Reaction-diffusion processes described by three-state quantum chains and integrability

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Abstract. The master equation of one-dimensional three-species reaction–diffusion processes is mapped onto an imaginary-time Schrödinger equation. In many cases the Hamiltonian obtained is that of an integrable quantum chain with known properties. Within this approach we search for three-state integrable quantum chains with known spectra and which are related to diffusive-reactive systems. Two integrable models are found to appear naturally in this context: the $U_q \widehat{SU(2)}$-invariant model with external fields and the three-state $U_q SU(P/M)$-invariant Perk–Schultz models with external fields. A non-local similarity transformation which brings the Hamiltonian governing the chemical processes to the known standard forms is described, leading in the case of periodic boundary conditions to a generalization of the Dzialoshinsky–Moriya interaction for N-state Hamiltonians ($N > 2$).

1. Introduction

Since the pioneering work of Smoluchowski in 1917 [1], reaction–diffusion-limited processes have had a forefront position in non-equilibrium statistical physics. They can be portrayed as bimolecular processes of the type

$$A + B \overset{k}{\underset{r}{\rightleftharpoons}} C + D \tag{1.1}$$

where species A and B (C and D) react to form C and D (A and B) with a reaction rate k (r). In the last decade much research has been reported mainly on irreversible ($r = 0$) and vacuum-driven chemical reactions, i.e. those for which at least one of the final products is an inert state, a precipitate or a non-reacting species (see [2–9] and references therein).

In spite of their apparent simplicity, tackling non-equilibrium problems described by (1.1) remains a most demanding task. Glauber [10] circumvented some of these difficulties, largely of a mathematical nature, by devising an ingenious way of using classical spin systems to study the problem of critical dynamics by means of a master equation approach. A major breakthrough was made by Kandel *et al* [11] who showed that another class of non-equilibrium problems, namely the shrinking domains of Ising spins, could also be understood in terms of the integrable six-vertex model in one of its critical manifolds [12]. This model has been one of the most fruitful paradigms of the mathematical theory of integrability [13] and it shed a new dimension into the possibilities of obtaining exact results in non-equilibrium problems. More recently Alcaraz *et al* [14] showed that the master equation for some particular reaction–diffusion processes could be mapped onto an

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imaginary-time Schrödinger equation for which the Hamiltonians were non-Hermitian and integrable q-deformed quantum chains.

The aim of the present paper is to extend [14] by finding three-state integrable quantum chains for which the Hamiltonians are time-evolution operators of diffusion–reaction processes and the spectra known or can easily be calculated. It is also our objective to obtain a better understanding of the role played by the boundaries in chemical reactions and how this can be understood in connection with quantum chains which arise from the mapping.

Our motivation is twofold: first, the equivalence of the spectra implicit in the equivalence of phase diagrams and the physical behaviour of chemical systems is then, in principle, determined by that of the chains they are mapped onto. For instance, if we consider the long-time behaviour of a system with its dynamics governed by (1.1), we expect the decay of the mean concentration for species j as a function of time to be of the form

$$c_j \sim \begin{cases} t^{-\alpha} \\ e^{-t/\tau} \end{cases} \tag{1.2}$$

where α and τ are characteristic of each problem. As an example, in the two-species annihilation process $(A + B \rightarrow \emptyset + \emptyset$ where $\emptyset$ is a vacancy), it has been found that in one dimension and for an initial random distribution of particles one has an algebraic fall-off with exponent $\alpha = \frac{1}{4}$ [15]. The other regime can be attained by the inclusion of certain processes (or reversible reactions) which lead to a local steady state and therefore a quicker (exponential) approach to equilibrium. These regimes correspond, respectively, to the massless and massive phases in the quantum chains mapping the chemical systems. Second, a major gain from the mapping is the existence of the Bethe ansatz for integrable models, which, in principle, allows one to calculate physical quantities exactly.

We summarize our results in what follows. We found that a large class of chemical reactions taking place on a one-dimensional lattice with open boundaries can be understood in terms of two integrable three-state quantum chains. The first one is a $U_q \widehat{SU(2)}$-invariant model for which the Hamiltonian, in the standard basis of matrices $(E^{kl})_{a,b} = \delta_{k,a}\delta_{l,b}$, reads

$$H' = H'_0 + H'_1$$

$$H'_0 = -\sum_{i=1}^{L-1} (E_i^{01} E_{i+1}^{10} + E_i^{10} E_{i+1}^{01} + E_i^{02} E_{i+1}^{20} + E_i^{20} E_{i+1}^{02}) + v\varepsilon_i^0 \varepsilon_{i+1}^0$$

$$+ w(\varepsilon_i^0 + \varepsilon_{i+1}^0) + a(\varepsilon_i^0 - \varepsilon_{i+1}^0) \tag{1.3}$$

$$H'_1 = -g \sum_{i=1}^{L} \varepsilon_i^z$$

$$\varepsilon^0 = E^{11} + E^{22} \qquad \varepsilon^z = E^{11} - E^{22}.$$

H'_0 is $U_q \widehat{SU(2)}$-invariant [17] and the symmetry-breaking H'_1, which commutes with H'_0, acts as an external field and does not spoil the integrability of the model. As shown in [18] H'_0 has the spectrum (apart from degeneracies) and phase diagram of the spin-$\frac{1}{2}$ XXZ model with an external field and a surface term, which reads

$$H^{XXZ} = -\frac{1}{2} \sum_{i}^{L-1} \left\{ \sigma_i^x \sigma_{i+1}^x + \sigma_i^y \sigma_{i+1}^y + \Delta \sigma_i^z \sigma_{i+1}^z + h(\sigma_i^z + \sigma_{i+1}^z) + a(\sigma_i^z - \sigma_{i+1}^z) + \beta \right\}. \tag{1.4}$$

This equivalence is crucial since the phase diagram for the XXZ chain has been known for many years [19] and we can, through the mapping, interpret it in the language of reaction–diffusion processes. For $h = 0$ this model has a massless and conformal invariant phase when $-1 \leqslant \Delta \leqslant 1$ and a massive antiferromagnetic (ferromagnetic) phase for $\Delta < -1$ ($\Delta > 1$). When $h \neq 0$ the system is massive commensurate for $\Delta > 1 - h$ and massless incommensurate otherwise, the line $\Delta = 1 - h$ corresponding to a Pokrovski–Talapov (PT) phase transition between these two regimes [20].

The equivalence between H_0' and H^{XXZ} can be established by rewriting the latter in the basis of E^{kl} matrices

$$H^{XXZ} = -\sum_{i=1}^{L-1}(E_i^{01} E_{i+1}^{10} + E_i^{10} E_{i+1}^{01}) + v E_i^{11} E_{i+1}^{11} + w(E_i^{11} + E_{i+1}^{11}) + a(E_i^{11} - E_{i+1}^{11}) + b$$

(1.5)

where

$$v = -2\Delta \qquad w = \Delta + h \qquad b = -(\tfrac{1}{2}(\Delta + \beta) + h).$$

(1.6)

H_0' is obtained from H^{XXZ} by adding the matrix elements $E_i^{02} E_{i+1}^{20}$ and $E_i^{20} E_{i+1}^{02}$ which do not affect the spectrum (only degeneracies). The diagonal terms are extended accordingly. The wavefunctions of H_0' have been calculated but the effect of H_1' on the phase diagram has not yet been studied [18].

As shown in [14], the second class of chains which naturally appear as time-evolution operators of chemical systems are the $(P + M)$-state $U_q SU(P/M)$-invariant Perk–Schultz (PS) models [21, 22]. The one-dimensional quantum Hamiltonian reads

$$H_{\{\epsilon_1,\dots,\epsilon_{P+M}\}} = \sum_{j=1}^{L-1} \left\{ \frac{q + q^{-1}}{2} - \left[\sum_{\alpha \neq \beta=0}^{P+M-1} E_j^{\alpha\beta} E_{j+1}^{\beta\alpha} + \frac{q + q^{-1}}{2} \sum_{\alpha=0}^{P+M-1} \epsilon_\alpha E_j^{\alpha\alpha} E_{j+1}^{\alpha\alpha} \right. \right.$$

$$\left. \left. + \frac{q - q^{-1}}{2} \sum_{\alpha \neq \beta=0}^{P+M-1} \text{sign}(\alpha - \beta) E_j^{\alpha\alpha} E_{j+1}^{\beta\beta} \right] \right\}$$

(1.7)

where, besides the anisotropy parameter q, one has an extra set of parameters $\{\epsilon_\alpha\}$ such that $\epsilon_0 = \epsilon_1 = \cdots = \epsilon_{P-1} = -\epsilon_P = -\epsilon_{P+1} = \cdots = -\epsilon_{P+M-1} = 1$. Their role can be better understood in the original two-dimensional formulation of the PS models, namely the multicolour ice-models (number of colours $= P + M$). In these models ferroelectric configurations (all links of a vertex having the same colour) are favoured for colours a having $\epsilon_a = +1$ and for colours b with $\epsilon_b = -1$ the corresponding vertex weights favour alternating coloured configurations [23]. Each possible set $\{\epsilon_\alpha\}$ defines therefore a completely different physical system (see e.g. [24–26]). From a mathematical point of view though, these chains have a rich underlying Hecke algebraic structure which yields important relations as regards their spectrum [27]. Our result extends that of [14] by showing that it is possible to encompass more general chemical reactions with the inclusion of external fields in the models given by $(P/M) = (3/0)$ and $(P/M) = (2/1)$.

