# Classical Mechanics *vs* Quantum Mechanics

Gert van der Zwan

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# *Is there anything $\rho$ can't do?*


❖ Overview

Classical and Damped Motion.

Quantum Dynamics in Hilbert and Liouville Space

Exercises and Problems


- *Fundamentals*
  - Dynamics
  - Statistical Mechanics
  - Pure and Mixed States
- *Applications*
  - (Non)–linear Optics
  - Quantum Dissipation
  - Proton Transfer
- *Connections*
  - QM–CM interaction
  - Measurement
  - Quantum Computing
- *Problems*
  - The Ehrenfest Problem
  - Quantum Dissipation
  - QM–CM Interaction

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

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- ❖ Classical conclusions

Quantum Dynamics in Hilbert and Liouville Space

Exercises and Problems


# *Classical and Damped Motion.*

# Review and Extension of Earlier Results


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

Time dependence follows from the Hamilton equations:

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

## Liouville's theorem:

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

or

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

# The One–Dimensional Oscillator


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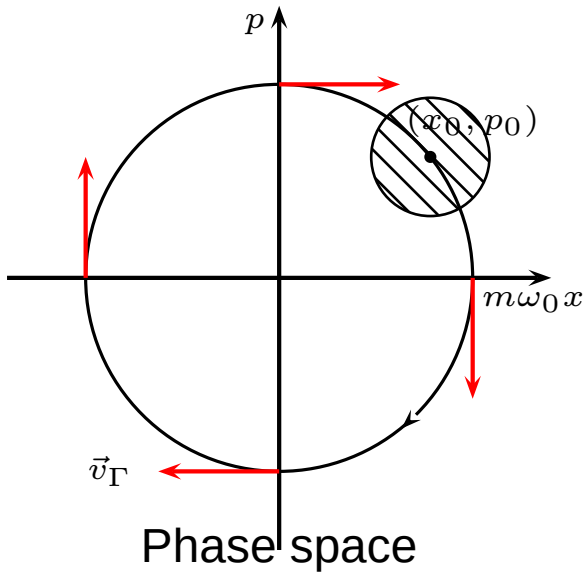
## Hamiltonian:

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

## Liouville equation:

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




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

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

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


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Inclusion of friction effects ("coupling to a bath") leads to

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

$\zeta$ = friction coefficient.

Alternative formulation:

$$\begin{aligned} \frac{dx}{dt} &= \frac{p}{m} \\ \frac{dp}{dt} &= -\zeta\frac{p}{m} - m\omega_0^2 x + F_R(t) \end{aligned} \qquad (1)$$

Random force

Fluctuation–dissipation theorem:

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

# The Brownian Oscillator


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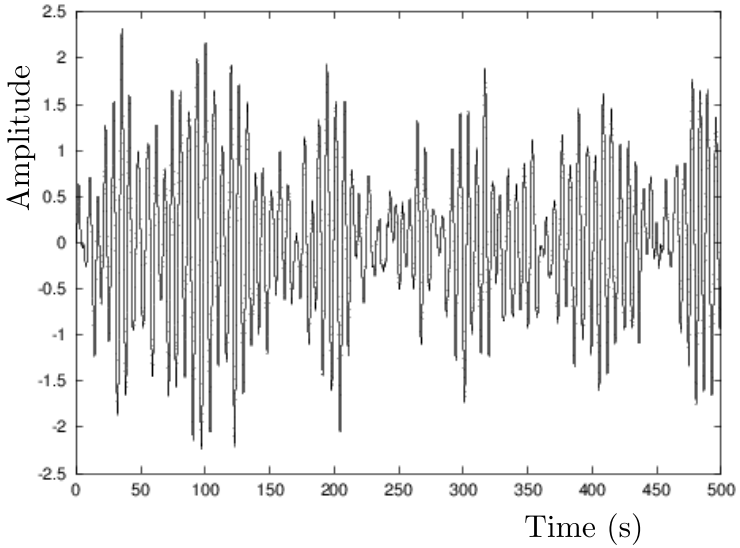
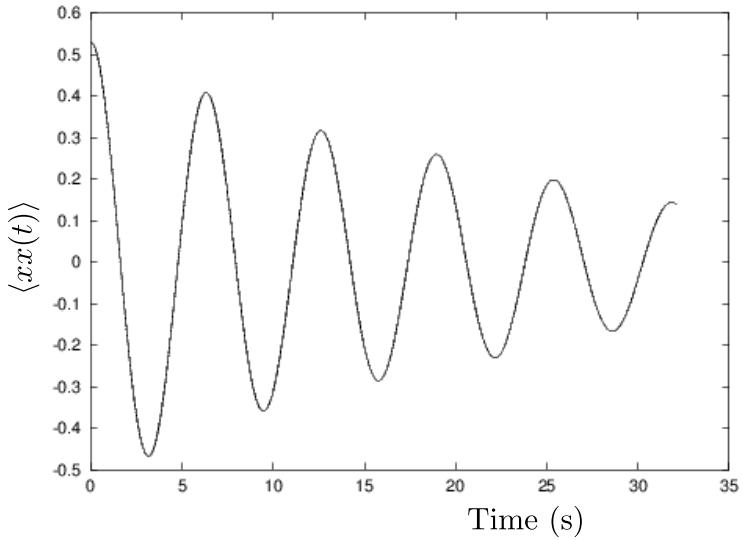
## Single damped oscillator with random force:




