Lausanne Lectures

Density Operator Formalism

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VU

Density operator and Liouville equation

- Fundamentals
  - CM and QM dynamics
  - Statistical Mechanics
  - Pure and mixed states
- Connections
  - QM–CM interactions
  - Measurement
  - Quantum computing
- Applications
  - (Non)–linear optics
  - Quantum dissipation
  - Excited state proton transfer
- Problems
  - The Ehrenfest problem
  - Quantum dissipation
  - Strong interaction

$$\boxed{\frac{\partial \,|\,\rho\rangle\rangle}{\partial t} = -2\pi i \mathcal{L}_0 \,|\,\rho\rangle\rangle - 2\pi i \mathcal{L}(t) \,|\,\rho\rangle\rangle}$$

Fundamentals: Classical Distribution Functions

Classical particle, position $\vec{r}(t)$, momentum $\vec{p}(t)$, governed by Hamiltonian $\mathcal{H}$.
Probability density of finding it at position $(\vec{r}(t), \vec{p}(t))$ in phase space Γ at time t:

$$\rho(\vec{r}(t), \vec{p}(t), t)$$

Time dependence follows from the Hamilton equations:

$$\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + \frac{\partial\rho}{\partial\vec{r}} \cdot \frac{d\vec{r}}{dt} + \frac{\partial\rho}{\partial\vec{p}} \cdot \frac{d\vec{p}}{dt} = \frac{\partial\rho}{\partial t} + \frac{\partial\rho}{\partial\vec{r}} \cdot \frac{\partial\mathcal{H}}{\partial\vec{p}} - \frac{\partial\rho}{\partial\vec{p}} \cdot \frac{\partial\mathcal{H}}{\partial\vec{r}} = \frac{\partial\rho}{\partial t} - \{\mathcal{H}, \rho\}$$

Poisson bracket:

$$\{A, B\} = \sum_i \left[\frac{\partial A}{\partial x_i} \frac{\partial B}{\partial p_i} - \frac{\partial B}{\partial x_i} \frac{\partial A}{\partial p_i} \right]$$

Liouville's theorem:

$$\frac{d\rho}{dt} = 0$$

or

$$\frac{\partial\rho}{\partial t} = \{\mathcal{H}, \rho\} \equiv -\vec{\nabla}_\Gamma \cdot \vec{j}_\rho = -\vec{\nabla}_\Gamma \cdot \vec{v}_\Gamma \rho$$

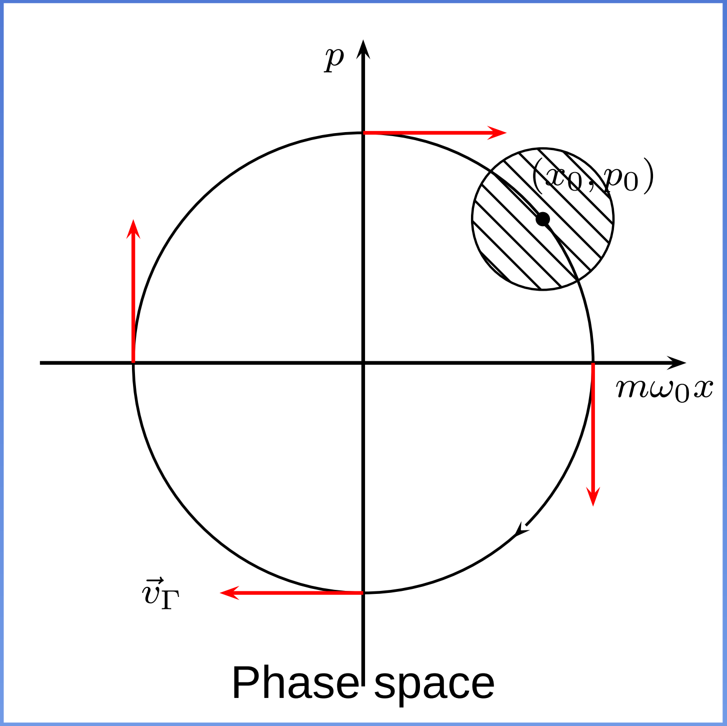
Example: The one–dimensional harmonic oscillator

Hamiltonian:

$$\mathcal{H} = \frac{p^2}{2m} + \frac{1}{2} m\omega_0^2 x^2$$

Liouville equation:

$$\frac{\partial \rho(x,p,t)}{\partial t} = -\frac{p}{m}\frac{\partial \rho}{\partial x} + m\omega_0^2 x \frac{\partial \rho}{\partial p}$$



Phase space

Fundamental solution:

$$\rho(x_1, p_1, t | x_0, p_0) = \delta(x_1 - x(t))\delta(p_1 - p(t))$$

with

$$\begin{aligned} x(t) &= x_0 \cos\omega_0 t + \frac{p_0}{m\omega_0}\sin\omega_0 t \\ p(t) &= -m\omega_0 x_0 \sin\omega_0 t + p_0 \cos\omega_0 t \end{aligned}$$

Equilibrium solution

Since $\{f(\mathcal{H}), \mathcal{H}\} = 0$,

$$\rho_{\mathrm{eq}} = \frac{e^{-\beta \mathcal{H}}}{\int dp \int dx\, e^{-\beta \mathcal{H}}}$$

is a solution of the Liouville equation.

Remarks:

- Liouville's theorem is derived from conservation of probability: area in phase space is conserved.
- Density in phase space behaves like an incompressible fluid.
- No decay to equilibrium, in general.
- Only for the harmonic oscillator: no distortion.

Fokker–Planck and Langevin equations

Inclusion of friction effects (“coupling to a bath”) leads to

$$\frac{\partial \rho(x,p,t)}{\partial t} = -\frac{p}{m}\frac{\partial \rho}{\partial x} + m\omega_0^2 x \frac{\partial \rho}{\partial p} + \zeta \frac{\partial}{\partial p}\left[k_B T \frac{\partial}{\partial p} + \frac{p}{m}\right]\rho$$

ζ = friction coefficient.

Alternative formulation:

Random force

$$\begin{aligned} \frac{dx}{dt} &= \frac{p}{m} \\ \frac{dp}{dt} &= -\zeta\frac{p}{m} - m\omega_0^2 x + F_R(t) \end{aligned}$$

Fluctuation–dissipation theorem:

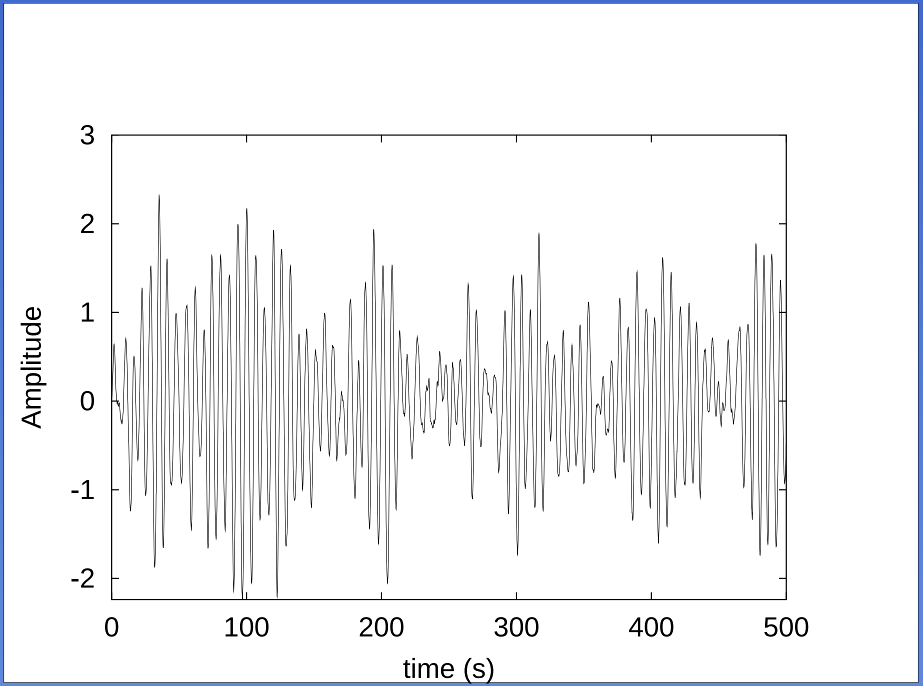
$$\langle F_R(t)F_R(t')\rangle = 2k_B T\zeta\delta(t-t')$$

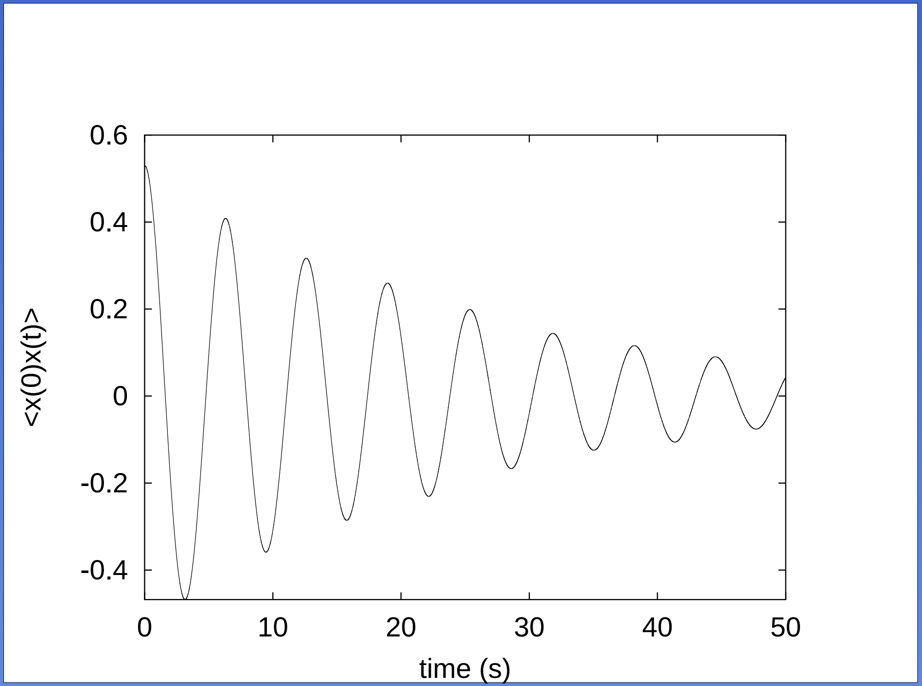
Literature: N.G. van Kampen, “Stochastic Processes in Physics and Chemistry”.

