Zombie Cats on the Quantum-Classical Frontier

Craig C. Martens
University of California, Irvine

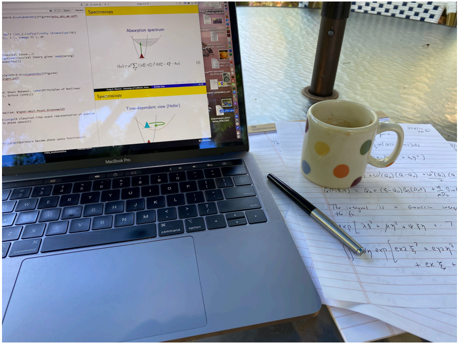
Virtual International Seminar on Theoretical Advancements
Cyberspace, March 17, 2021

Some people bake sourdough bread...

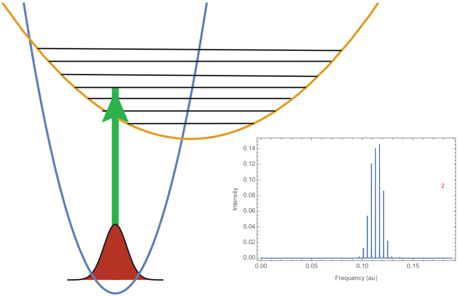
How to Survive the COVID-19 Apocalypse

...others home roast coffee beans...

The subject of this talk

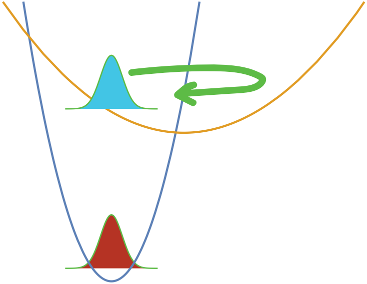


Absorption spectrum



$$I(\omega) \propto \mu^2 \sum_n |\langle \psi_0^g | \psi_n^e \rangle|^2 \, \delta(E_n^e - E_0^g - \hbar\omega) \tag{1}$$

Time-dependent view (Heller)



$$I(\omega) \propto \mu^2 \int_{-\infty}^{\infty} \langle \psi^g(0) \mid \psi^e(t) \rangle \, e^{i\omega t} \, dt$$

Quantum Coherence

Coherence $\hat{\rho}_{eg}$

$$\hat{\rho}_{eg} = |\psi^e(t)\rangle \langle\psi^g(t)|$$

Wavepacket correlation function

$$\langle\psi^g(t) \mid \psi^e(t)\rangle = \mathrm{Tr}\,\hat{\rho}_{eg}$$

This is often treated semiclassically

$$\mathrm{Tr}\,\hat{\rho}_{eg} \simeq \int \rho_{eg}^{SC}(q,p,t)dqdp$$

There is an issue...

Semiclassical theory gives *wrong* mechanical frequencies

us consider the time evolution of ρ_α in a period when the electronic state is $|n\rangle\langle m|$

$$\frac{d\rho_\alpha^{nm}(t)}{dt} = -\frac{i}{\hbar}[H_n\rho_\alpha^{nm}(t) - \rho_\alpha^{nm}(t)H_m], \tag{12.12}$$

where the choice $n, m = \mathrm{e}, \mathrm{g}$ depends on the path (α) as well as on the specific interval (t_1, t_2, or t_3). We next choose a *reference Hamiltonian* that is taken to be some weighted average of H_n and H_m, i.e.,

$$H_\alpha \equiv \eta H_n + (1-\eta)H_m, \tag{12.13}$$

where $0 \le \eta \le 1$. Some obvious choices that will be adopted below are $\eta = 1$ ($H_\alpha = H_n$), $\eta = 0$ ($H_\alpha = H_m$), or $\eta = 1/2$ $H_\alpha = (H_m + H_n)/2$. Using this definition, we can recast Eq. (12.12) in the form

$$\frac{d\rho_\alpha^{nm}}{dt} = -\frac{i}{\hbar}[H_\alpha, \rho_\alpha^{nm}] - \frac{i}{\hbar}[(1-\eta)U_{nm}\rho_\alpha^{nm} + \eta\rho_\alpha^{nm}U_{nm}], \tag{12.14}$$

where $U_{nm} \equiv W_n - W_m$ is the difference of the two adiabatic potentials.