## Input Parameters:

| | |
|---|---|
| $m$ | 1 |
| $\omega_0$ | 1 |
| $\zeta$ | 0.1 |
| $k_BT$ | $\approx 2$ |

Fit:

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

# Coupled Oscillators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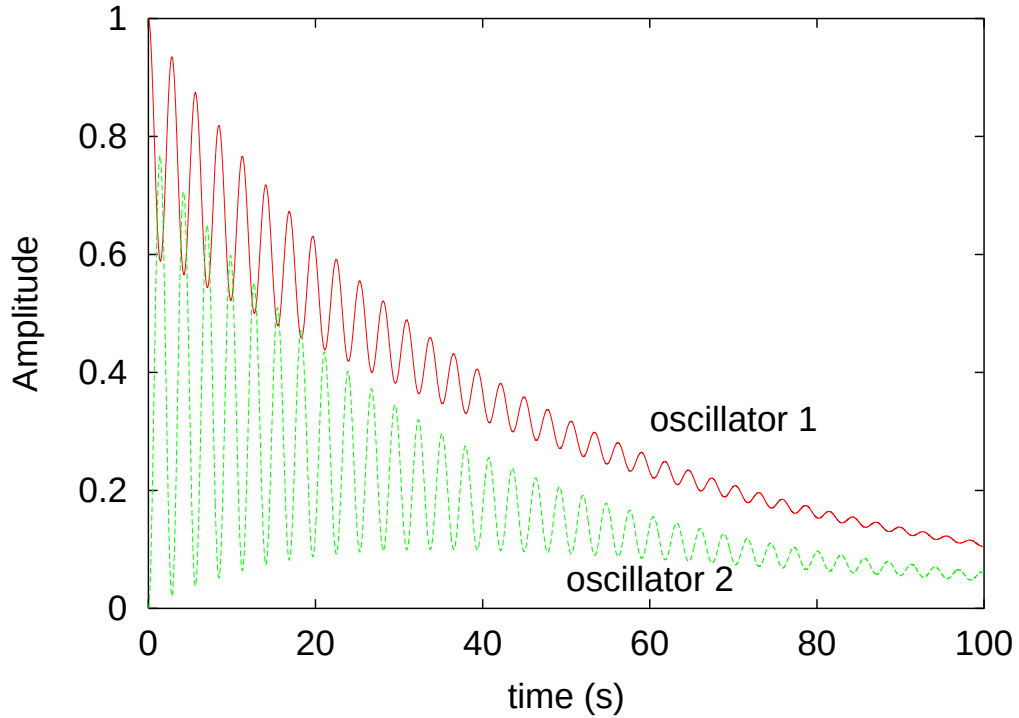


| | |
|---|---|
| $m_1$ | 1 |
| $m_2$ | 1 |
| $\omega_1$ | 1 |
| $\omega_2$ | 2 |
| $\gamma$ | 0.2 |
| $\zeta$ | 0.1 |

