

Sfb 450 Analysis and Control of Ultrafast Photoinduced Reactions

“Dissipation (dephasing and energy
relaxation) in the Harmonic Oscillator”

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How is this Talk Organized?

- Pure and Mixed States: The Statistical Operator.
- Coherence.
- Non-Perturbative Propagation of the Density Matrix (ρ).
- A Simple Example: Propagation in the H_2 Molecule within the Harmonic Oscillator Model.
- Collisions: Perturbative Propagation of ρ .
- The Redfield Theory of Relaxation.
- Linear Coupling to a Stochastic Bath Variable (ξ).
- Summary.

PART 1

Difference between Pure and Mixed States

The use of the Statistical or Density Operator to describe Mixed States

Propagation of a Superposition State in the absence of perturbation.

We illustrate these concepts with the aid of a simple *example* provided by the excitation of the hydrogen molecule to an ionic state with arbitrarily tunable and ultrashort laser pulses.

PART 2

Dephasing, Collisions and Relaxation after creation of a superposition state

Redfield theory of relaxation

We illustrate the previous concepts with a simple model in which a superposition state of a low-frequency monodimensional harmonic oscillator relaxes through interaction with a stochastic bath

Pure and Mixed States

The Representation or Basis

$$\{ |i\rangle \}$$

Pure States

$$|\psi\rangle = \sum_i a_i |i\rangle$$

Mixed States

$$|\psi\rangle = \sum_n W_n |n\rangle = \sum_{n,i} W_n a_i^n |i\rangle$$

$$\hat{Q} = \sum_n W_n \hat{Q}_n = \sum_n W_n \langle n | \hat{Q} | n \rangle$$

1. Most of the methods in Quantum Mechanics based on the Variational Theorem or the Perturbation Theory use basis states. Basis states are also the essence of the Heisenberg Matrix representation of Quantum Mechanics. By means of the basis states we are able to understand how similar is our actual system to some simpler model systems whose behaviour is well understood.
2. We express the wavefunction (**WF**) of our system as a linear combination of Basis States.
3. When working with ultrashort laser pulses, the excitation energy is imprecise and the state of the system after electronic optical excitation has to be described as a superposition state or wavepacket (**WP**). A **WP** is a linear combination of eigenstates of the system weighted by some probability. All these eigenstates can be themselves linear combinations of basis functions.
4. In the definition of the mean value of some observable \hat{Q} statistics enters in two ways: in the definition of mean value and in the average over the states.

The Statistical or Density Operator

The Density Matrix

$$\hat{\rho} = \sum_n W_n | \psi_n \rangle \langle \psi_n |$$

$$\hat{\rho}_{ij} = \sum_{n,i,j} W_n a_i^{n*} a_j^n$$

$$\hat{\rho}_{ij} = \sum_n W_n a_i^n a_j^{n*}$$

Properties

- i. Hermitian
- ii. ρ_{ii} means ensemble-averaged probability
- iii. $\text{Tr}(\hat{\rho}) = \sum_i \rho_{ii} = 1$
- iv. $\langle Q \rangle = \text{Tr}(\hat{\rho} Q)$

1. For the description of superposition systems it is more convenient to work with the density matrix instead of using the WF of the system.
2. The density or statistical operator is defined as the sum-over-the-states of the counter-product of the wavefunctions composing the superposition state and weighted by their respective probabilities.
3. The density matrix element ρ_{ij} is the average value over the states of the product of the contribution coefficient of the basis state ϕ_i by the contribution coefficient of the basis state ϕ_j (complex conjugate).

4. Important Properties:

It is hermitian.

The diagonal elements ρ_{ii} are the ensemble averaged probability of having a system described by the basis function ϕ_i .

As the meaning of the diagonal is probability the trace of the matrix has to be normalized to unity.

It can be shown that the mean value of the observable Q is the trace of the matrix $Q\rho$.