A classical approximation can now be obtained by replacing the commutator in the right-hand side with the classical Liouville equation and assuming that ρ_α^{nm} and U_{nm} commute. We then have

$$\frac{d\rho_\alpha^{nm}}{dt} = \left[\frac{\partial H_\alpha}{\partial \mathbf{q}}\frac{\partial \rho_\alpha^{nm}}{\partial \mathbf{p}} - \frac{\partial H_\alpha}{\partial \mathbf{p}}\frac{\partial \rho_\alpha^{nm}}{\partial \mathbf{q}}\right] - \frac{i}{\hbar}\rho_\alpha^{nm}U_{nm}. \tag{12.15}$$

A more systematic approach involves a switch to the Wigner representation. Making use of Eq. (3.110) and taking the classical ($\hbar \to 0$) limit we get Eq. (12.15) with the choice $\eta = 1/2$, i.e., $H_\alpha = (H_n + H_m)/2$. For physical reasons, as explained in Chapter 7, we may wish to retain the more general form (12.15) with some flexibility in the choice of η. The solution to this equation is

From: Shaul Mukamel, *Principles of Nonlinear Spectroscopy*, Oxford (1995)

Formalism: Wigner-Weyl-Moyal-Groenewold

An exact representation of quantum mechanics
in phase space

Operators become phase space functions

The density operator becomes a (quasi) probability
density in phase space

Weyl Symbols and Wigner Functions

The Weyl symbol of the operator $\hat{A}$:

$$A(q,p) = \int \left\langle q + \tfrac{y}{2} \right| \hat{A} \left| q - \tfrac{y}{2} \right\rangle e^{-ipy/\hbar}\, dy$$

The Wigner function of density operator $\hat{\rho}$:

$$\rho(q,p) = \frac{1}{2\pi\hbar} \int \left\langle q + \tfrac{y}{2} \right| \hat{\rho} \left| q - \tfrac{y}{2} \right\rangle e^{-ipy/\hbar}\, dy$$

For pure state $\psi(q) = \langle q \,|\, \psi \rangle$:

$$\rho(q,p) = \frac{1}{2\pi\hbar} \int \psi^*(q + \tfrac{y}{2}) \psi(q - \tfrac{y}{2}) e^{-ipy/\hbar}\, dy$$

Weyl symbol of an operator product:

$$(AB)(q,p) = \int \left\langle q + \tfrac{y}{2} \right| \hat{A}\hat{B} \left| q - \tfrac{y}{2} \right\rangle e^{-ipy/\hbar}\, dy = A(q,p) \star B(q,p).$$

The star product:

$$A \star B \equiv A e^{\frac{i\hbar}{2}\overleftrightarrow{\Lambda}} B$$

where

$$\overleftrightarrow{\Lambda} = \overleftarrow{\partial}_q \overrightarrow{\partial}_p - \overleftarrow{\partial}_p \overrightarrow{\partial}_q$$

Expansion in $\hbar$:

$$= AB + \frac{i\hbar}{2} A\overleftrightarrow{\Lambda} B - \frac{\hbar^2}{8} A\overleftrightarrow{\Lambda}^2 B + O(\hbar^3)$$

Commutator and Moyal Bracket

Weyl symbol of commutator $[\hat{A}, \hat{B}]$:

$$A \star B - B \star A = 2iA \sin\left(\frac{\hbar}{2}\overleftrightarrow{\Lambda}\right) B \equiv i\hbar\{\{A, B\}\}.$$

This defines the Moyal bracket:

$$\{\{A, B\}\} \equiv \frac{1}{i\hbar}(A \star B - B \star A).$$

or

$$\{\{A, B\}\} = \frac{2}{\hbar} A \sin\left(\frac{\hbar}{2}\overleftrightarrow{\Lambda}\right) B = \{A, B\} + O(\hbar^2).$$

Poisson bracket plus higher order terms in $\hbar$

Liouville Equation in Wigner-Moyal Representation

Quantum Liouville equation

$$i\hbar \frac{d\hat{\rho}}{dt} = [\hat{H}, \hat{\rho}] = \hat{H}\hat{\rho} - \hat{\rho}\hat{H}.$$

Moyal equation

$$\frac{\partial \rho}{\partial t} = \{\{H, \rho\}\} = \frac{2}{\hbar} H \sin\left(\frac{\hbar}{2} \overleftrightarrow{\Lambda}\right) \rho.$$

Moyal series (for $H = T + V$)

$$\frac{\partial \rho}{\partial t} = \{H, \rho\} - \frac{\hbar^2}{24} V'''(q) \frac{\partial^3 \rho}{\partial p^3} + \cdots$$

