
The Density Operator and Redfield Theory

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The Density Operator

- ❖ Postulate 1
- ❖ Equilibrium
- ❖ Postulate 2
- ❖ Postulate 3
- ❖ Postulate 4
- ❖ Reduction
- ❖ Example
- ❖ Dipole Operator
- ❖ Dipole Interaction
- ❖ The Dimer and Some Numbers
- ❖ Numerical Calculations for the Dimer
- ❖ The New States
- ❖ Reduction

Redfield Theory

Exercises and Problems

The Density Operator

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Redfield Theory

Exercises and Problems

What exactly qualifies some physical systems to play the role of ‘measurer’? Was the wavefunction of the world waiting to jump for thousands of millions of years until a single-celled living creature appeared? Or did it have to wait a little longer, for some better qualified system . . . with a PhD?

J.S. Bell, *Against Measurement*

Density Operator

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Redfield Theory

Exercises and Problems

- Operator Expectation Value in state $|\psi\rangle$ and expansion in orthonormal basis

$$\langle A \rangle = \langle \psi | A | \psi \rangle = \sum_{n,m} a_m^* a_n \langle m | A | n \rangle = \sum_{n,m} a_m^* a_n A_{mn} \quad (1)$$

- (Ensemble) Average

$$\overline{\langle A \rangle} = \sum_{n,m} \overline{a_m^* a_n} A_{mn} \equiv \sum_{n,m} \rho_{nm} A_{mn} = \sum_n (\rho A)_{nn} = \text{Tr}[\rho A] \quad (2)$$

- Density Operator, (or density matrix)

$$\rho_{nm} = \overline{a_m^* a_n} \quad (3)$$

Time-Dependence of $\rho(t) = |\psi(t)\rangle \langle \psi(t)|$

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Redfield Theory

Exercises and Problems

● Schrödinger Equation:

$$i\hbar \frac{\partial |\psi\rangle}{\partial t} = \mathcal{H} |\psi(t)\rangle \quad (4)$$

● Apply to $|\psi(t)\rangle \langle \psi(t)|$:

$$\frac{\partial \rho(t)}{\partial t} = -\frac{i}{\hbar} \mathcal{H} |\psi(t)\rangle \langle \psi(t)| + \frac{i}{\hbar} |\psi(t)\rangle \langle \psi(t)| \mathcal{H} = \frac{i}{\hbar} [\rho, \mathcal{H}] \quad (5)$$

Quantum Liouville Equation

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

Postulate 1

The Density Operator

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Redfield Theory

Exercises and Problems

Associated to any isolated physical system is a complex vector space with inner product, that is a Hilbert space, known as the *state space* of the system. The system is completely described by its *density operator* which is a positive operator ρ with trace one, acting on the state space of the system. If a system is in the state ρ_i with probability p_i , then the density operator of the system is $\sum_i p_i \rho_i$.

- Trace: Sum of the diagonal elements.
- Positive operator: Operator with non-negative eigenvalues

Examples & Properties

The Density Operator

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Redfield Theory

Exercises and Problems

- Quantum system with states $|\psi_i\rangle$ and probabilities p_i : the collection $\{p_i, |\psi_i\rangle\}$ is called *an ensemble of pure states*.

2LS or qubit with states $|0\rangle = |\uparrow\rangle$ and $|1\rangle = |\downarrow\rangle$

- Pure states are for instance $\rho_0 = |0\rangle\langle 0|$ and $\rho_1 = |1\rangle\langle 1|$. In matrixform:

$$\rho_0 = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \quad \text{and} \quad \rho_1 = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \quad (6)$$

- For pure states: $\text{Tr}[\rho^2] = 1$. In other cases this trace is smaller than 1.

