Non-stochastic matrix Schrödinger equation for open systems

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We propose an extension of the Schrödinger equation for a quantum system interacting with environment. This equation describes dynamics of auxiliary wave-functions $m$, from which the system density matrix can be reconstructed as $\hat{\rho} = m m\dagger$. We formulate a compatibility condition, which ensures that the reconstructed density satisfies a given quantum master equation for the system density. The resulting non-stochastic evolution equation preserves positive-definiteness of the system density and is applicable to both Markovian and non-Markovian system-bath treatments. Our formalism also resolves a long-standing problem of energy non-conservation in the time-dependent variational principle applied to mixed states of closed systems.

Introduction.— Quantum evolution of a statistical mixture of quantum states is governed by the Liouville-von Neumann (LvN) equation $\dot{\rho} = -i[\hat{H}, \hat{\rho}]$, where $\hat{H}$ is the Hamiltonian of a system and $\hat{\rho}$ is the corresponding density matrix (DM). The use of a DM in place of a Schrödinger wavefunction reflects a limited degree of knowledge about a quantum statistical mixture. The ability of a DM to describe statistical phenomena becomes essential in studies of an open quantum system interacting with its environment, since the exact quantum state of the environment is usually impossible to track or to control [1]. Dynamics of an open quantum system can be described by an appropriately modified LvN equation

$$\dot{\rho} = -i[\hat{H}, \hat{\rho}] + \mathcal{N}[\rho],$$

(1)

where a super-operator $\mathcal{N}$ describes non-unitary evolution of the system due to interaction with the environment and associated processes of relaxation, dissipation, and decoherence. We shall refer to Eq. (1) as the quantum master equation (QME). QME can be either postulated phenomenologically or derived from a microscopic Hamiltonian for the open system and its environment by integrating out environmental degrees of freedom (DOF) [1].

Despite its advantages, the DM-based formalism has a few problems. First, the number of variables that are necessary to describe a pure state $|\psi\rangle$ by a DM as $\hat{\rho} = |\psi\rangle\langle\psi|$ grows as a square of the Hilbert space size $\mathcal{D}_\mathcal{H}$ for the $|\psi\rangle$ representation. One might expect then for a mixture of $N$ states $\mathcal{D}_\mathcal{H} \times N$ variables are sufficient if an analog of a Schrödinger wavefunction would exist, whereas the DM formalism still depends on $\mathcal{D}_\mathcal{H}^2$ variables. Thus, if $N \ll \mathcal{D}_\mathcal{H}$, the DM representation seems to be excessively expensive.

Second, a reduction of the Hilbert space size in quantum propagations can be achieved by using time-evolving basis functions. The time-dependent variational principle (TDVP) has been successfully used to obtain equations of motion for time-evolving basis functions in wavefunction-based frameworks [2–6]. Attempts to generalize the TDVP to the density formalism leads to dynamics that does not conserve energy for isolated mixed-state systems. [7, 8] Mathematical roots of this problem is in conservation of the $\text{Tr}\{\hat{\rho}^2\hat{H}\}$ quantity by the density TDVP formulation instead of the system energy $E = \text{Tr}\{\hat{\rho}\hat{H}\}$.

Finally, when the non-unitary part $\mathcal{N}$ of Eq. (1) is not a generator of a completely positive map (e.g., not in the Lindblad form [9] for Markovian dynamics), the DM may cease to be positively definite [10–12], which was deemed to be unphysical [9, 13]. Later, it has been found [14, 15] that approximations used in derivation of Eq. (1) are not the only reason for non-positivity of the reduced density, and assumptions on the initial conditions of the full system + environment density can also destroy positivity of the system reduced density.