N. Wax, “Selected Papers on Noise and Stochastic Processes”.

The Brownian oscillator (1)

Single damped oscillator with random force:



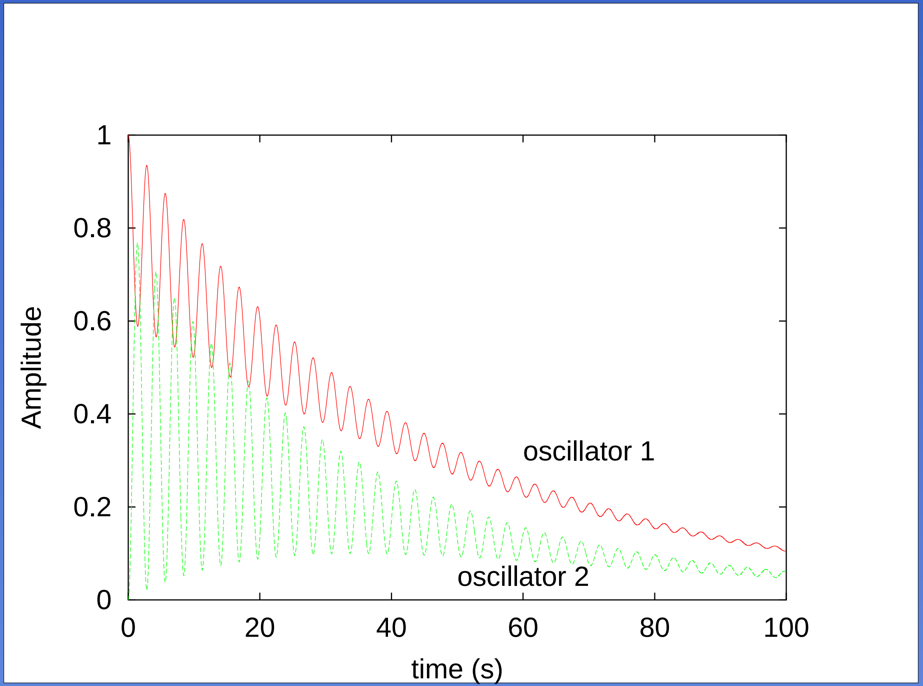


Parameters:

m	1
ω_0	1
ζ	0.1
$k_B T$	≈ 2

$$\langle x\, x(t)\rangle = \frac{k_B T}{m\omega_0^2} e^{-0.05t} \cos 0.999t$$

Brownian oscillators (2): coupled oscillators



m_1	1
m_2	1
ω_1	1
ω_2	2
γ	0.2
ζ	0.1

Equations of motion:

$$m_1 \frac{d^2 x_1}{dt^2} = -\omega_1^2 x_1 + \gamma x_2$$

$$m_2 \frac{d^2 x_2}{dt^2} = -\omega_2^2 x_2 - \zeta \frac{dx_2}{dt} + \gamma x_1$$

Note: see also lecture 2

Langevin equations: non–Markovian behavior (1)

Coupled equations

$$m_1 \frac{d^2 x_1}{dt^2} = -\omega_1^2 x_1 + \gamma x_2$$

$$m_2 \frac{d^2 x_2}{dt^2} = -\omega_2^2 x_2 - \zeta \frac{dx_2}{dt} + \gamma x_1 + F_R(t)$$

lead to non–Markovian behavior of oscillator 1:

Solve the second equation formally (use Fourier transforms this time)

$$x_2(\omega) = \frac{\gamma x_1(\omega) + F_R(\omega)}{-m_2\omega^2 - i\omega\zeta + \omega_2^2}$$

and substitute in the first:

$$-m_1\omega^2 x_1(\omega) + \omega_1^2 x_1(\omega) - \frac{\gamma^2 x_1(\omega)}{-m_2\omega^2 - i\omega\zeta + \omega_2^2} = \frac{\gamma F_R(\omega)}{-m_2\omega^2 - i\omega\zeta + \omega_2^2}$$

Langevin equations: non–Markovian behavior (2)

And do some minor rearrangement to get:

$$-m_1\omega^2 x_1(\omega) - i\omega\zeta_1(\omega)x_1(\omega) + \omega_{\mathrm{pmf}}^2 x_1(\omega) = \overline{F}_R(\omega)$$

- Potential of mean force (equilibrium solvation)

$$\omega_{\mathrm{pmf}}^2 = \omega_1^2\left(1 - \frac{\gamma^2}{\omega_1^2\omega_2^2}\right)$$

- Frequency dependent friction:

$$\zeta_1(\omega) = \frac{\gamma^2}{\omega_2^2}\frac{-i\omega m_2 + \zeta}{-m_2\omega^2 - i\omega\zeta + \omega_2^2}$$

- Random Force:

$$\left\langle \overline{F}_R(\omega)\overline{F}_R(\omega')\right\rangle = 2k_BT\zeta_1(\omega)2\pi\delta(\omega-\omega')$$

Note: frequency dependence reflects underlying dynamics.

D. Han, Y.S. Kim, and M.E. Noz, Am. J. Phys. 67, (1999), 61–66.

Classical conclusions

- Classical Liouville equation, Liouville’s theorem: conservation of probability.
- Fokker–Planck equation: approach to equilibrium.
- Coupled systems: Brownian oscillators, coupled to undamped systems lead to equilibrium for the initially undamped system.
- Langevin equations give equivalent description.
- Two simple examples: uncoupled and coupled oscillators.
- Application: Kramers theory for chemical reaction kinetics.
- Classical Brownian dynamics simulations* are simple (to a point).
- Non–Markovian behavior is the result of a lower layer of dynamics.

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*A.C. Brańka and D.M. Heyes, Phys. Rev. E60, (1999), 2381.
H.A. Forbert and S.A. Chin, Phys. Rev. E63, (2001), 016703.

Quantum dynamics (1): Hilbert Space

Schrödinger equation:

$$\frac{\partial \left|\psi\right\rangle}{\partial t} = -\frac{i}{\hbar}\mathcal{H}\left|\psi\right\rangle$$

Expansion in eigenfunctions of $\mathcal{H}$:

$$\left|\psi\right\rangle = \sum_n \psi_n \left|n\right\rangle$$

Expectation values of operators A:

$$\langle A\rangle = \langle\psi|\, A\,|\psi\rangle = \sum_{n,m}\psi_m^* \langle m|\, A\,|n\rangle\, \psi_n = \sum_{n,m}\psi_m^*\psi_n A_{mn} \equiv \sum_{n,m}\rho_{nm}A_{mn}$$

“Density matrix” (von Neumann, (1927))

$$\rho_{nm} = \psi_m^*\psi_n \;\;\Rightarrow\;\; \langle A\rangle = \mathrm{Tr}[\rho\cdot A]$$

- ρ_{nn}: populations
- ρ_{nm} $(n \neq m)$: coherences

R.C. Tolman, “The Principles of Statistical Mechanics”, Ch. IX.

R.P. Feynman, “Statistical Mechanics, A Set of Lectures”, Ch. 2.

Quantum dynamics (2). Liouville equation

Properties: ρ is hermitian ($\rho^\dagger = \rho$), and

$$\mathrm{Tr}[\rho] = 1$$

Equation of motion (quantum Liouville equation)

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar} [\mathcal{H}, \rho]$$

compare: Heisenberg picture for operator A:

$$\frac{dA}{dt} = \frac{i}{\hbar} [\mathcal{H}, A]$$

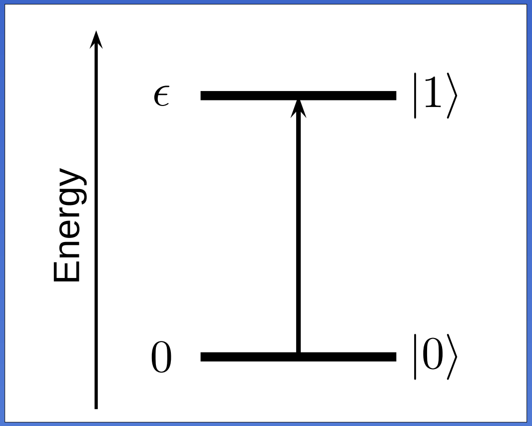
compare: Classical Liouville equation

$$-\frac{i}{\hbar} \{\mathcal{H}, \cdots\} \longleftrightarrow [\mathcal{H}, \cdots]$$

Commutator and Poisson brackets are both *Lie brackets*: antisymmetric, and satisfying the Jacobi identity:

$$[A, [B, C]] + [C, [A, B]] + [B, [C, A]] = 0$$

Example: two–level system (2LS)



Hamiltonian: $\mathcal{H} = \epsilon \left|1\right\rangle \left\langle 1\right|$

Dipole operator: $\hat{\vec{\mu}} = \vec{\mu}_0 \left|0\right\rangle \left\langle 0\right| + \vec{\mu}_1 \left|1\right\rangle \left\langle 1\right| + \vec{\mu}[\left|0\right\rangle \left\langle 1\right| + \left|1\right\rangle \left\langle 0\right|]$

Interaction Hamiltonian: $\mathcal{H}_{\mathrm{int}} = -\hat{\vec{\mu}} \cdot \vec{E}(t)$

- 🟩 Exact for spin 1/2 systems (ESR, NMR).
- 🟩 Good approximation for resonant electronic transitions.
- 🟩 In quantum computing: *qubit*.
- 🟩 Nontrivial (*e.g.* non–linear optics).

Quantum state: $\left|\psi\right\rangle = \cos\theta \left|0\right\rangle + \sin\theta e^{i\phi} \left|1\right\rangle$

Density matrix: $\rho = \begin{pmatrix} \cos^2\theta & \cos\theta\sin\theta e^{i\phi} \\ \cos\theta\sin\theta e^{-i\phi} & \sin^2\theta \end{pmatrix}$

Equilibrium

Ensemble average:

$$\rho = \sum_{\alpha} \psi_m^{(\alpha)*} \psi_n^{(\alpha)} = \overline{\psi_m^* \psi_n}$$

Equilibrium density matrix (coherences vanish, and diagonal elements become equilibrium populations):

$$\rho_{\mathrm{eq}} = \frac{e^{-\beta\mathcal{H}}}{Q} = \frac{1}{1+e^{\beta\epsilon}} \begin{pmatrix} 1 & 0 \\ 0 & e^{-\beta\epsilon} \end{pmatrix}$$

It is impossible to find a single quantum state that corresponds to this density matrix.