Equilibrium Density Matrix

The Density Operator

❖ Postulate 1

❖ **Equilibrium**

❖ Postulate 2

❖ Postulate 3

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Redfield Theory

Exercises and Problems

Equilibrium Density Operator:

$$\rho_{\text{eq}} = \frac{e^{-\beta\mathcal{H}}}{Q} \quad \text{with} \quad Q = \text{Tr} \left[e^{-\beta\mathcal{H}} \right] \quad (7)$$

- Diagonal elements of ρ are called populations.
- Off-diagonal elements of ρ are called coherences.
- Unperturbed 2LS Hamiltonian: $\mathcal{H}_0 = \epsilon |1\rangle \langle 1|$
- Transition dipole operator: $\hat{\mu} = \mu [|0\rangle \langle 1| + |1\rangle \langle 0|]$

Postulate 2

The Density Operator

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Redfield Theory

Exercises and Problems

The evolution of a closed quantum system is described by a *Unitary transformation*. That is, the state ρ at time t_1 is related to the state ρ' of the system at time t_2 by a unitary operator U which depends only on the times t_1 and t_2 ,

$$\rho' = U \rho U^\dagger$$

For Hamiltonian systems:

$$U = e^{-\frac{i}{\hbar} \mathcal{H}(t_2 - t_1)} \quad (8)$$

Postulate 3

The Density Operator

❖ Postulate 1

❖ Equilibrium

❖ Postulate 2

❖ **Postulate 3**

❖ Postulate 4

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Redfield Theory

Exercises and Problems

Quantum measurements are described by a collection $\{M_m\}$ of measurement operators. These are operators acting on the state space of the system being measured. The index m refers to the measurement outcomes that may occur in the experiment. If the state of the quantum system is ρ immediately before the measurement then the probability that result m occurs is given by

$$p(m) = \text{Tr}[M_m \rho M_m^\dagger] \quad (9)$$

and the state of the system after measurement is

$$\frac{M_m \rho M_m^\dagger}{\text{Tr}[M_m \rho M_m^\dagger]} \quad (10)$$

The measurement operators satisfy the *completeness relation*

$$\sum_m M_m^\dagger M_m = I \quad (11)$$

Postulate 4

The Density Operator

❖ Postulate 1

❖ Equilibrium

❖ Postulate 2

❖ Postulate 3

❖ **Postulate 4**

❖ Reduction

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Redfield Theory

Exercises and Problems

The state space of a composite physical system is the tensor product of the state spaces of the component physical systems. Moreover, if we have systems numbered 1 through n , and system i is prepared in state ρ_i then the joint state of the total system is $\rho_1 \otimes \rho_2 \otimes \cdots \otimes \rho_n$.

Two Coupled 2LS

- States are $|i\rangle \otimes |j\rangle \equiv |ik\rangle \equiv |2i + j\rangle$. For instance $|0\rangle \otimes |1\rangle = |1\rangle$.
- Inverse transformation: $|k\rangle = |k/2\rangle \otimes |k\%2\rangle$, using integer division and the mod operator. For instance $|3\rangle = |11\rangle = |1\rangle \otimes |1\rangle$.

Reduced Density Matrix

The Density Operator

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Redfield Theory

Exercises and Problems

When we solve a quantum–mechanical problem, what we really do is divide the universe into two parts — the system in which we are interested and the rest of the universe. We then usually act as if the system in which we are interested comprised the entire universe. To motivate the use of density matrices, let us see what happens when we include the part of the universe outside the system.

R.P. Feynman, *Statistical Mechanics*, p. 39

The reduced density matrix is obtained by taking the trace over the parts of the universe you don't want to deal with explicitly.

$$\sigma = \text{Tr}_2 \rho \quad (12)$$

A Dimer of 2-Level Systems

The Density Operator

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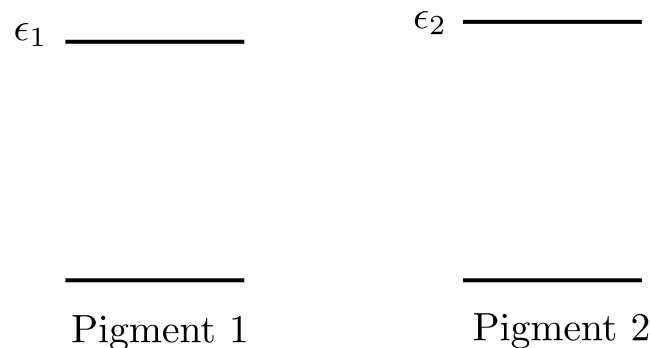
Redfield Theory