The second result in this paper is intimately related to the problem of boundary conditions. In the case of quantum chains appearing in equilibrium problems, the boundaries are expected to play no significant role in the determination of the phase diagram. However, for chemical processes where the Hamiltonian is non-Hermitian, this picture is far from correct and the physics is boundary-dependent. This is intuitively clear if one thinks of a biased ($k \neq r$) diffusion process

$$A + \emptyset \underset{r}{\overset{k}{\rightleftharpoons}} \emptyset + A.$$
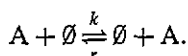
For open boundaries (equivalent to an impenetrable wall) one gets an asymptotic limit with particles concentrated on one side of the lattice [28]. For periodic boundaries, the same is not true. This problem was understood in connection with two-state spin systems where the biased diffusion Hamiltonian was shown to be equivalent, under a standard local similarity transformation, to an XXZ chain with a volume-dependent interaction at the boundary [29]. This boundary interaction term was also known [30] to arise in the XXZ chain through the inclusion of a Dzialoshinsky–Moryia exchange term over the bulk [31]. We show that for higher-state systems diffusing on a lattice with periodic boundary conditions, the *similarity transformation is non-local* and yields volume-dependent *bulk* interactions which cannot be written as a pure boundary interaction on the corresponding quantum chain.

The paper is organized as follows. In the second section we introduce the formalism of the master equation on lattices and its mapping onto nearest-neighbour quantum chains. In section 3 we treat the $U_q\widehat{SU(2)}$-invariant model as a workbench for the application of the method and reinterpret the phase diagram in the language of chemical processes. In section 4 we extend the known results for the PS models with the inclusion of external fields. We define also the non-local similarity transformation in terms of which we can understand the role played by the boundaries. Section 5 is of a more mathematical character. We study the transformation and generalize it to a system with an arbitrary number N of species, also deriving the volume-dependent bulk interactions which arise from the mapping. Finally in section 6 we summarize our results and some questions which we still face.

2. The master equation and quantum chains

The master equation, which governs the evolution of the probability distribution of Markov processes, is applied here in the description of chemical processes on a chain. Consider a one-dimensional lattice with L sites and open boundaries. At each site j we define a variable β_j taking N integer values $(0, 1, 2, \ldots, N-1)$. To each possible configuration $\{\beta\} = \{\beta_1, \ldots, \beta_L\}$ of the lattice realized at time t we attach a probability distribution $P(\{\beta\}, t)$ whose time evolution is given by the master equation

$$\frac{\partial P(\{\beta\}, t)}{\partial t} = \sum_{k=1}^{L-1} \left\{ - \Omega_{\beta_k, \beta_{k+1}} P(\beta_1, \ldots, \beta_L; t) \right.$$
$$\left. + \sum_{l,m=0}^{N-1}{}' \Gamma_{\beta_k, \beta_{k+1}}^{\beta_k+l, \beta_{k+1}+m} P(\beta_1, \ldots, \beta_k + l, \beta_{k+1} + m, \ldots, \beta_L; t) \right\}. \tag{2.1}$$

Here and henceforth the prime in a sum over l and m indicates exclusion of the pair $l = m = 0$. The $\Gamma_{c,d}^{a,b}$ are transition rates which equal the probability that, in a unit time step and at any site $j, j+1$ a state $(\beta_j, \beta_{j+1}) = (a, b)$ changes to a state $(\beta'_j, \beta'_{j+1}) = (c, d)$, pictorially $a + b \rightarrow c + d$. We will assume throughout this paper that the transition rates depend only on links (nearest-neighbour interaction) and are homogeneous, i.e. site independent. The $\Omega_{a,b}$ are related to the probability that a state (a, b) changes after a unit time step. Conservation of probability implies

$$\Omega_{a,b} = \sum_{r,s}{}' \Gamma_{r,s}^{a,b}. \tag{2.2}$$

Using the matrices E^{kl} we can rewrite the master equation (2.1) as

$$\frac{\partial |\psi\rangle}{\partial t} = -H |\psi\rangle \tag{2.3}$$

if we identify $|\psi\rangle$ as the probability $P(\{\beta\}, t)$ and H as

$$H = \sum_{j=1}^{L-1} H_j = \sum_{j=1}^{L-1} (U_j - T_j)$$

$$U_j = \sum_{a,b=0}^{N-1} \Omega_{a,b} E_j^{aa} E_{j+1}^{bb} \tag{2.4}$$

$$T_j = \sum_{a,b,c,d=0}^{N-1} {}' \Gamma_{c,d}^{a,b} E_j^{ca} E_{j+1}^{db}.$$

To identify the Hamiltonians of these chemical processes with those of known integrable quantum chains we must find the appropriate set of rates so that H can be recast as

$$H = H^0 + \sum_{j=1}^{L-1} (h_i + h_{i+1} + g_i - g_{i+1}) + H^1 \tag{2.5}$$

where H^0 is the integrable Hamiltonian and the terms under the summation sign are a field and a surface contribution, respectively. The spectrum of H is independent of H^1. We shall look only for those chemical processes with a spectrum equivalent to that of some quantum chain, therefore guaranteeing the equality of the phase diagram. The wavefunctions are not the same. For a *non-degenerate* spectrum it is, in principle, possible to define a similarity transformation of the form $A(\lambda)$ such that

$$A(\lambda) H A^{-1}(\lambda) = H^0 + \sum_{j=1}^{L-1} (h_i + h_{i+1} + g_i - g_{i+1}) + H^{1'}(\lambda) \tag{2.6}$$

such that for some given value $\lambda = \lambda_0$ we have $H^{1'}(\lambda_0) = 0$. If such a transformation were found, then the wavefunctions of the chemical problem could be obtained from that of the quantum chain.

3. The $U_q \widehat{SU(2)}$ model and the XXZ chain

In this section we address the problem of finding the set of chemical reactions associated with a given quantum chain based on the master equation approach. Our ultimate goal is to use the phase diagram of the chain to explain the chemistry of reaction–diffusion processes.

In what follows we identify particles with $A = 1$, $B = 2$ and inert state (or vacancy) $= \emptyset$. The boundaries are open. The symmetry requires that only left–right symmetric processes be taken into account. We therefore consider a system in which particles A and B diffuse symmetrically with rates equal to unity, i.e. $\Gamma_{0,1}^{1,0} = \Gamma_{1,0}^{0,1} = \Gamma_{0,2}^{2,0} = \Gamma_{2,0}^{0,2} = 1$. In addition, we also allow particles to react according to the following vacuum-driven rates:

(i) Annihilation: *pairwise destruction of particles with rates* $\Gamma_{0,0}^{1,1}, \Gamma_{0,0}^{2,2}, \Gamma_{0,0}^{1,2} = \Gamma_{0,0}^{2,1}$.

(ii) Coagulation: *pairwise aglutination of alike particles with rates* $\Gamma_{1,0}^{1,1} = \Gamma_{0,1}^{1,1}$ and $\Gamma_{2,0}^{2,2} = \Gamma_{0,2}^{2,2}$.

(iii) Death: *a particle vanishes from the system according to* $\Gamma_{0,0}^{1,0} = \Gamma_{0,0}^{0,1}$ and $\Gamma_{0,0}^{2,0} = \Gamma_{0,0}^{0,2}$.

(iv) Polymerization [32]: *mending of alike particles with rates* $\Gamma_{2,0}^{1,1} = \Gamma_{0,2}^{1,1}$ and $\Gamma_{1,0}^{2,2} = \Gamma_{0,1}^{2,2}$.

(v) Trapping [33]: *a particle traps its neighbour with rates* $\Gamma_{1,0}^{1,2} = \Gamma_{0,1}^{1,2} = \Gamma_{1,0}^{2,1} = \Gamma_{0,1}^{2,1}$ and $\Gamma_{2,0}^{1,2} = \Gamma_{0,2}^{2,1} = \Gamma_{0,2}^{1,2} = \Gamma_{2,0}^{2,1}$.