All these problems of the DM-based formalism prompted a search for an analog of the Schrödinger equation (SE) to describe statistical ensembles of states (mixed states). A handful of approaches of that spirit exist in the literature. Quantum state diffusion [16, 17] and quantum jumps [18, 19] methods are stochastic SE approaches which can describe both Markovian and non-Markovian dynamics via propagation of wavefunction realizations. However, the propagation is stochastic, and simulations must be converged in the number of stochastic trajectories. Another approach is propagation of a square-root of the density matrix [20]. This approach was developed only for the Lindblad type of QME [9], and even within the Lindblad scope the resulting equations of motion are not fully equivalent to the initial QME.

In what follows we introduce a formalism that generalizes the SE to mixed states and open systems. It leads to non-stochastic equations of motion that are completely equivalent to the solution of the corresponding QME, preserve the positive definiteness of the density matrix, are capable to describe the non-Markovian dynamics of mixed states in open systems, and conserve the energy of an isolated mixed-state when combined with the TDVP.
Theory.— We begin by considering the system and its environment as an isolated super-system described by a total wavefunction $|\Psi\rangle$. Introducing a complete set of individual states of the environment (“bath states”) $\{|\Psi_{B,s}\rangle\}_{s=1}^{\infty}$, we expand the total wavefunction as

$$|\Psi\rangle = \sum_s |\psi_s\rangle |\Psi_{B,s}\rangle.$$  

(2)

Coefficients $|\psi_s\rangle = \langle \Psi_{B,s}|\Psi\rangle$ are the functions of the system DOF because the integration is performed over the bath DOF only.

The reduced density matrix $\hat{\rho}$ of the system is obtained from the total density matrix $\hat{\rho}_{\text{tot}} = |\Psi\rangle \langle \Psi|$ by tracing out the bath, $\hat{\rho} = \text{Tr}_B \{\hat{\rho}_{\text{tot}}\} = \sum_s |\psi_s\rangle \langle \psi_s|$. Assuming a basis set representation for $|\psi_s\rangle$, the reduced density can be presented in the matrix form

$$\hat{\rho} = mm^\dagger,$$

(3)

Thus, $m$ is a matrix which can be thought of as a square root of $\hat{\rho}$. We will construct a non-stochastic open system Schrödinger equation (NOSSE) for the wavefunctions $m$ in the following general form [21]

$$m = -i\hat{H}m + \mathcal{O}[m],$$

(4)

where $\mathcal{O}[m]$ is a functional of $m$, which is responsible for relaxation, dissipation, and decoherence due to interaction with the environment. The central idea of this Letter is that the form of $\mathcal{O}[m]$ can be obtained exactly from the expression for the non-unitary propagator $\mathcal{N}[\hat{\rho}]$ of the QME in Eq. (1). Introducing the density decomposition of Eq. (3) into the QME and demanding that Eq. (4) is satisfied, $\mathcal{O}[m]$ is determined as a solution of the following equation:

$$\mathcal{O}[m]m^\dagger + mm^\dagger = \mathcal{N}[mm^\dagger].$$

(5)

Multiplication of Eq. (5) by $m^\dagger$ and $m$ from left and right, respectively, leads to a $\ast$-Sylvester equation [22]

$$m^\dagger \mathcal{O}[m] (m^\dagger m) + (m^\dagger m) \mathcal{O}[m] m^\dagger m = m^\dagger \mathcal{N}[mm^\dagger] m$$

(6)

with $m^\dagger \mathcal{O}[m]$ and its Hermitian conjugate as the new unknowns. The solution of Eq. (6) exists if and only if the $m^\dagger m$ matrix is invertible [22]. To recover $\mathcal{O}[m]$ from the solution of Eq. (6) one needs to compute $m^{-1}$. The existence of $m^{-1}$ guarantees positivity of all eigenvalues of the density $\hat{\rho}$.