Exercises and Problems

1. Basic States are $|0\rangle = |00\rangle$, $|1\rangle = |01\rangle$, $|2\rangle = |10\rangle$, and $|3\rangle = |11\rangle$
2. Unperturbed Hamiltonian is $\mathcal{H} = \mathcal{H}_1 \otimes \mathbb{1}_2 + \mathbb{1}_1 \otimes \mathcal{H}_2$
3. In matrix form the Hamiltonian in the Basic States basis is therefore

$$\mathcal{H} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & \epsilon_2 & 0 & 0 \\ 0 & 0 & \epsilon_1 & 0 \\ 0 & 0 & 0 & \epsilon_1 + \epsilon_2 \end{pmatrix} \quad (13)$$

Unperturbed System:



Dipole Operator

The Density Operator

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Redfield Theory

Exercises and Problems

Next to the Hamiltonian we also need the Dipole Operator

The dipole operator is more complex, since there are permanent dipole moments and transition dipole moments. And the dipole moments are vectors.

Most general case:

$$\hat{\vec{\mu}} = \vec{\mu}_0 |0\rangle \langle 0| + \vec{\mu}_1 |1\rangle \langle 1| + \vec{\mu}_{01} |0\rangle \langle 1| + \vec{\mu}_{10} |1\rangle \langle 0| \quad (14)$$

- The state dipole moments $\vec{\mu}_0$ and $\vec{\mu}_1$ need to be real.
- The transition dipole moments satisfy $\vec{\mu}_{10} = \vec{\mu}_{01}^*$.
- Since bacteriochlorophylls are almost symmetric, state dipole moments are very small.
- Transition dipole moments must satisfy $\vec{\mu}_{10} = \vec{\mu}_{01}^*$.
- For most applications $\vec{\mu}_{10}$ can be taken real. Exception: if the pigment is itself optically active. Bacteriochlorophyll is not.
- The total number of dipole moments for an N -level system is N state moments and $\frac{1}{2}N(N - 1)$ independent transition moments.

Dipole Interaction

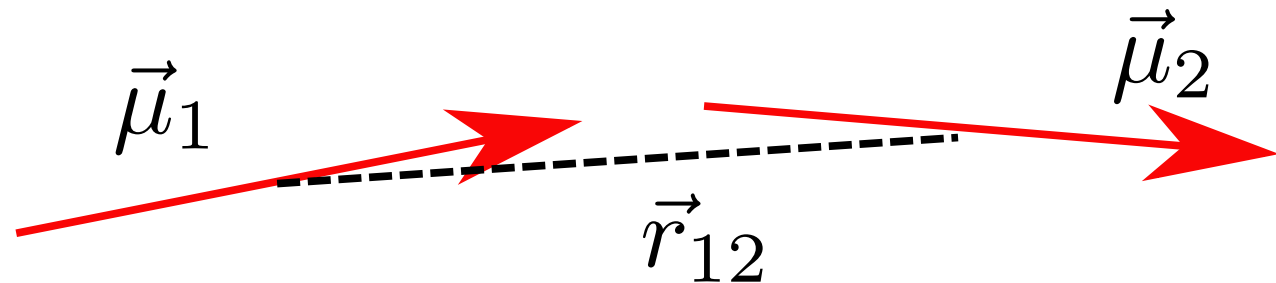
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- ## Redfield Theory
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- ## Exercises and Problems
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1. Interaction between dipole operators:

$$\hat{V}_{ij} = \frac{1}{4\pi\epsilon_0} \hat{\vec{\mu}}_i \cdot \left(1 - \frac{\vec{r}_{ij}\vec{r}_{ij}}{r_{ij}^2} \right) \cdot \hat{\vec{\mu}}_j \quad (15)$$

2. $\hat{\vec{\mu}}_i$ is the dipole operator of pigment i .
3. \vec{r}_{ij} is the vector connecting the positions of the pigment dipoles.
4. All dipole moments are supposed point dipoles.



Again the dipole operators need to be extended to the full M pigment N^M dimensional Hilbert space.

