The Backward Stochastic Liouville Equation[†]

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The backward stochastic Liouville equation is formulated in a Dirac-type notation in order to emphasize the kinship with the backward diffusion equation and the Heisenberg picture of quantum mechanics. The backward equations are useful both for analytic treatments and for numerical methods since the solution contains the average value of the observable for all initial spin and spatial conditions. The crucial point in using the backward equations is the boundary and initial conditions, which are derived for an arbitrary observable A and corresponding rate of change $\dot{A}$. The formalism is applied to derive explicit analytic expressions for the recombination yield of two radicals that performs a free diffusion in a liquid under high magnetic fields. It is shown that the nontrivial limit of diffusion-controlled reaction can be directly calculated by a careful choice of boundary conditions.

1. Introduction

The stochastic Liouville equation (SLE) has led to significant improvements in the description and understanding of quantum systems with a Hamiltonian that depends parametrically on a classical stochastic process. Perhaps the best known example is the electron spin resonance line shape of an anisotropic radical in a liquid or liquidlike environment. Prior to the SLE, only the rigid-limit spectrum and the motional-narrowed spectrum could be calculated accurately. The original application of the SLE to the line-shape problem by Freed et al.[1] showed the potential of the method and is now the standard method for these kind of problems.

The SLE has also been an essential tool for the description and understanding of the recombination of particles with spin. A physical example is delayed fluorescence where triplet excitons perform a random walk on the molecular crystal lattice until two excitons collide and annihilate.[2,3] The corresponding phenomena of short-lived radicals in liquids has many names, depending on the experimental conditions, e.g., CIDNP (chemically induced dynamic nuclear polarization) and RYDMR (reaction yield detected magnetic resonance).[4,5] In these examples, one measures the recombination (or escape) yield of a radical pair (RP) either as a function of the nuclear spin state (CIDNP) or as a function of the (static and/or radio frequency (rf)) magnetic field strength. Other observables, such as the electron spin polarization, may also be observed for the same systems.

The present work is concerned with a general description of both kind of problems, fluctuations in equilibrium systems and irreversible processes in nonequilibrium systems. The more specific parts of the work and the explicit calculations are, however, concerned with irreversible recombination problems.

A description based on the SLE is exact for the assumed Hamiltonian and stochastic process. The problem is to solve the SLE, which is a description in the direct product space of the spin superspace (or more generally the quantum mechanical superspace) and the space of the classical stochastic process. Obviously, one must be able to solve both the quantum part and the classical stochastic part separately in order to solve the combined system described by the SLE, but this is not a sufficient condition. In fact, only a few exact analytic solutions have appeared[6−8] for very simplified systems. But many approximate methods of solution have been developed, e.g., refs 9−12. Accurate numerical methods have been developed,[13,14] and with todays fast computers, they can easily be applied. However, analytic solutions display the various parameter dependences more clearly and are thus often preferable.

Although the SLE is now routinely used, the corresponding backward (or adjoint) equation is rarely used. Apparently, only an optimized numerical method[14] is directly based on the backward SLE.

In the present work, we derive a compact formulation of the backward SLE, which in an identical form can be applied to classical stochastic processes and to pure quantum dynamics. The goal was to let the time evolution of the system be contained in the physical observables and to derive an equation of motion for an arbitrary physical quantity. In quantum mechanics, this is clearly obtained by working in the Heisenberg picture and the backward equation is shown to be equal to the usual equation of motion for operators in this picture. The backward equation for a classical stochastic process is discussed, and a convenient Dirac notation is introduced. Equations of motion for an arbitrary observable $A(\mathbf{r},t)$ and its rate of change $\dot{A}(\mathbf{r},t)$ are derived in conjunction with the associated boundary conditions that are essential for the solution of the equations.

The backward SLE is convenient both for numerical solutions, as demonstrated in ref 14, and for deriving analytic solutions. It should also be a good platform for mixed analytic and numerical calculations. The backward SLE is a direct equation for the observable, and the solution contains the values of the observable for all initial spin states and all initial values of the stochastic parameters. The equation is well suited to be used in connection with symbolic computer systems. The method is used to derive analytic expressions for the recombination yield of a geminate pair of radicals in liquids under high magnetic fields. In connection with this derivation, we present a new scheme

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for a direct calculation of quantities in the diffusion-controlled limit, which is both simpler and faster than first solving the general case and then performing the limit.

The work is composed of four sections. The first three introduce the backward equation and a common Dirac notation to pure quantum systems, classical stochastic processes, and the combined systems, respectively. This exposition helps to understand the behavior and conditions of the backward SLE as it illustrates how they are built upon simpler parts from the underlaying systems. The final section demonstrates the usefulness of the backward SLE by deriving explicit expressions for the singlet recombination probability of a triplet, geminate radical pair in high magnetic fields.

2. Quantum Dynamics

The time development of a quantum system is in the Schrödinger picture given by

$$\frac{d\rho}{dt} = -i[H,\rho] \equiv -iH^\times \rho \qquad (1)$$

where ρ is the density operator of the system, H is the Hamiltonian (assumed to be Hermitian), and $H^\times$ is the commutator-generated superoperator. The Laplace transform of eq 1 is

$$[s + iH^\times]\rho(s) = \rho_0 \qquad (2)$$

where $\rho_0 = \rho(t = 0)$ is the initial density operator and s is the Laplace transform variable. By introducing the Green's superoperator by

$$[s + iH^\times]\hat{G}(s) = \mathbf{I} \qquad (3)$$

where $\mathbf{I}$ is the identity operator, the solution to eq 2 can be written as

$$\rho(s) = \hat{G}(s)\rho_0 \qquad (4)$$

The quantity of interest is the average value of an observable quantity. Let A be the operator that represents an observable that does not depend explicitly on time. The average value of A, at time t, is