The Off-Diagonal Terms in a Coherent Two-level System

Basis
 $\{ |a\rangle, |b\rangle \}$

Superposition State

$$| \psi_n(t) \rangle = a_n(0) \exp \left[-i \frac{E_a}{\hbar} t \right] | a \rangle + b_n(0) \exp \left[-i \frac{E_b}{\hbar} t + i \phi_0 \right] | b \rangle$$

Density Matrix

$$= \sum_n W_n \begin{bmatrix} |a_n(0)|^2 & a_n(0)b_n(0)^* \exp(i \phi_0) \\ a_n(0)^* b_n(0) \exp(-i \phi_0) & |b_n(0)|^2 \end{bmatrix}$$

1. Up to now we described the physical meaning of the diagonal elements of the density matrix. We now want to understand the meaning of the off-diagonal elements.
2. For simplicity, let's assume that we have a two-dimensional basis and a time-independent Hamiltonian. Any superposition state could be expressed as a linear combination of the two basis states. The time evolution of the **WF** is obtained by applying the time-dependent Schrödinger operator to it.
3. Now assume that we have control over the relative phases of the two basis-states. In other words, let's assume that we can “start” both states at exactly the same time for all the elements of the ensemble.
4. The values of the diagonal elements will depend only on the initial amplitudes of the basis states whereas the value of the off-diagonal elements will oscillate around the time-zero values with a frequency given by the energy difference of the basis states.

The Off-Diagonal Terms in a Non-Coherent Two-level System

State to State Random Phase

$$\bar{\theta}_n = \frac{E_b t_0^n}{\hbar}$$

Density Matrix

$$= \int_0^{2\pi} \frac{d\bar{\theta}_n}{2\pi} \begin{bmatrix} |a_n(0)|^2 & a_n(0)b_n(0)^* \exp[i(\bar{\theta}_n - \bar{\theta}_n)A_{ba}t] \\ a_n(0)^* b_n(0) \exp[Bi(\bar{\theta}_n - \bar{\theta}_n)A_{ba}t] & |b_n(0)|^2 \end{bmatrix}$$

$$= \int_0^{2\pi} \frac{d\bar{\theta}_n}{2\pi} \begin{bmatrix} |a_n(0)|^2 & a_n(0)b_n(0)^* \exp[i(\bar{\theta}_n - \bar{\theta}_n)A_{ba}t] \\ a_n(0)^* b_n(0) \exp[Bi(\bar{\theta}_n - \bar{\theta}_n)A_{ba}t] & |b_n(0)|^2 \end{bmatrix}$$

1. Let's assume now that we do not have control over the phases of the basis states or as we said before, that we can not "start" both states with some given phase difference for all the elements of the ensemble.
2. In this case, all the phase differences are equally probable and the probability of every phase in the superposition state is given by $1/2\pi$.
3. After integrating between 0 and 2π we observe that the off-diagonal elements vanish and the density matrix is diagonal.
4. Non-coherent creation of a superposition state leads to a dephased state. All the process by means of which an initial coherent state losses its coherence to give an uncoherent state are call **dephasing**.

Quantum Beats

Superposition State

$$|\psi(t)\rangle = a \exp\left[-i \frac{E_a}{\hbar} t\right] |a\rangle + b \exp\left[-i \frac{E_b}{\hbar} t\right] |b\rangle$$

Spontaneous Fluorescence

$$I(t) \propto |\langle \mu | \dot{\psi}(t) \rangle|^2 = |\dot{\mu}_0|^2$$

$$|\dot{\mu}_0|^2 = |a \mu_{0a}|^2 e^{B^2 - A^2 t} + |b \mu_{0b}|^2 e^{B^2 - A^2 t} + 2 \operatorname{Re} \left[a b^* \mu_{0a} \mu_{0b}^* \exp\left[-i \frac{E_a - E_b}{\hbar} t\right] \right]$$

$$a b^* \mu_{0a} \mu_{0b}^* \exp\left[-i \frac{E_a - E_b}{\hbar} t\right]$$

$$a^* b \mu_{0a}^* \mu_{0b} \exp\left[i \frac{E_a - E_b}{\hbar} t\right]$$

1. Coherence manifests itself in the signal of our experiments but the kind of manifestation depends on the kind of measurements we do.
2. We continue with our example of the superposition of two basis states evolving under a time-independent Hamiltonian.
3. Let's consider the example of *Spontaneous fluorescence*. The emitted signal, in the semiclassical treatment and within the Franck-Condon approximation is proportional to the electric transition dipole moment integral of the molecule. Here, we do not take polarization into account.
4. This integral can be expanded in four terms. The two first terms would correspond to the fluorescence intensity originating from the two basis states and weighted by their respective probabilities. The last two terms oscillate with a frequency given by the energy separation of the basis states and are proportional to the off-diagonal elements of the density matrix. If the system is dephased the last two terms vanish. The appearance of the "coherences" can be understood as an interference between the basis states.