The Dimer and Some Numbers

The Density Operator

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Numerical Calculations for the Dimer

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Redfield Theory

Exercises and Problems

1. To calculate $\langle k | \hat{V}_{ij} | l \rangle$ again expand the bra and the ket into pigment states. All pigments other than i and j should be in the same state left and right. The other elements are determined by the transitions of pigments i and j .
2. For the two level dimer with only transition moments the dipole interaction operator can be written:

$$\hat{V}_{12} = \begin{pmatrix} 0 & 0 & 0 & V \\ 0 & 0 & V & 0 \\ 0 & V & 0 & 0 \\ V & 0 & 0 & 0 \end{pmatrix} \quad (16)$$

3. The magnitude of V is determined by the magnitude and orientation of the dipole moments and the vector connecting them:

$$V = \frac{1}{4\pi\epsilon_0} \vec{\mu}_1 \cdot \left(1 - 3 \frac{\vec{r}_{12} \vec{r}_{12}}{r_{12}^2} \right) \cdot \vec{\mu}_2 \quad (17)$$

4. For $\mu = 1$ D dipoles at $a = 1$ nm distance:

$$V_0 = \frac{\mu^2}{4\pi\epsilon_0 a^3} = 5.035 \text{ cm}^{-1} \quad (18)$$

Numerical Calculations for the Dimer

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Redfield Theory

Exercises and Problems

1. The full Hamiltonian for the two-level dimer is

$$\mathcal{H} + \hat{V}_{12} = \begin{pmatrix} 0 & 0 & 0 & V \\ 0 & \epsilon_2 & V & 0 \\ 0 & V & \epsilon_1 & 0 \\ V & 0 & 0 & \epsilon_1 + \epsilon_2 \end{pmatrix} \quad (19)$$

2. The Hamiltonian falls into two blocks: the single excited states \mathcal{H}_s , and the ground and double excited state \mathcal{H}_d :

$$\mathcal{H}_s = \begin{pmatrix} \epsilon_2 & V \\ V & \epsilon_1 \end{pmatrix} \quad \text{and} \quad \mathcal{H}_d = \begin{pmatrix} 0 & V \\ V & \epsilon_1 + \epsilon_2 \end{pmatrix} \quad (20)$$

Both Hamiltonians are easily diagonalized.

3. Eigenvalues:

$$\lambda_{\pm}^s = \frac{1}{2} \left[\epsilon_1 + \epsilon_2 \pm \sqrt{(\epsilon_1 - \epsilon_2)^2 + 4V^2} \right] \quad (21)$$

$$\lambda_{\pm}^d = \frac{1}{2} \left[\epsilon_1 + \epsilon_2 \pm \sqrt{(\epsilon_1 + \epsilon_2)^2 + 4V^2} \right] \quad (22)$$

The New States

The Density Operator

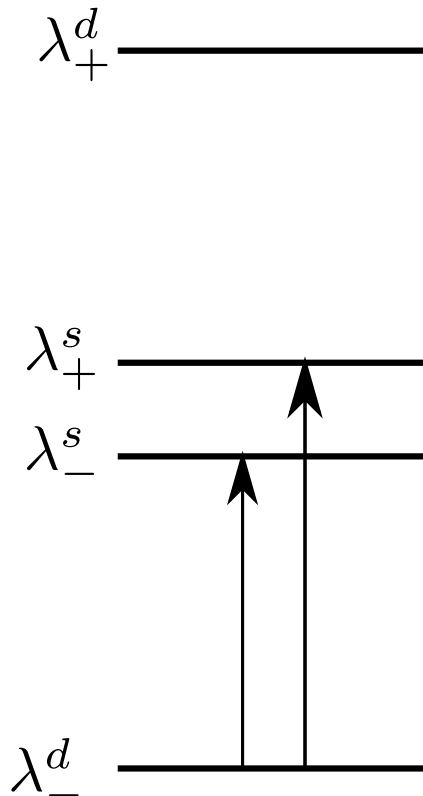
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Redfield Theory

Exercises and Problems



- The distance between the single excited states is $\sim 2V$ (this is exact when $\epsilon_1 = \epsilon_2$). This is called exciton splitting.
- The ground state is slightly lower than 0, the double excited state slightly higher than $\epsilon_1 + \epsilon_2$.
- Lowering of the ground state and raising the double excited state is much smaller than the exciton splitting because $V/(\epsilon_1 + \epsilon_2) \ll 1$. This is evidently not true for $V/(\epsilon_1 - \epsilon_2)$.
- The new states are labeled $|\psi_k\rangle$.