$$\langle A \rangle(t) = \text{Tr}[A\rho(t)] \qquad (5)$$

For the present application, it is more convenient to work with the Laplace-transformed quantities. The average value can be written in the following compact form

$$\langle A \rangle(s) = \text{Tr}[A\hat{G}(s)\rho_0] \equiv \langle A^\dagger | \hat{G}(s)|\rho_0 \rangle \qquad (6)$$

where we have introduced a Dirac notation in the space of operators on the relevant quantum mechanical vector space. The basis for this superspace is the shift operators $\{|j\rangle\langle k|\}$ where the set of vectors $\{|k\rangle\}$ forms an orthonormal basis of the vector space. The matrix element of the superoperator $H^\times$ in the superspace is related to the matrix elements of the Hamiltonian H by

$$(H^\times)_{ij,kl} = H_{ik}\delta_{jl} - H_{lj}\delta_{ik} \qquad (7)$$

In the superspace, superoperators are represented by matrices, and operators are represented by vectors. The kets and bras of the Dirac notation are then represented by column and row vectors, as usual, although a vector requires two state indices

and a matrix four state indices. More details on the properties of superoperators and scalar products in superspace can be found in refs 15 and 16.

The backward equation to eq 3 is defined as

$$[s - iH^\times]\hat{G}^+(s) = \mathbf{I} \qquad (8)$$

where the Laplace transform variable s is formally considered real. The superscript $+$ is used to denote the formal (or functional) adjoint. Comparison of this equation with the Hermitian conjugate of eq 3 yields

$$G^+ = G^\dagger \qquad (9)$$

Multiplication of eq 8 by $A^\dagger$ from the right leads to

$$[s - iH^\times]A^+(s) = A^\dagger \qquad (10)$$

where we have defined

$$A^+(s) \equiv G^+(s)A^\dagger \qquad (11)$$

Equation 10 is identical to the equation of motion of the operator $A^\dagger$ in the Heisenberg picture. The main difference between the Schödinger eq 2 and the Heisenberg eq 10 is well known. In the Schrödinger picture, the time evolution is contained in the density matrix (probability distribution) while the operators are independent of time (unless they have an explicit time dependence). In the Heisenberg picture, the time evolution is contained in the operators while the density matrix is constant. In analogy with the stochastic description, discussed below, it makes sense to call the Schrödinger equation for the forward equation and the Heisenberg equation for the backward equation.

The average value can be written in a number of equivalent ways that illustrate the different calculational procedures

$$\begin{aligned}
\langle A \rangle(s) &= \text{Tr}[A\rho(s)] = \langle A^\dagger|\rho(s)\rangle \\
&= \text{Tr}[A\hat{G}(s)\rho_0] = \langle A^\dagger|\hat{G}(s)|\rho_0\rangle \\
&= \text{Tr}[\rho_0^\dagger \hat{G}^\dagger(s)A^\dagger]^* = \langle \rho_0|G^+(s)|A^\dagger\rangle^* \\
&= \text{Tr}[\rho_0^\dagger A^+(s)]^* = \langle \rho_0|A^+(s)\rangle^* = \langle A^+(s)|\rho_0\rangle
\end{aligned} \qquad (12)$$

The complex conjugations (*) become superfluous if the average value is real. This is the case for Hermitian operators, if the Laplace transform variable s is real.

3. Stochastic Dynamics

Consider a stochastic process $\mathbf{r}(t)$ described by the probability density $P(\mathbf{r}, t)$, that satisfies

$$\frac{\partial}{\partial t}P(\mathbf{r},t) = \Gamma_\mathbf{r}P(\mathbf{r},t) \qquad (13)$$

and an associated set of boundary condition. In the diffusion approximation, $\Gamma_\mathbf{r}$ is a second-order differential operator. The Laplace transform of eq 13 and the corresponding definition of the Green's function are

$$(s - \Gamma_\mathbf{r})P(\mathbf{r},s) = P_0(\mathbf{r}) \qquad (14)$$

$$(s - \Gamma_\mathbf{r})G(\mathbf{r},\mathbf{r}_0;s) = \delta(\mathbf{r} - \mathbf{r}_0) \qquad (15)$$

where $P_0(\mathbf{r})$ is the initial distribution. Equation 15 and the well-known relation

$$P(\mathbf{r},s) = \int G(\mathbf{r},\mathbf{r}_0;s)P_0(\mathbf{r}_0)\,dV_0 \qquad (16)$$

illustrates that the Green's function is just the conditional probability density

$$P(\mathbf{r},s|\mathbf{r}_0) = G(\mathbf{r},\mathbf{r}_0;s) \qquad (17)$$

Let $A(\mathbf{r})$ represent some physical observable quantity A. The quantity of interest is the average value of A at time t or alternatively its Laplace transform, which can be written as

$$\langle A \rangle(s) = \int A(\mathbf{r})P(\mathbf{r},s)\,dV$$
$$= \int\int A(\mathbf{r})G(\mathbf{r},\mathbf{r}_0;s)P_0(\mathbf{r}_0)\,dV_0\,dV$$
$$\equiv \langle A^*|G(s)|P_0\rangle = \langle A^*|P(s)\rangle \qquad (18)$$

The formal Dirac notation is defined, as indicated, by integrations over adjacent variables.

