Variational principle for stochastic wave and density equations

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We develop a stochastic generalization of the McLachlan variational principle and show that it can be used to derive known stochastic wave equations. We then use it to obtain an exact probability preserving stochastic density decomposition for vibrational dynamics problems with pairwise interaction.

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The time-dependent McLachlan variational principle [1] can be employed to derive self-consistent field (SCF) equations [2,3] as well as multiconfiguration [4] and correlation correcting [5] generalizations of SCF. Since the McLachlan functional is the mean square error, the resulting equations are optimal for a given trial wave function. They usually also conserve norm.

Recently there have been a number of attempts to model the solutions of deterministic equations with sets of lower dimensional stochastic wave equations. For example, the reduced subsystem density of the completely-positive-dynamical-semigroup (CPDS) master equation [6] has been exactly decomposed as a stochastic average over diadics constructed from the solutions of stochastic wave equations [7]. Similar methods have been developed for master equations which are not of CPDS form [8]. Exact *N*-body solutions of the Liouville–von Neumann equation have also been obtained using one-body stochastic waves for pairwise interacting bosons [9] and fermions [10].

A variational principle could prove useful in deriving new stochastic decompositions. When a known stochastic decomposition is exact and the equations are norm conserving, then the decomposition is probably optimal. When the norm is not conserved (as in Refs. [9] and [10]) or the decomposition is only approximate, a variational principle could prove useful in determining the optimal equations.

In this manuscript we introduce a stochastic generalization of the McLachlan variational principle [1]. We first review the details of the deterministic variational principle. The stochastic generalization is best illustrated by example so we consider two different problems. We first use the variational principle to find the norm-conserving exact decomposition of the CPDS master equation, originally derived by Gisin and Percival [7]. Next we derive a new exact norm-conserving stochastic decomposition of the Liouville–von Neumann equation for vibrational dynamics with pairwise interactions. Finally, we discuss an alternative form for the variational principle. Throughout we use the Itô stochastic calculus [11] and units in which $\hbar=1$.

The deterministic McLachlan variational principle [1] for the Schrödinger wave equation $\dot{\psi}+iH\psi=0$ has a functional $\mathcal{F}=\|\dot{\psi}+iH\psi\|^2$ in which the wave function itself is assumed known but its rate of change $\dot{\psi}$ is to be determined. To obtain time-dependent SCF equations for vibrations, for example, we assume a trail wave function $\psi=\Pi_{j=1}^{N}\phi_j(x_j)$ for N modes with coordinates x_j. Allowing all possible variations $\delta\dot{\phi}_j$ then gives equations $\dot{\phi}_j+iH_j\phi_j=0$, where $H_j=\Pi_{k\neq j}\langle\phi_k|H|\phi_k\rangle$ is the SCF Hamiltonian of mode j. For the Liouville–von Neumann equation of the density matrix $\rho(t)$ the functional takes the form $\mathcal{F}=\|\dot{\rho}+iL\rho\|^2$ where $L=[H,\cdot\,]$ is the Liouville operator and the indicated norm is $\|x\|^2=\mathrm{Tr}\{x^\dagger x\}$. The unknown is again $\dot{\rho}$.

Generalizing the McLachlan variational principle [1] is straightforward. One simply replaces the unknown deterministic time derivative by the coefficients of the order dt terms from a stochastic differential. Consider the following examples.

(1) Stochastic waves for the CPDS master equation. Gisin and Percival [7] obtained an exact norm-preserving stochastic wave decomposition $\rho(t)=M[|\psi(t)\rangle\langle\psi(t)|]$ for the CPDS master equation

$$d\rho(t)/dt=-i[H,\rho(t)]-S^\dagger S\rho(t)-\rho(t)S^\dagger S+2S\rho(t)S^\dagger, \tag{1}$$

where $M[\ ]$ denotes an expectation over the stochastic waves $|\psi(t)\rangle$. We will now show that the stochastic wave equations they obtained for $|\psi(t)\rangle$ can be derived very simply from a stochastic generalization of the McLachlan variational principle.