Reduced Density Matrix

The Density Operator

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Redfield Theory

Exercises and Problems

- The dimer is in the ground state:

$$|\psi_0\rangle = c|0\rangle + s|3\rangle \quad (23)$$

s and c are constants such that $c^2 + s^2 = 1$.

- The density matrix can be written

$$\rho = \sum_{k,l=0}^3 \rho_{kl} |k\rangle \langle l| \quad (24)$$

- The reduced density matrix for system 1 can be written

$$\sigma = \text{Tr}_2 \rho = \begin{pmatrix} \rho_{00} + \rho_{11} & \rho_{02} + \rho_{13} \\ \rho_{20} + \rho_{31} & \rho_{22} + \rho_{33} \end{pmatrix} \quad (25)$$

Reduced Density Matrix 2

The Density Operator

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Redfield Theory

Exercises and Problems

- For the dimer in the ground state the density matrix is:

$$\begin{pmatrix} c^2 & 0 & 0 & cs \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ cs & 0 & 0 & s^2 \end{pmatrix} \quad (26)$$

- The reduced density matrix σ is:

$$\sigma = \begin{pmatrix} c^2 & 0 \\ 0 & s^2 \end{pmatrix} \quad (27)$$

- The reduced density matrix does not correspond to a pure state.

The Density
Operator

Redfield Theory

- ❖
- ❖ Assumptions
- ❖ Liouville Equation
- ❖ Hamiltonians
- ❖ Derivation
- ❖ Remarks

Exercises and
Problems

Redfield Theory



- ❖ Assumptions
- ❖ Liouville Equation
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- ❖ Derivation
- ❖ Remarks

Here we elucidate the role of coherence in determining the efficiency of charge separation in the plant photosystem II reaction center by comprehensively combining experiment (two-dimensional delectronic spectroscopy) and theory (standard Redfield theory).

E. Romero *et al.* preprint, (2012).

No spontaneous coherence arises in the standard Bloch–Redfield description, showing the essential need to go beyond such theories.

Chin *et al*, *Nat. Phys.*, **8**, (2013), 113

Assumptions

The Density Operator

Redfield Theory



❖ Assumptions

❖ Liouville Equation

❖ Hamiltonians

❖ Derivation

❖ Remarks

Exercises and Problems

- Theory designed for NMR relaxation, to give an underpinning to the Bloch equations.
- Bloch equations: coherences go to zero, populations go to equilibrium.
- In NMR relaxation is very slow (μs and longer).
- In NMR interaction between the spins and fluctuating fields in the environment is very weak.
- In NMR spin relaxation is much slower than decay of solvent correlation functions.

Liouville Equation

The Density Operator

Redfield Theory



❖ Assumptions

❖ **Liouville Equation**

❖ Hamiltonians

❖ Derivation

❖ Remarks

Exercises and Problems

$$\frac{\partial |\rho(t)\rangle\rangle}{\partial t} = -2\pi i \mathcal{L}_0 |\rho(t)\rangle\rangle - 2\pi i \mathcal{L}_r(t) |\rho(t)\rangle\rangle \quad (28)$$

- $|\rho\rangle\rangle$ is a vector in Liouville Space, the Hilbert space of density operators.
- For the 2SL $|\rho\rangle\rangle$ can be viewed as a vector with four elements. For instance $|0\rangle\rangle \equiv |0\rangle \langle 0|$. I find it convenient to use a similar bookkeeping device as for the dimer.
- \mathcal{L} is a Liouville operator, defined as

$$\mathcal{L} \cdots = [\mathcal{H}, \cdots] \quad (29)$$

- The notation hides the complexity, but makes it easier to do the formal steps.