Using (2.2)–(2.4) we find that the chemical Hamiltonian corresponding to these rates is given by

$$H = H^0 + H^1$$
$$= \sum_{i=1}^{L-1} (H^0_{i,i+1} + H^1_{i,i+1}) \tag{3.1}$$

where

$$H^0_{i,i+1} = \begin{pmatrix}
0 & & & & & & & & \\
\Gamma^{0,1}_{0,0}+1 & & -1 & & & & & & \\
& \Gamma^{0,2}_{0,0}+1 & & & & & -1 & & \\
-1 & & \Gamma^{0,1}_{0,0}+1 & & & & & & \\
& & & \Gamma^{1,1}_{0,0}+2\Gamma^{1,1}_{0,1} & & & & & \\
& & & +2\Gamma^{1,1}_{0,2} & & & & & \\
& & & & \Gamma^{1,2}_{0,0}+2\Gamma^{1,2}_{0,1} & & & & \\
& & & & +2\Gamma^{1,2}_{0,2} & & & & \\
& -1 & & & & \Gamma^{0,2}_{0,0}+1 & & & \\
& & & & & & \Gamma^{1,2}_{0,0}+2\Gamma^{1,2}_{0,1} & & \\
& & & & & & +2\Gamma^{1,2}_{0,2} & & \\
& & & & & & & \Gamma^{2,2}_{0,0}+2\Gamma^{2,2}_{0,1} & \\
& & & & & & & +2\Gamma^{2,2}_{0,2} &
\end{pmatrix}$$

$$H^1_{i,i+1} = \begin{pmatrix}
0 & \Gamma^{0,1}_{0,0} & \Gamma^{0,2}_{0,0} & \Gamma^{0,1}_{0,0} & \Gamma^{1,1}_{0,0} & \Gamma^{1,2}_{0,0} & \Gamma^{0,2}_{0,0} & \Gamma^{1,2}_{1,0} & \Gamma^{2,2}_{0,1} \\
& 0 & & & \Gamma^{1,1}_{0,1} & \Gamma^{1,2}_{0,1} & & \Gamma^{1,2}_{0,1} & \Gamma^{2,2}_{0,1} \\
& & 0 & & \Gamma^{1,1}_{0,2} & \Gamma^{1,2}_{0,2} & & \Gamma^{1,2}_{0,2} & \Gamma^{2,2}_{0,2} \\
& & & 0 & \Gamma^{1,1}_{0,1} & \Gamma^{1,2}_{0,1} & & \Gamma^{1,2}_{0,1} & \Gamma^{2,2}_{0,1} \\
& & & & 0 & & & & \\
& & & & & 0 & & & \\
& & & & \Gamma^{1,1}_{0,2} & \Gamma^{1,2}_{0,2} & 0 & \Gamma^{1,2}_{0,2} & \Gamma^{2,2}_{0,2} \\
& & & & & & & 0 & \\
& & & & & & & & 0
\end{pmatrix} \tag{3.2}$$

where the matrix elements not explicitly shown are zero. It is important to note that the spectrum of H coincides with that of H^0. This feature is encountered in many non-Hermitian chains and can be understood as follows: H^0 conserves the total number n_A of A particles and n_B of B particles separately and can therefore be brought into a block diagonal form. On the other hand, H^1 reduces the total particle number $n_A + n_B$ by one or two since it is made up of vacuum-driven processes. From linear algebra we know that the spectrum of matrices of the type $H = H^0 + H^1$ with such properties is independent of H^1. This has an important physical consequence: since the spectrum does not depend on each parameter of H^1 sepatately but only on their combinations which enter in H^0, the number of effective parameters is reduced to eight (see equation (3.2))†.

† Due to conservation of probability each diagonal element of a Hamiltonian must equal the sum of the non-diagonal entries in that same column. We can see this if we look at the definitions of rates in section 2 and realize that the conservation of the probabilities implies in a relation among rates which can be written as $\sum_{k \neq l} H_{kl} = H_{ll}$.

Our aim is to show that this Hamiltonian is equivalent to that of equation (1.3). To write it then in a more enlightening form, we first define some shorter notation by regrouping processes of the same category, as in table 1 ($i = 1, 2$).

Table 1.

Notation	Definition	Processes
A_i	$\Gamma_{0,0}^{i,i}$	Annihilation
$A_{1,2}^{\pm}$	$\Gamma_{0,0}^{1,2} \pm \Gamma_{0,0}^{2,1}$	Annihilation
$D_i^{\pm}$	$\Gamma_{0,0}^{0,i} \pm \Gamma_{0,0}^{i,0}$	Death
C_i^+	$\Gamma_{i,0}^{i,i} + \Gamma_{0,i}^{i,i}$	Coagulation
P_1^+	$\Gamma_{0,2}^{1,1} + \Gamma_{2,0}^{1,1}$	Polymerization
P_2^+	$\Gamma_{0,1}^{2,2} + \Gamma_{1,0}^{2,2}$	Polymerization
$T^{\pm}$	$[\Gamma_{1,0}^{1,2} \pm \Gamma_{0,1}^{2,1}] + [\Gamma_{0,1}^{1,2} \pm \Gamma_{1,0}^{2,1}] + [\Gamma_{2,0}^{1,2} \pm \Gamma_{0,2}^{2,1}] + [\Gamma_{0,2}^{1,2} \pm \Gamma_{2,0}^{2,1}]$	Trapping

It is clear that in the present problem only the symmetric combinations are non-zero, since the symmetry of the model so requires. If we make the following identifications

$$v = A_1 + C_1^+ + P_1^+ - D_1^+ - 2$$
$$w = \tfrac{1}{4}(D_1^+ + D_2^+) + 1$$

(3.3)

together with three constraints

$$2w + v = A_2 + C_2^+ + P_2^+$$
$$4w + 2v = A_{12}^+ + T^+$$
$$D_1^+ = D_2^+$$

(3.4)

we can rewrite H^0 of (3.1) as

$$H^0 = \sum_{i=1}^{L-1} -(E_i^{01} E_{i+1}^{10} + E_i^{10} E_{i+1}^{01} + E_i^{02} E_{i+1}^{20} + E_i^{20} E_{i+1}^{02}) + w(\varepsilon_i^0 + \varepsilon_{i+1}^0) + v\varepsilon_i^0 \varepsilon_{i+1}^0$$

(3.5)

$$\varepsilon^0 = E^{11} + E^{22} \qquad \varepsilon^z = E^{11} - E^{22}.$$

Comparing this expression with H_0' of equation (1.3) we conclude that they have the same phase diagram since the term in H_0' having the parameter a as coefficient is a surface contribution. To interpret the phase diagram in the language of reaction–diffusion processes, it suffices to identify the parameters of the Heisenberg chain with the rates of the chemical model. It gives (see (1.6))

$$h = \frac{A_1 + C_1^+ + P_1^+}{2}$$

$$\Delta = 1 + \frac{D_1^+ - (A_1 + C_1^+ + P_1^+)}{2}$$

(3.6)

$$\beta = -1 - \frac{A_1 + C_1^+ + P_1^+ + D_1^+}{2}.$$

The analysis is straightforward. $h = 0$ implies that all rates vanish *but* death. In this situation

$$\Delta = 1 + \tfrac{1}{2}D_1^+ \qquad \beta = -\Delta.$$

(3.7)

By varying the death rate we go from a massive regime to a massless one, that is, the time evolution for the concentration of particles has an exponential or algebraic fall-off,

respectively. This can be understood on physical grounds: being a 'one-particle' process, death happens irrespectively of any other processes occurring in the system, i.e. it is not diffusion-limited since any particle can die alone. It therefore outruns the characteristic time-scale set by diffusion and brings about a quicker decay. With an external field we have

$$\Delta + h - 1 = \tfrac{1}{2} D_1^+. \tag{3.8}$$

If death has a non-zero probability, then from the equation above one sees that the system is massive ferromagnetic. If we identify spin up in the Heisenberg model as a vacancy in chemistry, this means having a ground state with no particles. By varying the rate of death we approach the line on the phase diagram given by $\Delta + h = 1$. The system undergoes a PT transition [20] when the energy of the state with just one particle equals that of the state with no particles and it becomes the ground state. We have a level-crossing: since death is absent the system can evolve to a final steady state where only one particle is left. It is worth noting that in the massless regime (absence of death) many reactions besides diffusion still coexist, namely annihilation, coagulation, polymerization and trapping. This is so because the time-scale set by diffusion cannot be outrun, since all the remaining processes are two-particle ones. In other words, in a situation where the particles are some lattice spacings apart, they need first to diffuse before they reach each other and react—the processes are diffusion-limited. This observation is confirmed by results obtained in other studies where the time decay of the concentration of particles was shown to be algebraic in time (for pure annihilation $c_j \sim t^{1/4}$, see [15]). It also allows us to say that, qualitatively, the massless regime remains even if the other three reactions are present, as the previous equations show.

4. The Perk–Schultz chains

4.1. The $U_q SU(3/0)$, $U_q SU(2/1)$ and $U_q SU(1/2)$ chains

It is well known that the Hamiltonian of the six-vertex model is also the time-evolution operator for the two-state asymmetric diffusion process [11]. Recently this idea has been extended by Alcaraz and coworkers [14] who showed that the PS Hamiltonians appear as the corresponding operators for higher-state diffusive systems. Intuitively we can understand this if we recall that the quantum PS chains were originally obtained from the τ-continuum limit of the transfer matrix describing higher-state vertex models which obey the ice-rule. This picture is, however, far from complete and can be extended to encompass more general chemical systems if we reinterpret the additional reactions on chemical Hamiltonians as external fields in the PS chains onto which they are mapped. For the sake of completeness, we present first the results without external fields obtained in [14] and then proceed with the generalization of these results.

