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Quantum system-bath dynamics with Quantum Superposition Sampling and Coupled Generalised Coherent States.

Oliver Bramley[1)], Christopher Symonds[1),2)], and Dmitrii V. Shalashilin[1)]

1) School of Chemistry, University of Leeds, Leeds LS2 9JT, United Kingdom

2) School of Environment, University of Leeds, Leeds LS2 9JT, United Kingdom

(Supporting Information)

1. Coupled two level systems.

Coupled two level systems describe many problems in physics and chemistry, such as for example light harvesting complexes made of several chromophores each one of them having two electronic states, which also can interact with a number of vibrational modes considered as a bath.

Let us define Coherent State of a two level system (2L-CS) as simply a superposition of $|1\rangle$ and $|0\rangle$

$$|\zeta(a_1, a_2)\rangle = a_1|1\rangle + a_0|0\rangle \tag{1.1}$$

The kets $|1\rangle$ and $|0\rangle$ can represent the two different quantum states or a single mixed occupied/unoccupied state such as that described in ref[1]. Often 2L-CS is called SU(2) coherent state and is written as

$$|\zeta_{SU(2)}(\theta,\varphi)\rangle = \cos(\theta)e^{i\varphi}|1\rangle + \sin(\theta)|0\rangle \tag{1.2}$$

where one of the coefficients is assumed to be real, but it does not have to be. Having both a_0 and a_1 complex would introduce an insignificant phase factor, but the advantage is that both states are treated on equal footing.

Multidimensional 2L-CS representing M two-level systems (like several chromophores for example) is simply a Hartree product

$$\left|\zeta\right\rangle = \left|\zeta_1, \zeta_2, ..., \zeta_M\right\rangle = \prod_{m=1,M} \left(a_{1m}\left|1_m\right\rangle + a_{0m}\left|0_m\right\rangle\right). \tag{1.3}$$

The identity operator for a basis set of N 2L-CSs is

$$\hat{I} = \sum_{a,b=1,N} \left|\zeta^{(a)}\right\rangle \Omega^{(ab)^{-1}} \left\langle\zeta^{(b)}\right| \tag{1.4}$$

where their overlap matrix is

$$\begin{aligned}\Omega^{(ab)} &= \left\langle\zeta^{(a)}\middle|\zeta^{(b)}\right\rangle = \prod_{m=1,M} \left\langle\zeta_m^{(a)}\middle|\zeta_m^{(b)}\right\rangle = \\ &\prod_{m=1,M} \left(a_{1m}^{(a)} * a_{1m}^{(b)} + a_{0m}^{(a)} * a_{0m}^{(b)}\right) = \prod_{m=1,M} \omega_m^{(ab)}\end{aligned} \tag{1.5}$$

and $\omega_m^{(ab)}$ is a “1D-overlap”.

In this supporting material we will derive various forms of equations of motion for the wave functions represented as superposition of Generalized Coherent States $\left|\zeta,\ \mathbf{z}\right\rangle$ (GCS), which are a product of 2L-CSs $\left|\zeta\right\rangle$ and standard Harmonic oscillator Coherent states HO-CSs $\left|\mathbf{z}\right\rangle$:

$$\left|\Psi(t)\right\rangle = \sum_n A^{(n)}(t)\left|\zeta^{(n)}(t),\ \mathbf{z}^{(n)}(t)\right\rangle = \sum_n A^{(n)}(t)\left|\zeta^{(n)}(t)\right\rangle\left|\mathbf{z}^{(n)}(t)\right\rangle \tag{1.6}$$

We will rely on the general methodology of variational principle, as suggested in ref[2] and later adopted for HO CSs in ref[3]. The main idea is the following: if the wave function depends on a set of parameters its time dependence is that of the parameters $\Psi(t) = \Psi\left(\alpha_1(t), ..., \alpha_M(t)\right)$, which can be found either by substitution to the Schrödinger equation or more elegantly via variational principle which introduces the Lagrangian

$$\begin{aligned}L(\dot{\boldsymbol{\alpha}}*, \boldsymbol{\alpha}*, \dot{\boldsymbol{\alpha}}, \boldsymbol{\alpha}) &= L\left(\dot{\alpha}_1*, .., \dot{\alpha}_M*, \alpha_1*, ..., \alpha_M*, \dot{\alpha}_1, .., \dot{\alpha}_M, \alpha_1, ..., \alpha_M\right) = \\ &= \left\langle\Psi\right| \frac{i}{2}\left(\frac{\vec{\partial}}{\partial t} - \frac{\overleftarrow{\partial}}{\partial t}\right) - \hat{H}\left|\Psi\right\rangle\end{aligned} . \tag{1.7}$$

Then the equations of motion are simply the Lagrange equations.

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{\alpha}_j} - \frac{\partial L}{\partial \alpha_j} = 0 \tag{1.8}$$

which after introduction of the momenta

$$p_j = 2\frac{\partial L}{\partial \dot{\alpha}_j} \qquad (1.9)$$

can be written as the Hamilton's equation

$$\dot{\boldsymbol{\alpha}} = \left(\frac{\partial \mathbf{p}}{\partial \boldsymbol{\alpha}^*}\right)^{-1} \frac{\partial \langle \Psi | \hat{H} | \Psi \rangle}{\partial \boldsymbol{\alpha}^*} \qquad (1.10)$$

where $\left(\frac{\partial \mathbf{p}}{\partial \boldsymbol{\alpha}^*}\right)^{-1}$ is the inverse of the $\left(\frac{\partial \mathbf{p}}{\partial \boldsymbol{\alpha}^*}\right)$ matrix.