Classical Liouville equation plus higher order terms

Quantum-Classical *(Semiclassical)* Liouville Equation

Quantum Liouville equation

$$i\hbar \frac{d\hat{\rho}}{dt} = [\hat{H}, \hat{\rho}\,]$$

Two electronic states (diabatic representation)

$$\hat{H} = \begin{pmatrix} \hat{H}_{11} & \hat{V} \\ \hat{V} & \hat{H}_{22} \end{pmatrix} \qquad \hat{\rho} = \begin{pmatrix} \hat{\rho}_{11} & \hat{\rho}_{12} \\ \hat{\rho}_{21} & \hat{\rho}_{22} \end{pmatrix}$$

Quantum-Classical Liouville Equation (Martens *et al.* 1997)

$$\frac{\partial \rho_{11}}{\partial t} = \underbrace{\{H_{11}, \rho_{11}\}}_{\text{classical dynamics}} + \underbrace{\{V, \mathrm{Re}\,\rho_{12}\}}_{\text{nonclassical dynamics}} - \underbrace{\frac{2V}{\hbar}\mathrm{Im}\,\rho_{12}}_{\text{sink/source term}}$$

$$\frac{\partial \rho_{22}}{\partial t} = \underbrace{\{H_{22}, \rho_{22}\}}_{\text{classical dynamics}} + \underbrace{\{V, \mathrm{Re}\,\rho_{12}\}}_{\text{nonclassical dynamics}} + \underbrace{\frac{2V}{\hbar}\mathrm{Im}\,\rho_{12}}_{\text{sink/source term}}$$

$$\frac{\partial \rho_{12}}{\partial t} = \underbrace{\{H_0, \rho_{12}\} - i\omega\rho_{12}}_{\text{generalized classical dynamics}} + \underbrace{\frac{1}{2}\{V, \rho_{11} + \rho_{22}\}}_{\text{nonclassical dynamics}} + \underbrace{\frac{i}{\hbar}V(\rho_{11} - \rho_{22})}_{\text{coherence generation}}$$

$$H_o = (H_{11} + H_{22})/2 \qquad \omega = (H_{11} - H_{22})/\hbar$$

Focus on the evolution of coherence:

$$i\hbar\frac{d\hat{\rho}_{12}}{dt} = \hat{H}_1\hat{\rho}_{12} - \hat{\rho}_{12}\hat{H}_2$$

The Moyal equation becomes

$$\frac{\partial\rho_{12}}{\partial t} = \{H_o, \rho_{12}\} - i\omega\rho_{12} \underbrace{+ \frac{i\hbar^2\omega''}{8}\frac{\partial^2\rho_{12}}{\partial p^2} + \cdots}_{\text{higher order Moyal terms}}$$

Harmonic Potentials

For harmonic systems the series terminates:

$$\frac{\partial \rho_{12}}{\partial t} = \{H_o, \rho_{12}\} - i\omega\rho_{12} + \frac{i\hbar^2\,\omega''}{8}\frac{\partial^2 \rho_{12}}{\partial p^2}$$

$$H_o = (H_1 + H_2)/2 \qquad \omega = (U_1 - U_2)/\hbar$$

$$\Omega_o = \sqrt{(\Omega_1^2 + \Omega_2^2)/2} \qquad \omega'' = m(\Omega_1^2 - \Omega_2^2)/\hbar$$

The semiclassical limit:

$$\frac{\partial \rho_{12}}{\partial t} \simeq \{H_o, \rho_{12}\} - i\omega\rho_{12}$$

Note: coherence between two harmonic systems is *not* "classical" unless the frequencies are equal

The harmonic system is exactly soluble

$$\frac{\partial \rho_{12}}{\partial t} = \{H_o, \rho_{12}\} - i\omega\rho_{12} + \frac{i\hbar^2\omega''}{8}\frac{\partial^2 \rho_{12}}{\partial p^2}$$

Thawed phase space Gaussian ansatz:

$$\rho_{12}(q,p) = \exp[-a(q-Q)^2 - b(p-P)^2 + c(q-Q)(p-P) + u(q-Q) + v(p-P) + w]$$