Mixed states: density matrices to which no single quantum state corresponds

$$\mathrm{Tr}[\rho^2] < 1$$

Operators (and therefore the density operator) are vectors in Liouville space.

$$|\rho\rangle\rangle = \begin{pmatrix} \rho_{00} \\ \rho_{01} \\ \rho_{10} \\ \rho_{11} \end{pmatrix}$$

Quantum dynamics (3): Liouville space

Inner product:

$$\langle\langle A \mid B\rangle\rangle = \mathrm{Tr}[A^\dagger B]$$

Liouville equation:

$$\frac{\partial\,|\,\rho\rangle\rangle}{\partial t} = -\frac{i}{\hbar}\mathcal{L}\,|\,\rho\rangle\rangle \quad \text{with} \quad \mathcal{L}_{ij,kl} = \mathcal{H}_{ik}\delta_{jl} - \mathcal{H}_{lj}\delta_{ik}$$

System (2LS) Liouvillian:

$$-\frac{i}{\hbar}\mathcal{L}_0 = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & -2\pi i\nu_0 & 0 & 0 \\ 0 & 0 & 2\pi i\nu_0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \qquad \nu_0 = \text{transition frequency}$$

- Coupled systems, reduced density matrix.
- Coupling to external fields.
- Relaxation, Redfield theory.
- Mixed quantum–classical dynamics.

S. Mukamel, “Principles of Nonlinear Optical Spectroscopy”, Ch. 3.

Quantum dynamics (4)

Why not add friction to the Scrödinger equation

- We don’t want the wave functions to go to zero
- If we do it in the Heissenberg picture commutation relations go to zero, and we don’t want that either, we want decay to the ground state (for instance)
- Apart from the $T = 0$ case, equilibrium is not a *state*. An impure density matrix does not correspond to a quantum state, but to a mixture.
- So, if we want decay to an equilibrium density matrix, we need to start with a density matrix, even if it corresponds to a pure state.

Liouville space

Liouville space is the space of operators. It is also a Hilbert space.

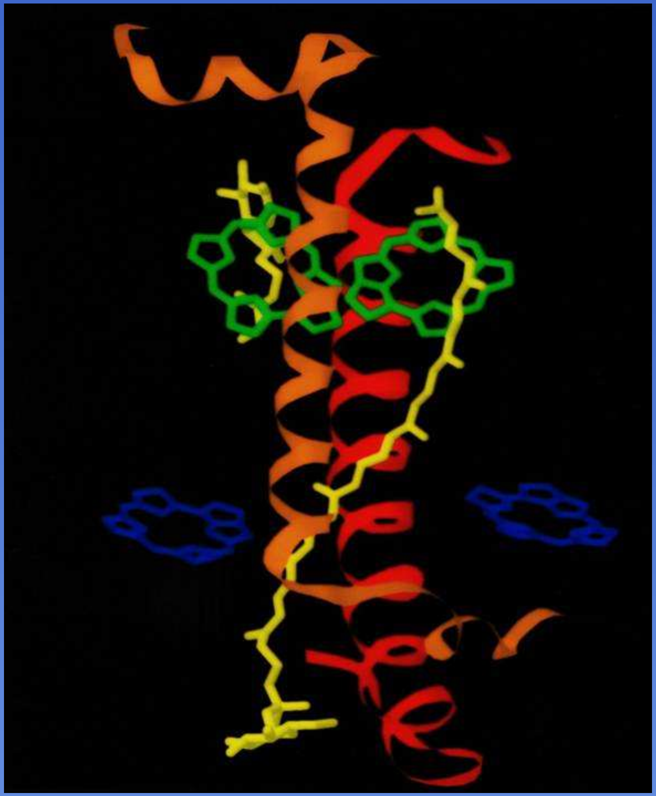
- It is a complex vector space.
  - Addition of operators is defined, and multiplication by complex numbers
  - Addition is commutative, multiplication distributive
  - There is a unit element.
- There is an inner product: $\langle\langle A \mid B \rangle\rangle = \mathrm{Tr}[A^\dagger B]$.
- It is complete: $\sum_n \mid n\rangle\rangle \, \langle\langle n \mid = \mathbf{1}$.

For a 2LS it is the space of vectors with four complex elements:

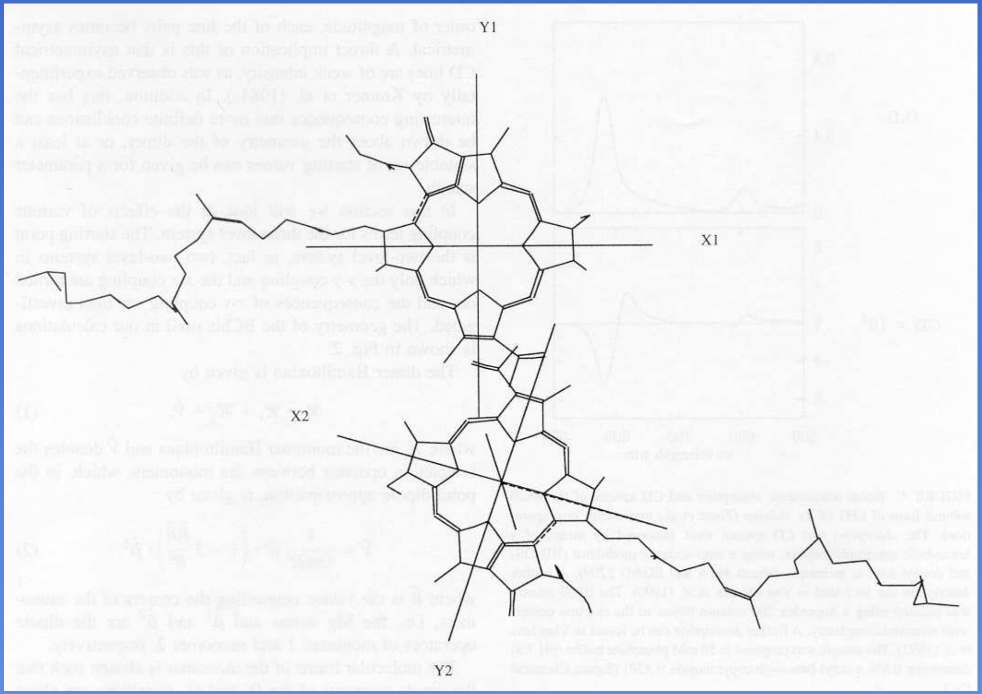
$$A = \begin{pmatrix} a_{00} & a_{01} \\ a_{10} & a_{11} \end{pmatrix} \quad \Leftrightarrow \quad \begin{pmatrix} a_{00} \\ a_{01} \\ a_{10} \\ a_{11} \end{pmatrix} \equiv \mid A \rangle\rangle \quad \text{and} \quad \langle\langle A \mid = \begin{pmatrix} a_{00}^* & a_{01}^* & a_{10}^* & a_{11}^* \end{pmatrix}$$

<u>Exercise:</u> calculate $\langle\langle A \mid A \rangle\rangle$ and $\mid A \rangle\rangle \, \langle\langle A \mid$.

Coupled systems, reduced density matrix (1)



The B820 subunit is a dimer of bacteriochlorophylls



Hamiltonian:

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_{\mathrm{int}} = \epsilon_1 \left|1\right\rangle \left\langle 1\right| \otimes \mathbf{1}_2 + \mathbf{1}_1 \otimes \epsilon_2 \left|1\right\rangle \left\langle 1\right| + \frac{1}{4\pi\epsilon_0\epsilon_r r^3} \hat{\vec{\mu}}_1 \cdot \left[1 - \hat{r}\hat{r}\right] \cdot \hat{\vec{\mu}}_2$$

M.H.C. Koolhaas, G. van der Zwan, F. van Mourik, and R. van Grondelle, Biophys. J. 72, (1997), 1828.

R.G. Stomphorst, T.J. Schaafsma, and G. van der Zwan, J. Phys. Chem. A, 105, (2001), 4226.

Coupled systems, reduced density matrix (2)

States of the dimer: $|ij\rangle = |i\rangle \otimes |j\rangle$, monomer 1 in state i, monomer 2 in state j.
Hamiltonian (only transition dipole moments):

$$\mathcal{H} = \begin{pmatrix} 0 & 0 & 0 & V \\ 0 & \epsilon_2 & V & 0 \\ 0 & V & \epsilon_1 & 0 \\ V & 0 & 0 & \epsilon_1 + \epsilon_2 \end{pmatrix}$$

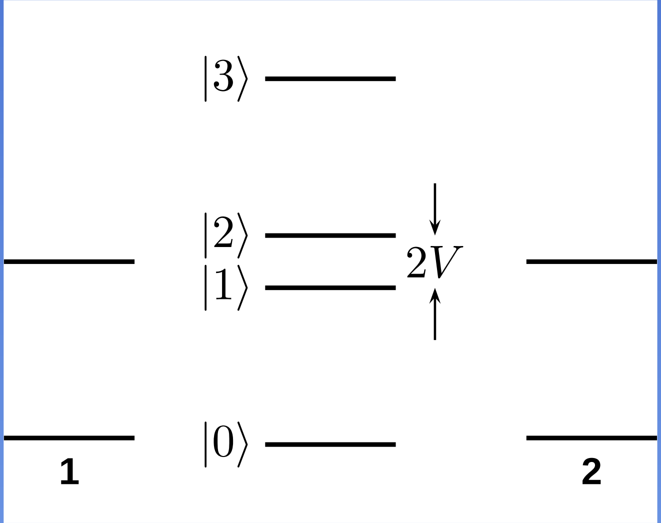
Diagonalize to get the new states:

$$|0\rangle = c_1 |00\rangle + s_1 |11\rangle$$

$$|1\rangle = c_2 |00\rangle + s_2 |11\rangle$$

$$|2\rangle = -s_2 |00\rangle + c_2 |11\rangle$$

$$|3\rangle = -s_1 |00\rangle + c_1 |11\rangle$$



Reduced density matrix for system 1, when total system is in the ground state:

$$\sigma_1 = \mathrm{Tr}_2[|0\rangle\langle 0|] = \begin{pmatrix} c_1^2 & 0 \\ 0 & s_1^2 \end{pmatrix}$$

Not a pure state

Coupling to external fields

External (electric) fields $\vec{E}(t)$ couple to the dipole operator. These fields can be due to

- Other systems (such as in previous slides): excitonic coupling.
- Optical fields $\vec{E}(t) = \vec{E}_0 e^{-i\vec{k}\cdot\vec{r}+i\omega t} +$ cc: linear and non–linear optics.
- Applied static electric fields (such as in Stark spectroscopy).
- Random fields in polarizable media: homogeneous and inhomogeneous broadening.
- Reaction fields in polarizable media: electronic structure changes.
- Damped fields in the environment: dissipation.