Kramer and Saraceno approach illustrates that quantum equations of motion have the same structure as those of classical mechanics. The evolution of the parameters of a quantum wave function can be described by the Hamilton's equation (1.10), regardless of the physical meaning of the parameters. Kramer and Saraceno also provided a mathematical tool for deriving quantum equations of motion for any parametrisation of the wave function.

Section 2 of this supporting material introduces the Hamiltonian in terms of GCSs. In the section 3 the equations of motion for the wave function made of single Generalised Coherent State in (1.6) are obtained, which are equivalent to those of a single Ehrenfest trajectory. Then in the section 4 the analogue of the MCEv2 approach[4] will be derived using the language of Generalised Coherent States. After that in the section 5 the analogue of the MCEv1[5] is derived. Finally in the section 6 a fully variational approach similar to vMCG[6] is developed, which can be called variational multiconfigurational Generalised Coherent States (vMCGCS).

vMCGCS can be derived easier if non-normalised Coherent States, which are sometimes are used. For HO CS they are defined as:

$$\| \mathbf{z} \rangle = | \mathbf{z} \rangle e^{\frac{|\mathbf{z}|^2}{2}} \qquad (1.11)$$

For the 2L-CSs there is no such difference between normalised and non-normalised 2L-CS, which both are given by (1.1) and we do not use separate notation for non-normalised 2L-CS. Conservation of norm $\langle \zeta | \zeta \rangle = 1$ is introduced as a constraint.

2. Generalised Coherent States Hamiltonian.

Creation and annihilation operators acting on a single 2L-CS (1.1) can be defined as follows:

$$
\begin{aligned}
&\hat{b}|1\rangle = |0\rangle && \langle 1|\hat{b} = 0\langle 0| \\
&\hat{b}|0\rangle = 0|1\rangle = 0 && \langle 0|\hat{b} = \langle 1| \\
&\hat{b}^+|0\rangle = |1\rangle && \langle 1|\hat{b}^+ = \langle 0| \\
&\hat{b}^+|1\rangle = 0|0\rangle = 0 && \langle 0|\hat{b}^+ = 0\langle 1|
\end{aligned}
\tag{2.1}
$$

So that

$$
\begin{aligned}
\hat{b}|\zeta\rangle &= \hat{b}\ \left(a_1|1\rangle + a_0|0\rangle\right) = \ a_1|0\rangle + 0|1\rangle \\
\hat{b}^+|\zeta\rangle &= \hat{b}^+\left(a_1|1\rangle + a_0|0\rangle\right) = \ 0|0\rangle + a_0|1\rangle
\end{aligned}
\tag{2.2}
$$

and

$$
\begin{aligned}
\langle\zeta|\hat{b} &= \left(a_1 * \langle 1| + a_0 * \langle 0|\right)\hat{b} \ = \ \left(0\langle 0| + a_0 * \langle 1|\right) \\
\langle\zeta|\hat{b}^+ &= \left(a_1 * \langle 1| + a_0 * \langle 0|\right)\hat{b}^+ \ = \ \left(a_1 * \langle 0| + 0\langle 1|\right)
\end{aligned}
\tag{2.3}
$$

Then the Hamiltonian of a set of coupled 2 level systems can be written as:

$$
\hat{H} = \sum_{m=1,M}\left(\hat{H}^{(11)}_{mm}\hat{b}^+_m\hat{b}_m + \hat{H}^{(00)}_{mm}\hat{b}_m\hat{b}^+_m\right) + \sum_{m=1,M}\hat{H}^{(01)}_{mm}\left(\hat{b}^+_m + \hat{b}_m\right) + \frac{1}{2}\sum_{m\neq n}\hat{H}_{nm}\left(\hat{b}^+_n\hat{b}_m + \hat{b}^+_m\hat{b}_n\right)
\tag{2.4}
$$

where the first term gives the energies of electronic states, the second term couples the states of single 2L system and the last term is responsible for the energy transfer between the coupled 2L systems.

The parameters of the Hamiltonian can depend on the nuclear motion creation and annihilation operators:

$$
\begin{aligned}
\hat{H}^{(11)}_{mm} &= H^{(11)}_{mm}\left(\hat{a}^+_1, \hat{a}^+_2 ... \hat{a}^+_L, \hat{a}_1, \hat{a}_2, ..., \hat{a}_L\right) \\
\hat{H}^{(00)}_{mm} &= H^{(00)}_{mm}\left(\hat{a}^+_1, \hat{a}^+_2 ... \hat{a}^+_L, \hat{a}_1, \hat{a}_2, ..., \hat{a}_L\right) \\
\hat{H}^{(10)}_{mm} &= H^{(10)}_{mm}\left(\hat{a}^+_1, \hat{a}^+_2 ... \hat{a}^+_L, \hat{a}_1, \hat{a}_2, ..., \hat{a}_L\right) \\
\hat{H}_{mn} &= H_{mn}\left(\hat{a}^+_1, \hat{a}^+_2 ... \hat{a}^+_L, \hat{a}_1, \hat{a}_2, ..., \hat{a}_L\right)
\end{aligned}
\tag{2.5}
$$

where L is the number of vibrational modes. The operators $\hat{a}^{+}, \hat{a}$ are standard creation and annihilation operators of a Harmonic Oscillator, which act on the ***z*** part of Generalised Coherent State.

