/\mathrm{d}t = -iL(c_{n-1} + c_{n+1}). \tag{4}$$

Replacements $c_n = (-i)^n b_n$ (the same will be used below for C_n's, too) and $\tau = 2Lt$ reduce Eq. (4) to $2\mathrm{d}b_m(\tau)/\mathrm{d}\tau = b_{m-1}(\tau) - b_{m+1}(\tau)$ which is the canonical relationship for Bessel functions $J_m(\tau)$, so we arrive at the known solution to set (4) with initial condition $b_m(0) = \delta_{m0}$, precisely, $c_m(t) = (-i)^m J_m(2Lt)$. Note that the integrals of the node probabilities $\int_0^\infty |c_m(t)|^2\mathrm{d}t$ are obviously divergent. By analogy with the previous case, it should mean that the quantum particle would be never 'lost in infinity', too. Let us address, however, the quantum yield from this chain in the presence of the trap.

The Schrödinger equation corresponding to Hamiltonian (3) reads

$$\mathrm{d}|\Psi(t)\rangle/\mathrm{d}\,t = -iH_0|\Psi(t)\rangle - (\chi/2)C_N(t)|N\rangle \tag{5}$$

and can be re-written, in dimensionless variables, in the equivalent integral form:

$$|\Psi(\tau)\rangle = |\psi(\tau)\rangle - a\int_0^\tau C_N(\theta)\left|\psi^{(N)}(\tau-\theta)\right\rangle \mathrm{d}\theta, \tag{6}$$

where $a = \chi/4L$, and, as earlier, the upper index labels the initial condition, $\left|\psi^{(N)}(0)\right\rangle = |N\rangle$. The identity of Eqs. (5) and (6) can be immediately verified by substituting (6) in (5) and differentiating the integral with the use of Leibniz's rule. Then one can easily obtain in Laplace transforms with respect to τ:

$$\tilde{C}_N^{(0)}(s) = (-i)^N\tilde{B}_N^{(0)}(s) = (-i)^N\frac{\tilde{b}_N^{(0)}(s)}{1+a\tilde{b}_N^{(N)}(s)} = (-i)^N\frac{\tilde{J}_N(s)}{1+a\tilde{J}_0(s)}, \tag{7}$$

where $\tilde{J}_m(s) = (\sqrt{s^2+1}-s)^m/\sqrt{s^2+1}\,(m \geqslant 0)$ [7], and $\tilde{J}_{-m} = (-1)^m\tilde{J}_m$. As all the functions of time considered here satisfy the condition $f(t<0) = 0$, their Fourier transforms $\tilde{f}(\omega)$ can be found simply by replacing $s \to i\omega$ in $\tilde{f}(s)$, and the sought quantum yield is:

$$W_N^{(0)} = \chi\int_0^\infty |B_N^{(0)}(t)|^2\mathrm{d}t = \frac{\chi}{2L}\int_0^\infty |B_N^{(0)}(\tau)|^2\mathrm{d}\tau$$
$$= \frac{a}{\pi}\int_{-\infty}^{\infty}|\tilde{B}_N^{(0)}(\omega)|^2\mathrm{d}\omega. \tag{8}$$

With the use of Eq. (7) we finally get:

$$W_N^{(0)}(a) = (2a/\pi)(A_1 + A_2),$$
$$A_1 = \int_0^1 \mathrm{d}\omega\left(\sqrt{1-\omega^2}+a\right)^{-2}, \tag{9}$$
$$A_2 = \int_1^\infty \left(\omega - \sqrt{\omega^2-1}\right)^{2N}\left(\omega^2+a^2-1\right)^{-1}\mathrm{d}\omega.$$

For $N = 0, 1, \infty$ the integrals in (9) can be written in elementary functions in a rather compact form omitted here for the sake of brevity. Instead, we present the corresponding plots in Fig. 2.

They illustrate a sharp distinction from the classical case. Now $W_N^{(0)}$ is *always less than* 1 *for any* $\chi > 0$ *and* N (except the obvious case of an infinitely intensive trap at the initial node, i.e. $\chi = \infty$, $N = 0$). In other words, there always exists a finite probability of the particle to be irreversibly lost in the chain (go off to infinity). Moreover, for any $N > 0$ the greater χ, the eventually less $W_N^{(0)}$. That is, increasing intensity of the trap makes its capture ability only worse, so that in the limit $\chi \to \infty$ the trap rather turns into a wall, blocking particle's return and capture.

Seeing such a nontrivial dependence $W_N^{(0)}$ on χ and N, it is natural to add one more trap into consideration. Let the traps be identical, $\chi_1 = \chi_2 = \chi$ for simplicity, and situated at nodes N_1 and $N_2(N_1 < N_2)$, so that

$$H = H_0 - (i\chi/2)(|N_1\rangle\langle N_1| + |N_2\rangle\langle N_2|).$$

Then the procedure described above leads to the following analogs to Eq. (7):

$$\tilde{B}_{N_1}^{(n_0)}(s) = \frac{\tilde{J}_{N_1-n_0}(1+a\tilde{J}_0) - a(-1)^{N_2-N_1}\tilde{J}_{N_2-N_1}\tilde{J}_{N_2-n_0}}{(1+a\tilde{J}_0)^2 - (-1)^{N_2-N_1}a^2\tilde{J}_{N_2-N_1}^2}$$
$$\tilde{B}_{N_2}^{(n_0)}(s) = \frac{\tilde{J}_{N_2-n_0}(1+a\tilde{J}_0) - a\tilde{J}_{N_2-N_1}\tilde{J}_{N_1-n_0}}{(1+a\tilde{J}_0)^2 - (-1)^{N_2-N_1}a^2\tilde{J}_{N_2-N_1}^2}, \tag{10}$$

and the total quantum yield is now $W^{(n_0)} = W_{N_1}^{(n_0)} + W_{N_2}^{(n_0)}$, with the recipe (8) for computing $W_{N_{1,2}}^{(n_0)}$. As earlier, the type of the curve $W^{(n_0)}(a)$ is critically dependent on the initial condition n_0 with three essentially different options: (i) $n_0 = N_1$ or N_2, (ii) $n_0 < N_1, N_2$ or $n_0 > N_1, N_2$, and finally (iii) $N_1 < n_0 < N_2$. It is clear that the first two result in the dependences which resemble those already shown in Fig. 2: in case (i) $W^{(n_0)}(a\to\infty) \to 1$ (we henceforth refer such a dependence as of type I), whereas in case (ii) $W^{(n_0)}(a\to\infty) \to 0$ (type II), see curves 1, 2 in Fig. 3.

To see what happens in case (iii), i.e. when the particle is initially placed between the traps, consider the simplest version: $N_1 = -1$, $n_0 = 0$, $N_2 = 1$. From (10) it then follows that $\tilde{B}_1^{(0)} = -\tilde{B}_{-1}^{(0)} = \frac{\tilde{J}_1}{1+a(\tilde{J}_0-\tilde{J}_2)}$, and the use of Eq. (8) leads to the curve 3 in Fig. 4, that is of type I again (no escape to infinity in the limit $a \to \infty$). 'Asymmetrical' initial conditions (like e.g.