The stochastic wave must satisfy an equation of the general form

$$d|\psi(t)\rangle=|v(t)\rangle dt+|u(t)\rangle d\alpha(t), \tag{2}$$

where $|v\rangle$ represents a deterministic drift term and $|u\rangle$ the stochastic part. Here $\alpha(t)$ is a real Wiener process satisfying $M[d\alpha(t)]=0$, $M[d\alpha(t)d\alpha(t)]=dt$. Consider a functional $\mathcal{F}$ of the unknowns $|v\rangle$ and $|u\rangle$ of the form

$$\begin{aligned}\mathcal{F}=\|&|v\rangle\langle\psi|+|\psi\rangle\langle v|+|u\rangle\langle u|+iH|\psi\rangle\langle\psi|-i|\psi\rangle\langle\psi|H\\&+S^\dagger S|\psi\rangle\langle\psi|+|\psi\rangle\langle\psi|S^\dagger S-2S|\psi\rangle\langle\psi|S^\dagger\|^2,\end{aligned} \tag{3}$$

where the norm is $\|x\|^2=\mathrm{Tr}\{x^\dagger x\}$. Note that we have simply replaced $d\rho(t)/dt$ in the density form of the McLachlan functional with the order dt terms of $d[|\psi\rangle\langle\psi|]=d[|\psi\rangle]\langle\psi|+|\psi\rangle d[\langle\psi|]+d[|\psi\rangle]d[\langle\psi|]$, in accord with the Itô calculus [11].

Allowing independent variations δv and δu, the minimum error is then given by the condition

$$\delta\mathcal{F}=0=2\,\mathrm{Tr}\{[|\delta v\rangle\langle\psi|+|\psi\rangle\langle\delta v|+|\delta u\rangle\langle u|+|u\rangle\langle\delta u|]\times[|v\rangle\langle\psi|+|\psi\rangle\langle v|+|u\rangle\langle u|+iH|\psi\rangle\langle\psi|-i|\psi\rangle\langle\psi|H+S^{\dagger}S|\psi\rangle\langle\psi|+|\psi\rangle\langle\psi|S^{\dagger}S-2S|\psi\rangle\langle\psi|S^{\dagger}]\}, \tag{4}$$

which leads [assuming that $\langle\psi(t)|\psi(t)\rangle=1$] to equations

$$|v\rangle+[\langle v|\psi\rangle-i\langle\psi|H|\psi\rangle+\langle\psi|S^{\dagger}S|\psi\rangle]|\psi\rangle+\langle u|\psi\rangle|u\rangle+iH|\psi\rangle+S^{\dagger}S|\psi\rangle-2\langle\psi|S^{\dagger}|\psi\rangle S|\psi\rangle=0, \tag{5}$$

$$\langle\psi|u\rangle|v\rangle+[\langle v|u\rangle-i\langle\psi|H|u\rangle+\langle\psi|S^{\dagger}S|u\rangle]|\psi\rangle+\langle u|u\rangle|u\rangle+i\langle\psi|u\rangle H|\psi\rangle+\langle\psi|u\rangle S^{\dagger}S|\psi\rangle-2\langle\psi|S^{\dagger}|u\rangle S|\psi\rangle=0. \tag{6}$$

Solving Eq. (5) for $|v\rangle$ and substituting into Eq. (6) gives the equation

$$[\langle u|u\rangle-\langle u|\psi\rangle\langle\psi|u\rangle]|u\rangle+[\langle v|u\rangle-\langle v|\psi\rangle\langle\psi|u\rangle-i\langle\psi|H|u\rangle+i\langle\psi|H|\psi\rangle\langle\psi|u\rangle+\langle\psi|S^{\dagger}S|u\rangle-\langle\psi|S^{\dagger}S|\psi\rangle\langle\psi|u\rangle]|\psi\rangle-2[\langle\psi|S^{\dagger}|u\rangle-\langle\psi|S^{\dagger}|\psi\rangle\langle\psi|u\rangle]S|\psi\rangle=0, \tag{7}$$

which [along with Eq. (5)] tells us that

$$|u\rangle=a|\psi\rangle+bS|\psi\rangle,$$

$$|v\rangle=c|\psi\rangle+dS|\psi\rangle-iH|\psi\rangle-S^{\dagger}S|\psi\rangle, \tag{8}$$

where a, b, c, and d are to be determined. Substituting Eq. (8) into Eq. (7) then gives

$$|u\rangle=-\frac{d^*}{b^*}|\psi\rangle+\frac{2}{b^*}S|\psi\rangle \tag{9}$$

which when compared with Eq. (8) implies that $|b|^2=2$ and so $b=\sqrt{2}=b^*$ is a solution. We also find that $a=-d^*/\sqrt{2}$.