Matrix elements of the Hamiltonian (2.4) with two Generalised Coherent States are as follows

$$\left\langle \zeta^{(a)}\mathbf{z}^{(a)} \middle| \hat{H} \middle| \zeta^{(b)}\mathbf{z}^{(b)} \right\rangle = \left\langle \zeta^{(a)}\mathbf{z}^{(a)} \middle| \zeta^{(b)}\mathbf{z}^{(b)} \right\rangle$$
$$\{ \sum_{m=1,M} \frac{\left(\tilde{H}^{(11)}_{mm} a^{(a)}_{1m} * a^{(b)}_{1m} + \tilde{H}^{(00)}_{mm} a^{(a)}_{0m} * a^{(b)}_{0m} + \tilde{H}^{(01)}_{mm}\left(a^{(a)}_{1m} * a^{(b)}_{0m} + a^{(a)}_{0m} * a^{(b)}_{1m}\right)\right)}{\left\langle \zeta^{(a)}_{m} \middle| \zeta^{(b)}_{m} \right\rangle} +$$
$$+ \frac{1}{2}\sum_{m\neq n} \frac{\tilde{H}_{nm}\left(a^{(a)}_{0n} * a^{(b)}_{1n}\; a^{(a)}_{1m} * a^{(b)}_{0m} + a^{(a)}_{0m} * a^{(b)}_{1m}\; a^{(a)}_{1n} * a^{(b)}_{0n}\right)}{\left\langle \zeta^{(a)}_{m} \middle| \zeta^{(b)}_{m} \right\rangle \left\langle \zeta^{(a)}_{n} \middle| \zeta^{(b)}_{n} \right\rangle} \}$$

(2.6)

and $\tilde{H}^{(11)}_{mm}$, $\tilde{H}^{(00)}_{mm}$, $\tilde{H}^{(10)}_{mm}$ and $\tilde{H}_{nm}$ are now functions of $z^{(a)}_{1}, z^{(a)}_{2}, \ldots, z^{(a)}_{L}$, $z^{(b)}_{1}, z^{(b)}_{2}, \ldots, z^{(b)}_{L}$ and their complex conjugate. The symbol " ~ " is equivalent to the index "ord" in our previous CCS work[7] and means that the functions were obtained by ordering the operators $\hat{a}^{+}_{m}$ and $\hat{a}_{m}$ such that the powers of creation operator are on the left and those of annihilation operator are on the right and then replacing them by the powers of $z_m *$ and z_m respectively.

3. Equations of motion for single Generalised Coherent State

The equations of motion for a single GCS

$$\left|\Psi\right\rangle = \left|\zeta\right\rangle\left|\mathbf{z}\right\rangle = \prod_{m=1,M}\left(a_{1m}\left|1_m\right\rangle + a_{0m}\left|0_m\right\rangle\right)\prod_{l=1,L}\left|z_l\right\rangle \quad (3.1)$$

can easily be obtained from the variational principle for the Lagrangian

$$L\left(a_{11} * \ldots a_{1M} *, a_{01} * \ldots a_{0M} *, z*, a_{11} * \ldots a_{1M}, a_{01} \ldots a_{0M}, z\right) =$$
$$\left\langle \Psi \right| \frac{i}{2}\left(\frac{\vec{\partial}}{\partial t} - \frac{\overleftarrow{\partial}}{\partial t}\right) - \hat{H} \left| \Psi \right\rangle =$$
$$\frac{i}{2}\left(\sum_{m=1,M}\left[\left(\dot{a}_{1m} a_{1m} * - a_{1m}\dot{a}_{1m} *\right) + \left(\dot{a}_{0m} a_{0m} * - a_{0m}\dot{a}_{0m} *\right)\right] + \sum_{l=1,L}\left(\dot{z}_l z_l * - z_l \dot{z}_l *\right)\right) - \left\langle \hat{H} \right\rangle$$

(3.2)

In (3.2)

$$\left\langle \hat{H} \right\rangle = \left\langle \Psi \middle| \hat{H} \middle| \Psi \right\rangle = \frac{\left\langle \boldsymbol{\zeta}, \mathbf{z} \middle| \hat{H} \middle| \boldsymbol{\zeta}, \mathbf{z} \right\rangle}{\left\langle \boldsymbol{\zeta}, \mathbf{z} \middle| \boldsymbol{\zeta}, \mathbf{z} \right\rangle} \tag{3.3}$$

is the Ehrenfest Hamiltonian and $\frac{\vec{\partial}}{\partial t}, \frac{\overleftarrow{\partial}}{\partial t}$ act on the right and left respectively.