A closed set of ODE's for (a, b, c, Q, P, u, v, w) result

The "Classical" Phase Space

Moyal term couples (Q, P) and (u, v) subsystems

$$\dot{Q} = \frac{P}{m}$$

$$\dot{P} = \underbrace{-U_o{}'(Q)}_{\Omega_o} - \underbrace{\frac{i\hbar^2}{4}\omega'' v}_{\text{Moyal}}$$

$$\dot{u} = -i\omega'(Q) + U_o{}'' v$$

$$\dot{v} = -\frac{1}{m} u$$

Complex phase space transformation

$$\xi_1 = Q + \frac{i\hbar}{2} v$$

$$\eta_1 = P - \frac{i\hbar}{2} u$$

$$\xi_2 = Q - \frac{i\hbar}{2} v$$

$$\eta_2 = P + \frac{i\hbar}{2} u$$

$$\longrightarrow$$

$$\dot{\xi}_1 = \frac{\eta_1}{m}$$

$$\dot{\eta}_1 = -U_1{}'(\xi)$$

$$\dot{\xi}_2 = \frac{\eta_2}{m}$$

$$\dot{\eta}_2 = -U_2{}'(\xi).$$

Classical dynamics on the individual surfaces!

The mechanical frequencies Ω_1 and Ω_2 reappear!

Q and P are superpositions of
two independent classical motions

$$\xi_1 \to Q_1$$

$$\xi_2 \to Q_2$$

$$\eta_1 \to P_1$$

$$\eta_1 \to P_1$$

$$Q = \frac{1}{2}(Q_1 + Q_2)$$

$$P = \frac{1}{2}(P_1 + P_2)$$

$$u = \frac{i(P_1 - P_2)}{\hbar}$$

$$v = -\frac{i(Q_1 - Q_2)}{\hbar}$$

(Q_j, P_j) simple harmonic motion on j^{th} state

Semiclassical limit solution

In the semiclassical limit:

$$\frac{\partial \rho_{12}}{\partial t} = \{H_o, \rho_{12}\} - i\omega\rho_{12}$$

(Q, P) and (u, v) *almost* uncouple

$$\dot{Q} = \frac{P}{m}$$

$$\dot{P} = -U_o{}'(Q)$$

Harmonic motion
with *single* frequency Ω_o

$$\dot{u} = U_o{}''v - i\omega'(Q(t))$$

$$\dot{v} = -\frac{1}{m}u$$

Resonantly driven
harmonic motion

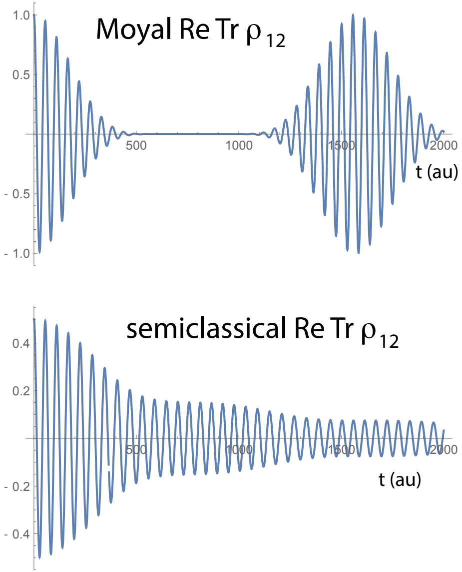
In the semiclassical limit:

$$u(t) = \frac{i\omega'' R(0)}{4\Omega_o}\left(\sin(\Omega_o t) - 2\Omega_o t \cos(\Omega_o t)\right)$$

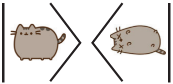
$$v(t) = \frac{i\omega'' R(0)}{4m\Omega_o^2}\left(3\cos(\Omega_o t) - 3 + 2\Omega_o t \sin(\Omega_o t)\right)$$

Secular terms in (u, v) lead to spurious decoherence of ρ_{12}

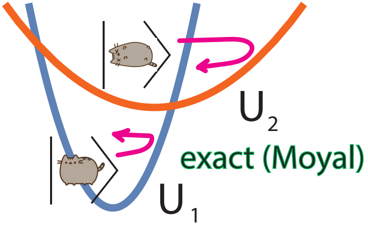
Exact Moyal and semiclassical trace



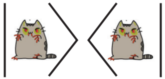
Exact Moyal: Schrödinger's Cats are Alive *and* Dead