Substituting these results into Eq. (5) then gives

$$|v\rangle=-\left[c^*+\frac{|d|^2}{2}\right]|\psi\rangle+dS|\psi\rangle-iH|\psi\rangle-S^{\dagger}S|\psi\rangle, \tag{10}$$

which when compared with Eq. (8) implies that $\mathrm{Re}(c)=-|d|^2/4$. Take $\mathrm{Im}(c)=0$ so that

$$|u\rangle=-\frac{d^*}{\sqrt{2}}|\psi\rangle+\sqrt{2}S|\psi\rangle,$$

$$|v\rangle=-\frac{|d|^2}{4}|\psi\rangle+dS|\psi\rangle-iH|\psi\rangle-S^{\dagger}S|\psi\rangle, \tag{11}$$

where d is now an arbitrary parameter. We set d by requiring that $\langle\psi|u\rangle=0$ which implies [via Eq. (11)] that $d=2\langle\psi|S^{\dagger}|\psi\rangle$ and we obtain the norm-conserving and exact equation

$$d|\psi\rangle=-iH|\psi\rangle dt+[2\langle\psi|S^{\dagger}|\psi\rangle S-S^{\dagger}S-|\langle\psi|S^{\dagger}|\psi\rangle|^2]|\psi\rangle dt+\sqrt{2}[S-\langle\psi|S|\psi\rangle]|\psi\rangle d\alpha \tag{12}$$

derived by Gisin and Percival [7].

(2) Stochastic densities for the Liouville–von Neumann equation. Here our goal is to reduce the N-body vibrational problem with pairwise interactions to N one-body problems by decomposing the full density matrix into a direct product of single mode densities, each of which satisfies a stochastic evolution equation. For small displacements nuclear exchange effects are unimportant and can be neglected. The restriction to pairwise interactions may seem unrealistic since higher order interactions occur in Born-Oppenheimer potentials. However, at low energies three phonon interactions should generally be much weaker than two phonon interactions. Hamiltonians with pairwise interactions should thus be representative of low energy vibrational dynamics in solids or in molecules near a potential minimum. Exact stochastic solutions of this restricted N-body problem could prove extremely useful for testing theories of decoherence and dissipation. For simplicity we consider the $N=2$ case. The generalization to larger N is straightforward.

We consider a decomposition $\rho(t)=M[\rho_1(t)\otimes\rho_2(t)]$ where $\rho_1(t)$ and $\rho_2(t)$ satisfy the following stochastic equations:

$$d\rho_1(t)=v_1(t)dt+u_1(t)d\alpha(t)+w_1(t)d\alpha^*(t),$$

$$d\rho_2(t)=v_2(t)dt+u_2(t)d\alpha^*(t)+w_2(t)d\alpha(t). \tag{13}$$

Here $M[\ ]$ denotes expectation over a complex Wiener process $\alpha(t)$, satisfying conditions $M[d\alpha(t)]=0$, $M[d\alpha(t)d\alpha(t)]=0$, and $M[d\alpha(t)d\alpha^*(t)]=dt$. In addition, we require that

$$\mathrm{Tr}_1\{v_1\}=\mathrm{Tr}_1\{u_1\}=\mathrm{Tr}_1\{w_1\}=0,$$

$$\mathrm{Tr}_2\{v_2\}=\mathrm{Tr}_2\{u_2\}=\mathrm{Tr}_2\{w_2\}=0, \tag{14}$$

so that trace norm is conserved by Eqs. (13). Consider the Hamiltonian

$$H=h_1+h_2+f_1f_2, \tag{15}$$

where h_1 and h_2 are single mode Hamiltonians and f_1 and f_2 generate a pairwise interaction. The appropriate form for the functional is

$$\mathcal{F}=\|v_1\rho_2+\rho_1v_2+u_1u_2+w_1w_2+i(h_1+h_2+f_1f_2)\rho_1\rho_2-i\rho_1\rho_2(h_1+h_2+f_1f_2)\|^2, \tag{16}$$

where the norm is $\|x\|^2=(x|x)$ with inner product $(x|y)=\mathrm{Tr}\{x^{\dagger}y\}$. (See Ref. [12] for a discussion of the Dirac notation in Liouville-Hilbert space.)