The adjoint equation to eq 15 is

$$[s - \Gamma_\mathbf{r}^+]G^+(\mathbf{r},\mathbf{r}_0;s) = \delta(\mathbf{r} - \mathbf{r}_0) \qquad (19)$$

where the adjoint operator $\Gamma_\mathbf{r}^+$ and the adjoint boundary condition follows from the requirement that Green's identity

$$\int (u(\mathbf{r})^*\Gamma_\mathbf{r}v(\mathbf{r}) - v(\mathbf{r})^*\Gamma_\mathbf{r}^+u(\mathbf{r}))\,dV = 0 \qquad (20)$$

must be satisfied for any two functions u and v satisfying the relevant boundary conditions.[17]

The forward boundary condition is determined by the physical problem. In the diffusion approximation, it can always be written as a so-called radiation boundary condition; i.e., the flux (probability current density) through the boundary is proportional to the probability density at the surface. The (forward) boundary condition will be symbolically written as

$$\Lambda_r v(\mathbf{r})|_S = 0 \qquad (21)$$

where S is the surface or boundary of the investigated volume. For a diffusion process, the operator Λ_r is a linear combination of first derivatives and constants. In one dimension, this is simply the Neumann condition, that states that a linear combination of the function and its derivative vanish at the boundary.

The adjoint boundary condition is determined by the requirement that Green's identity, eq 20, must be satisfied. The adjoint or backward boundary condition will be written as

$$\Lambda_\mathbf{r}^+ u(\mathbf{r})|_S = 0 \qquad (22)$$

The Green's function $G(\mathbf{r},\mathbf{r}_0;s)$ must satisfy the forward boundary condition (21) in the first argument ($\mathbf{r}$) and the backward boundary condition (22) in the second argument ($\mathbf{r}_0$).

Multiplication of eq 19 by $A^*(\mathbf{r}_0)$, integrating over $\mathbf{r}_0$, and finally renaming $\mathbf{r}$ and $\mathbf{r}_0$ lead to the backward equation

$$[s - \Gamma_{\mathbf{r}_0}^+]A^+(\mathbf{r}_0, s) = A^*(\mathbf{r}_0) \qquad (23)$$

where we have defined

$$A^+(\mathbf{r}_0,s) \equiv \int G^+(\mathbf{r}_0,\mathbf{r};s)A^*(\mathbf{r})\,dV \qquad (24)$$

Equation 23 is the backward equation to the forward eq 14. It is a direct equation in the dynamical variable $A^+(\mathbf{r}_0,s)$ with an initial value of $A^*(\mathbf{r}_0)$, and in this respect it corresponds to the Heisenberg picture.

The most fundamental relation for the Green's functions is, see, e.g., ref 17

$$G^+(\mathbf{r},\mathbf{r}_0;s) = G^*(\mathbf{r}_0,\mathbf{r};s) \qquad (25)$$

By inserting this relation into the definition (23) and applying $\Lambda_{\mathbf{r}_0}$ one immediately finds that $A^+(\mathbf{r}_0,s)$ satisfies the adjoint boundary condition

$$\Lambda_{\mathbf{r}_0}^+A^+(\mathbf{r}_0,s)|_S = 0 \qquad (26)$$

By rewriting eq 25 to

$$(G^+(\mathbf{r}_0,\mathbf{r};s))^* = G(\mathbf{r},\mathbf{r}_0;\,s) = P(\mathbf{r},\,s|\mathbf{r}_0) \qquad (27)$$

the average value of a dynamical variable A can be written alternatively as

$$\langle A \rangle(s) = (\int\int P_0^*(\mathbf{r}_0)G^+(\mathbf{r}_0,\mathbf{r};s)A^*(\mathbf{r})\,dV\,dV_0)^*$$
$$= \langle P_0|G^+(s)|A^*\rangle^*$$
$$= (\int P_0^*(\mathbf{r}_0)A^+(\mathbf{r}_0,s)\,dV_0)^*$$
$$= \langle P_0|A^+(s)\rangle^* = \langle A^+(s)|P_0\rangle \qquad (28)$$

This shows that the time (or Laplace variable) dependence has been moved from the probability density to the physical variable. This is formally equivalent with going from the Schrödinger picture to the Heisenberg picture. The equivalence and characteristics of the forward and backward descriptions may be illustrated by the identity

$$\langle A \rangle(s) = \langle A^*|P(s)\rangle = \langle A^+(s)|\,P_0\rangle \qquad (29)$$

Average quantities are often most conveniently calculated by the backward eq 23 since one of the integrations has already been performed. This has previously been demonstrated for calculations of the escape yield.[18] But, as shown above, the method is more general and can be applied to all dynamical variables.

The $t \to \infty$ limit of the average value can be calculated from the Laplace transformed quantity as

$$\lim_{t\to\infty} \langle A \rangle(t) = \lim_{s\to 0} s\,\langle A \rangle(s) \qquad (30)$$

but it is usually much easier to use the following trick. The rate of change of $A^+(r_0, s)$ is

$$\dot{A}^+(\mathbf{r}_0,t) = \frac{\partial}{\partial t}A^+(\mathbf{r}_0,t) \qquad (31)$$

Laplace transformation yields

$$\dot{A}^+(\mathbf{r}_0,s) = sA^+(\mathbf{r}_0,s) - A^*(\mathbf{r}_0) \qquad (32)$$

which shows that the wanted limit can be found as

$$\lim_{s\to 0} s\langle A \rangle(s) = \langle \dot{A} \rangle(s=0) + \langle A \rangle(t=0) \qquad (33)$$

By multiplying eq 23 by s and eliminating $A^+(\mathbf{r}_0,s)$ by use of eq 32, we find that the rate of change of A satisfies the following backward equation

$$[s - \Gamma_{\mathbf{r}_0}^+]\dot{A}^+(\mathbf{r}_0,s) = \Gamma_{\mathbf{r}_0}^+A^*(\mathbf{r}_0) \qquad (34)$$

Similarly, it follows from eqs 26 and 32 that $\dot{A}^+(\mathbf{r}_0,s)$ satisfies the inhomogeneous boundary condition

$$\Lambda^+_{\mathbf{r}_0}\dot{A}^+(\mathbf{r}_0,s)|_S = -\Lambda^+_{\mathbf{r}_0}\dot{A}^*(\mathbf{r}_0)|_S \qquad (35)$$

The $t \to \infty$ limit of $\langle A \rangle(t)$ can be found directly from eq 34 by setting $s = 0$, which leads to

$$\Gamma^+_{\mathbf{r}_0}\dot{A}^+(\mathbf{r}_0,s=0) = -\Gamma^+_{\mathbf{r}_0}A^*(\mathbf{r}_0) \qquad (36)$$

This may appear to be a singular equation, but the boundary conditions on $\dot{A}^+(\mathbf{r}_0,s)$ determine the solution uniquely, cf. the analytic examples.