## Equations of motion:

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

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

# Langevin Equations, Non–Markovian Behavior


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- Coupled equations

$$m_1 \frac{d^2 x_1}{dt^2} = -m_1 \omega_1^2 x + \gamma x_2$$
$$m_2 \frac{d^2 x_2}{dt^2} = -m_2 \omega_2^2 x - \zeta \frac{dx_2}{dt} + \gamma x_1 + F_R(t) \qquad (2)$$

lead to non–Markovian behavior of oscillator 1.

- Formally solve the second equation (use Fourier transforms):

$$x_2(\omega) = \frac{\gamma x_1(\omega) + F_R(\omega)}{m_2(\omega_2^2 - \omega^2) - i\omega\zeta} \qquad (3)$$

- And substitute in the first:

$$m_1(\omega_1^2 - \omega^2)x_1(\omega) - \frac{\gamma^2 x_1(\omega)}{m_2(\omega_2^2 - \omega^2) - i\omega\zeta} = \frac{\gamma F_R(\omega)}{m_2(\omega_2^2 - \omega^2) - i\omega\zeta} \qquad (4)$$

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- Some minor rearrangement:

$$m_1(\omega_{\rm pmf}^2 - \omega^2)x_1(\omega) - i\omega\zeta_1(\omega)x_1(\omega) = \overline{F}_R(\omega) \tag{5}$$

- Potential of Mean Force ("Equilibrium Solvation"):

$$\omega_{\rm pmf}^2 = \omega_1^2\left(1 - \frac{\gamma^2}{\omega_1^2\omega_2^2}\right) \tag{6}$$

- Frequency dependent friction:

$$\zeta_1(\omega) = \frac{\gamma^2}{\omega_2^2}\frac{-i\omega + \zeta/m_2}{m_2(\omega_2^2 - \omega^2) - i\omega\zeta} \tag{7}$$

- Fluctuation–Dissipation Theorem:

$$\left\langle \overline{F}_R(\omega)\overline{F}_R(\omega')\right\rangle = 2k_BT\zeta_1(\omega)2\pi\delta(\omega - \omega') \tag{8}$$

# Classical conclusions


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- 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.
- Brownian dynamics simulations are simple (up to a point).
- Non–Markovian behavior is the result of a lower layer of dynamics.
- Fluctuation–dissipation theorems, relating spontaneous fluctuations and dissipative aspects of an irreversible process are valid on all levels. No dissipation without fluctuations, and *vice versa*

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# *Quantum Dynamics in Hilbert and Liouville Space*

# Quantum dynamics (1): Hilbert Space


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Schrödinger equation:

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

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

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

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))

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

# Quantum dynamics (2). Liouville equation


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Properties: $\rho$ is hermitian ($\rho^\dagger = \rho$), and $\mathrm{Tr}[\rho] = 1$

Equation of motion (quantum Liouville equation)

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

compare: Heisenberg picture for operator $A$:

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

compare: Classical Liouville equation

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

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)


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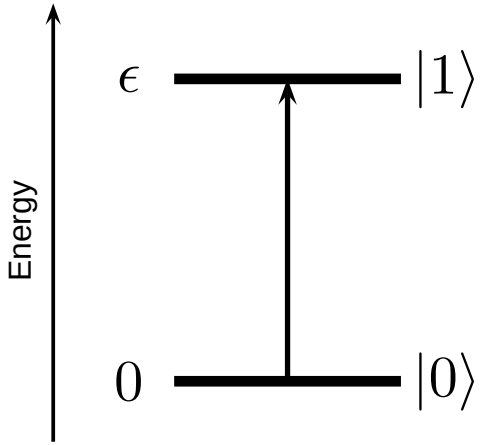