We first consider a system in which particles A and B diffuse on the lattice with rate Γ_R if the particle jumps to the right or Γ_L otherwise. For the interchange process we take the rates accordingly if B replaces A on the right or on the left. With the rates so defined

we get a Hamiltonian which reads

$$
H = \sum_{i=1}^{L-1} H_i
$$

$$
H_i = \begin{pmatrix}
0 & & & & & & & & \\
& \Gamma_L & & -\Gamma_R & & & & & \\
& & \Gamma_L & & & -\Gamma_R & & & \\
& -\Gamma_L & & \Gamma_R & & & & & \\
& & & & 0 & & & & \\
& & & & & \Gamma_L & & -\Gamma_R & \\
& & -\Gamma_L & & & & \Gamma_R & & \\
& & & & & -\Gamma_L & & \Gamma_R & \\
& & & & & & & & 0
\end{pmatrix} .
\tag{4.1}
$$

Defining $\sqrt{\Gamma_L/\Gamma_R} = q$, which measures the asymmetry of the diffusion, and the diffusion constant $\sqrt{\Gamma_L\Gamma_R} = \mathcal{D}$, which sets the time-scale of the problem, this can be rewritten as

$$
\frac{H_i}{\mathcal{D}} = \begin{pmatrix}
0 & & & & & & & & \\
& q & & -q^{-1} & & & & & \\
& & q & & & -q^{-1} & & & \\
& -q & & q^{-1} & & & & & \\
& & & & 0 & & & & \\
& & & & & q & & -q^{-1} & \\
& & -q & & & & q^{-1} & & \\
& & & & & -q & & q^{-1} & \\
& & & & & & & & 0
\end{pmatrix} .
\tag{4.2}
$$

In [14] it was observed that this non-Hermitian (q is real!) Hamiltonian is $U_q SU(3/0)$-invariant (cf equation (1.7)). They further observed that if one considered only a new set of processes corresponding to coagulation of B (B + B → B + Ø with rate $\Gamma_{2,0}^{2,2}$ and B + B → Ø + B with $\Gamma_{0,2}^{2,2}$) such that $\Gamma_{2,0}^{2,2} + \Gamma_{0,2}^{2,2} = \mathcal{D}(q + q^{-1})$ and the above plus coagulation of A (A + A → A + Ø with $\Gamma_{1,0}^{1,1}$ and A + A → Ø + A with $\Gamma_{0,1}^{1,1}$) with the restriction $\Gamma_{10}^{11} + \Gamma_{01}^{11} = \mathcal{D}(q + q^{-1})$ non-Hermitian $U_q SU(2/1)$-invariant and $U_q SU(1/2)$-invariant chains are obtained. The exact form of the transformation matrix which brings these chains to a Hermitian form was however still lacking. This motivated us to find this similarity transformation which, in contradistinction to the two-state case (see e.g. [29]), is non-local and reads

$$
\mathcal{F} = \sum_{\alpha_1,\alpha_2,\ldots,\alpha_L=0}^{2} q^{\frac{1}{2}\sum_{j>i=1}^{L} \text{sign}(\alpha_j-\alpha_i)} E^{\alpha_1\alpha_1} \otimes E^{\alpha_2\alpha_2} \otimes \cdots \otimes E^{\alpha_L\alpha_L}.
\tag{4.3}
$$

The physical features this matrix induces are also completely novel. We postpone a more detailed discussion of this topic to the next section, where we study its properties.

We note that the two last chains present a particular feature. From the spectrum of the (2/1) chain, the spectrum of the (1/2) can be obtained in a straighforward manner. We reverse the sign of the whole spectrum of the (2/1) model and add an overall constant equal to $(L-1)(q+q^{-1})$, which is the highest energy of the (2/1) chain (this value is indeed the highest energy for all L-site (P/M) chains with q real and non-zero P and M: an outline proof is given in [27]). In the chemical scenario, however, they correspond to different physical pictures and the reason is the positivity of the spectrum.

4.2. The chains with external fields

We now generalize the previously mentioned results to include the most general set of vacuum-driven processes which can be written as a pure non-Hermitian Hamiltonian H^1 which does not affect the spectrum of the PS chains. Beyond the 24 rates of section 3 (no left–right symmetry!) we can include one more set of reactions, namely those corresponding to mutation and transmutation of A. The corresponding rates are $\Gamma_{2,0}^{1,0}$, $\Gamma_{0,2}^{0,1}$, $\Gamma_{0,2}^{1,0}$ and $\Gamma_{2,0}^{0,1}$. For these reactions we define the following combination

$$M_1^{\pm} = \Gamma_{0,2}^{0,1} \pm \Gamma_{2,0}^{1,0} \qquad X_1^{\pm} = \Gamma_{2,0}^{0,1} \pm \Gamma_{0,2}^{1,0}. \tag{4.4}$$

Using the master-equation approach we get a Hamiltonian which can be written as follows

$$\frac{H'}{D} = \frac{H}{D} + \sum_{i=1}^{L-1}(h_i + h_{i+1} + g_i - g_{i+1}) + H^1 \tag{4.5}$$

where H is given by (4.2) and $H^1 = \sum_i H_i^1$, being the same in all cases, reads

$$H_i^1 = \begin{pmatrix} 0 & \Gamma_{0,0}^{0,1} & \Gamma_{0,0}^{0,2} & \Gamma_{0,0}^{1,0} & \Gamma_{0,0}^{1,1} & \Gamma_{0,0}^{1,2} & \Gamma_{0,0}^{2,0} & \Gamma_{0,0}^{2,1} & \Gamma_{0,0}^{2,2} \\ & 0 & & & \Gamma_{0,1}^{1,1} & \Gamma_{0,1}^{1,2} & & \Gamma_{0,1}^{2,1} & \Gamma_{0,1}^{2,2} \\ & \Gamma_{0,2}^{0,1} & 0 & \Gamma_{0,2}^{1,0} & \Gamma_{0,2}^{1,1} & \Gamma_{0,2}^{1,2} & & \Gamma_{0,2}^{2,1} & \Gamma_{0,2}^{2,2} \\ & & & 0 & \Gamma_{1,0}^{1,1} & \Gamma_{1,0}^{1,2} & & \Gamma_{1,0}^{2,1} & \Gamma_{1,0}^{2,2} \\ & & & & 0 & & & & \\ & & & & & 0 & & & \\ & \Gamma_{2,0}^{0,1} & & \Gamma_{2,0}^{1,0} & \Gamma_{2,0}^{1,1} & \Gamma_{2,0}^{1,2} & 0 & \Gamma_{2,0}^{2,1} & \Gamma_{2,0}^{2,2} \\ & & & & & & & 0 & \\ & & & & & & & & 0 \end{pmatrix}. \tag{4.6}$$

It is important to note, as in the last section, that the spectrum of H' depends on H^1 only through the h's and g's which are diagonal contributions arising due to conservation of probabilities. They commute with H, playing the role of external fields and surface terms, respectively. Their values differ for each particular chain as can be seen in table 2.

Table 2.

Model	h_1	h_2	g_1	g_2	Constraints
$U_q SU(3/0)$	$\frac{M_1^+ + X_1^+ + D_1^+}{2D}$	$\frac{D_2^+}{2D}$	$-\frac{M_1^- + X_1^- + D_1^-}{2D}$	$-\frac{D_2^-}{2D}$	$M_1^+ + T_1^+ + D_1^+ = C_1^+ + P_1^+ + A_1$ $D_2^+ = C_2^+ + P_2^+ + A_2$ $A_{12}^+ + T^+ = M_1^+ + X_1^+ + D_1^+ + D_2^+$ $A_{12}^- + T^- = D_2^- - M_1^- - X_1^- - D_1^-$
$U_q SU(2/1)$	$\frac{M_1^+ + X_1^+ + D_1^+}{2D}$	$-\frac{D_2^+}{2D}$	$-\frac{M_1^- + X_1^- + D_1^-}{2D}$	$-\frac{D_2^-}{2D}$	$M_1^+ + T_1^+ + D_1^+ = C_1^+ + P_1^+ + A_1$ $D_2^+ = C_2^+ + P_2^+ + A_2 - \mathcal{D}(q + q^{-1})$ $A_{12}^+ + T^+ = M_1^+ + X_1^+ + D_1^+ + D_2^+$ $A_{12}^- + T^- = D_2^- - M_1^- - X_1^- - D_1^-$
$U_q SU(1/2)$	$-\frac{M_1^+ + X_1^+ + D_1^+}{2D}$	$-\frac{D_2^+}{2D}$	$-\frac{M_1^- + X_1^- + D_1^-}{2D}$	$-\frac{D_2^-}{2D}$	$M_1^+ + T_1^+ + D_1^+ = C_1^+ + P_1^+ + A_1 - \mathcal{D}(q + q^{-1})$ $D_2^+ = C_2^+ + P_2^+ + A_2 - \mathcal{D}(q + q^{-1})$ $A_{12}^+ + T^+ = M_1^+ + X_1^+ + D_1^+ + D_2^+$ $A_{12}^- + T^- = D_2^- - M_1^- - X_1^- - D_1^-$

The constraints arise from the fact the number of parameters in the original chemical problem exceeds those of the quantum chains they are mapped onto and must therefore be

related. Due to the symmetry properties of the PS chains, the field (and surface contribution) were decomposed into three independent variables h_α (g_α), one for each conserved particle of type α. Since one of our particles is an inert state, we took the corresponding variables h_0 (g_0) to be equal to zero.

