Quantum-classical dynamics in the mapping basis

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October 2, 2016

Motivation

- As Dirac remarked, Maxwell's equations of light, and the relativistic wave equation, which he was too modest to call the Dirac equation, govern most of physics, and all of chemistry and biology. So in principle, we ought to be able to predict human behavior, though I can't say I have had much success myself.

Classical mechanics

- Classical mechanics occur on phase space which consists of one dimension (axe) for each coordinate and each momenta.
- The state of a system is determined by a single point in phase space.
- Every property of the system, f, is a function of coordinate, r, and momenta, p.
- Hamiltonian, H: Total energy of the system.
- Dynamics: $\frac{\partial f}{\partial t} = \{f, H\}$
- Poisson bracket: $\{f, g\} = \frac{\partial f}{\partial r}\frac{\partial g}{\partial p} - \frac{\partial f}{\partial p}\frac{\partial g}{\partial r}$

Introduction-Quantum mechanics

- Quantum mechanics lives in the Hilbert spae where there is no hole.
- A vector, C, is denoted by a ket $|C\rangle$. Complex conjugate of such a vector, $C^{\dagger}$, is denoted by a bra $\langle C|$
- bra * ket = bracket, $\langle D|C\rangle$
- ket * bra = operator, $|C\rangle\langle D|$
- Operator acts on a vector to produce another vector

Introduction-Quantum mechanics

- Every observable is represented by an operator, $\hat{E}$, $\hat{X}$, $\hat{P}$
- Density matrix, $\hat{\rho}$, contains all information that can be known about a system.
- For a pure state, $\rho = |\psi\rangle\langle\psi|$
- Quantum Liouville equation $\frac{\partial \hat{\rho}(t)}{\partial t} = \frac{i}{\hbar}[\hat{\rho}(t), \hat{H}]$
- $\{\cdot, \cdot\} \leftrightarrow \frac{i}{\hbar}[\cdot, \cdot]$

Motivation

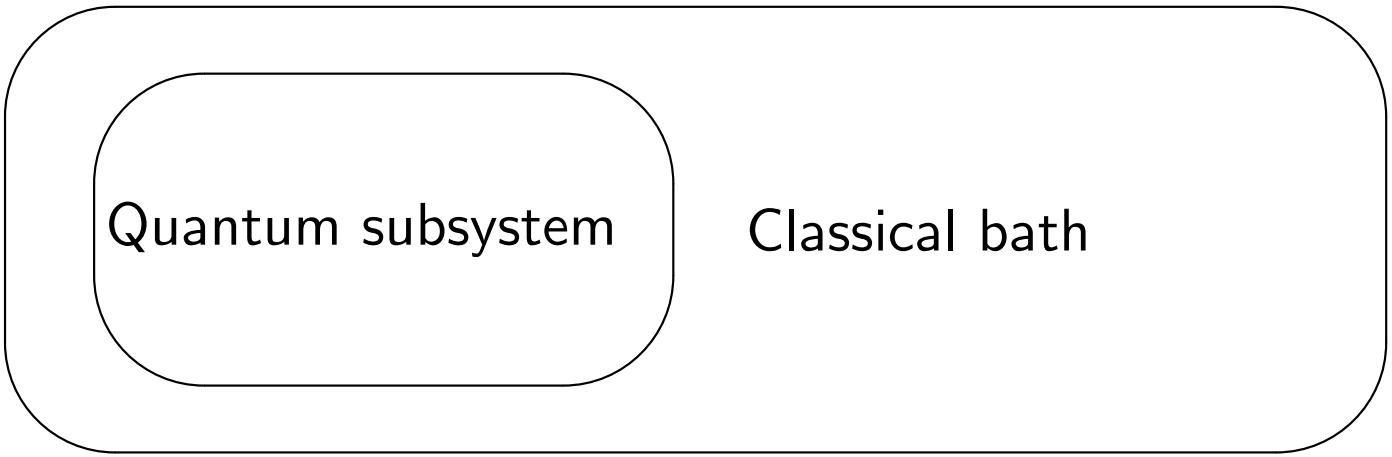
- The computational power and memory of a classical computer linearly scales with its size, while the complexity of a quantum dynamical problem scales exponentially with the size of the system. This point renders a quantum calculation very difficult except for the smallest of systems.
- Considering a number of degrees of freedom as quantum mechanical and approximating the remainder of the system with classical mechanics, seems a viable path for many problems.