Equations (4) and (5) constitute a set of coupled equations, whose solution is entirely equivalent to the solution of QME with a positive-defined density matrix $\hat{\rho}$. In many important cases one can bypass the numerical solution of Eq. (5) by obtaining the form of $\mathcal{O}[m]$ through visual inspection. For example, if $\mathcal{N}[\hat{\rho}]$ is in the Lindblad form [9], $\mathcal{N}[\hat{\rho}] = \sum_j 2\hat{L}_j\hat{\rho}\hat{L}_j - \hat{L}_j\hat{\rho}\hat{L}_j - \hat{\rho}\hat{L}_j\hat{L}_j$, then it is easy to check that $\mathcal{O}[m] = \sum_j \hat{L}_j m (m^{-1}\hat{L}_j m)^\dagger - \hat{L}_j^\dagger \hat{L}_j m$. Another example of the explicit solution of Eq. (5) is the time convolutionless master equation [1] considered as a numerical illustration below.

In fact, Eq. (5) admits a whole family of solutions: if $\mathcal{O}[m]$ obeys Eq. (5) then $\mathcal{O}'[m] = \mathcal{O}[m] + imG$ with a Hermitian matrix $G$ also satisfies the same equation. $G$ gives rise to phase dynamics that is insignificant for any observable properties. To show this, let us expand $m$ in an orthonormal basis set as $m = \varphi^T A$, where $\varphi^T = (|\varphi_1\rangle |\varphi_2\rangle \ldots)$ is a vector of basis functions, and $A$ is a matrix of coefficients. Introducing this expansion into Eq. (4) and considering for the simplicity a closed system ($N = 0$, $\mathcal{O}[m] = imG$), we obtain

$$\varphi^T A \varphi^T \hat{A} = -i\hat{H} \varphi^T A + i\varphi^T AG.$$  

(7)

If we substitute $A$ by $A \exp(itG)$, then the last term in the right-hand side of Eq. (7) will be cancelled. The reduced density $\hat{\rho}$ assembled from $m_G = \varphi^T A \exp(itG)$ by Eq. (3) does not depend on $G$. Thus, the ambiguity in the solution of Eq. (5) is compensated by the phase transformation of $A$ providing the $G$-invariant formalism.

The proposed approach allows for extremely simple calculations of eigen-spectra for both closed and open systems. The autocorrelation function $C(t)$ of the “system+environment” super-system is

$$C(t) = \langle \Psi(0)|\Psi(t)\rangle = \sum_s \langle \psi_s(0)|\psi_s(t)\rangle_s \equiv \text{Tr}_S \{m(0)m^\dagger(t)\}.$$  

(8)

The Fourier transform of $C(t)$ gives the spectrum [23]

$$I(E) = \int_{-\infty}^{+\infty} C(t) \exp(-itE) \, dt.$$  

(9)

To solve Eq. (4) numerically, we specify $m$ at $t = 0$ using the Schmidt decomposition [24] of the initial density matrix:

$$\hat{\rho}(0) = \sum_{j=1}^N \omega_j |\varphi_j(0)\rangle \langle \varphi_j(0)|,$$

(10)

and assigning the components of $m$ to be $|\psi_j\rangle = \sqrt{\omega_j}|\varphi_j(0)\rangle$. In Eq. (10), $N$ is the number of states in the ensemble, and if each of $|\varphi_j(0)\rangle$ is described by a linear combination of $\mathcal{D}_H$ Hilbert space vectors, then $m(0)$ is a $\mathcal{D}_H \times N$ rectangular matrix. In some cases (e.g., the environment heats up the initially cold system or one starts from a pure state) the states that were not populated initially but are expected to be populated later should be added (with numerically small weights) to the ensemble. In such cases $N$ should be adjusted accordingly, but if $N \ll \mathcal{D}_H$, the $m$ representation is still more compact and efficient than the DM counterpart.
Numerical examples. — Our first example shows the NOSSE ability to recover the exact solution of the QME equation for non-adiabatic non-Markovian dynamics of an open system. We demonstrate that our approach allows for a flexible control of the numerical efforts needed to obtain converged results. Also, we employ our formalism to calculate the spectrum of the system in the presence of a bath. It is noteworthy that the non-zero widths of spectral lines come out naturally—a result, which is very hard to obtain with other methods.