Hamiltonians

The Density Operator

Redfield Theory

❖

❖ Assumptions

❖ Liouville Equation

❖ Hamiltonians

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Exercises and Problems

- System Hamiltonian: \mathcal{H}_0 .
- Random Hamiltonian :

$$\mathcal{H}_r(t) = \sum_k \hat{A}_k B_k(t) \quad (30)$$

with \hat{A}_k a set of system operators, and $B_k(t)$ a set of fluctuating environment ('bath') functions.

- Properties of B :
 - ❖ Averages are zero: $\langle B_k(t) \rangle = 0$
 - ❖ Correlation functions:
 $\langle B_k(t) B_l(t + \tau) \rangle = \langle B_k(0) B_l(\tau) \rangle \equiv J_{kl}(\tau)$
are rapidly decaying in time.
- Example for NMR: \hat{A} are the spin operators, B magnetic field fluctuations.
- Example for electronic transitions: \hat{A} is the dipole operator, B polarization fluctuations.

The Derivation in Eight Steps

The Density Operator

Redfield Theory

- ❖
- ❖ Assumptions
- ❖ Liouville Equation
- ❖ Hamiltonians

❖ Derivation

❖ Remarks

Exercises and Problems

1. Go to the interaction picture:

$$\frac{\partial |\rho_I(t)\rangle\rangle}{\partial t} = -2\pi i \mathcal{L}_{r,I}(t) |\rho_I(t)\rangle\rangle \quad (31)$$

with

$$|\rho_I(t)\rangle\rangle = e^{2\pi i \mathcal{L}_0 t} |\rho(t)\rangle\rangle \mathcal{L}_r(t) e^{-2\pi i \mathcal{L}_0 t} \quad (32)$$

and

$$\mathcal{L}_{r,I}(t) = e^{2\pi i \mathcal{L}_0 t} \mathcal{L}_r(t) e^{-2\pi i \mathcal{L}_0 t} \quad (33)$$

- If there is no interaction with the environment the density operator in the interaction picture is a constant.
- The Liouville operators do not commute.

Interaction Picture

The Density Operator

Redfield Theory

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Exercises and Problems

2. Formal solution in the interaction picture:

$$|\rho_I(t)\rangle\rangle = |\rho_I(0)\rangle\rangle - 2\pi i \int_0^t d\tau \mathcal{L}_{r,I}(\tau) |\rho_I(\tau)\rangle\rangle \quad (34)$$

- Not really a *solution*, rather writing a differential equation as an equivalent integral equation.
- Nevertheless a commonly used technique: see for instance the Feynman expansion for quantum electrodynamics, or Mukamel's expansion for the derivation of non-linear optics.

3. Expand to second order

$$\begin{aligned} |\rho_I(t)\rangle\rangle &= |\rho_I(0)\rangle\rangle - 2\pi i \int_0^t d\tau \mathcal{L}_{r,I}(\tau) |\rho_I(0)\rangle\rangle \\ &\quad - 4\pi^2 \int_0^t d\tau \int_0^\tau d\tau' \mathcal{L}_{r,I}(\tau) \mathcal{L}_{r,I}(\tau') |\rho_I(0)\rangle\rangle + \dots \end{aligned} \tag{35}$$

- Not much to argue with here.
- I have no idea if anyone ever proved that the series expansion converges.

Truncation and Derivation

The Density Operator

Redfield Theory

❖

❖ Assumptions

❖ Liouville Equation

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❖ Remarks

Exercises and Problems

4. Truncate after the second order term, and take the time derivative

$$\begin{aligned} \frac{\partial |\rho_I(t)\rangle\rangle}{\partial t} &= -2\pi i \mathcal{L}_{r,I}(t) |\rho_I(0)\rangle\rangle \\ &\quad - 4\pi^2 \int_0^t d\tau \mathcal{L}_{r,I}(t) \mathcal{L}_{r,I}(\tau) |\rho_I(0)\rangle\rangle \end{aligned} \quad (36)$$

- This is some form of *coarse graining* I assume.
- I know of no other cases in which this procedure is used.
- But we do get a new differential equation for $|\rho\rangle\rangle$.

5. Average over the bath variables

$$\frac{\partial |\rho_I(t)\rangle\rangle}{\partial t} = -4\pi^2 \int_0^t d\tau \langle \mathcal{L}_{r,I}(t) \mathcal{L}_{r,I}(\tau) \rangle |\rho_I(0)\rangle\rangle \quad (37)$$

- Average over the bath function is zero, only the correlation functions remain.