Unfortunately little is known about the phase diagram of the PS chains on an external field. Since the field commutes with the particle number operators, its effect on the spectrum is trivial and one may use the Bethe ansatz equations to obtain reliable finite-size data and consequently determine the phase diagram. Apart from the difficulties in analysing these equations, there is an additional subtlety: the non-Hermitian chemical Hamiltonians are related under $\mathcal{F}$ to PS chains with different properties, whether the boundaries in the original formulation are open or periodic. This reflects the fact that the chemistry of reaction–diffusion models is boundary-dependent (see the discussion in the introduction of this paper) and in our case this is brought about by the non-locality of $\mathcal{F}$. For periodic boundaries, we found that the bias-dependent chemical system is similar through $\mathcal{F}$ to a PS Hamiltonian with volume-dependent interactions spread through the bulk in a highly non-trivial way (see section 6). In this case the Bethe ansatz equations are given by [34]

$$e^{\gamma(N_0+N_1)} \epsilon_1^{M_1} \left(\frac{\sinh(\lambda_k^{(0)} + \epsilon_0\gamma/2)}{\sinh(\lambda_k^{(0)} - \epsilon_0\gamma/2)} \right)^L = \prod_{\alpha=1}^{M_0} \frac{\sinh(\lambda_k^{(0)} - \lambda_\alpha^{(0)} + \epsilon_1\gamma)}{\sinh(\lambda_k^{(0)} - \lambda_\alpha^{(0)} - \epsilon_0\gamma)}$$
$$\times \prod_{\alpha=1}^{M_1} \frac{\sinh(\lambda_k^{(0)} - \lambda_\alpha^{(1)} - \epsilon_1\gamma/2)}{\sinh(\lambda_k^{(0)} - \lambda_\alpha^{(1)} + \epsilon_1\gamma/2)} \tag{4.7}$$
$$e^{\gamma(N_1+N_2)} \epsilon_2^{M_2} \epsilon_0^{M_0} = \prod_{\alpha=1}^{M_0} \frac{\sinh(\lambda_\alpha^{(0)} - \lambda_l^{(1)} + \epsilon_1\gamma/2)}{\sinh(\lambda_\alpha^{(0)} - \lambda_l^{(1)} - \epsilon_1\gamma/2)} \prod_{\alpha=1}^{M_1} \frac{\sinh(\lambda_\alpha^{(1)} - \lambda_l^{(1)} - \epsilon_2\gamma)}{\sinh(\lambda_\alpha^{(1)} - \lambda_l^{(1)} + \epsilon_1\gamma)}$$

where $\{\epsilon_\alpha\}$ are the parameters of the PS chains, and γ is related to q through $q = \exp(\gamma)$. The N_i's correspond to the particular number of particles of type i in each charge sector and the M_i's equal the number of roots of the set of coupled equations. They are obtained from the N_i's through

$$M_i = L - (N_0 + N_1 + \cdots + N_i) \tag{4.8}$$

where L is the lattice size. These equations were also derived by Lopes and de Vega [23] but without the bias-dependent non-local interactions. We shall return to this problem in a future publication.

5. Similarity transformation and boundary conditions

In this section we consider thoroughly the transformation given by the matrix $\mathcal{F}$ introduced in the last section. We shall address two points: the first regards the extention of $\mathcal{F}$ not only to higher-state models but also to multi-parameter diffusion processes, i.e. those characterized by a larger set $\{q\} = \{q_1, q_2, \ldots\}$ of parameters in contradistinction to the one-parameter diffusion we dealt with so far. Second, we want to look at the effect of $\mathcal{F}$ on periodic chains and the physical features it induces. We would like to note that this matrix is implicitly used by Reshetikhin in his paper on multi-parameter quantum groups [35].

5.1. Multi-parameter and higher-state diffusion processes

As before, we consider a system in which $(N - 1)$ different species diffuse and interchange places on a one-dimensional lattice with open boundary conditions with rates

$$A_x + A_y \rightleftharpoons A_y + A_x \quad \Gamma^{A_x,A_y}_{A_y,A_x}; \Gamma^{A_y,A_x}_{A_x,A_y} \qquad x > y = 0, 1, \cdots, N - 1 \qquad (5.1)$$

from which we define $\frac{1}{2}N(N - 1)$ parameters q_{xy}

$$\sqrt{\frac{\Gamma^{A_y,A_x}_{A_x,A_y}}{\Gamma^{A_x,A_y}_{A_y,A_x}}} = q_{xy} \qquad (5.2)$$

with $q_{xy} = q_{yx}^{-1}$. We impose a homogeneous time-scale

$$\sqrt{\Gamma^{0,A_1}_{A_1,0}\Gamma^{A_1,0}_{0,A_1}} = \sqrt{\Gamma^{0,A_2}_{A_2,0}\Gamma^{A_2,0}_{0,A_2}} = \cdots = \sqrt{\Gamma^{A_{N-2},A_{N-1}}_{A_{N-1},A_{N-2}}\Gamma^{A_{N-1},A_{N-2}}_{A_{N-2},A_{N-1}}} = \mathcal{D} \qquad (5.3)$$

and obtain a non-Hermitian Hamiltonian

$$\frac{H}{\mathcal{D}} = \sum_{k=1}^{L-1}\left\{ \sum_{x\neq y=0}^{N-1} q_{xy}(E_k^{xx}E_{k+1}^{yy} - E_k^{xy}E_{k+1}^{yx})\right\} \qquad (5.4)$$

which governs the time evolution of the chemical system defined above. Our goal is to find a similarity transformation which makes H Hermitian. The (non-local!) similarity transformation which accomplishes this reads

$$\mathcal{F} = \sum_{\alpha_1,\alpha_2,\dots,\alpha_L=0}^{N-1} \left(\prod_{x>y=0}^{N-1} (q_{xy})^{f_{xy}(\alpha_1,\alpha_2,\dots,\alpha_L)} \right) E^{\alpha_1\alpha_1} \otimes E^{\alpha_2\alpha_2} \otimes \cdots \otimes E^{\alpha_L\alpha_L} \qquad (5.5)$$

with the functions f_{xy} given by

$$f_{xy}(\alpha_1, \alpha_2, \dots, \alpha_L) = \frac{1}{2} \sum_{n>m=1}^{L} (\delta_{\alpha_n,x}\delta_{\alpha_m,y} - \delta_{\alpha_n,y}\delta_{\alpha_m,x}). \qquad (5.6)$$

We point out in the expression for the function that the order of its arguments is very important since they index the sites on the chain, that is, $f(\dots, \alpha_j, \alpha_{j+1}, \dots) \neq f(\dots, \alpha_{j+1}, \alpha_j, \dots)$.

Proof. For clarity, we consider the diagonal and non-diagonal parts of the Hamiltonian separately. Since $\mathcal{F}(\sum_j H_{j,j+1})\mathcal{F}^{-1} = \sum_j \mathcal{F}H_{j,j+1}\mathcal{F}^{-1}$, it suffices to consider the action of S on the two-site operator $H_{j,j+1}$.