The model describes population transfer between two electronic states, donor and acceptor, which are interacting with a harmonic bath. The system is characterized by a two-dimensional linear vibronic coupling (LVC) Hamiltonian written in frequency- and mass-weighted coordinates

$$\hat{H} = \sum_{j=1}^{2} \frac{\omega_j}{2} (\hat{p}_j^2 + \hat{x}_j^2) 1_2 + \left( \frac{A}{2} - d \hat{x}_1 \right) \sigma_z + c \hat{x}_2 \sigma_x,$$

(11)

where $1_2$ is the $2 \times 2$ unit matrix, $\sigma_x$ and $\sigma_z$ are the Pauli matrices. A discretized Ohmic spectral density bath of $N_b$ harmonic oscillators with frequencies $\Omega_k$ is coupled linearly to the $\hat{x}_2$ coordinate with coupling strengths $\lambda_k$. Numerical values of all parameters as well as initial conditions are given in the supplemental material [25].

The QME is obtained using the time convolutionless approach up to the second order in the system-bath interaction [1]

$$\dot{\hat{\rho}} = -i \left[ \hat{H}, \hat{\rho} \right] - \left( [\hat{x}_2, \hat{x}_2(t)] \hat{\rho} + [\hat{\rho} \hat{x}_2(t)^\dagger, \hat{x}_2] \right), \quad (12)$$

$$\hat{x}_2(t) = -\int_0^t e^{-i t' H} \hat{x}_2 e^{i t' H} \sum_{k=1}^{N_b} \frac{\lambda_k^2}{2} e^{i \Omega_k t'} dt'.$$

(13)

The non-unitary part $O[m]$ of NOSSE directly follows from Eqs. (12) and (5)

$$O[m] = \hat{x}_2 m \left( [m^{-1} \hat{x}_2(t) m]^{\dagger} - [m^{-1} \hat{x}_2(t) m] \right). \quad (14)$$

The inverse of the rectangular matrix $m$ in Eq. (14) is understood as the pseudo-inverse [26]: $m^{-1} = (m^\dagger m)^{-1} m^\dagger$, so that the inversion is possible if and only if Eq. (6) admits a solution at time $t$.

To simulate converged population dynamics (Fig. 1) the QME approach employed 240 basis functions, which correspond to 28920 independent matrix elements in $\hat{\rho}$. As few as $N = 14$ states in the ensemble provided a very good agreement between NOSSE and QME calculations, and with $N = 34$ the results are converged. This leads to only 3360 and 8160 matrix elements in NOSSE propagations for $N = 14$ and $N = 34$, respectively. To choose the ensemble states we use not only the population criterion in the initial density Schmidt decomposition but also the system and environment energy scales corresponding to the model dynamics [25].

Spectrum calculations [Eq. (9)] for this model require more ensemble states to obtain converged results ($N = 96$, Fig. 2) than in the population dynamics simulations. QME-based autocorrelation functions provide not eigenvalue spectra but rather transition spectra where peaks are associated with eigenvalue differences. Hence, we compare the open-system eigen-spectrum computed within the NOSSE formalism against its closed-system counterpart calculated by the exact diagonalization of the Hamiltonian in Eq. (11). The spectrum of the open system indeed shows all expected features: red shifts due to the system-bath interaction (friction) and finite spectral widths due to finite lifetimes of system states.