6. Stationarity and Rapid decay of the bath functions

$$\frac{\partial |\rho_I(t)\rangle\rangle}{\partial t} = -4\pi^2 \int_0^\infty d\tau \langle \mathcal{L}_{r,I}(0) \mathcal{L}_{r,I}(t - \tau) \rangle |\rho_I(0)\rangle\rangle \quad (38)$$

- This equation holds for times longer than bath correlation decay times.

Assume Slow Change

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- ❖
- ❖ Assumptions
- ❖ Liouville Equation
- ❖ Hamiltonians

❖ Derivation

❖ Remarks

Exercises and Problems

7. Assume slow change of $|\rho_I\rangle\rangle$

$$\frac{\partial |\rho_I(t)\rangle\rangle}{\partial t} = -4\pi^2 \int_0^\infty d\tau \langle \mathcal{L}_{r,I}(0) \mathcal{L}_{r,I}(t - \tau) \rangle |\rho_I(0)\rangle\rangle \quad (39)$$

- Since $|\rho_I(t)\rangle\rangle$ has not changed within the bath correlation time, we can replace $|\rho_I(0)\rangle\rangle$ by $|\rho_I(t)\rangle\rangle$

8. Work out the correlation functions.

$$\begin{aligned} \frac{\partial \rho_{\alpha\alpha'}(t)}{\partial t} = & -2\pi i(\alpha - \alpha')\rho_{\alpha\alpha'}(t) - 2\pi \sum_{\beta,\beta'} \left[\delta_{\alpha'\beta'} \sum_{\gamma} J(\beta - \gamma) A_{\gamma\beta} \cdot A_{\alpha\gamma} \right. \\ & \left. - [J(\alpha' - \beta') + J(\beta - \alpha)] A_{\beta'\alpha'} \cdot A_{\alpha\beta} + \delta_{\alpha\beta} \sum_{\gamma} J(\gamma - \beta') A_{\beta'\gamma} \cdot A_{\gamma\alpha'} \right] \rho_{\beta\beta'}(t) \end{aligned} \quad (40)$$

Remarks

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❖ Assumptions

❖ Liouville Equation

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❖ Derivation

❖ **Remarks**

Exercises and Problems

- Eq. (40) is the so-called *Redfield Equation*, an equation for the decay of a quantum system due to external fluctuations for weak system–bath interaction.
- The functions $J(\omega)$ (note that $\alpha - \beta$ is an energy difference, and hence a frequency) are the Fourier transforms of the correlation functions $J(t)$. They are called *Spectral Densities*.
- The term in brackets contains both so-called secular terms (shifts in energy) as well as damping terms: coherences go to zero, and the population goes to the ground state.
- The decay of the quantum system must be much slower than the decay of bath correlations. This is *not* satisfied for coherence decay in excitonically coupled systems.

Remarks 2

The Density Operator

Redfield Theory

- ❖
- ❖ Assumptions
- ❖ Liouville Equation
- ❖ Hamiltonians
- ❖ Derivation
- ❖ **Remarks**

Exercises and Problems

- The derivation is rather weird, and as far as I know has no equivalents in other fields. There are other derivations based on a projection operator formalism (see the Argyres and Kelley paper)
- Two worked out examples, spin 1/2 relaxation and electronic relaxation are given in the document Redfield.pdf
- The Redfield equation can be written as:

$$\frac{\partial |\rho\rangle\rangle}{\partial t} = -2\pi i \mathcal{L}_0 |\rho\rangle\rangle - \Gamma_d |\rho\rangle\rangle \quad (41)$$

where Γ_d represents the damping. This is a *superoperator*, the action of which can be written as

$$[\Gamma_d |\rho\rangle\rangle]_{ij} = \sum_{k,l} [\Gamma_d]_{ij;kl} \rho_{kl} \quad (42)$$

Remarks 3

The Density Operator

Redfield Theory



❖ Assumptions

❖ Liouville Equation

❖ Hamiltonians

❖ Derivation

❖ **Remarks**

Exercises and Problems

- There is no decay to the equilibrium density operator for finite temperatures.
- If $\Gamma_d e^{-\beta \mathcal{H}_0} = 0$ it is argued that the Redfield equation also holds for deviations from equilibrium.
- As far as I know there is no proof that any initial density operator decays to equilibrium.
- There are a number of other theories with super operators, see for instance the Kossakowski–Lindblad equation (sometimes a bunch of other names are also attached to this).