Consider first the action of $\mathcal{F}$ on the diagonal piece of the Hamiltonian. We have

$$\mathcal{F}\frac{H^{diag}_{j,j+1}}{\mathcal{D}}\mathcal{F}^{-1} = \sum_{\{\alpha\}=0}^{N-1} \prod_{x>y}(q_{xy}^{f_{xy}(\alpha_1,\alpha_2,\dots,\bar{\alpha}_L)} E^{\alpha_1\alpha_1} \otimes E^{\alpha_2\alpha_2} \otimes \cdots \otimes E^{\alpha_L\alpha_L}) \left(\sum_{a\neq b=0}^{N-1} q_{ab}E_j^{aa}E_{j+1}^{bb} \right)$$

$$\times \sum_{\{\beta\}=0}^{N-1} \prod_{w>z}(q_{wz}^{-f_{wz}(\beta_1,\beta_2,\dots,\beta_L)} E^{\beta_1\beta_1} \otimes E^{\beta_2\beta_2} \otimes \cdots \otimes E^{\beta_L\beta_L}). \qquad (5.7)$$

Reordering the terms, one has

$$\mathcal{F}\frac{H^{diag}_{j,j+1}}{\mathcal{D}}\mathcal{F}^{-1} = \sum_{[\alpha]}\sum_{[\beta]} \prod_{x>y=0}^{N-1} \prod_{w>z=0}^{N-1} (q_{xy}^{f_{xy}(\alpha_1,\alpha_2,\dots,\alpha_L)} q_{wz}^{-f_{wz}(\beta_1,\beta_2,\dots,\beta_L)})$$

$$\times E^{\alpha_1\alpha_1}E^{\beta_1\beta_1} \otimes E^{\alpha_2\alpha_2}E^{\beta_2\beta_2} \otimes \cdots \otimes \mathbb{1}^{(j)} \otimes \mathbb{1}^{(j+1)} \otimes \cdots \otimes E^{\alpha_L\alpha_L}E^{\beta_L\beta_L}$$

$$\times \sum_{\substack{\alpha_j,\alpha_{j+1} \\ \beta_j,\beta_{j+1}}} \sum_{a\neq b=0}^{N-1} (q_{ab} E^{\alpha_j\alpha_j} E^{aa} E^{\beta_j\beta_j} \otimes E^{\alpha_{j+1}\alpha_{j+1}} E^{bb} E^{\beta_{j+1}\beta_{j+1}}).$$ (5.8)

Since x, y, w and z serve only to index the same set $\{q\}$ of diffusion parameters, we can take $x=w$, $y=z$. Using the multiplication properties of the matrices $E^{\alpha\beta}$, namely

$$E^{pq} E^{rs} = \delta_{q,r} E^{ps}$$ (5.9)

we get

$$\mathcal{F}\frac{H_{j,j+1}^{\mathrm{diag}}}{\mathcal{D}}\mathcal{F}^{-1} = \sum_{\{\alpha\}}^{N-1}\sum_{\{\beta\}}^{N-1}\prod_{x>y=0}^{N-1} (q_{xy}^{f_{xy}(\alpha_1,\alpha_2,...,\alpha_L)-f_{xy}(\beta_1,\beta_2,...,\beta_L)})$$
$$\times E^{\alpha_1\alpha_1}\delta_{\alpha_1,\beta_1} \otimes E^{\alpha_2\alpha_2}\delta_{\alpha_2,\beta_2} \otimes \cdots \otimes \mathbf{1}^{(j)} \otimes \mathbf{1}^{(j+1)} \otimes \cdots \otimes E^{\alpha_L\alpha_L}\delta_{\alpha_L,\beta_L}$$
$$\times \sum_{\substack{\alpha_j,\alpha_{j+1} \\ \beta_j,\beta_{j+1}}} \sum_{a\neq b=0}^{N-1} (q_{ab} E_j^{aa} E_{j+1}^{bb}\delta_{\alpha_j,a}\delta_{\alpha_{j+1},b}\delta_{\alpha_j,\beta_j}\delta_{\alpha_{j+1},\beta_{j+1}}).$$ (5.10)

Taking into account the Kronecker's deltas we have

$$\mathcal{F}\frac{H_{j,j+1}^{\mathrm{diag}}}{\mathcal{D}}\mathcal{F}^{-1} = \sum_{\{\alpha\}}^{N-1}\prod_{x>y=0}^{N-1} q_{xy}^{f_{xy}(\alpha_1,\alpha_2,...,\alpha_L)-f_{xy}(\alpha_1,\alpha_2,...,\alpha_L)} \left(\sum_{a\neq b=0}^{N-1} q_{ab} E_j^{aa} E_{j+1}^{bb} \right)$$
$$\times E^{\alpha_1\alpha_1} \otimes E^{\alpha_2\alpha_2} \otimes \cdots \otimes \mathbf{1}^{(j)} \otimes \mathbf{1}^{(j+1)} \otimes \cdots \otimes E^{\alpha_L\alpha_L}.$$ (5.11)

The exponent of q_{xy} is clearly zero. Summing over $\{\alpha\}$ we have finally

$$\mathcal{F}\frac{H_{j,j+1}^{\mathrm{diag}}}{\mathcal{D}}\mathcal{F}^{-1} = \sum_{a\neq b=0}^{N-1} q_{ab}\mathbf{1}\otimes\mathbf{1}\otimes\cdots\otimes E_{(j)}^{aa}\otimes E_{(j+1)}^{bb}\otimes\cdots\otimes\mathbf{1}$$
$$= \frac{H_{j,j+1}^{\mathrm{diag}}}{\mathcal{D}}.$$ (5.12)

This shows that the diagonal elements of the Hamiltonian are not changed by the transformation generated by $\mathcal{F}$.

To see the effect of $\mathcal{F}$ on the non-diagonal part we consider only the two-body operator for a given value of the pair (a,b). We have

$$\mathcal{F}\frac{H_{j,j+1}^{\mathrm{nond}}}{\mathcal{D}}\mathcal{F}^{-1} = S(q_{ab} E_j^{ab} E_{j+1}^{ba} + q_{ab}^{-1} E_j^{ba} E_{j+1}^{ab})_{a>b}S^{-1}.$$ (5.13)

As in the diagonal case, after multiplying the $E^{\alpha\beta}$ matrices on each site we obtain

$$\mathcal{F}\frac{H_{j,j+1}^{\mathrm{nond}}}{\mathcal{D}}\mathcal{F}^{-1} = \sum_{\{\alpha\}}^{N-1}\sum_{\{\beta\}}^{N-1}\prod_{x>y=0}^{N-1} (q_{xy}^{f_{xy}(\alpha_1,\alpha_2,...,\alpha_L)-f_{xy}(\beta_1,\beta_2,...,\beta_L)})$$
$$\times E^{\alpha_1\alpha_1}\delta_{\alpha_1,\beta_1} \otimes \cdots \otimes \mathbf{1}^{(j)} \otimes \mathbf{1}^{(j+1)} \otimes \cdots \otimes E^{\alpha_L\alpha_L}\delta_{\alpha_L,\beta_L}$$
$$\times \sum_{\substack{\alpha_j,\alpha_{j+1} \\ \beta_j,\beta_{j+1}}} (q_{ab} E_j^{ab} E_{j+1}^{ab}\delta_{\alpha_j,a}\delta_{\beta_j,b} + q_{ab}^{-1} E_j^{ba} E_{j+1}^{ab}\delta_{\alpha_j,b}\delta_{\beta_j,a})_{a>b}\delta_{\alpha_{j+1},\beta_j}\delta_{\alpha_j,\beta_{j+1}}.$$

(5.14)

This reduces to

$$
\mathcal{F}\frac{H^{\text{nond}}_{j,j+1}}{D}\mathcal{F}^{-1} = \sum_{\{\alpha\}} \prod_{x>y=0}^{N-1} q_{xy}^{f_{xy}(\alpha_1,\dots,\alpha_j,\alpha_{j+1},\dots,\alpha_L)-f_{xy}(\alpha_1,\dots,\alpha_{j+1},\alpha_j,\dots,\alpha_L)}
$$

$$
\times E^{\alpha_1\alpha_1} \otimes E^{\alpha_2\alpha_2} \otimes \cdots \otimes 1^{(j)} \otimes 1^{(j+1)} \otimes \cdots \otimes E^{\alpha_L\alpha_L}
$$

$$
\times (q_{ab}E^{ab}_j E^{ab}_{j+1}\delta_{\alpha_j,a}\delta_{\alpha_{j+1},b} + q^{-1}_{ab} E^{ba}_j E^{ab}_{j+1}\delta_{\alpha_j,b}\delta_{\alpha_{j+1},a})_{a>b}. \tag{5.15}
$$

Note the interchanged arguments in the exponent of q_{xy}, that is

$$
f_{xy}(\alpha_1,\dots,\alpha_j,\alpha_{j+1},\dots,\alpha_L) - f_{xy}(\alpha_1,\dots,\alpha_{j+1},\alpha_j,\dots,\alpha_L)
$$

$$
= \tfrac{1}{2}(\delta_{\alpha_{j+1},x}\delta_{\alpha_j,y} - \delta_{\alpha_{j+1},y}\delta_{\alpha_j,x}) - \tfrac{1}{2}(\delta_{\alpha_j,x}\delta_{\alpha_{j+1},y} - \delta_{\alpha_j,y}\delta_{\alpha_{j+1},x})
$$

$$
= \delta_{\alpha_{j+1},x}\delta_{\alpha_j,y} - \delta_{\alpha_{j+1},y}\delta_{\alpha_j,x}. \tag{5.16}
$$

Substituting this expression on (5.15) we get

$$
\mathcal{F}\frac{H^{\text{nond}}_{j,j+1}}{D}\mathcal{F}^{-1} = \sum_{\{\alpha\}} \prod_{x>y=0}^{N-1} q_{xy}^{\delta_{\alpha_{j+1},x}\delta_{\alpha_j,y} - \delta_{\alpha_{j+1},y}\delta_{\alpha_j,x}}
$$

$$
\times (q_{ab}E^{ab}_j E^{ab}_{j+1}\delta_{\alpha_j,a}\delta_{\alpha_{j+1},b} + q^{-1}_{ab} E^{ba}_j E^{ab}_{j+1}\delta_{\alpha_j,b}\delta_{\alpha_{j+1},a})_{a>b}
$$

$$
\times E^{\alpha_1\alpha_1} \otimes E^{\alpha_2\alpha_2} \otimes \cdots \otimes 1^{(j)} \otimes 1^{(j+1)} \otimes \cdots \otimes E^{\alpha_L\alpha_L}. \tag{5.17}
$$