Our second example shows how the NOSSE formalism combined with the TDVP leads to a set of equations of

![FIG. 1. Dynamics of the donor state population $P(t) = \text{Tr} \{ \hat{\rho}(t) [1 + \sigma_z] \}] / 2$ starting from the Boltzmann distribution of the donor state at $T = 1000K$. The bath is at the Boltzmann distribution with $T = 0K$.](image)

![FIG. 2. The eigen-spectrum [Eq. (9)] obtained from the dynamics of the open system using NOSSE (solid black). Red sticks are the eigenvalues from the exact diagonalization of the Hamiltonian in Eq. (11).](image)
motion that conserve the energy of an isolated system. The TDVP allows one to derive approximate equations of motion when basis functions and their coefficients are time-dependent [7]. For the DM formalism the TDVP amounts to minimization of the Hilbert-Schmidt norm of an operator $\|\hat{\rho} + i[H, \hat{\rho}]\|$. In the NOSSE formalism we minimize $\|\hat{m} + iH\hat{m}\|$.

Consider an isolated system described by the Hamiltonian in Eq. (11). To apply the TDVP, we employ a linear combination of Gaussian products

$$\hat{\rho} = \sum_{j,k=1}^{N_d} |g_j\rangle B_{jk} \langle g_k|,$$

(15)

$$\langle x_1 x_2 | g_k \rangle = \exp \left[ \sum_{j=1}^{2} \left( -\frac{\omega_j}{2} x_j^2 + \xi_{j,k} x_j \right) \right].$$

(16)

The widths of Gaussian functions $g_k$ are frozen ($\omega_j = 0$), whereas $B = \{B_{jk}\}$ and $\xi = \{\xi_{j,k}\}$ are the time-dependent quantities to be optimized via the TDVP. The resulting equations of motion are

$$\dot{B} = -S^{-1}(iH + \tau)B + B(iH - \tau)S^{-1},$$

$$\dot{\xi} = C^{-1}Y,$$

(17)

(18)

where $S_{kl} = \langle g_k | g_l \rangle$, $\tau_{kl} = \langle g_k | \frac{\partial \rho}{\partial t} \rangle$, $H_{kl} = \langle g_k | \hat{H} | g_l \rangle$, $C_{\alpha\beta}^{k l} = \left\langle \frac{\partial g_k}{\partial \lambda_{\alpha,k}} \left[ \hat{1} - \hat{P}_{N_N} \right] \frac{\partial g_l}{\partial \lambda_{\beta,l}} \right\rangle [BSB]_{jk}$, $[Y]_{kl}^\alpha = -i \sum_t \left\langle \frac{\partial g_k}{\partial \lambda_{\alpha,k}} \left[ \hat{1} - \hat{P}_{N_N} \right] \hat{H} \hat{\rho} \right\rangle B_{lk}$,

(19)

(20)

and $\hat{P}_{N_N} = \sum_{m,n} |g_m\rangle [S^{-1}]_{mn} |g_n\rangle$. On the other hand, applying the TDVP to NOSSE recovers Eqs. (17) and (18) with new $C$ and $Y$

$$C_{\alpha\beta}^{k l} = \left\langle \frac{\partial g_k}{\partial \lambda_{\alpha,k}} \left[ \hat{1} - \hat{P}_{N_N} \right] \frac{\partial g_l}{\partial \lambda_{\beta,l}} \right\rangle B_{lk},$$

(21)

$$[Y]_{kl}^\alpha = -i \sum_t \left\langle \frac{\partial g_k}{\partial \lambda_{\alpha,k}} \left[ \hat{1} - \hat{P}_{N_N} \right] \hat{H} \right\rangle B_{lk}.$$  

(22)

To expose the problem of energy conservation we used a different set of parameters and initial conditions [25]. The total energy of the system as a function of time is plotted in Fig. 3. It is clear, that TDVP equations based on NOSSE definitions [Eqs. (21) and (22)] are able to conserve the total energy of an isolated system, whereas the DM counterparts [Eqs. (19) and (20)] are not.