Hamiltonian:

$$\mathcal{H} = \mathcal{H}_0 - \hat{\vec{\mu}} \cdot \vec{E}(t)$$

Liouville equation:

$$\frac{\partial \,|\,\rho(t)\rangle\rangle}{\partial t} = -\frac{i}{\hbar}\,[\mathcal{L}_0 + \mathcal{L}_{\text{int}}]\,|\,\rho(t)\rangle\rangle$$

with

$$\mathcal{L}_{\text{int}} \cdots = [\mathcal{H}_{\text{int}}, \cdots] = -[\hat{\vec{\mu}}, \cdots] \cdot \vec{E}(t)$$

Example: 2LS in external optical field

Liouville space dipole operator, neglecting permanent moments:

$$\mathcal{L}_{\text{int}} = \begin{pmatrix} 0 & -\vec{\mu}\cdot\vec{E}(t) & \vec{\mu}\cdot\vec{E}(t) & 0 \\ \vec{\mu}\cdot\vec{E}(t) & 0 & 0 & -\vec{\mu}\cdot\vec{E}(t) \\ -\vec{\mu}\cdot\vec{E}(t) & 0 & 0 & \vec{\mu}\cdot\vec{E}(t) \\ 0 & \vec{\mu}\cdot\vec{E}(t) & -\vec{\mu}\cdot\vec{E}(t) & 0 \end{pmatrix}$$

From now on: $h = c = 1$ (so everything can be expressed in cm^{-1}).

Equation of motion:

$$\frac{\partial \,|\,\rho\rangle\rangle}{\partial t} = -2\pi i[\mathcal{L}_0 + \mathcal{L}_{\text{int}}(t)]\,|\,\rho\rangle\rangle$$

Formal solution (system initially in state $|\,0\rangle\rangle$):

$$|\,\rho(t)\rangle\rangle = e^{-2\pi i\mathcal{L}_0 t}\,|\,0\rangle\rangle - 2\pi i\int_0^t d\tau\, e^{2\pi i\mathcal{L}_0(\tau-t)}\mathcal{L}_{\text{int}}(\tau)\,|\,\rho(\tau)\rangle\rangle$$

Resulting polarisation:

$$\vec{P}(t) = \langle\langle\hat{\vec{\mu}}|\rho(t)\rangle\rangle$$

Linear and non–linear optics

Expand the formal solution to the desired order:

$$\begin{aligned}
&|\,\rho(t)\rangle\rangle = e^{-2\pi i\mathcal{L}_0 t}\,|\,0\rangle\rangle - 2\pi i\int_0^t d\tau\, e^{2\pi i\mathcal{L}_0(\tau-t)}\mathcal{L}_{\rm int}(\tau)\,|\,0\rangle\rangle - \\
&4\pi^2\int_0^t d\tau\int_0^\tau d\tau_1\, e^{2\pi i\mathcal{L}_0(\tau-t)}\mathcal{L}_{\rm int}(\tau)e^{2\pi i\mathcal{L}_0(\tau_1-\tau)}\mathcal{L}_{\rm int}(\tau_1)\,|\,0\rangle\rangle + \\
&8\pi^3 i\int_0^t d\tau\int_0^\tau d\tau_1\int_0^{\tau_1} d\tau_2\, e^{2\pi i\mathcal{L}_0(\tau-t)}\mathcal{L}_{\rm int}(\tau)e^{2\pi i\mathcal{L}_0(\tau_1-\tau)}\mathcal{L}_{\rm int}(\tau_1)e^{2\pi i\mathcal{L}_0(\tau_2-\tau_1)}\mathcal{L}_{\rm int}(\tau_2)\,|\,0\rangle\rangle \\
&\ldots\ldots
\end{aligned}$$

Thus we get for $\vec{P}(t)$ (in isotropic systems)

Linear optics, absorption, CD, LD, etc.

$$\begin{aligned}
&\vec{P}(t) = -2\pi i\int_0^t d\tau\,\langle\langle\hat{\vec{\mu}}|e^{2\pi i\mathcal{L}_0(\tau-t)}\mathcal{L}_{\rm int}(\tau)\,|\,0\rangle\rangle - \\
&8\pi^3 i\int_0^t d\tau\int_0^\tau d\tau_1\int_0^{\tau_1} d\tau_2\,\langle\langle\hat{\vec{\mu}}|e^{2\pi i\mathcal{L}_0(\tau-t)}\mathcal{L}_{\rm int}(\tau)e^{2\pi i\mathcal{L}_0(\tau_1-\tau)}\mathcal{L}_{\rm int}(\tau_1)e^{2\pi i\mathcal{L}_0(\tau_2-\tau_1)}\mathcal{L}_{\rm int}(\tau_2)\,|\,0\rangle\rangle \\
&\ldots\ldots
\end{aligned}$$

Third order non–linearities; TG, 3PEPS, PP, etc.

S. Mukamel, “Principles of Nonlinear Optical Spectroscopy”

Coupling to a heat bath

- Schrödinger equation does not offer the option for dissipation: there is no *state* corresponding to equilibrium. Liouville space is much bigger.
- Since $[f(\mathcal{H}), \mathcal{H}] = 0$, the equilibrium distribution is a stationary solution to the quantum Liouville equation. As in the classical case, there is no approach to this solution, without introducing a decay mechanism.
- Some equilibrium considerations: 2LS in polarizable media; symmetry breaking, lineshapes, and (fluorescence) Stark spectroscopy.
- Redfield theory: weak coupling, and slow relaxation (NMR). Projection operator formalism.
- Mixed classical–quantum theories. Strong coupling. Formalities and direct simulation.

Systems:

(1) 2LS in a cavity in a polarizable medium.

(2) 2LS coupled to (quantum, classical, damped, fluctuating) oscillator(s).

2LS in constant electric field

Hamiltonian:

$$\mathcal{H} = \epsilon\,|1\rangle\langle 1| - \hat{\vec{\mu}}\cdot\vec{E} = \begin{pmatrix} -\vec{\mu}_0\cdot\vec{E} & -\vec{\mu}\cdot\vec{E} \\ -\vec{\mu}\cdot\vec{E} & \epsilon-\vec{\mu}_1\cdot\vec{E} \end{pmatrix}$$

Diagonalize: new energies

$$\epsilon_{g,e} = \frac{1}{2}\left[\epsilon - (\vec{\mu}_0+\vec{\mu}_1)\cdot\vec{E} \mp \sqrt{(\epsilon-(\vec{\mu}_1-\vec{\mu}_0)\cdot\vec{E})^2 + 4(\vec{\mu}\cdot\vec{E})^2}\right]$$

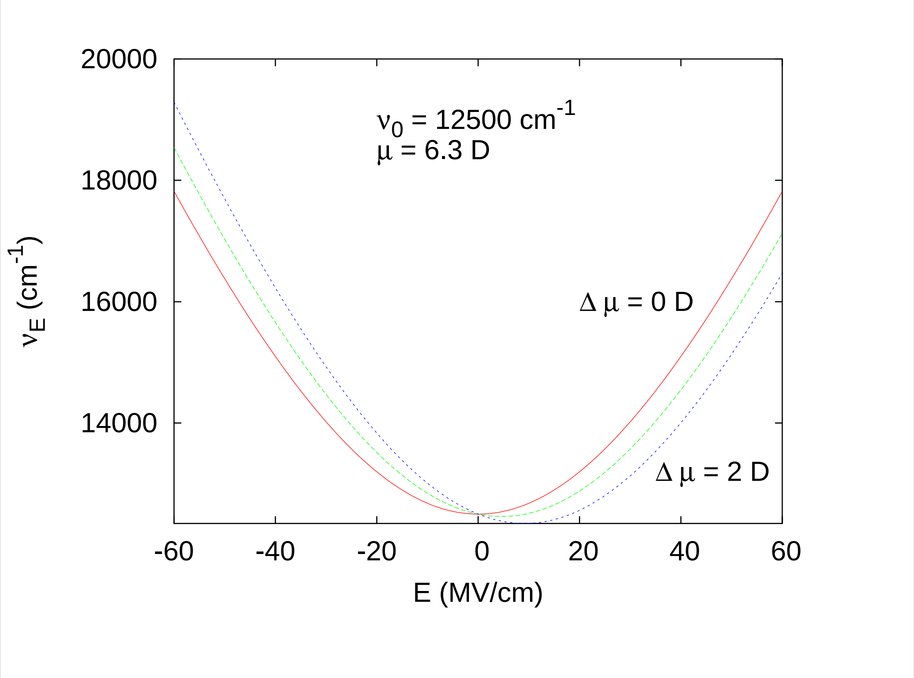
New states

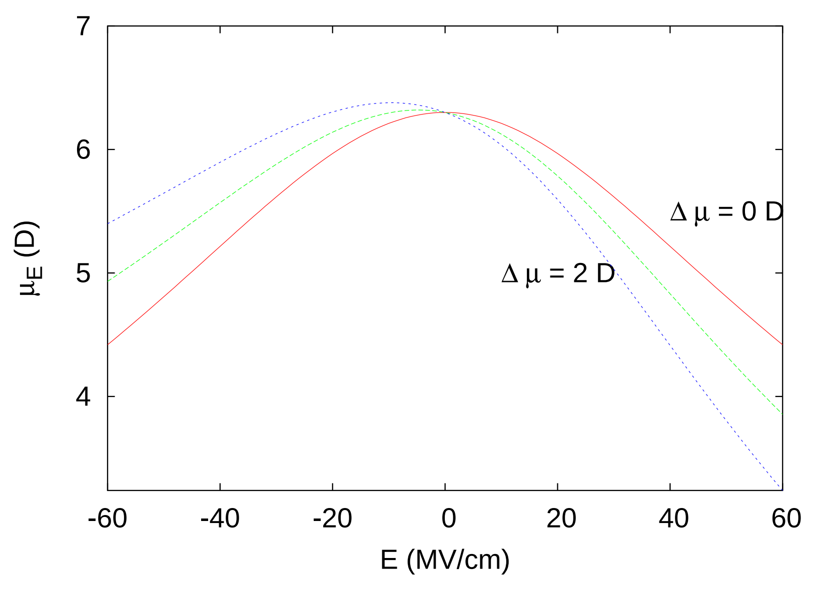
$$\begin{aligned} |g\rangle &= \frac{1}{\sqrt{1+t^2}}\,|0\rangle + \frac{t}{\sqrt{1+t^2}}\,|1\rangle \\ |e\rangle &= -\frac{t}{\sqrt{1+t^2}}\,|0\rangle + \frac{1}{\sqrt{1+t^2}}\,|1\rangle \end{aligned}$$

with

$$t = \frac{\epsilon - \Delta\vec{\mu}\cdot\vec{E} - \sqrt{(\epsilon-\Delta\vec{\mu}\cdot\vec{E})^2 + 4(\vec{\mu}\cdot\vec{E})^2}}{2\vec{\mu}\cdot\vec{E}}$$