The Lagrange equations

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{\boldsymbol{\alpha}}} - \frac{\partial L}{\partial \boldsymbol{\alpha}} = 0 \tag{3.4}$$

where $\boldsymbol{\alpha} = (a, a^*, z, z^*)$ become

$$\begin{aligned} \frac{d\mathbf{z}^*}{dt} &= i\frac{\partial \left\langle H \right\rangle}{\partial \mathbf{z}} \quad , \quad \frac{d\mathbf{z}}{dt} = -i\frac{\partial \left\langle H \right\rangle}{\partial \mathbf{z}^*} \\ \frac{d\zeta^*}{dt} &= i\frac{\partial \left\langle H \right\rangle}{\partial \zeta} \quad , \quad \frac{d\zeta}{dt} = -i\frac{\partial \left\langle H \right\rangle}{\partial \zeta^*} \end{aligned} \tag{3.5}$$

which are the standard Ehrenfest equations. It is easy to see that for a single 2-level system they become

$$\begin{aligned} i\dot{a}_1 &= H_{11}a_1 + H_{10}a_0 \\ i\dot{a}_0 &= H_{01}a_1 + H_{00}a_0 \\ \dot{\mathbf{z}} &= -i\frac{\partial \left\langle H \right\rangle}{\partial \mathbf{z}^*} \end{aligned} \tag{3.6}$$

The equations (3.6) also can be obtain simply by substitution of (3.1) into the Schrödinger equation.

4. The equations for A and D coefficients - the analogue of MCEv2

The Ehrenfest wave function (3.1) is not flexible enough to represent quantum dynamics accurately, but a superposition of several GCSs

$$\left|\Psi(t)\right\rangle = \sum_n A^{(n)}(t)\left|\zeta^{(n)}(t),\ \mathbf{z}^{(n)}(t)\right\rangle = \sum_n A^{(n)}(t)\left|\zeta^{(n)}(t)\right\rangle\left|\mathbf{z}^{(n)}(t)\right\rangle \tag{4.1}$$

can be converged to the exact quantum result. In the spirit of the CCS method[7] we can use the equations (3.5) above to move the basis of $\left|\zeta^{(n)}(t),\ \mathbf{z}^{(n)}(t)\right\rangle$ and then to get the equations for $A^{(i)}(t)$ by simple substitution to the Schrödinger equation, or by applying the variational principle to *A*-

coefficients only. It is also useful to represent the coefficient *A* as a product of rapidly oscillation exponent and smooth preexponential factor:

$$\left|\Psi\right\rangle = \sum_{n} D^{(n)} e^{iS^{(n)}} \left|\zeta^{(n)}(t), \mathbf{z}^{(n)}(t)\right\rangle \tag{4.2}$$

where $S^{(n)} = \int L^{(n)} dt$ is the action with the Lagrangian (3.2) along the Ehrenfest trajectory of configuration $\left|\zeta^{(n)}(t), \mathbf{z}^{(n)}(t)\right\rangle$. The time dependence of the action is given by

$$\begin{aligned}
\frac{dS^{(n)}}{dt} = L^{(n)} &= \frac{i}{2}\sum_{j}\left(a_{0j}^{(n)} * \dot{a}_{0j}^{(n)} - \dot{a}_{0j}^{(n)} * a_{0j}^{(n)}\right) + \frac{i}{2}\sum_{j}\left(a_{1j}^{(n)} * \dot{a}_{1j}^{(n)} - \dot{a}_{1j}^{(n)} * a_{1j}^{(n)}\right) \\
&+ \frac{i}{2}\sum_{j}\left(z_{j}^{(n)} * \dot{z}_{j}^{(n)} - \dot{z}_{j}^{(n)} * z_{j}^{(n)}\right) - \\
&\left\langle \mathbf{z}^{(n)}\zeta^{(n)}\right|\hat{H}\left|\zeta^{(n)}\mathbf{z}^{(n)}\right\rangle = \\
\frac{i}{2}\left(\mathbf{a}_{0}^{(n)} * \dot{\mathbf{a}}_{0}^{(n)} - \dot{\mathbf{a}}_{0}^{(n)} * \mathbf{a}_{0}^{(n)}\right) &+ \frac{i}{2}\left(\mathbf{a}_{1}^{(n)} * \dot{\mathbf{a}}_{1}^{(n)} - \dot{\mathbf{a}}_{1}^{(n)} * \mathbf{a}_{1}^{(n)}\right) \\
&+ \frac{i}{2}\left(\mathbf{z}^{(n)} * \dot{\mathbf{z}}^{(n)} - \dot{\mathbf{z}}^{(n)} * \mathbf{z}^{(n)}\right) - \left\langle \mathbf{z}^{(n)}\zeta^{(n)}\right|\hat{H}\left|\zeta^{(n)}\mathbf{z}^{(n)}\right\rangle =
\end{aligned} \tag{4.3}$$