3.1. Specific Diffusion Operators and Boundary Conditions. For the sake of completeness, two common diffusion operators and associated boundary conditions will be explicitly considered.

The traditional diffusion operator is[19]

$$\Gamma\phi = \nabla\cdot(e^{-V}\mathbf{D}\nabla(e^V\phi)) = \nabla\cdot(\phi\mathbf{D}\nabla V + \mathbf{D}\nabla\phi) \qquad (37)$$

where $\mathbf{D}$ is the diffusion tensor and V is a potential of interaction measured in units of kT. The formal adjoint operator

$$\Gamma^+\psi = e^V\nabla\cdot(e^{-V}\mathbf{D}\nabla\psi) = \nabla\cdot(\mathbf{D}\nabla\psi) - (\nabla V)\mathbf{D}(\nabla\psi) \qquad (38)$$

The precise form of the operators and the possible identity of the two depends on the coordinate system used, i.e., on the interpretation of the derivative ∇. The surface terms resulting from eq 20 are

$$Q_S[\psi,\phi] = \int_S \mathbf{n}(\psi^*\phi\mathbf{D}\nabla V + \psi^*\mathbf{D}\nabla\phi - \phi\mathbf{D}\nabla\psi^*)\,\mathrm{d}S = 0 \qquad (39)$$

where $\mathbf{n}$ is the surface normal pointing out of the volume. The radiation boundary condition is used for reactions of intermediate strength and is a mixed boundary condition that states that the flux through the reactive surface is proportional to the density at the surface. Since any diffusion equation must be a continuity equation for the probability, it must have the general form

$$\frac{\partial P(\mathbf{r},t)}{\partial t} = -\nabla\cdot\mathbf{j}(\mathbf{r},t) \qquad (40)$$

where $\mathbf{j}(\mathbf{r},t)$ is flux (current density). By comparison with eq 37, the radiation boundary condition with reaction strength $k \geq 0$ is easily constructed

$$\mathbf{n}\cdot\mathbf{j}|_S = k\phi|_S \Rightarrow (\mathbf{n}(\mathbf{D}\nabla\phi + \phi\mathbf{D}\nabla V) + k\phi)|_S = 0 \qquad (41)$$

The adjoint boundary condition then follows immediately from eq 39

$$(\mathbf{n}\mathbf{D}\nabla\psi + k\psi)|_S = 0 \qquad (42)$$

It follows that the diffusion operator (eq 37) is self-adjoint in Cartesian coordinates only if the potential is constant.

Reflecting boundary conditions are obtained by letting $k \to 0$ in eqs 41 and 42. The adjoint boundary condition becomes particularly simple, $\mathbf{n}\mathbf{D}\nabla\psi|_S = 0$.

Diffusion-controlled boundary conditions are obtained by letting $k \to \infty$, which implies a vanishing probability at the surface, $\phi|_S = 0$, and an identical adjoint boundary condition, $\psi|_S = 0$.

It has recently been argued[20,21] that the alternative diffusion operator

$$\Gamma\phi = \nabla\cdot(e^{-V}\nabla(\mathbf{D}e^V\phi)) = \nabla\cdot(\phi\mathbf{D}\nabla V + \phi\nabla\cdot\mathbf{D} + \mathbf{D}\nabla\phi) \qquad (43)$$

might provide a better description for electrons in solids and particles suspended in denser media (liquids). For isotropic systems, the two operators are mathematically (but not physically) equivalent, in the sense that the substitution $V \to V + \log D$ transforms the standard operator (eq 37) into the alternative operator (eq 43).

The formal adjoint operator to the alternative operator is

$$\Gamma^+\psi = \mathbf{D}{:}e^V\nabla(e^{-V}\nabla\psi) = \mathbf{D}{:}\nabla\nabla\psi - (\nabla V)\mathbf{D}(\nabla\psi) \qquad (44)$$

which contains no derivatives of $\mathbf{D}$ but instead has a double contraction. The surface term

$$Q_S[\psi,\phi] = \int_S \mathbf{n}(\psi^*\phi\mathbf{D}\nabla V + \psi^*\phi\nabla\cdot\mathbf{D} + \psi^*\mathbf{D}\nabla\phi - \phi\mathbf{D}\nabla\psi^*)\,\mathrm{d}S = 0 \qquad (45)$$

has an additional term compared to eq 39. Obviously, the diffusion-controlled and reflecting boundary conditions are identical to the previous case. But the more general radiation boundary condition has a slightly different appearance

$$(\mathbf{n}(\mathbf{D}\nabla\phi + \phi\nabla\cdot\mathbf{D} + \phi\mathbf{D}\nabla V) + k\phi)|_S = 0 \qquad (46)$$

Nevertheless the adjoint boundary condition remains identical to that of the traditional operator.