Adiabatic (BO) approximation

- The lightest nuclei is 1800 times heavier than electron.
- Thus one might be justified to assume, $\Psi(R, r) = \phi(r; R)\chi(R)$
- It is common to assume classical nuclear degrees of freedom under the effect of electronic potential $\epsilon_n(R)$
- This work addresses many cases where adiabatic approximation fails. The most obvious examples are proton or electron transfer reactions and excitation energy transfer among chromophores.

Partitioning

- Define degrees of freedom to be dealt with quantum mechanically as subsystem with a characteristic mass m. Those to be dealt with classically as bath with a characteristic mass M.



Wigner transform

- Mr. Wigner didn't liked quantum mechanics in a bizarre Hilbert space. So he invented a method to do quantum mechanics in the phase space.
- Wigner transformation

$$A_w(Q,P) = \int dZ \langle Q - \frac{Z}{2}|\hat{A}|Q + \frac{Z}{2}\rangle e^{iPZ/\hbar}$$

  relates every operator in the Hilbert space to a function in the phase space and Weyl transformation do the reverse.
- $\hat{\rho} = \sum_i p_i |\psi_i\rangle\langle\psi_i|$

QCLE

- Liouville-von Neumann equation: $\frac{\partial}{\partial t}\hat{\rho}(t) = -\frac{i}{\hbar}\left[\hat{H}, \hat{\rho}\right]$
- Taking a partial Wigner transform

$$\frac{\partial}{\partial t}\hat{\rho}_W(X,t) = -\frac{i}{\hbar}\Big[(\hat{H}\hat{\rho})_W - (\hat{\rho}\hat{H})_W\Big]$$

- Using

$$(\hat{A}\hat{B})_w = A_w e^{\hbar\Lambda/2i} B_w$$

where

$$\Lambda = \frac{\overleftarrow{\partial}}{\partial p}\frac{\overrightarrow{\partial}}{\partial q} - \frac{\overleftarrow{\partial}}{\partial q}\frac{\overrightarrow{\partial}}{\partial p} = -\{\cdot,\cdot\}$$

and some more manipulation of the Liouville equation in the limit of $\mu = (\frac{m}{M})^{1/2} \to 0$ gives the quantum-classical Liouville equation (QCLE).

- $$\frac{\partial}{\partial t}\hat{\rho}w(X,t) = -\frac{i}{\hbar}[\hat{H}w, \hat{\rho}w] + \frac{1}{2}(\{\hat{H}w, \hat{\rho}w\} - \{\hat{\rho}w, \hat{H}w\})$$

- $$\begin{aligned}\hat{H}_w =& \frac{P^2}{2M} + V_b(R) + \hat{V}_c(R,\hat{r}) + \hat{h}_s(\hat{r},\hat{p}) \\ =& \frac{P^2}{2M} + \hat{h}(R,\hat{r},\hat{p}),\end{aligned}$$

where $\hat{h}_s = \frac{\hat{p}^2}{2m} + \hat{V}_s$.

Solving QCLE

- There have been various attempts for solving QCLE, e.g., in subsystem,

$$\hat{h}_S|\lambda\rangle = \epsilon_\lambda|\lambda\rangle,$$

adiabatic,

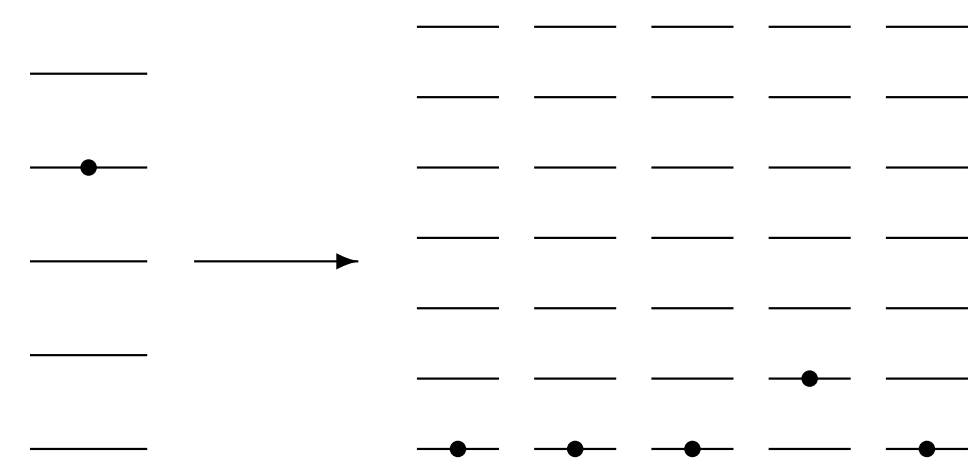
$$\hat{h}(R)|\lambda; R\rangle = \epsilon_\lambda(R)|\lambda; R\rangle,$$

and force bases, but there always have been some difficulties, partly due to the fact that the subsystem and bath degrees of freedom are treated on different footings.