Transition energies and dipole moments





New transition frequency, and new dipole moments:

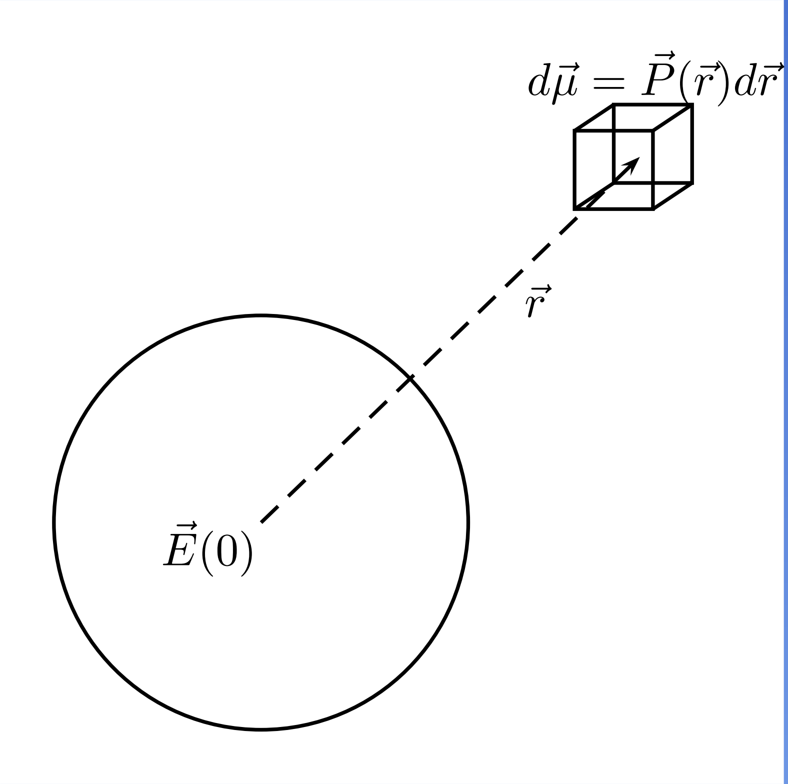
$$
\begin{aligned}
h\nu_E &= \epsilon_e - \epsilon_g = \sqrt{(h\nu_0 - \Delta\vec{\mu}\cdot\vec{E})^2 + 4(\vec{\mu}\cdot\vec{E})^2} \\
\vec{\mu}_g &= \frac{1}{1+t^2}\left(\vec{\mu}_0 + 2t\vec{\mu} + t^2\vec{\mu}_1\right) \\
\vec{\mu}_e &= \frac{1}{1+t^2}\left(t^2\vec{\mu}_0 - 2t\vec{\mu} + \vec{\mu}_1\right) \\
\vec{\mu}_E &= \frac{1}{1+t^2}\left(t\Delta\vec{\mu} + (1-t^2)\vec{\mu}\right)
\end{aligned}
$$

F. van Mourik, M. Chergui, and G. van der Zwan, J. Phys. Chem. B, 105, (2001), 9715.

Random fields and the absorption spectrum (1).

Polarization in the medium means fluctuations of the electric field at the center of a cavity.
Probability for finding polarization $\vec{P}$ at position $\vec{r}$:

$$P \propto e^{-\beta G[\vec{P}]}$$



Free energy functional:

$$\begin{aligned} G[\vec{P}] &= \frac{1}{2\chi}\int d\vec{r}\vec{P}(\vec{r})\cdot\vec{P}(\vec{r}) + \\ &\quad \frac{1}{2}\int d\vec{r}\int d\vec{r}\,'\frac{\vec{\nabla}\cdot\vec{P}(\vec{r})\vec{\nabla}\,'\cdot\vec{P}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} \end{aligned}$$

Electric field at the origin:

$$d\vec{E} = \frac{3\epsilon_r}{2\epsilon_r+1}\frac{1}{4\pi\epsilon_0\epsilon_r r^3}[1-3\hat{r}\hat{r}]\cdot\vec{P}(\vec{r})d\vec{r}$$

$$\left\langle \vec{E}(0)\right\rangle = 0 \quad \text{and} \quad \left\langle \vec{E}(0)\cdot\vec{E}(0)\right\rangle = \frac{1}{4\pi\epsilon_0 a^3}\frac{2(\epsilon_r-1)}{2\epsilon_r+1}k_B T$$

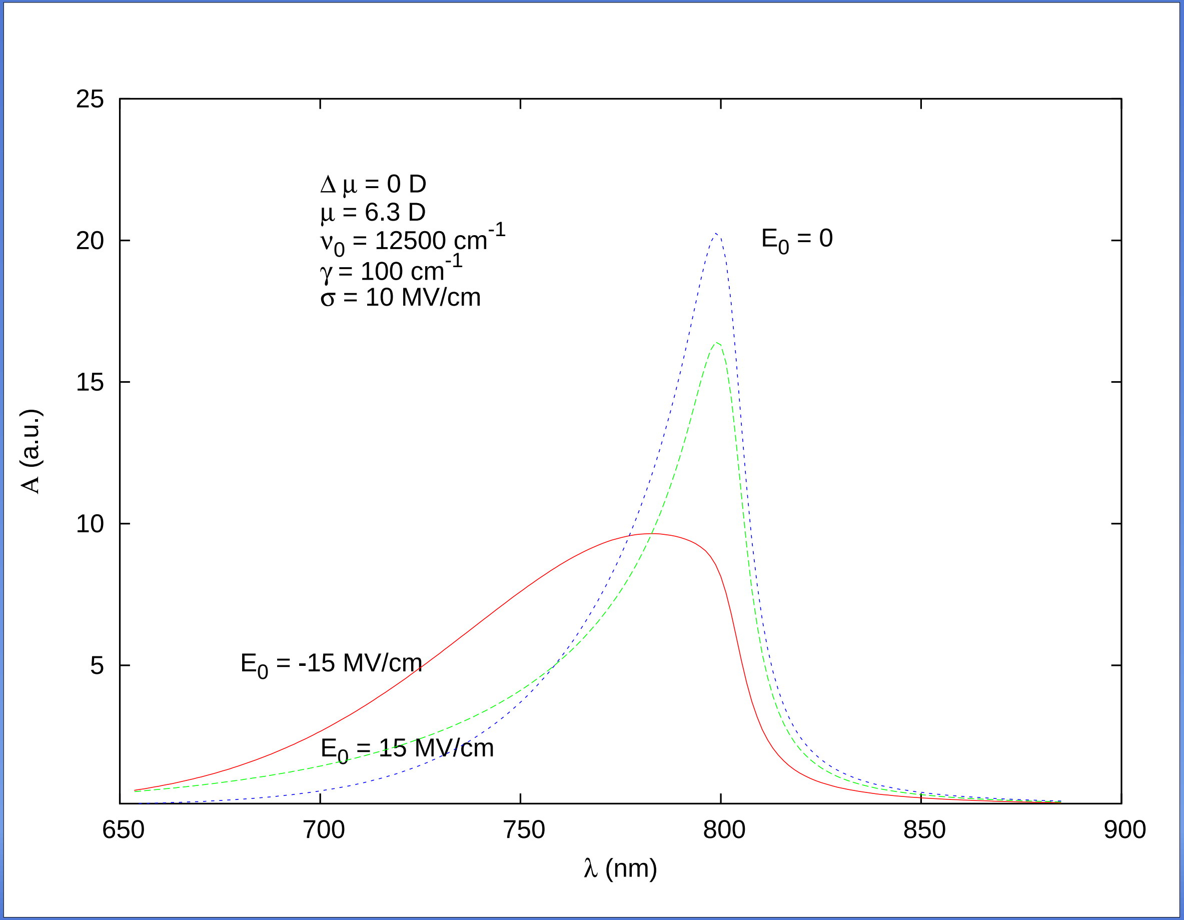
B.U. Felderhof, J. Chem. Phys. 67, (1977), 493.

Random fields and the absorption spectrum (2).

For a cavity of diameter 4Å, $\sqrt{\langle E^2 \rangle} \approx 20$ MV/cm.
Absorption spectrum (see sheet 20):

$$A(\nu) = \left\langle \mathrm{Im}[\chi^{(1)}(\nu)] \right\rangle = \frac{2\gamma}{3h} \left\langle \frac{\nu_E \mu_E^2}{(\nu - \nu_E)^2 + \gamma^2} \right\rangle$$

Averaging is over the electric field fluctuations (more).



Self–consistency: Onsager revisited (1)

2LS in a spherical cavity in polarizable medium.