The Liouville-Von Neumann Equations

The TimeB dependent Hamiltonian

$$\hat{\mathcal{H}}(t) = \hat{\mathcal{H}}_0 + \hat{\mathcal{V}}(t)$$

The TimeB dependent Schrödinger Equation

$$i \frac{d}{dt} |\psi(t)\rangle = \hat{\mathcal{H}}(t) |\psi(t)\rangle$$

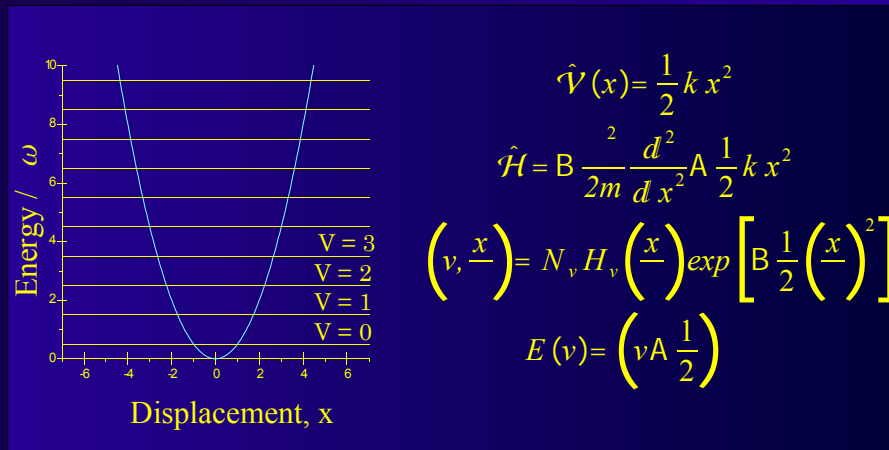
The LiouvilleB Von Neumann Equations

$$i \frac{d}{dt} \hat{\rho}(t) = [\hat{\mathcal{H}}(t), \hat{\rho}(t)]$$

$$i \frac{d}{dt} \rho_{ij}(t) = (E_i - E_j) \rho_{ij}(t) + i [\hat{\mathcal{V}}(t), \hat{\rho}(t)]_{ij}$$

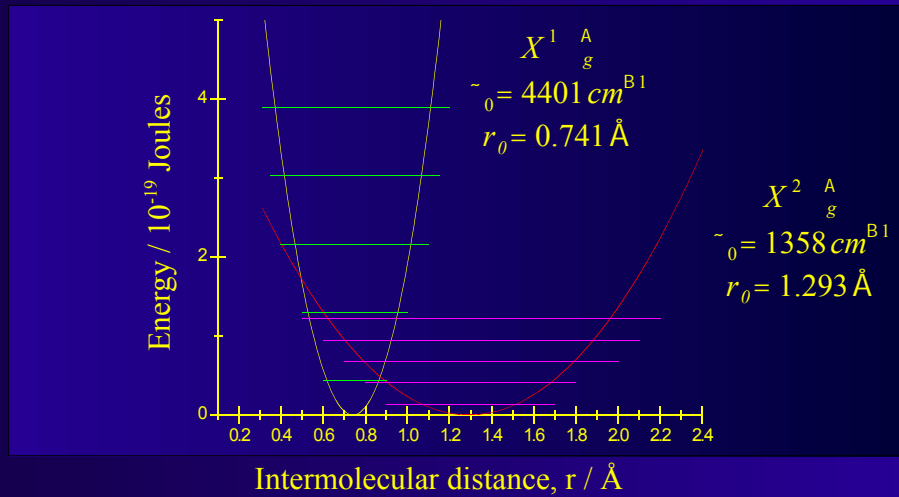
1. The time-evolution of a quantum mechanical system is given by the time-dependent Schrödinger Equation.
2. By using the time-dependent Schrödinger Equation and the definition of the Density operator we arrive at the Liouville-Von Neumann Equation which propagates the density operator in time. The commutator in the *rhs* is the Liouville operator.
3. In the second part of our talk we will use the Liouville-Von Neumann equation for the elements of the density matrix. As it is clear in the last of this equations, the first term of the *rhs* corresponds to the evolution of a superposition state in the absence of perturbation, whereas the second term accounts for an external perturbation $\mathcal{V}(t)$.
4. Therefore, there is a direct correspondence between the **WF** and the density matrix and the time-dependent Schrödinger Equation and the Liouville-Von Neumann Equation.