Mapping

- Mapping recipe for states,

$$
\begin{aligned}
|\lambda\rangle \rightarrow \quad & |m_\lambda\rangle = |0_1, ..., 1_\lambda, ..., 0_N\rangle, \\
\langle q|m_\lambda\rangle = \quad & \langle q_1, q_2, ..., q_N|0_1, ..., 1_\lambda, ..., 0_N\rangle \\
= \quad & \phi_0(q_1)...\phi_0(q_{\lambda-1})\phi_1(q_\lambda)...\phi_0(q_N).
\end{aligned}
$$



$$|4\rangle \longrightarrow |0, 0, 0, 1, 0\rangle$$

Mapping

- Mapping recipe for operators

$$\hat{A} = \sum_{\lambda\lambda'} A^{\lambda\lambda'} |\lambda\rangle\langle\lambda'| \rightarrow \hat{A}_m = \sum_{\lambda\lambda'} A_m^{\lambda\lambda'} \hat{a}_\lambda^\dagger \hat{a}_{\lambda'}$$

$$\hat{a}_\lambda = \sqrt{\frac{1}{2\hbar}}(\hat{q}_\lambda + i\hat{p}_\lambda), \qquad \text{and} \qquad \hat{\mathrm{a}}_\lambda^\dagger = \sqrt{\frac{1}{2\hbar}}(\hat{\mathrm{q}}_\lambda - \mathrm{i}\hat{\mathrm{p}}_\lambda).$$

- $$\hat{a}_\lambda^\dagger \hat{a}_{\lambda'} |m_\mu\rangle = \delta_{\lambda'\mu} |m_\lambda\rangle$$

- Using this mapping formalism we transform discrete quantum states to continuous mapping states. Putting all degrees of freedom on the same footing.

Mapping Expectation value

$$\begin{aligned}\overline{A(t)} =& \mathrm{Tr}(\hat{A}(t)\hat{\rho}) \\ =& \int dXdxdx'\ A_m(x,X,t)f(x,x')\rho_m(x',X) \\ =& \int dXdx\ A_m(x,X,t)\tilde{\rho}_m(x,X),\end{aligned}$$

where $\tilde{\rho}_m(x,X) = \int dx' f(x,x')\rho_m(x',X)$ and

$$\begin{aligned}f(x,x') =& \frac{1}{(2\pi\hbar)^N}\sum_{\lambda\lambda'}\int dzdz' \langle m_\lambda | r - \frac{z}{2}\rangle\langle r + \frac{z}{2}|m_{\lambda'}\rangle \\ & \times \langle m_{\lambda'}|r' - \frac{z'}{2}\rangle\langle r' + \frac{z'}{2}|m_\lambda\rangle e^{-i(p\cdot z + p'\cdot z')/\hbar} \\ =& (\frac{2}{\pi\hbar})^N 4\Big[(r\cdot r' + p\cdot p')^2 + (r\cdot p' - r'\cdot p)^2 \\ & - \frac{1}{2}(x^2 + x'^2) + \frac{N}{2}\Big] e^{-(x^2+x'^2)}.\end{aligned}$$

Mapping QCLE

- Casting the QCLE in the subsystem basis and performing the mapping we end up with an equation which can be partially Wigner transformed over the mapping degrees of freedom to yield the mapping QCLE

$$\frac{\partial}{\partial t}\rho_m(t) = -\frac{1}{\hbar}\sum_{\lambda,\lambda'} h_{\lambda\lambda'}\left(p_{\lambda'}\frac{\partial}{\partial r_\lambda} - r_{\lambda'}\frac{\partial}{\partial p_\lambda}\right)\rho_m + \frac{\partial H_m}{\partial R}\frac{\partial \rho_m}{\partial P}$$

$$-\frac{P}{M}\frac{\partial \rho_m}{\partial R} - \frac{\hbar}{8}\sum_{\lambda,\lambda'}\left[\frac{\partial h_{\lambda\lambda'}}{\partial R}\left(\frac{\partial^2}{\partial r_\lambda \partial r_{\lambda'}} + \frac{\partial^2}{\partial p_\lambda \partial p_{\lambda'}}\right)\frac{\partial \rho_m}{\partial P}\right]$$

$$= \{H_m, \rho_m\}_{x,x} - \frac{\hbar}{8}\sum_{\lambda,\lambda'}\left[\frac{\partial h_{\lambda\lambda'}}{\partial R}\left(\frac{\partial^2}{\partial r_\lambda \partial r_{\lambda'}} + \frac{\partial^2}{\partial p_\lambda \partial p_{\lambda'}}\right)\frac{\partial \rho_m}{\partial P}\right].$$