- Hamiltonian: $\mathcal{H} = \epsilon \left|1\right\rangle \left\langle 1\right|$
- Dipole operator:

$$\hat{\vec{\mu}} = \vec{\mu}_g \left|0\right\rangle \left\langle 0\right| + \vec{\mu}_e \left|1\right\rangle \left\langle 1\right| + \vec{\mu}[\left|0\right\rangle \left\langle 1\right| + \left|1\right\rangle \left\langle 0\right|]$$

- Interaction Hamiltonian:

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

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

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


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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):

$$\rho_{\mathrm{eq}} = \frac{e^{-\beta \mathcal{H}}}{Q} = \frac{1}{1+e^{\beta\epsilon}} \begin{pmatrix} 1 & 0 \\ 0 & e^{-\beta\epsilon} \end{pmatrix} \tag{9}$$

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

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

# *Liouville space*


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

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

## Inner product:

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

## Liouville equation:

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

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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: $\sum_n |n\rangle\rangle \langle\langle n| = \mathbf{1}$.

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

$$A = \begin{pmatrix} a_{00} & a_{01} \\ a_{10} & a_{11} \end{pmatrix} \quad \Leftrightarrow \quad \begin{pmatrix} a_{00} \\ a_{01} \\ a_{10} \\ a_{11} \end{pmatrix} \equiv |A\rangle\rangle \tag{10}$$

and

$$\langle\langle A| = \begin{pmatrix} a_{00}^* & a_{01}^* & a_{10}^* & a_{11}^* \end{pmatrix} \tag{11}$$

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System (2LS) Liouvillian:

$$-\frac{i}{\hbar}\mathcal{L}_0 = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & -2\pi i\nu_0 & 0 & 0 \\ 0 & 0 & 2\pi i\nu_0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \tag{12}$$

where $\nu_0 =$ transition frequency.

Liouville Space, what is it good for?

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

# Quantum Dissipation?


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Why not just add friction to the Schrödinger equation?

- We dont want the wave functions to go to zero.
- If we do it in the Heissenberg picture, commutation relations go to zero, and we dont 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.
- 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.

# Coupled systems.


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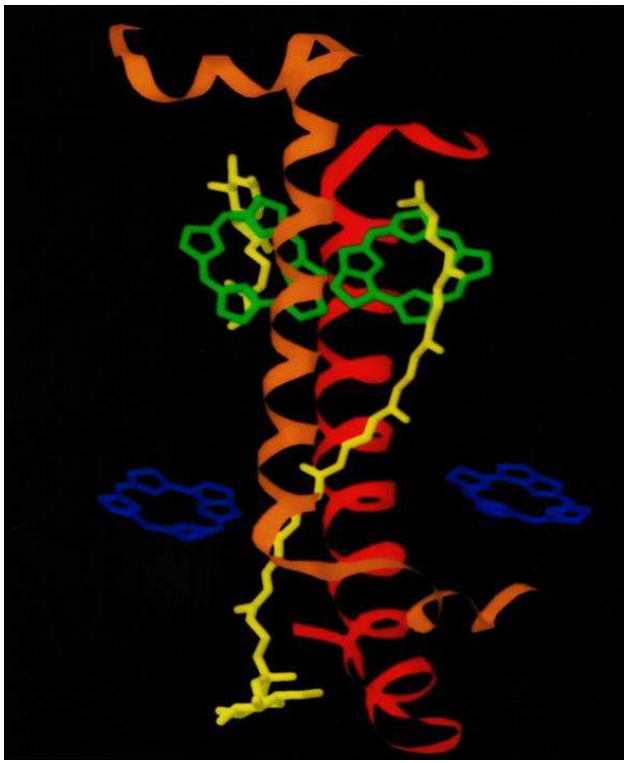