**Conclusions.**—We introduced a non-stochastic analog of the Schrödinger equation for open systems that involves the ensemble of wave functions. The equations of motion for the ensemble is made to reproduce the QME evolution for the system density. Our formalism possesses many virtues: it guarantees completely positive evolution of the density matrix (as long as the solution exists), it is applicable to Markovian and non-Markovian treatments of system-bath interaction, and it provides an easy access to the system spectrum. From a numerical standpoint, our formalism is more computationally efficient since the number of dynamical variables is no longer quadratic with respect to size of the Hilbert space. The new approach is compatible with the TDVP formalism, since it leads to total energy conservation for closed systems and can be applied in investigating photochemical reactions induced by incoherent light.

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[1] H.-P. Breuer and F. Petruccione, eds., *The Theory of Open Quantum Systems* (Oxford University Press, New York, 2002).
[2] M. Beck, A. Jäckle, G. Worth, and H.-D. Meyer, Phys. Rep. **324**, 1 (2000).
[3] G. A. Worth, M. A. Robb, and I. Burghardt, Farad. Discuss. **127**, 307 (2004).
[4] M. Ben-Nun and T. J. Martinez, Adv. Chem. Phys. **121**, 439 (2002).
[5] K. Saita and D. V. Shalashilin, J. Chem. Phys. **137**, 22A506 (2012).
[6] A. F. Izmaylov, J. Chem. Phys. **138**, 104115 (2013).
[7] A. McLachlan, Mol. Phys. **8**, 39 (1964).
[8] A. Raab and H.-D. Meyer, Theor. Chem. Acc. **104**, 358 (2000).
[9] G. Lindblad, Commun. Math. Phys. **48**, 119 (1976).
[10] R. Düümecke and H. Spohn, Z. Physik B **34**, 419 (1979).
[11] A. van Wonderen and K. Lendi, J. Stat. Phys. **80**, 273 (1995).
[12] F. Benatti, R. Floreanini, and M. Piani, Phys. Rev. A 67, 042110 (2003).
[13] R. Alicki, in Quantum Dynamical Semigroups and Applications, Lecture Notes in Physics, Vol. 286 (Springer Berlin Heidelberg, 1987) pp. 1–94.
[14] P. Pechukas, Phys. Rev. Lett. 73, 1060 (1994).
[15] R. Alicki, Phys. Rev. Lett. 75, 3020 (1995).
[16] L. Diosi and W. T. Strunz, Phys. Lett. A 235, 569 (1997); W. T. Strunz, L. Diosi, and N. Gisin, Phys. Rev. Lett. 82, 1801 (1999).
[17] J. T. Stockburger and H. Grabert, Chem. Phys. 268, 249 (2001); Phys. Rev. Lett. 88, 170407 (2002).
[18] J. Piilo, S. Maniscalco, K. Härkönen, and K.-A. Suominen, Phys. Rev. Lett. 100, 180402 (2008).
[19] P. Rebentrost, R. Chakraborty, and A. Aspuru-Guzik, J. Chem. Phys. 131, 184102 (2009).
[20] A. Yahalom and R. Englman, Physica A 371, 368 (2006); J. Mol. Struct. Proceedings of the Symposium on the Jahn-Teller Effect, 838, 27 (2007).
[21] S. Mukamel, in Principles of Nonlinear Optical Spectroscopy (Oxford University Press, New York, 1995) p. 35.
[22] D. Kressner, C. Schröder, and D. S. Watkins, Numer. Algorithms 51, 209 (2009).
[23] D. J. Tannor, in Introduction to Quantum Mechanics: A Time-Dependent Perspective (University Science Books, Sausalito, California, 2007) p. 82.
[24] I. Peschel, Braz. J. Phys. 42, 267 (2012).
[25] L. Joubert-Doriol, I. G. Ryabinkin, and A. F. Izmaylov, “Non-stochastic matrix Schrödinger equation for open systems: Supplemental material,” (2014).
[26] E. H. Moore, Bull. Amer. Math. Soc. 26, 394395 (1920); R. Penrose, Math. Proc. Cambridge 51, 406 (1955).