Solution

- Consider the continuity equation for the phase space density

$$\frac{\partial}{\partial t}\rho_m(\chi,t) = -\nabla \cdot j(\chi,t)$$

where flux $j = v \cdot \rho_m$

- Comparing to MQCLE one has

$$v_{r_\lambda} = \dot{r}_\lambda = -\frac{h_{\lambda'\lambda}}{\hbar}p_{\lambda'},\ v_{p_\lambda} = \dot{p}_\lambda = \frac{h_{\lambda\lambda'}}{\hbar}r_{\lambda'}\ , v_R = \dot{R} = -\frac{P}{M}$$

$$v_P = \dot{P} = \frac{\partial H_m}{\partial R} - \frac{\hbar}{8\rho_m}\sum_{\lambda,\lambda'}\left[\frac{\partial h_{\lambda\lambda'}}{\partial R}\left(\frac{\partial^2}{\partial r_\lambda \partial r_{\lambda'}} + \frac{\partial^2}{\partial p_\lambda \partial p_{\lambda'}}\right)\right]\rho_m.$$

Solution

- Ensemble of trajectories

$$\rho(t) = \frac{1}{N}\sum_{i}^{N}\delta(\chi - \chi_i(t))$$

- If one neglects the last term of the dynamics our PDE can be transformed into a number of ODE's

$$\frac{dr_\lambda(t)}{dt} = \sum_{\lambda'} h_{\lambda\lambda'}(R(t))p_{\lambda'}(t),$$

$$\frac{dp_\lambda(t)}{dt} = -\sum_{\lambda'} h_{\lambda\lambda'}(R(t))r_{\lambda'}(t),$$

$$\frac{dR(t)}{dt} = \frac{P(t)}{M}, \quad \frac{dP(t)}{dt} = -\frac{\partial H_m}{\partial R(t)}.$$

Back transformation

- When is the last term of the dynamics negligible? What are we missing by neglecting it and how its effect can be incorporated into the dynamics.
- Motivated by these questions we back transformed every term of the mapping dynamics to the subsystem basis.
- The last term is one forth of effect of the subsystem on the bath dynamics.

Spin-boson model

- $$h_W = \begin{pmatrix} \hbar\gamma(R) & -\hbar\Omega \\ -\hbar\Omega & -\hbar\gamma(R) \end{pmatrix},$$

  and $\gamma(R) = -\sum c_j R_j$. The energy gap of the isolated two-state system is $2\hbar\Omega$.