3.2. Diffusion-Controlled Recombination Probability. As an illustration of the formalism we calculate the recombination probability for a pair of particles that performs a free diffusion and recombine with certainty when the interparticle distance become equal to the distance of closest approach d. The probability that the particles have a separation r then satisfies the diffusion equation

$$\frac{\partial P(r,t)}{\partial t} = \frac{D}{r}\frac{\partial^2}{\partial r^2}rP(r,t) \qquad (47)$$

where $D = D_1 + D_2$ is the diffusion coefficient for the relative diffusion of the two particles (1 and 2). The boundary conditions for diffusion-controlled recombination are

$$P(d,t) = 0 \quad \text{and} \quad \lim_{r\to\infty} r^2P(r,t) = 0 \qquad (48)$$

The free diffusion operator is self-adjoint with these boundary conditions, so the backward equation has the same form. The survival probability $N(t)$ is obtained by setting $A(r) = 1$, and the recombination probability is calculated as $R(t) = 1 - N(t)$. The rate of recombination is thus $\dot{R}(t) = -\dot{N}(t)$. According to eq 34, the Laplace transformed rate of recombination satisfies

$$\left[s - \frac{D}{r_0}\frac{\partial^2}{\partial r_0^2}r_0\right]\dot{R}(r_0,s) = \left(\frac{D}{r_0}\frac{\mathrm{d}^2}{\mathrm{d}r_0^2}r_0\right)(-1) = 0 \qquad (49)$$

The inner boundary condition for $\dot{R}(r_0,s)$ follows from eq 35 by noting that the inner boundary condition in eq 48 implies that the boundary operator introduced in eq 21 is $\Lambda_r = \Lambda_{r_0} = 1$. This leads to

$$\dot{R}(d,s) = 1 \quad \text{and} \quad \lim_{r_0\to\infty}\dot{R}(r_0,s) = 0 \qquad (50)$$

The solution is immediately obtained as

$$\dot{R}(r_0,s) = \frac{d}{r_0}e^{-(s(r_0-d)^2/D)^{1/2}} \qquad (51)$$

By adding a term $-sP(r,t)$ to the right-hand side of eq 47, it is seen that the Laplace-transformed rate of the geminate recombination of a pair of particles with initial separation r_0 can be interpreted as the total (or ultimate) recombination probability in the presence of a homogeneously distributed scavenger with first-order rate constant s.[22]

4. The Stochastic Liouville Equation

We consider a quantum system with a Hamiltonian, and possibly other interactions, that depends on one or more classical parameters (denoted **r**) that are stochastic processes. The SLE describes the combined time evolution of the system and is

$$\frac{\partial}{\partial t}\rho(\mathbf{r},t) = [-i\mathrm{H}^\times(\mathbf{r}) + \Gamma_\mathbf{r}]\rho(\mathbf{r},t) \tag{52}$$

The Laplace-transformed SLE, for a more general situation, is

$$[s + i\mathrm{H}^\times(\mathbf{r}) + \hat{K}(\mathbf{r}) + \hat{R} - \Gamma_\mathbf{r}]\rho(\mathbf{r},s) = \rho_0(\mathbf{r}) \tag{53}$$

where we have included a superoperator $\hat{K}$ to describe spin-dependent recombination and a superoperator $\hat{R}$ for a phenomenological description of spin relaxation, e.g., by Bloch equations or Redfield theory. For typographical reasons, the quantum superoperators will be combined into

$$\hat{Q}(\mathbf{r}) = \mathrm{H}^\times(\mathbf{r}) - i\hat{K}(\mathbf{r}) - i\hat{R} \tag{54}$$

The hermitian and functionally adjoint operator is

$$\hat{Q}^\dagger(\mathbf{r}) = \mathrm{H}^\times(\mathbf{r}) + i\hat{K}(\mathbf{r}) + i\hat{R} \tag{55}$$

The Green's superoperator is defined by

$$[s + i\hat{Q}(\mathbf{r}) - \Gamma_\mathbf{r}]\hat{G}(\mathbf{r},\mathbf{r}_0;s) = \mathbf{I}\delta(\mathbf{r} - \mathbf{r}_0) \tag{56}$$

and the average value of an operator $A(\mathbf{r})$ can then be written as

$$\langle A\rangle(s) = \int\int\mathrm{Tr}[A(\mathbf{r})\hat{G}(\mathbf{r},\mathbf{r}_0;s)\rho_0(\mathbf{r}_0)]\,dV_0\,dV$$
$$= \langle A^\dagger|\hat{G}(s)|\rho_0\rangle = \langle A^\dagger|\rho(s)\rangle \tag{57}$$

where the Dirac notation combines the definitions from the pure quantum and the classical stochastic cases, cf. eqs 6 and 18. Equations 53 and 56 will both be denoted the forward SLE. The backward SLE corresponding to eq 56 is

$$[s - i\hat{Q}^\dagger(\mathbf{r}) - \Gamma_\mathbf{r}^+]\hat{G}^+(\mathbf{r},\mathbf{r}_0;s) = \mathbf{I}\delta(\mathbf{r} - \mathbf{r}_0) \tag{58}$$

In analogy with the classical stochastic processes, cf. eq 24, we define

$$A^+(\mathbf{r}_0,s) \equiv \int\hat{G}^+(\mathbf{r}_0,\mathbf{r};s)A^\dagger(\mathbf{r})\,dV \tag{59}$$

which satisfies the backward SLE

$$[s - i\hat{Q}^\dagger(\mathbf{r}_0) - \Gamma_{\mathbf{r}_0}^+]A^+(\mathbf{r}_0,s) = A^\dagger(\mathbf{r}_0) \tag{60}$$

The latter equation is proved from eq 58 by interchanging **r** and $\mathbf{r}_0$, multiplying from the right by $A^\dagger(\mathbf{r})$, and integrating over **r**.