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Exercises and Problems

Exercises and Problems

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1. Prove: If V is a finite-dimensional inner product space over \mathbb{C} , and if $A : V \rightarrow V$ satisfies $\langle Av|v \rangle \geq 0$ for all $v \in V$, then A is Hermitian.
2. Show that $\frac{1}{2} [|0\rangle + |1\rangle] [\langle 0| + \langle 1|]$ is a pure state.
3. Show that for qubits we can not find a state $|\psi\rangle$ such that $\rho = |\psi\rangle \langle \psi|$ if $\rho = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{pmatrix}$.
4. Calculate the equilibrium density operator for a qubit in a static electric field E : $\mathcal{H} = \mathcal{H}_0 - \mu E$. Plot the ground state population as function of E and T .
5. Plot the change in transition dipole moment as a function of E and T for the density of the previous problem.
6. Calculate Q for the harmonic oscillator: $\mathcal{H} = \sum_{n=0}^{\infty} (n + \frac{1}{2}) |n\rangle \langle n|$
7. Prove that there is no quantum mechanical state corresponding to thermal equilibrium unless $T = 0$. In other words, prove that for finite temperatures the equilibrium density operator is not pure.
8. Show that the properties (symmetry, Jacobi identity) of the commutator and the Poisson bracket are the same.

Exercises

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9. Prove that if for a combined system $\rho = \rho^1 \otimes \rho^2$, the reduced density matrix for system 1 is

$$\sigma = \text{Tr}_2(\rho) = \rho^1 \quad (43)$$

10. Find explicit expressions for the constants c and s in Eq. (23).
11. Prove Eq. (25).
12. In a paper by Fuchs and Peres the following statement is made:

For example, there is no way to ascertain whether a single system is in a pure state or is part of an entangled composite system.

Do you agree?

13. Derive an equation of motion for the reduced density operator. Is this a closed equation?
14. The derivation of ref. 6 is similar to that of Redfield theory. Why does energy or momentum conservation not bother the Redfield approach introduced here. Or does it?

Exercises

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15. Show that with Eq.(8) $\rho' = U\rho U^\dagger$ solves the quantum Liouville equation.
16. Papers on the role of coherence in photosynthesis are always based on fs pulsed experiments. Do you think that the photosynthetic complex is optimized for fs pulses? Is the difference between sunlight and very intense fs laserpulses irrelevant?
17. Work out the relaxation of an electronic state due to electric field fluctuations. The interaction Hamiltonian is

$$\mathcal{H}_r = -\hat{\vec{\mu}} \cdot \vec{E} \quad (44)$$

The electric field correlations can be written as

$$\langle E_i E_j(t) \rangle = \frac{1}{3} \delta_{ij} \langle E^2 \rangle e^{-\zeta t} \quad (45)$$

so that

$$J(\omega) = \frac{\langle E^2 \rangle}{\zeta - i\omega} \quad (46)$$

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18. Show that from Eq. (28) it follows that not only $\text{Tr}[\rho]$ is a constant, but also $\text{Tr}[\rho^2]$. In other words, a pure state remains a pure state under the action of this equation. Hint: it is easier to use the commutator representation of the Liouville operator for this proof.
19. For those who do not want to use commutators: first show that $\text{Tr}[\rho] = \langle\langle \mathbb{1} | \rho \rangle\rangle$, where $|\mathbb{1}\rangle\rangle \equiv \sum_k |k\rangle \langle k|$.
20. At the end of the derivation of the Redfield equation, coherences decay and populations decay to the ground state. So even when we start with an impure state, the final state is pure. At which step of the derivation is purity no longer a conserved quantity?
21. What does the result of the previous exercise tell you about the series expansion of the integral form of the Liouville equation?

Literature

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