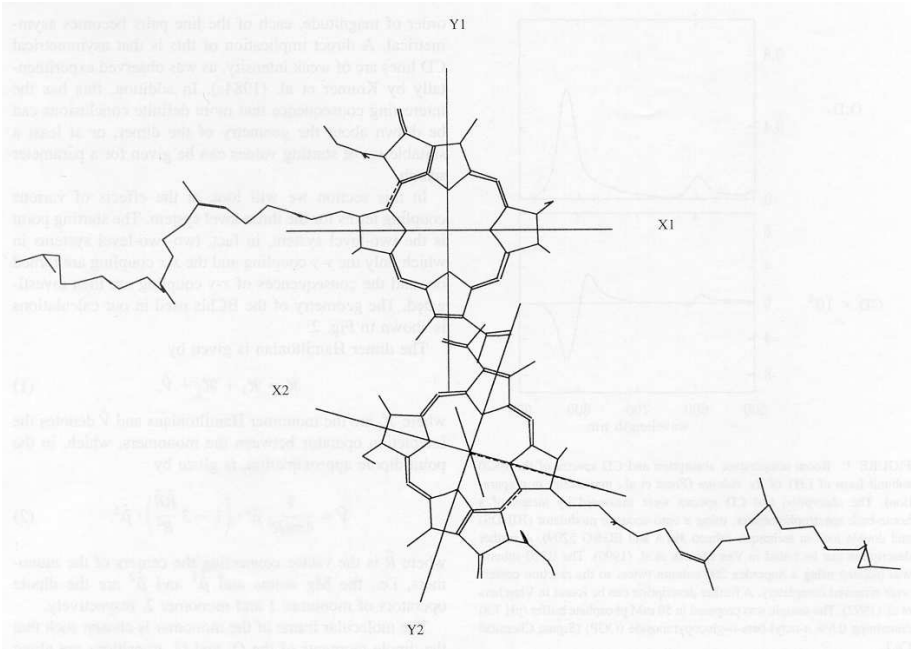


The B820 subunit is a dimer of bacteriochlorophylls.

Hamiltonian:

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_{\text{int}} = \epsilon_1 |1\rangle\langle 1| \otimes \mathbf{1}_2 + \mathbf{1}_1 \otimes \epsilon_2 |1\rangle\langle 1| + \frac{1}{4\pi\epsilon_0\epsilon_r r^3} \hat{\vec{\mu}}_1 \otimes \hat{\vec{\mu}}_2 : [1 - \hat{r}\hat{r}] \quad (13)$$

M.H.C. Koolhaas, *et al*, *Biophys. J.*, **72**, (1997), 1828.

# Coupled systems, reduced density matrix


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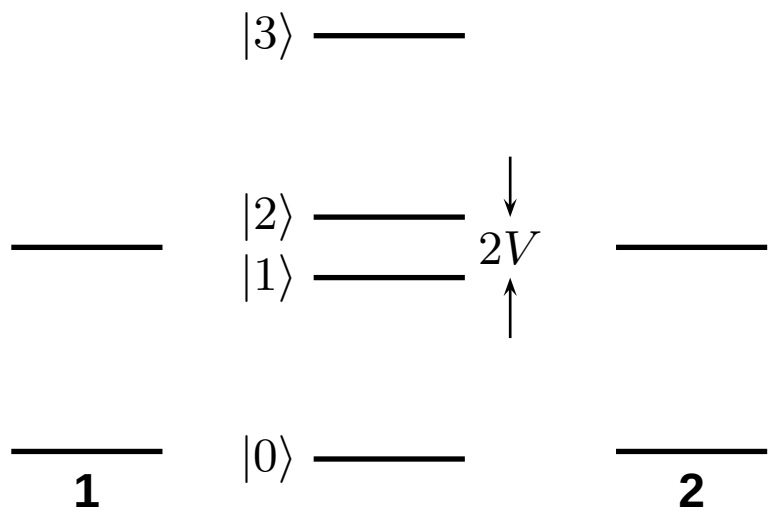
States of the dimer: $|ij\rangle = |i\rangle \otimes |j\rangle$, monomer 1 in state $i$, monomer 2 in state $j$.