Allowing independent variations δv_1, δu_1, δw_1, δv_2, δu_2, and δw_2 we then obtain the following condition for minimum global error:

$$\delta\mathcal{F}=0=2(\delta v_1\rho_2+\rho_1\delta v_2+\delta u_1u_2+u_1\delta u_2+\delta w_1w_2 + w_1\delta w_2|v_1\rho_2+\rho_1v_2+u_1u_2+w_1w_2+i(h_1+h_2 + f_1f_2)\rho_1\rho_2-i\rho_1\rho_2(h_1+h_2+f_1f_2)) \quad (17)$$

This condition leads to the set of equations

$$(\rho_2|\rho_2)v_1+(\rho_2|u_2)u_1+(\rho_2|w_2)w_1+i(\rho_2|\rho_2)(h_1\rho_1-\rho_1h_1) + i(\rho_2|f_2|\rho_2)(f_1\rho_1-\rho_1f_1)=0, \quad (18)$$

$$(\rho_1|\rho_1)v_2+(\rho_1|u_1)u_2+(\rho_1|w_1)w_2+i(\rho_1|\rho_1)(h_2\rho_2-\rho_2h_2) + i(\rho_1|f_1|\rho_1)(f_2\rho_2-\rho_2f_2)=0, \quad (19)$$

$$(u_2|\rho_2)v_1+(u_2|u_2)u_1+(u_2|w_2)w_1+i(u_2|\rho_2)(h_1\rho_1-\rho_1h_1) + i(u_2|f_2|\rho_2)(f_1\rho_1-\rho_1f_1)=0, \quad (20)$$

$$(u_1|\rho_1)v_2+(u_1|u_1)u_2+(u_1|w_1)w_2+i(u_1|\rho_1)(h_2\rho_2-\rho_2h_2) + i(u_1|f_1|\rho_1)(f_2\rho_2-\rho_2f_2)=0, \quad (21)$$

$$(w_2|\rho_2)v_1+(w_2|u_2)u_1+(w_2|w_2)w_1+i(w_2|\rho_2)(h_1\rho_1 - \rho_1h_1)+i(w_2|f_2|\rho_2)(f_1\rho_1-\rho_1f_1)=0, \quad (22)$$

$$(w_1|\rho_1)v_2+(w_1|u_1)u_2+(w_1|w_1)w_2+i(w_1|\rho_1)(h_2\rho_2 - \rho_2h_2)+i(w_1|f_1|\rho_1)(f_2\rho_2-\rho_2f_2)=0, \quad (23)$$

which we have simplified somewhat using conditions (14). Solving Eqs. (18) and (19) for v_1 and v_2, and substituting v_1 into Eqs. (20) and (22), and v_2 into Eqs. (21) and (23) gives

$$\left[(u_2|u_2)-\frac{(u_2|\rho_2)(\rho_2|u_2)}{(\rho_2|\rho_2)}\right]u_1+\left[(u_2|w_2) - \frac{(u_2|\rho_2)(\rho_2|w_2)}{(\rho_2|\rho_2)}\right]w_1+i\left[(u_2|f_2|\rho_2) - \frac{(u_2|\rho_2)(\rho_2|f_2|\rho_2)}{(\rho_2|\rho_2)}\right](f_1\rho_1-\rho_1f_1)=0, \quad (24)$$

$$\left[(u_1|u_1)-\frac{(u_1|\rho_1)(\rho_1|u_1)}{(\rho_1|\rho_1)}\right]u_2+\left[(u_1|w_1) - \frac{(u_1|\rho_1)(\rho_1|w_1)}{(\rho_1|\rho_1)}\right]w_2+i\left[(u_1|f_1|\rho_1) - \frac{(u_1|\rho_1)(\rho_1|f_1|\rho_1)}{(\rho_1|\rho_1)}\right](f_2\rho_2-\rho_2f_2)=0, \quad (25)$$

$$\left[(w_2|u_2)-\frac{(w_2|\rho_2)(\rho_2|u_2)}{(\rho_2|\rho_2)}\right]u_1+\left[(w_2|w_2) - \frac{(w_2|\rho_2)(\rho_2|w_2)}{(\rho_2|\rho_2)}\right]w_1+i\left[(w_2|f_2|\rho_2) - \frac{(w_2|\rho_2)(\rho_2|f_2|\rho_2)}{(\rho_2|\rho_2)}\right](f_1\rho_1-\rho_1f_1)=0, \quad (26)$$

$$\left[(w_1|u_1)-\frac{(w_1|\rho_1)(\rho_1|u_1)}{(\rho_1|\rho_1)}\right]u_2+\left[(w_1|w_1) - \frac{(w_1|\rho_1)(\rho_1|w_1)}{(\rho_1|\rho_1)}\right]w_2+i\left[(w_1|f_1|\rho_1) - \frac{(w_1|\rho_1)(\rho_1|f_1|\rho_1)}{(\rho_1|\rho_1)}\right](f_2\rho_2-\rho_2f_2)=0. \quad (27)$$