The Green's superoperator has properties that combine those of the pure quantum, eq 9, and the classical stochastic case, eq 25. The fundamental relation is

$$\hat{G}^+(\mathbf{r},\mathbf{r}_0;s) = \hat{G}^\dagger(\mathbf{r}_0,\mathbf{r};s) \tag{61}$$

By using this property the average value of any physical observable can be written as

$$\langle A\rangle(s) = \int\int\mathrm{Tr}[\rho_0^\dagger(\mathbf{r}_0)\hat{G}^+(\mathbf{r}_0,\mathbf{r};s)A^\dagger(\mathbf{r})]^*\,dV_0\,dV \tag{62}$$

The average value can now be compactly written in a number of equivalent ways

$$\langle A\rangle(s) = \langle A^+(s)|\rho_0\rangle = \langle\rho_0|A^+(s)\rangle^*$$
$$= \langle\rho_0|\hat{G}^+(s)|A^\dagger\rangle^*$$
$$= \langle A^\dagger|\hat{G}(s)|\rho_0\rangle = \langle A^\dagger|\rho(s)\rangle \tag{63}$$

Equation 63 illustrates the different calculational procedures one can use to calculate the average value. One can calculate $\rho(\mathbf{r},s)$ from the forward eq 53 for a specific initial situation, specified by $\rho_0(\mathbf{r})$, and then take the scalar product with the observable $A(\mathbf{r})$. The advantage of this approach is that the average value of any observable can be calculated after the time-consuming step of solving the forward SLE has been performed. And several averages can be calculated as easily as a single one.

Alternatively, one can solve the backward eq 60 for a specific choice of the observable; the specification of the initial condition can be delayed to after the solution step. This method is often advantageous, as usually only one, or a few, observables are needed, and the solution is directly obtained for all initial conditions. The final scalar product with $\rho_0(\mathbf{r})$ just projects out the solution for a particular initial conditions.

A backward SLE for the rate of change of an observable A can also be derived. The derivation parallels that used for the classical stochastic processes, cf. eqs 31−36. By Laplace transforming the definition of the rate

$$\dot{A}(\mathbf{r}_0,t) = \frac{\partial A(\mathbf{r}_0,t)}{\partial t} \tag{64}$$

one gets

$$\dot{A}(\mathbf{r}_0,s) = sA(\mathbf{r}_0,s) - A(\mathbf{r}_0) \tag{65}$$

Multiplication of eq 60 with s and insertion of eq 65 gives

$$[s - i\hat{Q}^\dagger(\mathbf{r}_0) - \Gamma_{\mathbf{r}_0}^+]\dot{A}^+(\mathbf{r}_0,s) = [i\hat{Q}^\dagger(\mathbf{r}_0) + \Gamma_{\mathbf{r}_0}^+]A^\dagger(\mathbf{r}_0) \tag{66}$$

Once again, this equation is particularly useful for a calculation of the $t \to \infty$ limit of $\langle A\rangle(t)$, which, due to eq 33, can be obtained as the solution to eq 66 with $s = 0$, i.e., by solving

$$[i\hat{Q}^\dagger(\mathbf{r}_0) + \Gamma_{\mathbf{r}_0}^+]\dot{A}^+(\mathbf{r}_0,s=0) = -[i\hat{Q}^\dagger(\mathbf{r}_0) + \Gamma_{\mathbf{r}_0}^+]A^\dagger(\mathbf{r}_0) \tag{67}$$

This is generally much simpler to solve than eq 66. The boundary conditions for $A^+(\mathbf{r}_0)$ and $\dot{A}^+(\mathbf{r}_0)$ are identical to those for the classical case, eqs 26 and 35, with the exception that in general they contain a quantum operator which however is the same in all the boundary conditions.

5. Spin-Dependent Recombination

As an example of applications of the backward SLE, we calculate the singlet recombination yield of a geminate radical pair that is created in an unpolarized triplet state

$$\rho_0 = \frac{1}{3} (|T_0\rangle\langle T_0| + |T_+\rangle\langle T_+| + |T_-\rangle\langle T_-|) \qquad (68)$$

The effective initial separation of the RP, i.e., after any initial, fast relaxation of excess kinetic energy, is denoted r_0. The recombination is assumed to be local at the distance of closest approach d, and only singlet pairs are allowed to react. The superoperator describing the recombination (irreducible decay through the singlet channel) is thus

$$\hat{K}(r) = \frac{K\delta(r-d)}{4\pi d^2} \{|S\rangle\langle S|, \cdot\} \qquad (69)$$

where $\{,\}$ denotes the anticommutator. The value of the decay constant K must be chosen as the integral value of the short range $K(r)$ that it approximates, i.e.

$$K = \int_d^\infty K(r) 4\pi r^2 \, dr \qquad (70)$$

In high magnetic fields, the spin Hamiltonian of the RP can be written as

$$H = H_0 + H_{ex}(r) \qquad (71)$$

where H_0, the Hamiltonian of the free (separated) radicals, is the sum of the individual Hamiltonians

$$H_0 = \omega_{01}S_{12} + \omega_{02}S_{2z} \qquad (72)$$

with the effective Larmor frequencies, ω_{0n} ($n = 1$ and 2), depending on the nuclear spin state through the hyperfine interaction

$$\omega_{0n} = g_n\beta B + \sum_{j\in n} A_j m_j \qquad (73)$$

The inter-radical interaction, represented by $H_{ex}(r)$, is usually dominated by the exchange interaction. However, in the present example, we will neglect both inter-radical interactions and spin relaxation. Both interactions can be included but at the expense of significantly more complicated results.

Since the Hamiltonian H_0 conserves the projection of the total electron spin on the z axis, only the T_0 part of the initial triplet RP can be mixed with the reactive singlet state (S) and thus have a chance to react. Consequently, it is sufficient to work in the S$-$T$_0$ subspace.