- Expectation value of the dipole operator in the ground state causes polarization in the medium, and a reaction field.
- Reaction field changes the state of the system

Hamiltonian:

$$\mathcal{H} = \epsilon \left|0\right\rangle \left\langle 0\right| - \hat{\vec{\mu}} \cdot \vec{E}_R$$

Reaction field:

$$\vec{E}_R = \frac{1}{4\pi\epsilon_0 a^3} \frac{2(\epsilon_r - 1)}{2\epsilon_r + 1} \left\langle \hat{\vec{\mu}} \right\rangle_g \equiv A\vec{\mu}_g$$

Remember: a rotation over θ with:

$$t = \tan\theta = \frac{\epsilon - \Delta\vec{\mu} \cdot \vec{E}_R - \sqrt{(\epsilon - \Delta\vec{\mu} \cdot \vec{E}_R)^2 + 4(\vec{\mu} \cdot \vec{E}_R)^2}}{2\vec{\mu} \cdot \vec{E}_R}$$

diagonalizes the Hamiltonian, and

$$\vec{\mu}_g = \frac{1}{1+t^2} \left(\vec{\mu}_0 + 2t\vec{\mu} + t^2\vec{\mu}_1\right)$$

Onsager revisited (2). Symmetry breaking.

This leads to a fourth order equation in t:

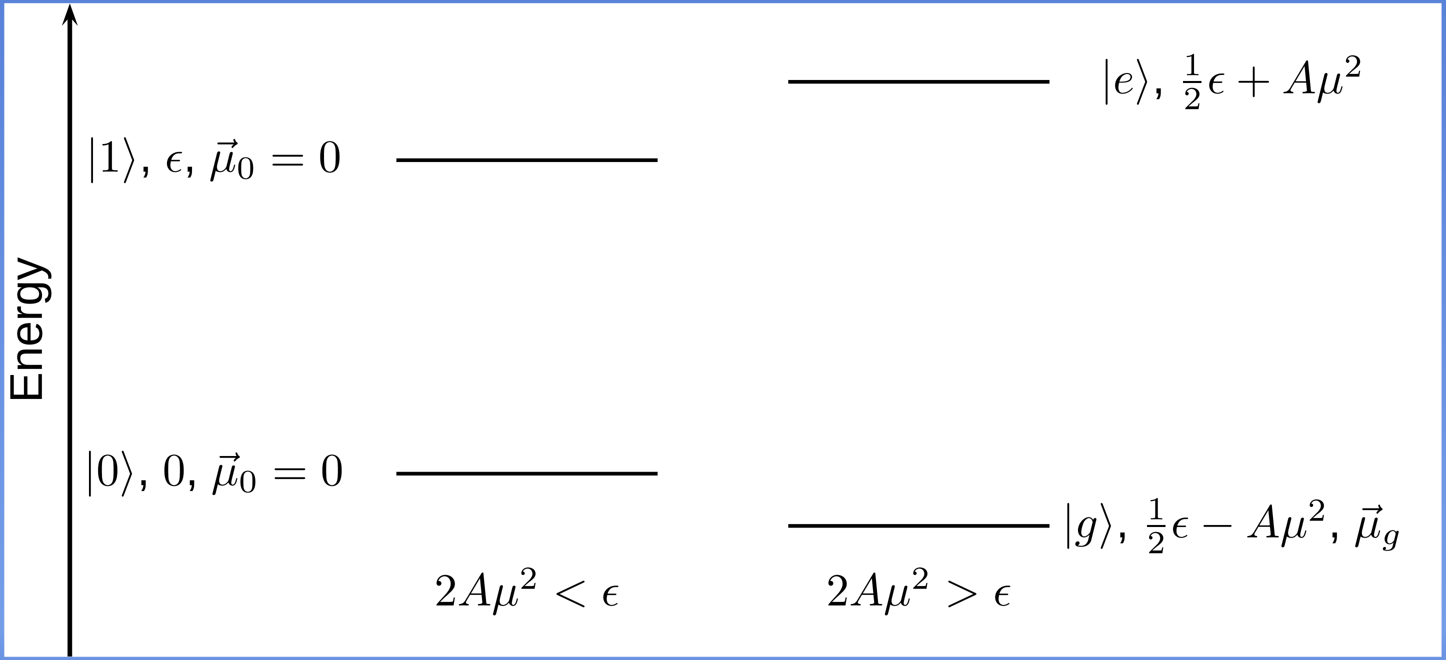
$$A\vec{\mu}\cdot\vec{\mu}_1 t^4 + t^3\left[2A\mu^2 + A\mu_1^2 - \epsilon\right] + A\vec{\mu}\cdot\Delta\vec{\mu}t^2 + t\left[A\vec{\mu}_0\cdot\Delta\vec{\mu} - 2A\mu^2 - \epsilon\right] - A\vec{\mu}_0\cdot\vec{\mu} = 0$$

Simple case: $\vec{\mu}_0 = \vec{\mu}_1 = 0$

$$t^3\left[2A\mu^2 - \epsilon\right] - t\left[2A\mu^2 + \epsilon\right] = 0$$

Solution:

$$t = 0 \quad \text{and} \quad t^2 = \frac{2A\mu^2 + \epsilon}{2A\mu^2 - \epsilon} \quad \text{if} \quad 2A\mu^2 \geq \epsilon$$



Onsager revisited (3). Free energy and polarization fluctuations.

Free energy related to electric field fluctuations at the origin of the cavity (see also sheet 27):

$$G[\vec{E}] = \frac{E^2}{2A} \quad \text{with} \quad A = \frac{1}{4\pi\epsilon_0 a^3} \frac{2(\epsilon_r - 1)}{2\epsilon_r + 1}$$

Free energy of quantum system in fluctuating field:

$$G[\Psi, \vec{E}] = \langle\Psi|\, \mathcal{H}_0 \,|\Psi\rangle - \langle\Psi|\, \hat{\vec{\mu}} \,|\Psi\rangle \cdot \vec{E} + \frac{E^2}{2A}$$

Minimize G with respect to the state, and to the fields:

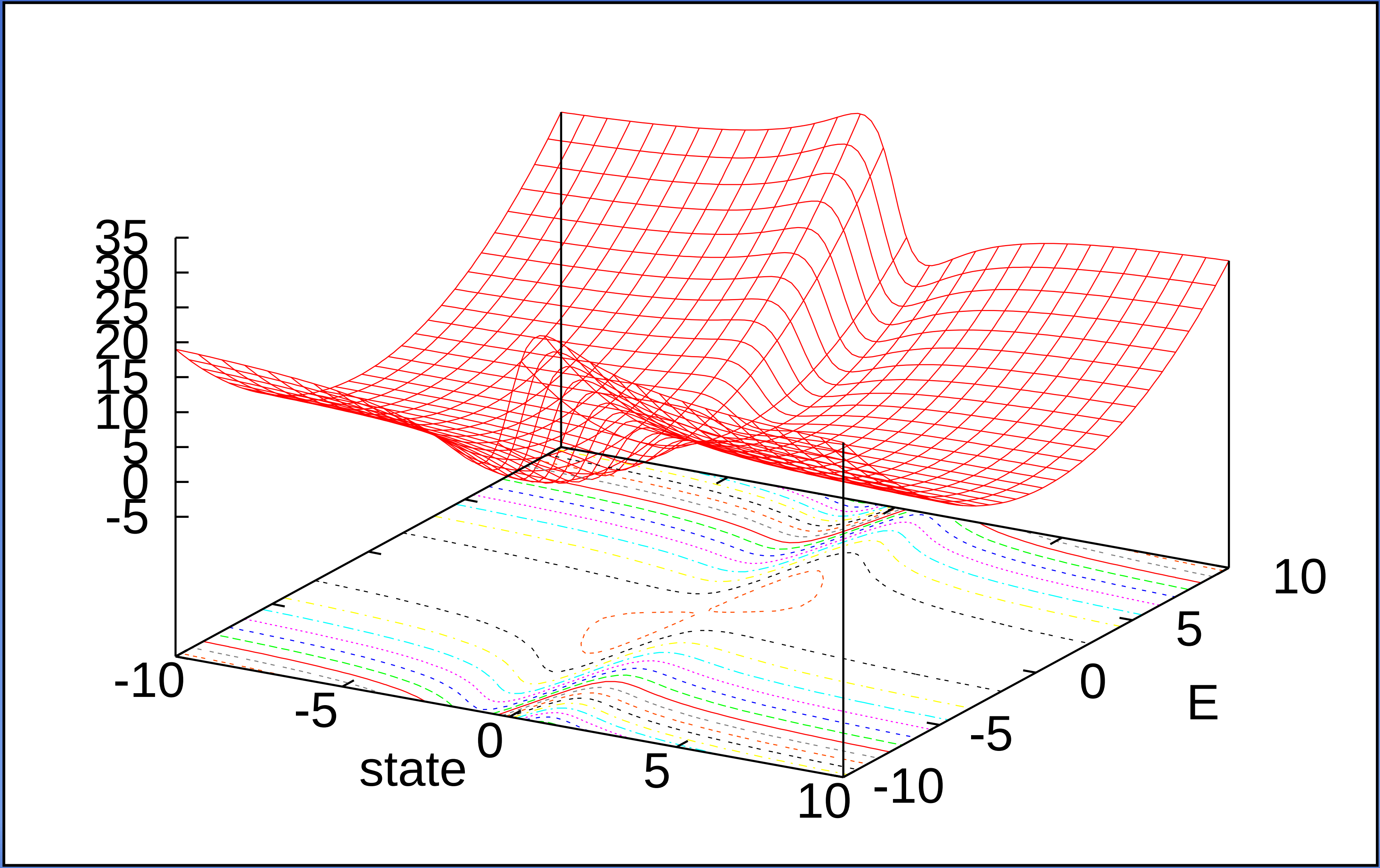
$$\frac{\delta G}{\delta \Psi} = 0 \quad \text{gives} \quad \left[\mathcal{H}_0 - \hat{\vec{\mu}} \cdot \vec{E}\right] |\Psi\rangle = \epsilon\, |\Psi\rangle$$

(ϵ is an undetermined Lagrange multiplier put in to keep $|\Psi\rangle$ normalized), and

$$\frac{\delta G}{\delta \vec{E}} = 0 \quad \text{gives} \quad \vec{E} = A\, \langle\Psi|\, \hat{\vec{\mu}} \,|\Psi\rangle$$

Onsager revisited (4). Free energy surface.