We now set

$$u_1=a_1\rho_1+b_1f_1\rho_1, \quad u_2=a_2\rho_2+b_2f_2\rho_2,$$
$$w_1=c_1\rho_1+d_1\rho_1f_1, \quad w_2=c_2\rho_2+d_2\rho_2f_2 \quad (28)$$

where a_1, a_2, b_1, b_2, c_1, c_2, d_1, and d_2 are complex quantities to be determined. When Eqs. (28) are substituted into Eqs. (24)–(27) we obtain the conditions

$$b_2a_1+d_2c_1=0, \quad b_1a_2+d_1c_2=0,$$
$$b_1b_2=-i, \quad d_1d_2=i \quad (29)$$

from which we immediately deduce that $b_1=\sqrt{-i}=b_2$ and $d_1=\sqrt{i}=d_2$. Thus,

$$u_1=a_1\rho_1+\sqrt{-i}f_1\rho_1, \quad u_2=a_2\rho_2+\sqrt{-i}f_2\rho_2,$$
$$w_1=c_1\rho_1+\sqrt{i}\rho_1f_1, \quad w_2=c_2\rho_2+\sqrt{i}\rho_2f_2 \quad (30)$$

and requirements (14) then imply that

$$a_1=-\sqrt{-i\overline{f_1}}, \quad a_2=-\sqrt{-i\overline{f_2}},$$
$$c_1=-\sqrt{i\overline{f_1}}, \quad c_2=-\sqrt{i\overline{f_2}}, \quad (31)$$

where $\overline{f_1}=\mathrm{Tr}_1\{f_1\rho_1\}$ and $\overline{f_2}=\mathrm{Tr}_2\{f_2\rho_2\}$. Conditions (31) satisfy Eqs. (29). Thus, we obtain

$$u_1=\sqrt{-i}(f_1-\overline{f_1})\rho_1, \quad u_2=\sqrt{-i}(f_2-\overline{f_2})\rho_2,$$
$$w_1=\sqrt{i}\rho_1(f_1-\overline{f_1}), \quad w_2=\sqrt{i}\rho_2(f_2-\overline{f_2}) \quad (32)$$

and substituting these results back into Eqs. (18) and (19) gives

$$v_1=-i(h_1\rho_1-\rho_1h_1)-i\overline{f_2}(f_1\rho_1-\rho_1f_1),$$
$$v_2=-i(h_2\rho_2-\rho_2h_2)-i\overline{f_1}(f_2\rho_2-\rho_2f_2). \quad (33)$$

Thus, the variational principle (17) gives the set of stochastic density equations

$$d\rho_1(t)=-i(h_1\rho_1-\rho_1h_1)dt-i\overline{f_2}(f_1\rho_1-\rho_1f_1)dt + \sqrt{-i}(f_1-\overline{f_1})\rho_1d\alpha(t)+\sqrt{i}\rho_1(f_1-\overline{f_1})d\alpha^*(t),$$
$$d\rho_2(t)=-i(h_2\rho_2-\rho_2h_2)dt-i\overline{f_1}(f_2\rho_2-\rho_2f_2)dt+\sqrt{-i}(f_2 - \overline{f_2})\rho_2d\alpha^*(t)+\sqrt{i}\rho_2(f_2-\overline{f_2})d\alpha(t). \quad (34)$$

These equations clearly preserve probability since $\mathrm{Tr}_1\{d\rho_1(t)\}=0=\mathrm{Tr}_2\{d\rho_2(t)\}$. It can be really verified using Eqs. (34) and the properties of the Wiener process that $d\rho = M[d\rho_1\rho_2+\rho_1 d\rho_2+d\rho_1 d\rho_2]=-i(H\rho-\rho H)dt$, so that Eqs. (34) are exact in the mean. Generalization to N modes is straightforward.

The variational principle can also be employed in a wave equation form. Suppose we wish to find a stochastic decomposition of the form $\psi(t)=M[\Pi_{j=1}^{N}\phi_j]$ where each ϕ_j satisfies a stochastic wave equation. Consider the $N=2$ case for simplicity. If $d\phi_1=v_1dt+u_1d\alpha$ and $d\phi_2=v_2dt+u_2d\alpha$ then the functional would take the form $\mathcal{F}=\|v_1\phi_2+\phi_1v_2+u_1u_2+iH\phi_1\phi_2\|^2$. We used this variational principle to show that while there is a class of exact vibrational wave function decompositions, none conserve norm.

In summary, we have developed a stochastic generalization of the McLachlan variational principle. We illustrated the method by finding norm-conserving exact stochastic decompositions for the CPDS master equation, and for the vibrational dynamics problem with pairwise interactions. The approach could prove useful in deriving new stochastic decompositions and for improving existing decompositions which do not conserve norm.

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