Hamiltonian (only transition dipole moments):

$$\mathcal{H} = \begin{pmatrix} 0 & 0 & 0 & V \\ 0 & \epsilon_2 & V & 0 \\ 0 & V & \epsilon_1 & 0 \\ V & 0 & 0 & \epsilon_1 + \epsilon_2 \end{pmatrix} \tag{14}$$

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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The reduced density matrix is obtained by taking the partial trace.
Reduced density matrix for system 1, when total system is in the ground state:

$$\sigma_1 = \mathrm{Tr}_2[|0\rangle\langle 0|] = \begin{pmatrix} c_1^2 & 0 \\ 0 & s_1^2 \end{pmatrix} \quad \text{Not a pure state} \qquad (15)$$

System + Bath Hamitonian:

$$\mathcal{H} = \mathcal{H}_S + \mathcal{H}_B + \mathcal{H}_{int} \qquad (16)$$

Reduced Density Matrix:

$$\sigma_S = \mathrm{Tr}_B \rho \qquad (17)$$

# Coupling to external fields


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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:

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

with

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

# Example: Linear and Nonlinear Optics


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- Equation of motion:

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

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

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

- Resulting polarisation (which is what we measure):

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

# *Linear and non–linear optics*


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Classical and Damped Motion.

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Exercises and Problems


Expand the formal solution to the desired order:

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

$$4\pi^2\int_0^t d\tau\int_0^\tau d\tau_1\, e^{2\pi i\mathcal{L}_0(\tau-t)}\mathcal{L}_{\rm int}(\tau)e^{2\pi i\mathcal{L}_0(\tau_1-\tau)}\mathcal{L}_{\rm int}(\tau_1)\,|0\rangle\rangle +$$

$$8\pi^3 i\int_0^t d\tau\int_0^\tau d\tau_1\int_0^{\tau_1} d\tau_2\, e^{2\pi i\mathcal{L}_0(\tau-t)}\mathcal{L}_{\rm int}(\tau)e^{2\pi i\mathcal{L}_0(\tau_1-\tau)}\mathcal{L}_{\rm int}(\tau_1)$$

$$e^{2\pi i\mathcal{L}_0(\tau_2-\tau_1)}\mathcal{L}_{\rm int}(\tau_2)\,|0\rangle\rangle\cdots\cdots \qquad (18)$$

# Linear and non–linear optics


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

Linear optics, absorption, CD, LD, etc.

$$\vec{P}(t) = -2\pi i \int_0^t d\tau \left\langle\left\langle \hat{\vec{\mu}} \right| e^{2\pi i \mathcal{L}_0(\tau - t)} \mathcal{L}_{\rm int}(\tau) \left| 0 \right\rangle\right\rangle -$$

$$8\pi^3 i \int_0^t d\tau \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 \left\langle\left\langle \hat{\vec{\mu}} \right| e^{2\pi i \mathcal{L}_0(\tau - t)} \mathcal{L}_{\rm int}(\tau) e^{2\pi i \mathcal{L}_0(\tau_1 - \tau)} \mathcal{L}_{\rm int}(\tau_1)$$

$$e^{2\pi i \mathcal{L}_0(\tau_2 - \tau_1)} \mathcal{L}_{\rm int}(\tau_2) \left| 0 \right\rangle\right\rangle \cdots\cdots \qquad (19)$$

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

# Coupling to a Heat Bath


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- 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 Stark spectroscopy.
- Redfield theory: weak coupling, and slow relaxation (NMR). Projection operator formalism (see Lausanne4.pdf).
- 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).

# *Mixed Classical–Quantum Coupling.*


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Classical and Damped Motion.

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Exercises and Problems


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.

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

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

Major Problem:

- The quantum backreaction

A. Anderson, Quantum backreaction on “classical” variables, *Phys. Rev. Lett.*, **74**, (1995), 621–625

# Simulations


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Exercises and Problems


Many systems can be solved or simulated directly:

- Action of a Stark field on a molecule
- Interaction of molecules with electromagnetic fields (NMR, optical spectroscopy)

Some systems need a backreaction:

- Reaction field in polarizable media
- QM–MM methods.