Free energy surface above symmetry breaking threshold:



Classical–Quantum coupling in equilibrium

Equilibrium density operator:

$$\rho_{eq} = \frac{1}{Q} e^{-\beta\left[\mathcal{H}_0 - \hat{\vec{\mu}}\cdot\vec{E} + E^2/2A\right]} = \frac{1}{Q}\left[e^{-\beta(\epsilon_g + E^2/2A)} \left|g\right\rangle \left\langle g\right| + e^{-\beta(\epsilon_e + E^2/2A)} \left|e\right\rangle \left\langle e\right|\right]$$

with

$$Q = \int d\vec{E}\, \mathrm{Tr} e^{-\beta\left[\mathcal{H}_0 - \hat{\vec{\mu}}\cdot\vec{E} + E^2/2A\right]}$$

Quantum equivalent of potential of mean force (“average Hamiltonian”):

$$\overline{\rho}_{eq} \equiv \sigma_{eq} = \int d\vec{E}\, \rho_{eq}$$

also called: reduced density matrix

Some conclusions

- For pure states Schrödinger and Liouville are equivalent descriptions.
- “purity” is conserved by unitary transformations (Hamiltonian dynamics)
- Impure states can be the result of reducing the density matrix by
  - coupling to other quantum systems
  - coupling to classical fluctuations
  - equilibrium statistical mechanics
- impure (density operator) states have no Hilbert space equivalent.
- No inconsistency problems are apparent in equilibrium
- Coupling to (classical) optical fields $\longrightarrow$ linear/non linear optics
- Coupling to static fields: Stark effect, lineshapes, possible symmetry breaking
- Approach to equilibrium (non–conservation of purity)?
- Dynamical coupling (“quantum backreaction”)?

The need for quantum–classical dynamics

Some systems need to be described quantum mechanically:

- Proton transfer reactions (even at high temperatures), high frequency vibrations, spin.
- Changes in electronic density of the molecule (including electron transfer reactions).
- (High energy physics).

Some things are very hard or impossible to describe quantum mechanically:

- Solvents and proteins that constitute the environment of the quantum system.
- (Gravitational fields)

A. Anderson, Phys. Rev. Lett. 74, 1995, 621–625.

Direct simulation of the Liouville equation

$$\frac{\partial \,|\, \rho\rangle\rangle}{\partial t} = -2\pi i \mathcal{L}_0 \,|\, \rho\rangle\rangle - 2\pi i \mathcal{L}(t) \,|\, \rho\rangle\rangle$$

with

$$\mathcal{L}(t) = -\left[\hat{\vec{\mu}}, \cdots\right] \cdot \vec{E}_0(t) e^{2\pi i \nu_f t}$$

where the (slowly developing) envelope of the field is given by a Gaussian shaped pulse:

$$\vec{E}_0(t)\vec{E}_0 e^{-(t-T)^2/2\sigma^2}$$

The transition dipole moments of the system, between the different vibrational levels, are given by

$$\langle 0; n|\, \hat{\vec{\mu}} \,|1; m\rangle = \vec{\mu} \,\langle n|\; m\rangle$$

with $\vec{\mu}$ the electronic transition dipole moment, and $\langle n|\; m\rangle$ the overlap between ground and excited state vibrational wavefunctions.

For results see webpage.

Note: em field is classical, but quantum backreaction can be ignored.

Coupled quantum and classical dynamics.

Question: Why not simulate Liouville equation coupled to classical field directly?

$$\frac{\partial \rho}{\partial t} = -2\pi i[\mathcal{H}_0, \rho(t)] - 2\pi i[\hat{\vec{\mu}}, \rho(t)] \cdot \vec{E}(t)$$

$\vec{E}(t)$: electric field at the center of the cavity. Assume damped oscillatory behavior

$$\frac{d^2\vec{E}}{dt^2} = -\omega_s^2\vec{E} - \gamma\frac{d\vec{E}}{dt} + A\left\langle\hat{\vec{\mu}}\right\rangle$$

with (as usual)

$$\left\langle\hat{\vec{\mu}}\right\rangle = \mathrm{Tr}[\hat{\vec{\mu}}\rho(t)]$$

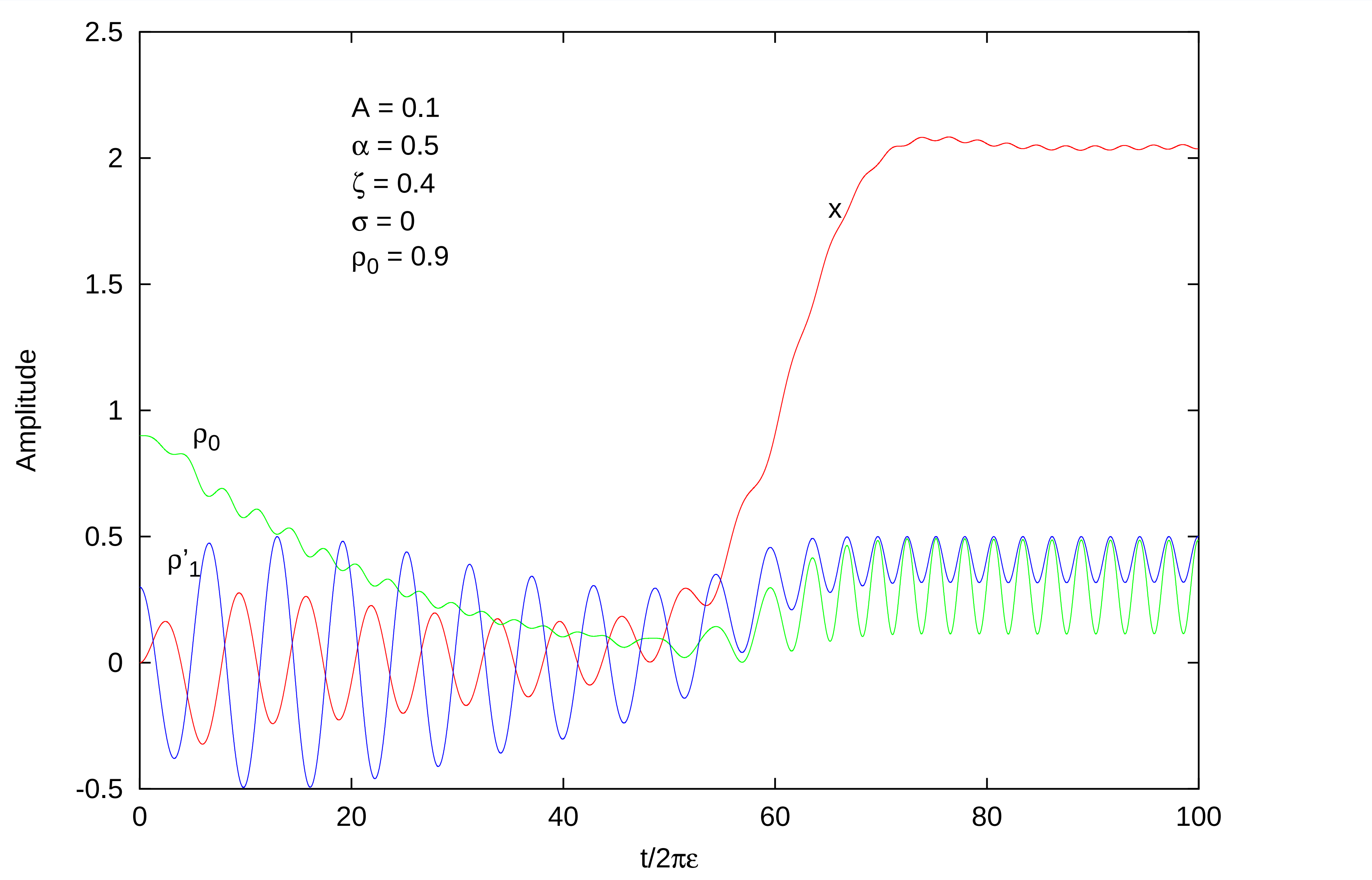
major problem: classical system only feels the average field

For all the gory details about this type of simulations: see simulations.pdf

Note the similarity with the traditional Redfield approach, where the second equation is used implicitly to calculate solvent correlation functions.

HOWEVER

Coupled quantum and classical dynamics. No Relaxation



Coupled quantum and classical dynamics. Relaxation

Problem: Starting from any non–equilibrium situation we want the density operator to go to the equilibrium density.

Projection operator formalism

System+bath hamiltonian:

$$\mathcal{H} = \mathcal{H}_s + \mathcal{H}_b + \mathcal{H}_{\rm int}$$

where

$\mathcal{H}_s$:	system Hamiltonian
$\mathcal{H}_b$:	bath Hamiltonian
$\mathcal{H}_{\rm int}$:	system–bath interaction Hamiltonian

Interaction Hamiltonian:

$$\mathcal{H}_{\rm int} = \sum_{k,l} \alpha_{kl} s_k b_l$$

where

$\{s_k\}$:	complete set of system operators
$\{b_l\}$:	complete set of bath operators

Projection operator formalism (2)

System+bath are described by a density operator $\rho(s,b,t)$.
Concentrating on the system:

$$\sigma(s,t) = \mathrm{Tr}_b[\rho(s,b,t)]$$

Projection operator

$$\mathcal{P} = \sigma_{eq}(b)\mathrm{Tr}_b[\rho(s,b,t)]$$

where $\sigma_{eq}(b)$ is the bath equilibrium density operator, found by Tr$_s[\rho_{eq}(s,b)]$.
Note: before any experiment system+bath are in equilibrium.
Starting point:

$$\frac{\partial\rho(b,s,t)}{\partial t} = -2\pi i\mathcal{L}\rho(b,s,t)$$

Separating the equation

$$\begin{aligned}
\frac{\partial\mathcal{P}\rho(b,s,t)}{\partial t} &= -2\pi i\mathcal{P}\mathcal{L}\mathcal{P}\rho(b,s,t) - \mathcal{P}\mathcal{L}\left[1-\mathcal{P}\right]\rho(b,s,t)\\
\frac{\partial\left[1-\mathcal{P}\right]\rho(b,s,t)}{\partial t} &= -2\pi i[1-\mathcal{P}]\mathcal{L}\mathcal{P}\rho(b,s,t) - 2\pi i[1-\mathcal{P}]\mathcal{L}[1-\mathcal{P}]\rho(b,s,t)
\end{aligned}$$

Projection operator formalism (3)