Then similarly to refs[3, 7] the equations for the amplitudes *D* become

$$\sum_{n} \dot{D}^{(n)} e^{i(S^{(n)}-S^{(n)})} \left\langle \zeta^{(m)}\mathbf{z}^{(m)} \middle| \zeta^{(n)}\mathbf{z}^{(n)}\right\rangle = -i\sum_{n}\left(\Delta^{2}H^{SU(2)}\right)^{(mn)} D^{(n)} e^{i(S^{(n)}-S^{(n)})} \tag{4.4}$$

which is a system of linear equations for the derivatives of the amplitudes $D^{(n)}$. In (4.4)

$$\begin{aligned}
\left(\Delta^{2}H^{SU(2)}\right)^{(mn)} &= \left\langle \zeta^{(m)}\mathbf{z}^{(m)} \middle| \zeta^{(n)}\mathbf{z}^{(n)}\right\rangle L_{n} + \left\langle \zeta^{(m)}\mathbf{z}^{(m)}\right|\hat{H}\left|\zeta^{(n)}\mathbf{z}^{(n)}\right\rangle \\
&- i\left\langle \zeta^{(m)} \middle| \dot{\zeta}^{(n)}\right\rangle\left\langle \mathbf{z}^{(m)} \middle| \mathbf{z}^{(n)}\right\rangle - i\left\langle \zeta^{(m)} \middle| \zeta^{(n)}\right\rangle\left\langle \mathbf{z}^{(m)} \middle| \dot{\mathbf{z}}^{(n)}\right\rangle
\end{aligned} \tag{4.5}$$

and $\left\langle \zeta^{(m)} \middle| \dot{\zeta}^{(n)}\right\rangle$ and $\left\langle \mathbf{z}^{(m)} \middle| \dot{\mathbf{z}}^{(n)}\right\rangle$ are given as

$$\begin{aligned}
\left\langle \mathbf{z}^{(j)}(t) \middle| \dot{\mathbf{z}}^{(n)}(t)\right\rangle &= \sum_{l}\left(z_{l}^{(j)} * \dot{z}_{l}^{(n)} - \frac{\dot{z}_{l}^{(n)} * z_{l}^{(n)} - z_{l}^{(n)} * \dot{z}_{l}^{(n)}}{2}\right)\left\langle \mathbf{z}^{(j)}(t) \middle| \mathbf{z}^{(n)}(t)\right\rangle = \\
&= \sum_{l}\left((z_{l}^{(j)} * - z_{l}^{(n)} *)\dot{z}_{l}^{(n)} + \frac{z_{l}^{(n)} * \dot{z}_{l}^{(n)} - \dot{z}_{l}^{(n)} * z_{l}^{(n)}}{2}\right)\left\langle \mathbf{z}^{(j)}(t) \middle| \mathbf{z}^{(n)}(t)\right\rangle
\end{aligned} \tag{4.6}$$

and

$$\left\langle \zeta^{(j)}(t) \middle| \dot{\zeta}^{(n)}(t) \right\rangle = \sum_{m=1,M} (a_{1m}^{(j)*} \dot{a}_{1m}^{(n)} + a_{0m}^{(j)*} \dot{a}_{0m}^{(n)}) \prod_{m'=m} \left(a_{1m'}^{(j)*} a_{1m'}^{(n)} + a_{0m'}^{(j)*} a_{0m'}^{(n)} \right) =$$

$$\sum_{m=1,M} ((a_{1m}^{(j)*} - a_{1m}^{(n)*}) \dot{a}_{1m}^{(n)} + a_{1m}^{(n)*} \dot{a}_{1m}^{(n)} + (a_{0m}^{(j)*} - a_{0m}^{(n)*}) \dot{a}_{0m}^{(n)} + a_{0m}^{(n)*} \dot{a}_{0m}^{(n)})$$

$$\prod_{m'=m} \left(a_{1m'}^{(j)*} a_{1m'}^{(n)} + a_{0m'}^{(j)*} a_{0m'}^{(n)} \right) =$$

$$\sum_{m=1,M} ((a_{1m}^{(j)*} - a_{1m}^{(n)*}) \dot{a}_{1m}^{(n)} + \frac{a_{1m}^{(n)*} \dot{a}_{1m}^{(n)} - \dot{a}_{1m}^{(n)*} a_{1m}^{(n)}}{2} + (a_{0m}^{(j)*} - a_{0m}^{(n)*}) \dot{a}_{0m}^{(n)} + \frac{a_{0m}^{(n)*} \dot{a}_{0m}^{(n)} - \dot{a}_{0m}^{(n)*} a_{0m}^{(n)}}{2})$$

$$\prod_{m'=m} \left(a_{1m'}^{(j)*} a_{1m'}^{(n)} + a_{0m'}^{(j)*} a_{0m'}^{(n)} \right)$$

(4.7)

Similarly to the previously developed CCS method[7, 8] the diagonal elements of $\left(\Delta^2 H^{SU(2)}\right)^{(mn)}$ in (4.4) are zero and the off-diagonal elements are always small. Thus, in this section it is shown that the MCEv2 method can be viewed as a generalisation of the Coupled Coherent States approach, which uses Generalised Coherent States instead of Gaussian Coherent States of the Harmonic oscillator. This property of Coupled Generalised Coherent States equations has already been demonstrated in ref[9]