The SLE for the system is

$$\frac{\partial\rho}{\partial t} = [-iH_0^\times - \hat{K}(r) + \Gamma_r]\rho(r,t) \qquad (74)$$

with a reflecting boundary conditions at the contact distance d

$$\frac{\partial\rho}{\partial r}\Big|_{r=d} = 0 \quad \text{and} \quad \lim_{r\to\infty} r^2\rho(r,t) = 0 \qquad (75)$$

If the relative motion of the radicals is assumed to be a free diffusion, then

$$\Gamma_r = D \frac{1}{r}\frac{\partial^2}{\partial r^2} r \qquad (76)$$

where $D = D_1 + D_2$ is the diffusion coefficient for the relative motion.

In the classical theory of diffusion-influenced reactions, it is well known that a local sink term describing the reaction can be included in the boundary condition rather than as a separate

term in the diffusion equation. Similarly, the spin-dependent recombination superoperator $\hat{K}(r)$ can be removed from the SLE (eq 74) by changing the boundary condition at $r = d$ to

$$-\frac{\partial\rho}{\partial r}\Big|_{r=d} + k\{|S\rangle\langle S|,\rho(d)\} = 0 \qquad (77)$$

In accordance with the classical recombination case, the average value of the identity operator is the survival probability

$$N(t) = 1 - R(t) = \langle\mathbf{I}\rangle = \text{Tr}[\rho(t)] \qquad (78)$$

The rate of change of the recombination probability $\dot{R}$ is therefore represented by the operator $-\mathbf{I}$, and it follows from eq 66 that the corresponding backward SLE is

$$\left[s - iH_0^\times - \frac{D}{r_0}\frac{\partial^2}{\partial r_0^2} r_0\right]\dot{R}(r_0,s) = 0 \qquad (79)$$

since the right-hand side of the equation vanishes

$$-\left[iH_0^\times + \frac{D}{r_0}\frac{\partial^2}{\partial r_0^2} r_0\right]\mathbf{I} = 0 \qquad (80)$$

To calculate the total recombination probability, we only have to solve eq 79 with $s = 0$. The matrix representation of this equation is diagonal in the direct product basis and can be written as

$$\frac{1}{x}\frac{d^2}{dx^2} x \begin{pmatrix} \dot{R}_1 \\ \dot{R}_2 \\ \dot{R}_3 \\ \dot{R}_3 \end{pmatrix} = -i \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 2q & 0 & 0 \\ 0 & 0 & -2q & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \dot{R}_1 \\ \dot{R}_2 \\ \dot{R}_3 \\ \dot{R}_3 \end{pmatrix} \qquad (81)$$

where the matrix elements have been enumerated in the following way

$$\{1, 2, 3, 4\} = \{(\alpha\beta, \alpha\beta), (\alpha\beta, \beta\alpha), (\beta\alpha, \alpha\beta), (\beta\alpha, \beta\alpha)\} \qquad (82)$$

and we have introduced the dimensionless variables

$$x = r_0/d \qquad (83)$$

$$q = \frac{|\omega_1 - \omega_2|}{2}\frac{d^2}{D} \qquad (84)$$

Equation 81 is a set of independent differential equations that are easily solved. The solution that vanishes for $x \to \infty$ can be written as

$$\dot{\mathbf{R}}(x) = \frac{1}{x}\begin{pmatrix} a_1 \\ a_2 \, e^{-q^{1/2}(x-1)} \, e^{-iq^{1/2}(x-1)} \\ a_3 \, e^{-q^{1/2}(x-1)} \, e^{-iq^{1/2}(x-1)} \\ a_4 \end{pmatrix} \qquad (85)$$

where, for convenience, the components of the solutions have been constructed such that their values at the distance of closest approach ($x = 1$) are equal to the coefficients a_j, which may be complex.

The inner boundary condition that follows from eqs 77 and 36 can be written in dimensionless form as

$$-\frac{d}{dx}\dot{\mathbf{R}}(x)_{x=1} + k\dot{\mathbf{R}}(1) = k\mathbf{I} \qquad (86)$$

where **k** and **I** are the matrix representations in superspace of the recombination superoperator and the identity operator, respectively. In the direct product basis of the superspace, with the numbering given by eq 82, these matrix representations are

$$\mathbf{k} = \frac{k}{2}\begin{pmatrix} 2 & -1 & -1 & 0 \\ -1 & 2 & 0 & -1 \\ -1 & 0 & 2 & -1 \\ 0 & -1 & -1 & 2 \end{pmatrix} \quad \mathbf{I} = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 1 \end{pmatrix} \quad (87)$$

with $k = K/(4\pi dD)$. Since **k** is nondiagonal in the direct product basis, it induces a coupling of the solutions in $\dot{\mathbf{R}}$. But the solutions are coupled only at the point $x = 1$ and thus it gives a set of simple algebraic equations in the four coefficients a_j

$$a_1(1 + k) - k(a_2 + a_3)/2 = k$$

$$a_4(1 + k) - k(a_2 + a_3)/2 = k$$

$$a_2(1 + q^{1/2}(1 - i) + k) - k(a_1 + a_4)/2 = -k$$

$$a_3(1 + q^{1/2}(1 + i) + k) - k(a_1 + a_4)/2 = -k \quad (88)$$

The decay constant k is not a particularly useful parameter as it cannot be measured. A more convenient parameter is $\Lambda = k/(1 + k)$ that equals the recombination yield of a singlet RP created at contact in the absence of spin effects.[13] The diffusion-controlled case corresponds to $\Lambda = 1$, and the effect of small deviations from diffusion controlled are then easily seen.