Define

$$\begin{aligned}\sigma_{eq}(b)\sigma(s,t) &= \mathcal{P}\rho(s,b,t)\\ \eta(s,b,t) &= [1-\mathcal{P}]\rho(s,b,t)\end{aligned}$$

To get

$$\begin{aligned}\frac{\partial\sigma(s,t)}{\partial t} &= -2\pi i\mathcal{L}_s\sigma(s,t) - 2\pi i\mathrm{Tr}_b[\mathcal{L}_{\mathrm{int}}\eta(s,b,t)]\\ \frac{\partial\eta(s,b,t)}{\partial t} &= -2\pi i\mathcal{L}_{\mathrm{int}}\sigma_{eq}(b)\sigma(s,t) - 2\pi i[\mathcal{L}_s+\mathcal{L}_b+(1-\mathcal{P})\mathcal{L}_{\mathrm{int}}]\eta(s,b,t)\end{aligned}$$

Solve the second equation formally:

$$\begin{aligned}\eta(s,b,t) &= e^{-2\pi i[\mathcal{L}_s+\mathcal{L}_b+(1-\mathcal{P})\mathcal{L}_{\mathrm{int}}]t}\eta(s,b,0)\\ &\quad -2\pi i\int_0^t d\tau\, e^{-2\pi i[\mathcal{L}_s+\mathcal{L}_b+(1-\mathcal{P})\mathcal{L}_{\mathrm{int}}](t-\tau)}\mathcal{L}_{\mathrm{int}}\sigma_{eq}(b)\sigma(s,\tau)\end{aligned}$$

And substitute in the first

Projection operator formalism (4)

$$\begin{aligned}\frac{\partial\sigma(s,t)}{\partial t} &= -2\pi i\mathcal{L}_s\sigma(s,t) - 2\pi i\mathrm{Tr}_b\left[\mathcal{L}_{\mathrm{int}}e^{-2\pi i[\mathcal{L}_s+\mathcal{L}_b+(1-\mathcal{P})\mathcal{L}_{\mathrm{int}}]t}\eta(s,b,0)\right]\\ &\quad -4\pi^2\int_0^t d\tau\ \mathrm{Tr}_b\left[\mathcal{L}_{\mathrm{int}}e^{-2\pi i[\mathcal{L}_s+\mathcal{L}_b+(1-\mathcal{P})\mathcal{L}_{\mathrm{int}}](t-\tau)}\mathcal{L}_{\mathrm{int}}\sigma_{eq}(b)\sigma(s,\tau)\right]\end{aligned}$$

- This is still *exact*: no weak coupling, no separation of time scales.
- $\mathcal{L}_s$ can contain coupling to for instance optical field if the system is molecule and the bath a solvent.
- Initial condition: $\eta(s,b,0)=\rho_{eq}(s,b)-\sigma_{eq}(s)\sigma_{eq}(b)$ could be important for short time dynamics upon excitation, and for consistency (stationary solution)
- No “slow” or “fast” variables. (*cf.* Mori).
- Last term is already second order in the interaction.
- Second order will give Redfield^{++}, a modification of Redfield theory, but no “backreaction”.
- The initial value term also contains second order contributions (see classical example).

Projection operator formalims (5)

Up to second order (neglecting the initial condition term):

$$\frac{\partial\sigma(s,t)}{\partial t} = -2\pi i \mathcal{L}_s \sigma(s,t) - 4\pi^2 \int_0^t d\tau \, \mathrm{Tr}_b \left[\mathcal{L}_{\mathrm{int}} e^{-2\pi i [\mathcal{L}_s + \mathcal{L}_b](t-\tau)} \mathcal{L}_{\mathrm{int}} \rho_{eq}(b) \sigma(s,\tau) \right]$$

- $\mathcal{L}_{\mathrm{int}}$ in the exponential vanishes.
- $\sigma_{eq}(b)$ replaced by $\rho_{eq}(b) = e^{-\beta\mathcal{H}_b}/Q$.
- no “backreaction”.
- The initial condition term is a source term, which should vanish for long times, and not contribute to the approach to equilibrium. It is likely to be important for the short time dynamics.

Projection operator formalism (6)

Bath correlation functions.
In order to get to the bath correlation functions we use the explicit form of the interaction Hamiltonian

$$\frac{\partial\sigma(t)}{\partial t} = -2\pi i\mathcal{L}\sigma(t) - 4\pi^2\int_0^t d\tau\,\mathrm{Tr}_b\left[\mathcal{H}_{\mathrm{int}}, e^{-2\pi i\mathcal{L}_s(t-\tau)}e^{-2\pi i\mathcal{L}_b(t-\tau)}\left[\mathcal{H}_{\mathrm{int}}, \rho_{eq}(b)\sigma(\tau)\right]\right]$$

With

$$\mathcal{H}_{\mathrm{int}} = \sum_{k,l}\alpha_{kl}s_k b_l$$

this gives for the integrand:

$$\sum_{k,l}\sum_{k',l'}\alpha_{kl}\alpha_{k'l'}\mathrm{Tr}_b\left[s_k b_l, e^{-2\pi i\mathcal{L}_s(t-\tau)}e^{-2\pi i\mathcal{L}_b(t-\tau)}\left[s_{k'}b_{l'}, \rho_{eq}(b)\sigma(\tau)\right]\right]$$

This can be worked out further to give bath correlation functions:

Projection operator formalism (7)

$$\begin{aligned}
&\sum_{k,l}\sum_{k',l'} \alpha_{kl}\alpha_{k'l'} \Big\{ \Big(s_k e^{-2\pi i \mathcal{L}_s(t-\tau)} s_{k'}\sigma(\tau)\Big) \mathrm{Tr}_b \Big[b_l e^{-2\pi i \mathcal{L}_b(t-\tau)} [b_{l'}, \rho_{eq}(b)]\Big] + \\
&\Big[s_k, e^{-2\pi i \mathcal{L}_s(t-\tau)} s_{k'}\sigma(\tau)\Big] \mathrm{Tr}_b \Big[b_l e^{-2\pi i \mathcal{L}_b(t-\tau)} b_{l'} \rho_{eq}(b)\Big]\Big\} = \\
&\sum_{k,l}\sum_{k',l'} \alpha_{kl}\alpha_{k'l'} \Big\{ \Big(s_k e^{-2\pi i \mathcal{L}_s(t-\tau)} s_{k'}\sigma(\tau)\Big) \left\langle [b_l, b_{l'}(t-\tau)]\right\rangle_{eq} + \\
&\Big[s_k, e^{-2\pi i \mathcal{L}_s(t-\tau)} s_{k'}\sigma(\tau)\Big] \left\langle b_l b_{l'}(t-\tau)\right\rangle_{eq} \Big\}
\end{aligned}$$

Exercise: Take the classical limit of the bath correlation functions.

- Result is Redfield^{++} (some extra terms, better behavior for $t->\infty$)
- Bath dynamics not influenced by system dynamics: only for weak coupling.
- Bath equilibrium distribution is also not influenced by the presence of the system.
- Initial condition terms can be included for short time behavior.
- Higher orders give more bath system interaction, but:

Exercise: Show that summing over all higher order terms neglecting the change of bath dynamics and bath equilibrium distribution leads to the cumulant expansion.

Strange issues remaining

- If we only add a random force, or non–Markovian force to a *classical* system, it does not relax. For instance
$$\frac{d^2x}{dt^2} = -\omega_0^2 x + F_R(t)$$
with solution
$$x(t) = x_0 \cos\omega_0 t + \frac{v_0}{\omega_0}\sin\omega_0 t + \frac{1}{2\pi i}\int_{-i\infty}^{i\infty} ds\, \frac{F_R(s)e^{st}}{s^2+\omega_0^2}$$
so how come Redfield theory actually does give relaxation?

- For a *quantum* oscillator we could start with
$$\frac{\partial\rho(t)}{\partial t} = -2\pi i[\mathcal{H}_0, \rho] - 2\pi i[x, \rho(t)]F_R(t)$$
but the operators on the right are hermitian, so the “purity” of ρ is conserved.
So how come after all the manipulations the theory describes decay to equilibrium (an impure state) from any, possibly pure, state?

A very fundamental problem

Coupling classical and quantum mechanics.

Classically:

$$\frac{\partial \rho}{\partial t} = \{\mathcal{H}, \rho\}$$

Quantum mechanically:

$$\frac{\partial \rho}{\partial t} = -2\pi i[\mathcal{H}, \rho]$$

Both $[,]$ and $\{,\}$ are Lie brackets, satisfying the Jacobi identity:

$$[A,[B,C]] + [C,[A,B]] + [B,[C,A]] = 0$$

A quantum classical bracket has been proposed:

$$[fA, gB]_{gc} = fg[A,B] + \{f,g\}BA$$

(f, g functions, A, B operators). But this is no Lie bracket, and furthermore not even in general $[\mathcal{H}^2, \mathcal{H}]_{qc} = 0$. (Prove this).

So far it has been impossible to combine Hilbert and phase space into one space.

A. Anderson, Phys. Rev. Lett. 74, (1995), 621.

J. Caro and L.L. Salcedo, Phys. Rev. A 60, (1999), 842

A few further remarks

The limit $\hbar \to 0$ is by no means trivial.

- Certainly it can not be done in the Schrödinger equation.
- Often it is stated that in the limit $\hbar \to 0$ the commutators reduce to Poisson brackets, but there is no mathematical procedure to do that.
- Some coherent states may go to classical states.
- Does the Wigner distribution help? (Only for quadratic Hamiltonians, (A.J. Dragt, S. Habib, ArXiv:quant-ph 9808056).
- Can it be done on a correlation function level? In the projection operator formalism we encounter the following bath correlation functions:

  $$c_{ll'}(t) = \mathrm{Tr}_b\left[\rho_{eq}(b) b_l b_{l'}(t)\right]$$

  and

  $$\phi_{ll'}(t) = \mathrm{Tr}_b\left[b_l[b_{l'}(t), \rho_{eq}(b)]\right] = i\frac{\partial}{\partial t}\int_0^\beta d\lambda c_{ll'}(t - i\hbar\lambda)$$

  Often it is stated that in the classical limit the trace over Hilbert space goes to a phase space integral, but there is no mathematical procedure to do that.
- Bohm Theory? Hydrodynamic approach (works for quadratic Hamiltonians)?
- QM/MM?
- Feynman path integrals?

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