5. The analogue of MCEv1

We should be able to develop the MCEv1 approach using the language of Generalised Coherent States. For the simple spin-boson model, comprised of a single 2-level system, MCEv1 has shown excellent convergence[5]. One can represent a wave function as a superposition of several Generalised Coherent States

$$\left| \Psi(t) \right\rangle = \sum_n \left| \zeta^{(n)}(t) \right\rangle \left| \mathbf{z}^{(n)}(t) \right\rangle \quad , \tag{5.1}$$

but without the *A* coefficients present in the MCEv2 ansatz, which are not needed if the norm conservation $\left\langle \zeta^{(n)}(t) \middle| \zeta^{(n)}(t) \right\rangle = 1$ is no longer assumed. We still assume however that the trajectories of ***z*** are the Ehrenfest ones

$$\frac{d\mathbf{z}^*}{dt} = i \frac{\partial \langle H \rangle}{\partial \mathbf{z}} \quad , \quad \frac{d\mathbf{z}}{dt} = -i \frac{\partial \langle H \rangle}{\partial \mathbf{z}^*} \tag{5.2}$$

with the Ehrenfest Hamiltonian given by Eq(3.3)

The equation of motion for ζ in (5.1) can then be obtained by substituting (5.1) to the Schrödinger equation:

$$\mathrm{i}\frac{\partial}{\partial t}\left|\Psi(t)\right\rangle = \mathrm{i}\sum_n \left|\dot{\zeta}^{(n)}(t)\right\rangle\left|\mathbf{z}^{(n)}(t)\right\rangle + \mathrm{i}\sum_n \left|\zeta^{(n)}(t)\right\rangle\left|\dot{\mathbf{z}}^{(n)}(t)\right\rangle = \hat{H}\sum_n \left|\zeta^{(n)}(t)\right\rangle\left|\mathbf{z}^{(n)}(t)\right\rangle$$

(5.3)

which can be rearranged as

$$\mathrm{i}\sum_n \left|\dot{\zeta}^{(n)}(t)\right\rangle\left|\mathbf{z}^{(n)}(t)\right\rangle = \hat{H}\sum_n \left|\zeta^{(n)}(t)\right\rangle\left|\mathbf{z}^{(n)}(t)\right\rangle - \mathrm{i}\sum_n \left|\zeta^{(n)}(t)\right\rangle\left|\dot{\mathbf{z}}^{(n)}(t)\right\rangle \qquad (5.4)$$

or more specifically

$$\begin{aligned}\mathrm{i}\sum_{n,j}\left(\dot{a}_{1j}^{(n)}\left|1_j\right\rangle + \dot{a}_{oj}^{(n)}\left|0_j\right\rangle\right)\prod_{k\neq j}\left(a_{1k}^{(n)}\left|1_k\right\rangle + a_{ok}^{(n)}\left|0_k\right\rangle\right)\left|\mathbf{z}^{(n)}(t)\right\rangle = \\ \hat{H}\sum_n \left|\zeta^{(n)}(t)\right\rangle\left|\mathbf{z}^{(n)}(t)\right\rangle - \mathrm{i}\sum_n \left|\zeta^{(n)}(t)\right\rangle\left|\dot{\mathbf{z}}^{(n)}(t)\right\rangle\end{aligned} \quad . \qquad (5.5)$$

By multiplying (5.5) by $\left\langle \mathbf{z}^{(m)}\right|\left\langle 1_l\right|\prod_{k\neq l}\left(a_{1k}^{(m}\left\langle 1_k\right| + a_{ok}^{(m)}\left\langle 0_k\right|\right)$ a system of linear equations for the derivatives $\dot{a}_{1l}^{(n)}$ and $\dot{a}_{0l}^{(n)}$ can be obtained,

$$\begin{aligned}\mathrm{i}\left[\dot{a}_{1l}^{(n)}\prod_{k\neq l}\left(a_{1k}^{(m)}*a_{1k}^{(n)} + a_{ok}^{(m)}*a_{ok}^{(n)}\right) + a_{1l}^{(n)}\sum_{j\neq l}\left(a_{1j}^{(m)}*\dot{a}_{1j}^{(n)} + a_{oj}^{(m)}*\dot{a}_{oj}^{(n)}\right)\prod_{k\neq j,k\neq l}\left(a_{1k}^{(m)}*a_{1k}^{(n)} + a_{ok}^{(m)}*a_{ok}^{(n)}\right)\right] \\ \left\langle \mathbf{z}^{(m)}(t)\middle|\mathbf{z}^{(n)}(t)\right\rangle = \\ \sum_n\left\langle \mathbf{z}^{(m)}(t)\right|\left\langle 1_l\right|\prod_{k\neq l}\left\langle \zeta_k^{(n)}\right|\hat{H}\left|\zeta^{(n)}(t)\mathbf{z}^{(n)}(t)\right\rangle - \mathrm{i}\sum_n\left\langle 1_l\right|\left\langle\prod_{k\neq l}\left\langle \zeta_k^{(n)}\right|\middle|\zeta^{(n)}(t)\right\rangle\left\langle \mathbf{z}^{(m)}(t)\middle|\dot{\mathbf{z}}^{(n)}(t)\right\rangle\end{aligned}$$