The solution to eq 88 with k replaced by Λ was derived by the symbolic computation system Maple and is

$$\dot{\mathbf{R}}(1) = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{pmatrix} = \frac{\Lambda}{\mathcal{N}}\begin{pmatrix} 1 + q^{1/2}(2 - \Lambda) + 2q(1 - \Lambda) \\ -1 - q^{1/2}(1 - \Lambda)(1 - i) \\ -1 - q^{1/2}(1 - \Lambda)(1 + i) \\ 1 + q^{1/2}(2 - \Lambda) + 2q(1 - \Lambda) \end{pmatrix} \quad (89)$$

where

$$\mathcal{N} = 1 + \Lambda + (2 - \Lambda^2)q^{1/2} + 2(1 - \Lambda)q \quad (90)$$

In the diffusion-controlled limit ($\Lambda = 1$), the solution simplifies significantly to

$$\dot{\mathbf{R}}(1) = \frac{1}{1 + 2q^{1/2}}\begin{pmatrix} 1 + q^{1/2} \\ -1 \\ -1 \\ 1 + q^{1/2} \end{pmatrix} \quad (91)$$

In the following, we utilize the previous notation for the fractional recombination yield, $F(x)$.[13] According to eq 63, the recombination probability for a specific initial spin configuration ρ_0 is obtained by the scalar product

$$\mathcal{F}(x) = \langle \rho_0 | \dot{R}(x) \rangle \quad (92)$$

For an unpolarized triplet, the initial spin density matrix is

$$\rho_0^{\dagger} = (1, 1, 1, 1)/6 \quad (93)$$

and the recombination probability for a RP created at the contact distance d ($x = 1$) is immediately obtained as

$$\mathcal{F}(1) = \frac{1}{3}\frac{\Lambda[q^{1/2} + 2(1 - \Lambda)q]}{1 + \Lambda + (2 - \Lambda^2)q^{1/2} + 2(1 - \Lambda)q} \quad (94)$$

which in the diffusion-controlled limit simplifies to the well-known expression

$$\mathcal{F}(1) = \frac{1}{6}\sum_{j=1}^{4} a_j = \frac{1}{3}\frac{q^{1/2}}{2 + q^{1/2}} \quad (95)$$

Equation 95 and, in a differrent form, eq 94 have been derived before by other techniques[7,9,12] which, however, involves significantly more complicated mathematics. Another advantage of the present method is that the recombination probability for an arbitrary initial separation can be obtained immediately. One simply has to substitute the calculated values of the coefficients a_j into the solution vector (eq 85) and calculate the scalar product (eq 92) for the specified value of x. This immediately leads to

$$\mathcal{F}(x) = \frac{\Lambda}{x\mathcal{N}}\{1 + q^{1/2} - e^{-q^{1/2}(x-1)}\cos(q^{1/2}(x - 1)) + (1 - \Lambda)q^{1/2}[1 + 2q^{1/2} - (\cos(q^{1/2}(x - 1)) + \sin(q^{1/2}(x - 1)))\,e^{-q^{1/2}(x-1)}]\} \quad (96)$$

which for $\Lambda = 1$ reduces to a previously derived expression.[23]

Radical pair reactions are usually considered to be diffusion controlled, and the expressions are also simpler in this limit. Thus it would be convenient to be able to calculate these limiting results directly. This, however, is not straightforward. Taking the $K \to \infty$ limit of the boundary conditions (eq 88) gives a set of useless equations, and a different strategy is needed.

In the diffusion-controlled limit, the singlet probability must satisfy the absorbing boundary condition, i.e., $\rho_{SS}(d) = 0$ while the unreactive triplet RPs must satisfy the reflecting boundary condition, i.e., $\partial\rho_{T_0T_0}(x)/\partial x|_{x=1} = 0$. By transforming these two equations into the direct product basis, one gets

$$a_1 + a_4 - (a_2 + a_3) = 2$$

$$a_1 + a_4 + (a_2 + a_3)(1 + q^{1/2}) - iq^{1/2}(a_2 - a_3) = 0 \quad (97)$$

It is not clear what kind of boundary conditions the off-diagonal elements should have in the singlet−triplet basis. Fortunately, they are not needed. It follows from the definition of the matrix elements that $a_2 = a_3^*$. Moreover, $a_1 = a_4$ due to the permutation symmetry. But the crucial point is that a diffusion-controlled reaction will destroy all phase elements at the reaction distance. Consequently, the off-diagonal elements a_2 and a_3 must be equal and real. Inserting these relations into eq 97 yields

$$a_1 + a_2(1 + q^{1/2}) = 0$$

$$a_1 - a_2 = 1 \quad (98)$$

It is immediately seen that these simple relations have the previously found solution, eq 91.

6. Conclusion

The backward SLE has some advantages compared to the usual SLE with respect to obtaining analytical and numerical results. However, to apply the backward SLE, the correct boundary conditions are needed, and these are usually different from those used for the forward SLE. The general boundary conditions were derived above and exemplified to standard

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recombination problems of particles with spins. These boundary conditions contain elements from the quantum part as well as from the stochastic part. Therefore we have included a complete derivation of the backward diffusion equation and added a simple but important application. In this new approach, we derived all the relevant boundary conditions for the backward diffusion equations corresponding to the two standard diffusion equations.

The $t \to \infty$ limit of the average value of an observable A can be calculated directly, i.e., without performing any limiting process, by introduction of the rate of change of the observable ($\dot{A}$). These two quantities have different initial and boundary conditions to be used in the backward SLE. It was also shown that the diffusion-controlled limit can be calculated directly, rather than as the limit of a general solution. This procedure requires a careful consideration of the boundary conditions.

It was demonstrated that the backward SLE is useful for deriving analytic results. For a local interaction, the calculation essentially consists of solving the backward diffusion equation for various values of the Laplace transform variable and then combining these functions into a combination that satisfies the boundary conditions. These relatively simple operations can be time consuming with voluminous intermediate expressions, but this can be taken care of by symbolic computation (algebra) systems that are well suited for such operations. With the continuous development of such systems, more and more complicated problems may be expected to be solved analytically. In particular, one may expect to see more analytic solutions for the diffusion-controlled case. New computational procedures with partly analytic and partly numerical calculations may also be expected to appear. The backward SLE is an ideal platform for such calculations.

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