$\rho_{12} =$  $e^{i\phi}$

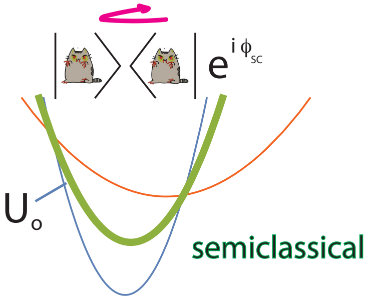
Multiple paths—independent evolution of live and dead cats



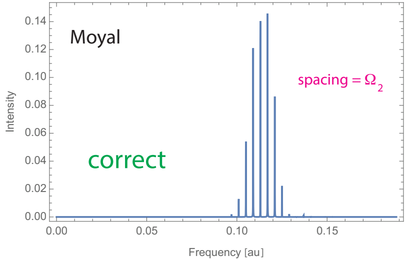
Semiclassical ZOMBIE CATS

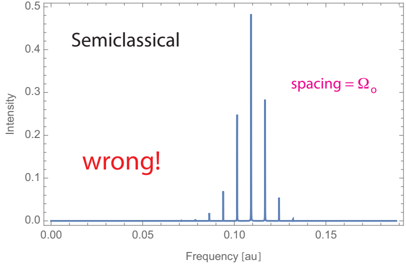
$\rho^{SC}_{12} =$  $e^{i\phi_{SC}}$

Single path evolution on average potential
—neither alive nor dead!



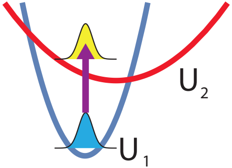
Experimental Evidence for ZOMBIES?





Model system

$$\Omega_1 = 0.01 \qquad \Omega_2 = 0.004$$



(To obtain semiclassical spectrum, further approximation: linearize difference potential!)

Motivation and Future Work

The semiclassical coherence has issues:

$$\frac{\partial \rho_{12}}{\partial t} = \{H_o, \rho_{12}\} - i\omega\rho_{12}$$

- Incorrect mechanical frequencies
- Spurious *decoherence*

Motivation and Future Work

The first Moyal correction solves these problems (for harmonic systems)

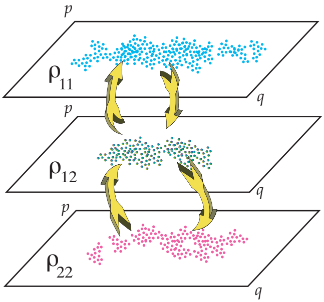
$$\frac{\partial \rho_{12}}{\partial t} = \{H_o, \rho_{12}\} - i\omega\rho_{12} + \frac{i\hbar^2\omega''}{8}\frac{\partial^2 \rho_{12}}{\partial p^2}$$

Future work:

Approximations to Moyal term in trajectory-based methods

Surface Hopping Methodology

- Improve absolute accuracy of individual trajectory phases
- More accurate overall fidelity of ensemble coherence



Ehrenfest dynamics: A zombie apocalypse

Motivation and Future Work

Moyal correction: Vaccine against quantum zombies?

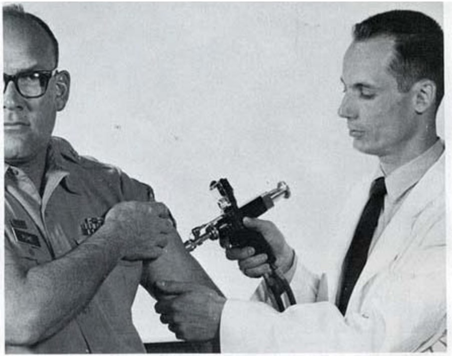


FIGURE 12.—Hypodermic jet injection gun, developed by the U.S. Army Medical Research and Development Command, being used to administer an inoculation. This device provides a fast, safe method for giving mass inoculations to troops.

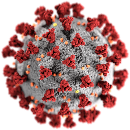
Acknowledgments

Thanks to:

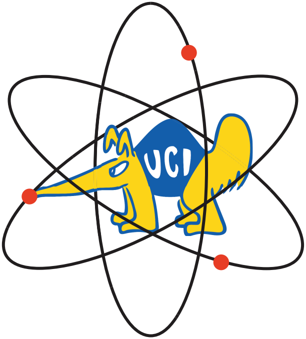
Shaul Mukamel, Vladimir Mandelshtam, Filipp Furche (UCI)
Greg Ezra (Cornell)
Austin Green (UCI)

Telluride Science Research Center (TSRC) Workshops 2013–2020
UCI Liquid Theory Lunch (LTL) @ Anthill Pub

National Science Foundation



Thanks for listening!



Questions?