(5.6)

which becomes:

$$\begin{aligned}\mathrm{i}\left[\dot{a}_{1l}^{(n)}\left(\omega_l^{(mn)}\right)^{-1} + a_{1l}^{(n)}\left(\omega_l^{(mn)}\omega_j^{(mn)}\right)^{-1}\sum_{j\neq l}\left(a_{1j}^{(m)}*\dot{a}_{1j}^{(n)} + a_{oj}^{(m)}*\dot{a}_{oj}^{(n)}\right)\right] \\ \left\langle \zeta^{(m)}(t)\mathbf{z}^{(m)}(t)\middle|\zeta^{(n)}(t)\mathbf{z}^{(n)}(t)\right\rangle = \\ \sum_n\frac{\partial\left\langle \zeta^{(m)}(t)\mathbf{z}^{(m)}(t)\right|\hat{H}\left|\zeta^{(n)}(t)\mathbf{z}^{(n)}(t)\right\rangle}{\partial a_{1l}^{(n)}} - \mathrm{i}\sum_n\frac{\partial\left\langle \zeta^{(m)}(t)\middle|\zeta^{(n)}(t)\right\rangle}{\partial a_{1l}^{(n)}}\left\langle \mathbf{z}^{(m)}(t)\middle|\dot{\mathbf{z}}^{(n)}(t)\right\rangle\end{aligned}$$

(5.7)

where

$$\omega_j^{(mn)} = a_{1j}^{(m)} * a_{1j}^{(n)} + a_{oj}^{(m)} * a_{oj}^{(n)}$$
$$\omega_l^{(mn)} = a_{1l}^{(m)} * a_{1l}^{(n)} + a_{ol}^{(m)} * a_{ol}^{(n)} \tag{5.8}$$

are the 1D overlaps

A similar system of linear equations

$$i\left[\dot{a}_{0l}^{(n)}\left(\omega_l^{(mn)}\right)^{-1} + a_{0l}^{(n)}\left(\omega_l^{(mn)}\omega_j^{(mn)}\right)^{-1}\sum_{j\neq l}\left(a_{1j}^{(m)} * \dot{a}_{1j}^{(n)} + a_{oj}^{(m)} * \dot{a}_{oj}^{(n)}\right)\right]$$
$$\left\langle \zeta^{(m)}(t)\mathbf{z}^{(m)}(t) \middle| \zeta^{(n)}(t)\mathbf{z}^{(n)}(t)\right\rangle =$$
$$\sum_n \frac{\partial\left\langle \zeta^{(m)}(t)\mathbf{z}^{(m)}(t)\middle|\hat{H}\middle|\zeta^{(n)}(t)\mathbf{z}^{(n)}(t)\right\rangle}{\partial a_{0l}^{(n)}} - i\sum_n \frac{\partial\left\langle \zeta^{(m)}(t)\middle|\zeta^{(n)}(t)\right\rangle}{\partial a_{0l}^{(n)}}\left\langle \mathbf{z}^{(m)}(t)\middle|\dot{\mathbf{z}}^{(n)}(t)\right\rangle$$

(5.9)

can be obtained by multiplication of (5.5) by $\left\langle z^{(m)}\right|\left\langle 0_l\right|\prod_{k\neq l}\left(a_{1k}^{(m}\left\langle 1_k\right| + a_{ok}^{(m)}\left\langle 0_k\right|\right)$

The equations (5.7) and (5.9) for $\zeta(t)$ together with the equation (3.5) for the trajectories ***z(t)*** represent a generalisation of the MCEv1 approach[5]. As the norm of individual Generalised CS is not conserved the Ehrehnfest Hamiltonian

$$\left\langle \hat{H}\right\rangle = \frac{\left\langle \zeta^{(n)}(t)\mathbf{z}^{(n)}(t)\middle|\hat{H}\middle|\zeta^{(n)}(t)\mathbf{z}^{(n)}(t)\right\rangle}{\left\langle \zeta^{(n)}(t)\mathbf{z}^{(n)}(t)\middle|\zeta^{(n)}(t)\mathbf{z}^{(n)}(t)\right\rangle} \tag{5.10}$$

must explicitly include the overlap $\left\langle \zeta^{(n)}(t)\middle|\zeta^{(n)}(t)\right\rangle$ in the denominator.

6. Fully variational approach.

For Generalized Coherent States a fully variational approach can be developed as well. Let us represent the wave function as a superposition

$$\left|\Psi(t)\right\rangle = \sum_n \left|\zeta^{(n)}(t)\right\rangle\left|\tilde{\mathbf{z}}^{(n)}(t)\right\rangle \tag{6.1}$$

where $\left\|\tilde{\mathbf{z}}^{(n)}(t)\right\rangle$ is the non-normalised Coherent State (1.11) so that the overlap of two non-normalised CSs is now

$$\left\langle \mathbf{z}^{(m)} \middle\| \mathbf{z}^{(n)} \right\rangle = \exp\left(\mathbf{z}^{(m)} * \mathbf{z}^{(n)}\right) \ , \qquad (6.2)$$

an analytical function of $\mathbf{z}^{(m)} *$ and $\mathbf{z}^{(n)}$. Using non-normalised CSs makes all algebra required by variational principle easier.