Summing over $\{\alpha\}$ gives us an identity matrix on each site. Kronecker's delta eliminates the sum over α_j, α_{j+1} such that we are left with

$$
\mathcal{F}\frac{H^{\text{nond}}_{j,j+1}}{D}\mathcal{F}^{-1} = \prod_{x>y=0}^{N-1} (q_{xy}^{\delta_{b,x}\delta_{a,y}-\delta_{a,x}\delta_{b,y}} q_{ab}E^{ab}_j E^{ba}_{j+1} + q_{xy}^{\delta_{a,x}\delta_{b,y}-\delta_{a,y}\delta_{b,x}} q^{-1}_{ab} E^{ba}_j E^{ab}_{j+1})_{a>b}
$$

$$
= (q^{-1}_{ab} q_{ab} E^{ab}_j E^{ba}_{j+1} + q_{ab}q^{-1}_{ab} E^{ba}_j E^{ab}_{j+1})_{a>b}
$$

$$
= (E^{ab}_j E^{ba}_{j+1} + E^{ba}_j E^{ab}_{j+1})_{a>b}. \tag{5.18}
$$

The above term is clearly Hermitian. This concludes our proof. □

To finish we would like to indicate how in the one-parameter N-state diffusion process this expression simplifies. The rates are defined according to

$$
A_x + A_y \rightleftharpoons A_y + A_x \qquad \Gamma_R, \Gamma_L \qquad x > y = 0, 1, \dots, N-1 \tag{5.19}
$$

for which the L-site Hamiltonian reads

$$
\frac{H}{D} = \sum_{k=1}^{L-1} \left\{ \frac{q+q^{-1}}{2} - \left[q^{-1} \sum_{\alpha>\beta=0}^{N-1} E^{\alpha\beta}_k E^{\beta\alpha}_{k+1} + q \sum_{\alpha<\beta=0}^{N-1} E^{\alpha\beta}_k E^{\beta\alpha}_{k+1} \right. \right.
$$

$$
\left. \left. + \frac{q+q^{-1}}{2} \sum_{\alpha=0}^{N-1} E^{\alpha\alpha}_k E^{\alpha\alpha}_{k+1} + \frac{q-q^{-1}}{2} \sum_{\alpha\neq\beta=0}^{N-1} \text{sign}(\alpha-\beta)E^{\alpha\alpha}_k E^{\beta\beta}_{k+1} \right] \right\}. \tag{5.20}
$$

In this situation the operator $\mathcal{F}$ from equation (5.5) with $q_{xy} = q$ reduces to a much simpler form. By observing that in this case we have

$$
f_1(\alpha_1,\alpha_2,\dots,\alpha_L) + \cdots + f_{N-1}(\alpha_1,\alpha_2,\dots,\alpha_L) = \tfrac{1}{2} \sum_{n>m=1}^{L} \text{sign}(\alpha_n - \alpha_m) \tag{5.21}
$$

$\mathcal{F}$ is reduced to (see section 4)

$$
\mathcal{F} = \sum_{\alpha_1,\alpha_2,\dots,\alpha_L=0}^{N-1} q^{\frac{1}{2}\sum_{n>m=1}^{L} \text{sign}(\alpha_n-\alpha_m)} E^{\alpha_1\alpha_1} \otimes E^{\alpha_2\alpha_2} \otimes \cdots \otimes E^{\alpha_L\alpha_L}. \tag{5.22}
$$

The results presented here hold for any of the $U_q SU(P/M)$-invariant PS chains with $P + M = N$.

5.2. Periodic boundary conditions

Due to the non-locality of the similarity transformation, the chemical chains with free or periodic boundaries transform differently under $\mathcal{F}$. In the first case the non-Hermitian chemical Hamiltonian is transformed into a Hermitian PS chain. In the second case, the Hamiltonian is similar under $\mathcal{F}$ to a quantum chain with non-trivial bulk interactions. In the two-state model, this simplifies to a volume-dependent boundary interaction which, on its turn, was understood to arise from a Dzialoshinsky–Moriya interaction in the bulk [31]. This has been known for years and we review it shortly.

Consider as before particles diffusing on a one-dimensional lattice with *periodic* boundaries. The rates are given by

$$A + \emptyset \rightleftharpoons \emptyset + A \quad \Gamma_R, \Gamma_L \tag{5.23}$$

where $\mathcal{D}$ and q are defined in the usual way (see section 4). The Hamiltonian thus generated reads

$$\frac{H}{\mathcal{D}} = \sum_{k=1}^{L} \left\{ \frac{q+q^{-1}}{2} - \frac{q+q^{-1}}{2} \sum_{\alpha=0}^{1} E_k^{\alpha\alpha} E_{k+1}^{\alpha\alpha} - \frac{q-q^{-1}}{2} \sum_{\alpha \neq \beta=0}^{1} \text{sign}(\alpha-\beta) E_k^{\alpha\alpha} E_{k+1}^{\beta\beta} \right.$$
$$\left. -q^{-1} E_k^{10} E_{k+1}^{01} - q E_k^{01} E_{k+1}^{10} \right\}. \tag{5.24}$$

It is convenient to change to the more familiar basis of Pauli matrices, by making the identification

$$\begin{aligned}
E^{00} &= \tfrac{1}{2}(1+\sigma^z) \\
E^{11} &= \tfrac{1}{2}(1-\sigma^z) \\
E^{01} &= \sigma^+ \\
E^{10} &= \sigma^-.
\end{aligned} \tag{5.25}$$

In this basis the Hamiltonian can be written as

$$\frac{H}{\mathcal{D}} = -\frac{1}{2} \sum_{k=1}^{L} \left\{ 2q^{-1}\sigma_k^+\sigma_{k+1}^- + 2q\sigma_k^-\sigma_{k+1}^+ + \frac{q+q^{-1}}{2}\sigma_k^z\sigma_{k+1}^z - \frac{q-q^{-1}}{4} \right\}. \tag{5.26}$$

The constant term is irrelevant in our discussion and we will drop it for the time being. Applying equation (5.22) to the remaining terms in the chain we get

$$\mathcal{F}\frac{H}{\mathcal{D}}\mathcal{F}^{-1} = \frac{\widetilde{H}}{\mathcal{D}} = -\frac{1}{2}\sum_{k=1}^{L-1} \left\{ 2\sigma_k^+\sigma_{k+1}^- + 2\sigma_k^-\sigma_{k+1}^+ + \frac{q+q^{-1}}{2}\sigma_k^z\sigma_{k+1}^z \right\}$$
$$-\frac{1}{2}\left\{ 2q^L\sigma_L^+\sigma_1^- + 2q^{-L}\sigma_L^-\sigma_1^+ + \frac{q+q^{-1}}{2}\sigma_L^z\sigma_1^z \right\}. \tag{5.27}$$

Since q is real, we have a boundary term which is proportional to the volume of the system, changing the whole structure of the problem. In other words, the dynamics of diffusion processes in a chain with open boundaries are different from that of a periodic chain [29].

To explicitly see the Dzialoshinsky–Moryia interaction in (5.26), redefine q in terms of a new variable η

$$q = \sqrt{\frac{1-\eta}{1+\eta}} \tag{5.28}$$

in terms of which $\Gamma_R = \frac{1}{2}(1 + \eta)$ and $\Gamma_L = \frac{1}{2}(1 - \eta)$. After some simple algebraic manipulation one can write (5.26) apart from the constant as

$$\frac{H}{\mathcal{D}} = -\frac{1}{2} \sum_{k=1}^{L} \{2\sigma_k^+ \sigma_{k+1}^- + 2\sigma_k^- \sigma_{k+1}^+ + \sigma_k^z \sigma_{k+1}^z + 2\eta(\sigma_k^+ \sigma_{k+1}^- - \sigma_k^- \sigma_{k+1}^+)\}. \tag{5.29}$$

The new term is clearly recognizable as a Dzialoshinsky–Moryia interaction term.

For higher-state diffusion models on periodic lattices we get interactions other than the ones obtained in the two-state case, after applying $\mathcal{F}$. To see this we first note that the whole effect of $\mathcal{F}$ is to change the off-diagonal terms of the two-body chemical Hamiltonian at the boundary, namely $E_L^{ab} E_1^{ba}$ and $E_L^{ba} E_1^{ab}$. In the two-state case there are only two possibilities for the pair (a, b): $(1, 0)$ and $(0, 1)$. Since opposite pairs are related by an inversion of the power of q, we have effectively one result which is q^L. In higher-state cases, the power depends on the particular (a, b) chosen. We present the results for the three-state model and the for the general N-state case in what follows.