Results

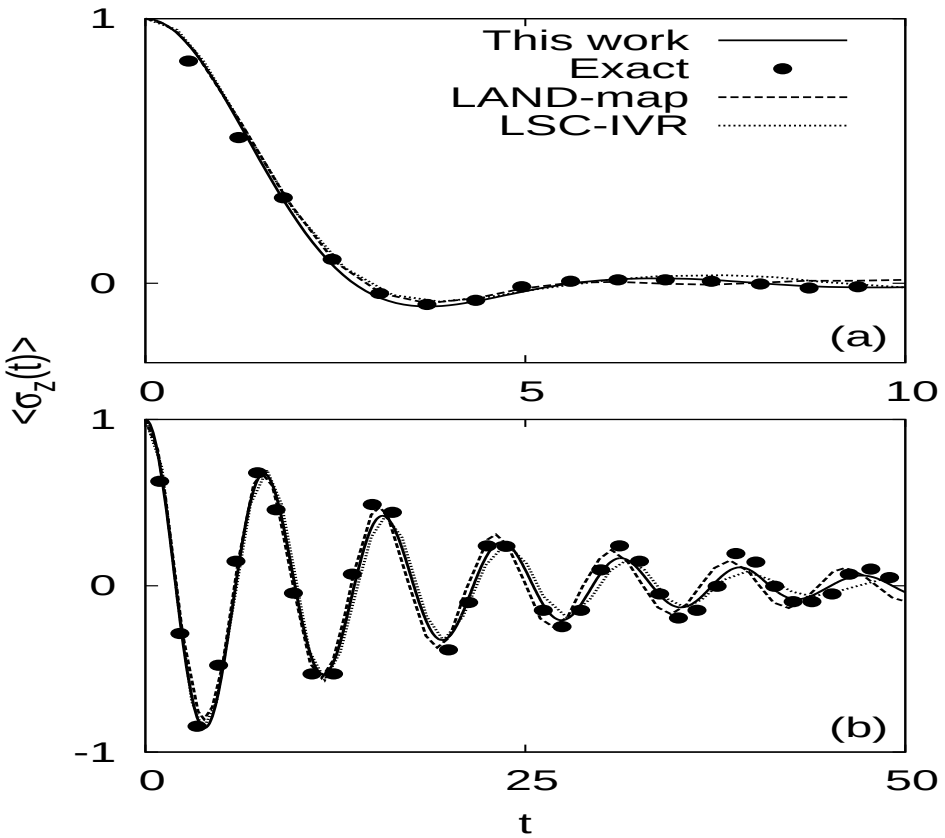


Figure: Electronic population difference $\langle \sigma_z(t) \rangle$ as a function of t for two dimensionless parameter sets: $\Omega = 0.4$, $\xi = 0.09$, and $\beta = 0.25$ (a) or 12.5 (b). The solid points are exact results, the dashed lines are the LAND-map results and the dotted lines are the LSC-IVR results.

Results

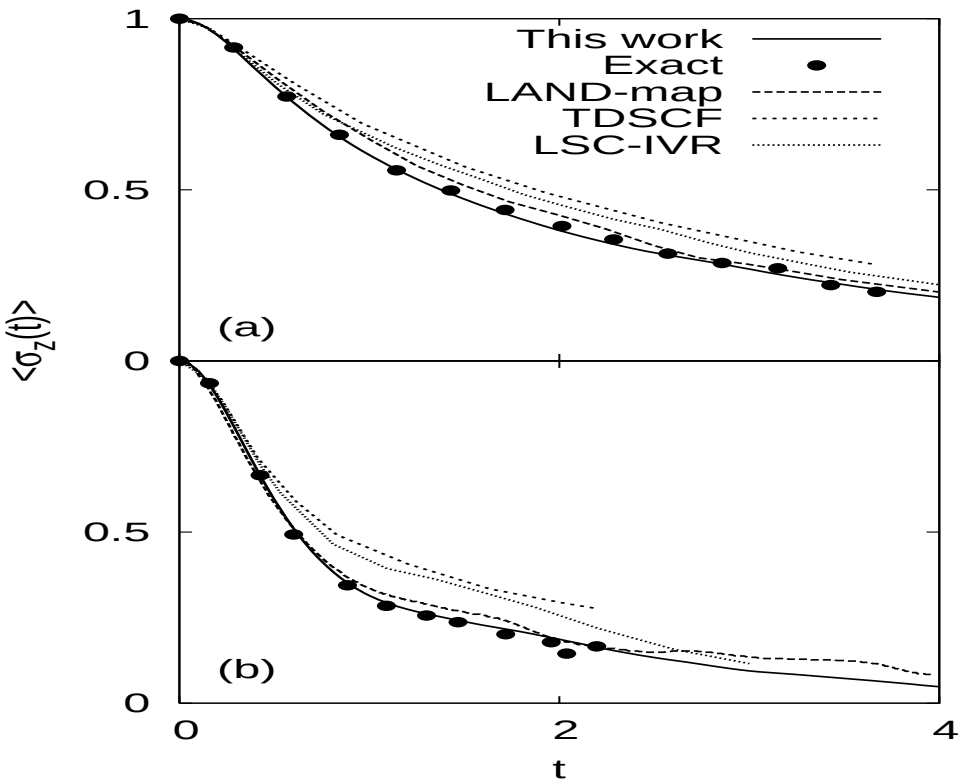


Figure: Electronic population difference $\langle\sigma_z(t)\rangle$ as a function of t for two parameter sets: $\xi = 2$, $\beta = 0.25$, and $\Omega = 0.8$ (a) or 1.2 (b). The solid points are exact results, the dashed lines are the LAND-map results, the dot-dashed lines are the TDSCF results and the dotted lines are the LSC-IVR results.

Result

- In order to save in computational cost of quantum dynamic problems, a semi-consistent quantum-classical dynamics can be derived by approximating quantum dynamics. In this work, using the mapping basis we construct a simulation algorithm to solve quantum-classical Liouville dynamics without suffering from the limitations of surface hoping trajectories.
- Note that one assumes a knowledge of Hamiltonian in this formalism, which is not obvious for any realistic system.

Acknowledgment

- Thanks to my PhD supervisor Prof. Kapral and University of Toronto for financial support during this work.

- Thank you for listening and the floor is yours for questions and discussions.