The Lagrangian then becomes

$$\begin{aligned}
&L\left(a_1^{(1)} * \ldots a_1^{(n)} *, a_0^{(1)} * \ldots a_0^{(n)} *, z^{(1)} * \ldots z^{(n)} *, a_1^{(1)} \ldots a_1^{(n)}, a_0^{(1)} .. a_0^{(n)}, z^{(1)} .. z^{(n)}\right) = \\
&\qquad \left\langle \Psi \right| \frac{i}{2}\left(\frac{\vec{\partial}}{\partial t} - \frac{\overleftarrow{\partial}}{\partial t}\right) - \hat{H} \left| \Psi \right\rangle = \\
&\sum_{m,n}\left\{\frac{i}{2}\left[\left\langle \zeta^{(m)} \middle| \dot{\zeta}^{(n)} \right\rangle - \left\langle \dot{\zeta}^{(m)} \middle| \zeta^{(n)} \right\rangle\right]\left\langle \mathbf{z}^{(m)} \middle\| \mathbf{z}^{(n)} \right\rangle + \left[\left\langle \mathbf{z}^{(m)} \middle\| \dot{\mathbf{z}}^{(n)} \right\rangle - \left\langle \dot{\mathbf{z}}^{(m)} \middle\| \mathbf{z}^{(n)} \right\rangle\right]\left\langle \zeta^{(m)} \middle| \zeta^{(n)} \right\rangle - \left\langle \mathbf{z}^{(m)} \middle\| \left\langle \zeta^{(m)} \middle| \hat{H} \middle| \zeta^{(n)} \right\rangle \middle\| \mathbf{z}^{(n)} \right\rangle\right\} = \\
&\sum_{m,n}\frac{i}{2}\left\{\sum_j\left[a_{1j}^{(m)} * \dot{a}_{1j}^{(n)} - \dot{a}_{1j}^{(m)} * a_{1j}^{(n)} + a_{0j}^{(m)} * \dot{a}_{0j}^{(n)} - \dot{a}_{0j}^{(m)} * a_{0j}^{(n)}\right]\prod_{k\neq j}\left(a_{1k}^{(m)} * a_{1k}^{(n)} + a_{0k}^{(m)} * a_{0k}^{(n)}\right)\right\} \\
&\qquad \exp\left(\sum_l z_l^{(m)} * z_l^{(n)}\right) + \\
&\sum_{m,n}\frac{i}{2}\left\{\sum_l\left[z_l^{(m)} * \dot{z}_l^{(n)} - \dot{z}_l^{(m)} * z_l^{(n)}\right]\right\}\exp\left(\sum_l z_l^{(m)} * z_l^{(n)}\right)\prod_k\left(a_{1k}^{(m)} * a_{1k}^{(n)} + a_{0k}^{(m)} * a_{0k}^{(n)}\right) \\
&\qquad - \left\langle \mathbf{z}^{(m)} \middle\| \left\langle \zeta^{(m)} \middle| \hat{H} \middle| \zeta^{(n)} \right\rangle \middle\| \mathbf{z}^{(n)} \right\rangle
\end{aligned}$$

(6.3)

The momenta are

$$\begin{aligned}
p_{1j}^{(n)} &= 2\frac{\partial L}{\partial \dot{a}_{1j}^{(n)}} = \sum_m a_{1j}^{(m)} * \exp\left(\sum_l z_l^{(m)} * z_l^{(n)}\right)\prod_{k\neq j}\left(a_{1k}^{(m)} * a_{1k}^{(n)} + a_{0k}^{(m)} * a_{0k}^{(n)}\right) \\
p_{0j}^{(n)} &= 2\frac{\partial L}{\partial \dot{a}_{0j}^{(n)}} = \sum_m a_{0j}^{(m)} * \exp\left(\sum_l z_l^{(m)} * z_l^{(n)}\right)\prod_{k\neq j}\left(a_{1k}^{(m)} * a_{1k}^{(n)} + a_{0k}^{(m)} * a_{0k}^{(n)}\right) \\
p_{zl}^{(n)} &= 2\frac{\partial L}{\partial \dot{z}_l^{(n)}} = \sum_m z_l^{(m)} * \exp\left(\sum_l z_l^{(m)} * z_l^{(n)}\right)\prod_k\left(a_{1k}^{(m)} * a_{1k}^{(n)} + a_{0k}^{(m)} * a_{0k}^{(n)}\right)
\end{aligned}$$

(6.4)

Then the elements of the parameter matrix $\frac{\partial \mathbf{p}}{\partial \boldsymbol{\alpha} *}$

$$\frac{\partial p_{1j}^{(n)}}{\partial a_{1i}^{(m)*}}, \frac{\partial p_{1j}^{(n)}}{\partial a_{0i}^{(m)*}}, \frac{\partial p_{1j}^{(n)}}{\partial z_{i}^{(m)*}}$$
$$\frac{\partial p_{0j}^{(n)}}{\partial a_{1i}^{(m)*}}, \frac{\partial p_{0j}^{(n)}}{\partial a_{0i}^{(m)*}}, \frac{\partial p_{0j}^{(n)}}{\partial z_{i}^{(m)*}} \qquad (6.5)$$
$$\frac{\partial p_{zj}^{(n)}}{\partial a_{1i}^{(m)*}}, \frac{\partial p_{zj}^{(n)}}{\partial a_{0i}^{(m)*}}, \frac{\partial p_{zj}^{(n)}}{\partial z_{i}^{(m)*}}$$

required for the variational equations (1.10) can be obtained by simple differentiation which yields a fully variational Generalilsed Coherent States method very similar in spirit to variational Multiconfigurational Gaussians (vMCG) approach[3, 10] or variational Davydov ansatz[11, 12].

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