5.2.1. Three-state diffusion process Here we have $(a, b) = (0, 1); (0, 2); (1, 2)$ and the reversed pairs. The action of $\mathcal{F}$ yields

$$\mathcal{F}\{q^{-1} E_1^{01} E_L^{10}\}\mathcal{F}^{-1} = q^{-2} E_1^{01} \otimes M_1 \otimes M_1 \otimes \cdots \otimes M_1 \otimes E_L^{10}$$

$$M_1 = \begin{pmatrix} q & & \\ & q & \\ & & 1 \end{pmatrix} \tag{5.30}$$

for $(a, b) = (0, 1)$. Exchanging a, b we get the same structure but with q replaced by q^{-1}, as expected. For the pair $(a, b) = (1, 2)$ we obtain

$$\mathcal{F}\{q^{-1} E_1^{12} E_L^{21}\}\mathcal{F}^{-1} = q^{-2} E_1^{12} \otimes M_2 \otimes M_2 \otimes \cdots \otimes M_2 \otimes E_L^{21}$$

$$M_2 = \begin{pmatrix} 1 & & \\ & q & \\ & & q \end{pmatrix}. \tag{5.31}$$

Finally for $(a, b) = (0, 2)$ we have

$$\mathcal{F}\{q^{-1} E_1^{02} E_L^{20}\}\mathcal{F}^{-1} = q^{-2} E_1^{02} \otimes M_1 M_2 \otimes M_1 M_2 \otimes \cdots \otimes M_1 M_2 \otimes E_L^{21}. \tag{5.32}$$

We see now that, in the case under study, the effect of the transformation cannot be understood in terms of boundary interactions, in contradistinction to the two-state problem— the interaction is 'spread' over the bulk. The structure is analogous in higher-state models as is shown next.

5.2.2. N-state diffusion process Assume that $(a, b) = (i, j)$ such that $i < j = 0, 1, \ldots, N - 1$. We obtain in this case

$$\mathcal{F}\{q^{-1} E_1^{ij} E_L^{ji}\}\mathcal{F}^{-1} = q^{-2} E_1^{ij} \otimes M \otimes M \otimes \cdots \otimes M \otimes E_L^{ji} \tag{5.33}$$

where M is an $N \times N$ matrix which reads

$$M = \begin{pmatrix} 1 & & & & & & & & & \\ & \ddots & & & & & & & & \\ & & 1 & & & & & & & \\ & & & q & & & & & & \\ & & & & q^2 & & & & & \\ & & & & & \ddots & & & & \\ & & & & & & q^2 & & & \\ & & & & & & & q & & \\ & & & & & & & & 1 & \\ & & & & & & & & & \ddots & \\ & & & & & & & & & & 1 \end{pmatrix} \qquad (5.34)$$

where q appears at the ith and jth positions in the diagonal. All other M_{kk} are equal to 1 for $k < i$ and $k > j$ and equal to q^2 in the case $i < k < j$. The interaction is spread along the bulk as we can see from equation (5.33).

6. Conclusions

In this paper we have shown that: (i) the Hamiltonian obtained from the master equation of general three-state diffusion–reaction systems is related to two known integrable chains, namely the $U_q\widehat{SU(2)}$-invariant model and the PS Hamiltonian with external fields. In these mappings, not all rates governing the chemical processes are important in determining the phase diagram of the the system; and (ii) the presence of asymmetic diffusion for three- and higher-state systems reflects itself in the structure of the related quantum chains through the appearance of a non-local bias-dependent interaction term, in contradistinction to the two-state case, where such asymmetry leads to a volume-dependent interaction for the boundary spins of the associated quantum chain. This novel interaction can be understood as an extension of a Dzialoshinsky–Moryia interaction for higher-state chains.

The mapping used in this paper preserves the spectrum of the chains, implying that the phase diagram of the chemical model is completely settled by that of the integrable chain. As an example, we showed in section 3 how the massless and massive regimes of the quantum chains yields two types of time dependence for the decay of the particles' concentration, which are in agreement with other studies [15]. In the PS models with external fields, where little about the phase diagram is known, we went beyond the mapping by deriving the Bethe ansatz equations for the three-state chemical processes taking place on a lattice with periodic boundaries which is related through a similarity transformation to a PS chain with the novel bulk interactions. Much is still to be done in the exploration of this mapping and we expect it will enable us in the near future to gain some new insights and shed some light onto the physics of reaction–diffusion models.

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References

[1] Smoluchowski M V 1917 *Z. Phys. Chem.* **92** 215
[2] Bramson M and Griffeath D 1980 *Ann. Prob.* **8** 183
[3] Torney D C and McConnel H M 1983 *J. Phys. Chem.* **87** 1941
[4] Kang K, Meakin P, Oh J H and Redner S 1984 *J. Phys. A: Math. Gen.* **17** L60
[5] Racz Z 1985 *Phys. Rev. Lett.* **55** 1107
[6] Lushnikov A A 1987 *Phys. Lett.* **120A** 135
[7] Bramson M and Lebowitz J L 1988 *Phys. Rev. Lett.* **61** 2397
[8] Kusovkov V and Kotomin E 1988 *Rep. Prog. Phys.* **51** 2397
[9] ben-Avraham D, Burschka M A and Doering C R 1990 *J. Stat. Phys.* **60** 695
[10] Glauber R J 1963 *J. Math. Phys.* **4** 294
[11] Kandel D, Domany E and Nienhuis B 1990 *J. Phys. A: Math. Gen.* **23** L755 and references therein
[12] Baxter R J 1982 *Exactly Solved Models in Statistical Mechanics* (London: Academic)
[13] De Vega H J 1989 *Int. J. Mod. Phys.* A **4** 2371
[14] Alcaraz F C, Droz M, Henkel M and Rittenberg V 1994 *Ann. Phys.* **230** 250
[15] Toussaint D and Wilczek F 1983 *J. Chem. Phys.* **78** 2642
    Kang K and Redner S 1984 *Phys. Rev. Lett.* **52** 955; 1984 *Phys. Rev.* A **30** 2833
[16] Alcaraz F C and Rittenberg V 1993 *Phys. Lett.* **314B** 377
[17] Saleur H 1989 *Trieste Conf. on Recent Developments in Conformal Field Theories* (Singapore: World Scientific)
[18] Alcaraz F C, Arnaudon D, Rittenberg V and Scheunert M 1994 *Int. J. Mod. Phys.* A **9/19** 3473
[19] Johnson J D and Mckoy B M 1972 *Phys. Rev.* A **46** 1613
    Takahashi M and Suzuki M 1972 *Prog. Theor. Phys.* **48** 2187
[20] Pokrovskii V L and Talapov A L 1980 *Sov. Phys.–JETP* **51** 134
[21] Sutherland B 1975 *Phys. Rev.* B **12** 3795
[22] Perk J H H and Schultz C L 1981 *Non-Linear Integrable Systems, Classical Theory and Quantum Theory* ed M Jimbo and T Miwa (Singapore: World Scientific)
    Schultz C L 1981 *Phys. Rev. Lett.* **46** 629; 1983 *Physica* **122** 71
[23] Lopes E and De Vega H 1992 *Nucl. Phys.* B **370**
[24] Hinrichsen H and Rittenberg V 1992 *Phys. Lett.* **275B** 350
[25] Jaubert M, Glachand A, Bienfat M and Boato G 1981 *Phys. Rev. Lett.* **46** 1676
[26] Anderson P W 1987 *Science* **235** 1196
    Bares P A and Blatter G 1990 *Phys. Rev. Lett.* **64** 2567
[27] Martin P P and Rittenberg V 1992 *Int. J. Mod. Phys.* A **7** Suppl. 1B 707 and references therein
[28] Schütz G 1993 *J. Stat. Phys.* **71** 471; 1993 *Phys. Rev.* E **47** 4265
[29] Henkel M and Schütz G 1994 *Physica* A **206** 187
    Alcaraz F C 1994 Exact steady states of asymmetric diffusion and two-species annihilation with back reaction from the ground state of quantum spin models *Preprint* Universidade Federal de São Carlos, Brazil
[30] The general discussion in connection to the XXZ-spin 1/2 model can be found in
    Alcaraz F C and Wreszinski W F 1990 *J. Stat. Phys.* **58** 45
[31] Dzialoshinsky I 1958 *J. Phys. Chem. Solids* **4** 241
    Moriya T 1960 *Phys. Rev.* **117** 635; 1963 *Magnetism* ed G T Rado and H Suhl (London: Academic)
[32] Spouge J L 1988 *Phys. Rev. Lett.* **60** 871
[33] Chopard D, Droz M, Karapiperis T and Rácz Z 1993 *Phys. Rev.* E **47** R40
    Rodriguez M A, Abramson G, Wio H and Bru A 1993 *Phys. Rev.* E **48** 829
[34] Dahmen S R in preparation
[35] Reshetikhin N 1990 *Lett. Math. Phys.* **20** 331