# Simulations


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Attempt along the lines of the classical methods:

- Motion of the quantum system

$$\frac{\partial \rho}{\partial t} = -2\pi i[\mathcal{H}_0, \rho] + 2\pi i \vec{E} \cdot [\hat{\vec{\mu}}, \rho] \tag{20}$$

- Motion of the classical system (modelled as a damped Harmonic Oscillator):

$$\frac{d^2\vec{E}}{dt^2} = -\omega_s^2 \vec{E} - \zeta \frac{d\vec{E}}{dt} + A \left\langle \hat{\vec{\mu}} \right\rangle \tag{21}$$

- Coupling: the bath feels the expectation value of the dipole operator

$$\left\langle \hat{\vec{\mu}} \right\rangle = \mathrm{Tr}[\hat{\vec{\mu}}\rho] \tag{22}$$

# Results


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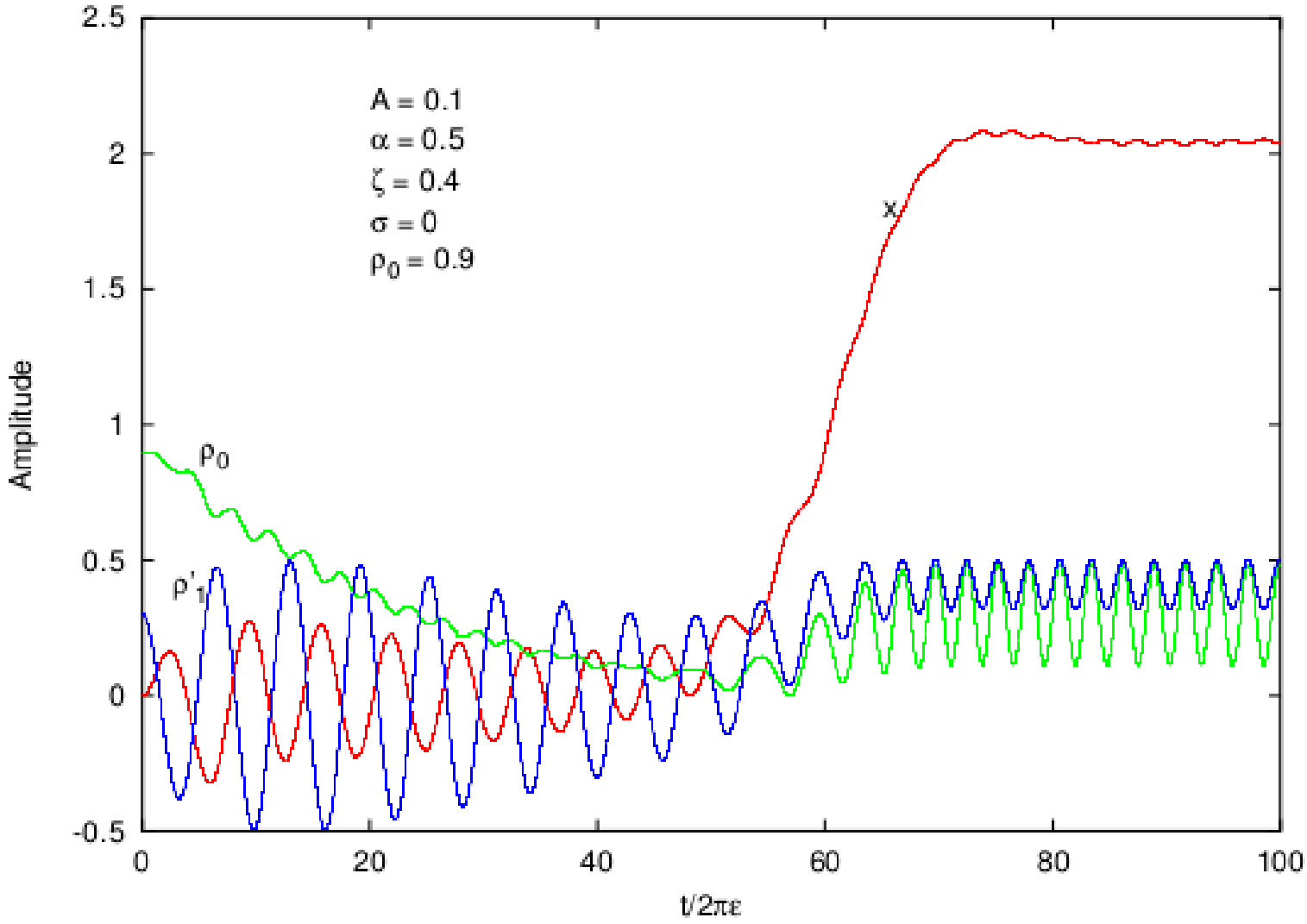

# Results 2


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- The oscillator position ($x$ in the picture) does not decay to zero.
- The coherences (the real part of $\rho_{01}$ is depicted as $\rho_1'$) does not decay to zero.
- The population does not decay to the ground state.

Thus: this problem is completely unlike the classical equivalent where

- The system oscillator decays to average position $x = 0$.
- The bath oscillator decays to average position $x = 0$.
- The system oscillator satisfies a generalized Langevin equation.

# Remarks


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- This is what people do in QM–MM methods (and worse)
- Almost, if not all, work on so–called non–linear Schrödinger equations suffers from the same problem.
- The equation is non–linear, and solutions are sensitive to initial conditions (rather irrelevant in view of the larger problems).
- It will never work since Eq. (20) conserves purity.
- Classical systems do not ‘feel’ expectation values, they perform measurements. Measurement do not preserve purity.

❖ Overview

Classical and Damped Motion.

Quantum Dynamics in Hilbert and Liouville Space

Exercises and Problems

❖ Exercises

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# *Exercises and Problems*

# Exercises and Problems


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1. Solve Eq. (1) formally. Give expressions for the average position and deviations from it, and shows that the fluctuation dissipation theorem gives the correct equilibrium value for $\langle x^2 \rangle$.
2. Do some simulations with the program langevin.c. You need to have a c compiler (or c++) with the gsl library installed. Otherwise, write a similar program in your prefered programming language.
3. Derive Eqs. (5)–(8). Show that both oscillators go to thermal equilibrium, with the correct equilibrium positions, and widths.
4. Show that it is impossible to find a quantum state corresponding to the density matrix in Eq. (9).
5. Show that Eq. (12) is indeed the propagator for the unperturbed 2LS.
6. Calculate $\langle\langle A \mid A \rangle\rangle$ and $|A\rangle\rangle \langle\langle A|$ for $A$ in Eqs. (10) and (11)
7. Write the Hamiltonian and the dipole operators as a vector in Liouville space (*cf.* Eqs. (10) and (11)).
8. Perform the diagonalization of Eq. (14), find explicit expressions for the eigenvalues, and eigenfunctions (the coefficients $c$ and $s$).

# Exercises and Problems


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9. The following states of a coupled system are called *Bell States*, the *Bell basis*, or *EPR pairs*.

$$|\beta_{00}\rangle = \frac{|00\rangle + |11\rangle}{\sqrt{2}} \qquad |\beta_{10}\rangle = \frac{|00\rangle - |11\rangle}{\sqrt{2}} \tag{23}$$

$$|\beta_{01}\rangle = \frac{|01\rangle + |10\rangle}{\sqrt{2}} \qquad |\beta_{11}\rangle = \frac{|01\rangle - |10\rangle}{\sqrt{2}} \tag{24}$$

   Prove that these states form an orthonormal basis of the two qubit Hilbert space.

10. For each of the Bell states, find the reduced density operator for each of the qubits.

11. Show that the entropy defined for the whole system $S = -k_B T \mathrm{Tr}[\rho \ln \rho]$ does not change in time.

12. Show that the entropy for a reduced subsystem $S = -k_B T \mathrm{Tr}[\sigma \ln \sigma]$ does change in time. What are the causes of this change?

13. Why does the second order term in Eq. (18) vanish for isotropic systems?

# Exercises and Problems


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14. Calculate the first term (the absorption spectrum) in Eq. (19) for a two–level system.
15. Mukamel makes the following remark (*Nonlinear Optical Spectroscopy*, p. 135): “The entropy of the universe is time independent, whereas the entropy of a subsystem is a significant and useful measure of the amount of missing information about the system”. Can you agree with that statement?
16. Give the explicit expression of $\mathcal{L}_{\mathrm{int}}$ for a 2LS in a time–dependent electric field.
17. Write down Hamiltonians for the systems on slide 30, for the appropriate cases.

# Literature


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