The Unidimensional Harmonic Oscillator



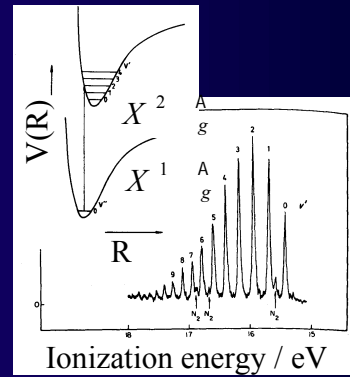
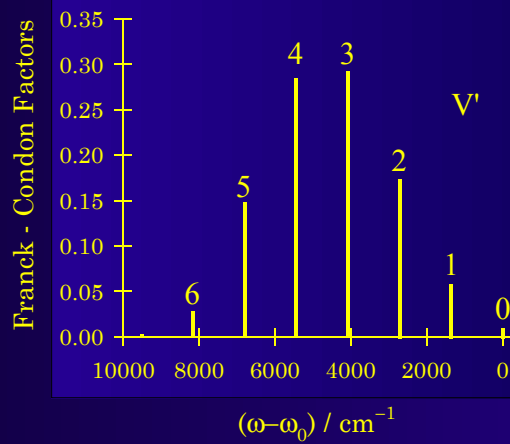
1. In order to illustrate the previous concepts we will use the unidimensional harmonic oscillator model system. We will describe it briefly.
2. The hamiltonian of the harmonic oscillator consists of two terms: the kinetic energy and the parabolic potential.
3. The eigenfunctions of this operator are the hermite polinomials multiplied by a gaussian function which concentrates most of the probability of finding our oscillator within the potential curve. The function is normalized.
4. The energy separation between consecutive quantum energy levels is $\hbar \omega$, where ω is the oscillation frequency.

A Model for the H₂ Molecule



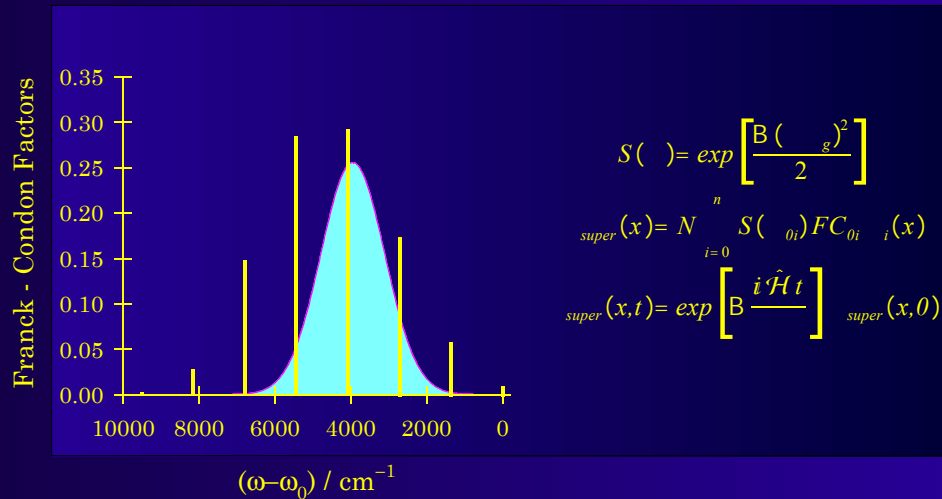
1. We use the harmonic oscillator model to describe the evolution of an ensemble of hydrogen molecules after **impulsive** electronic excitation with imprecise energy from the ground vibronic state to multiple vibronic states of the ionic doublet state.
2. Vibrational energy gap and equilibrium position of the harmonic oscillator change appreciably on going from the ground electronic state to the excited ionic state, namely, the bonding character of the ground state is significantly stronger.
3. Frequencies and equilibrium positions shown are experimental values. We will model the behaviour of this molecule with harmonic potential energy surfaces although the true potential energy surfaces could be highly anharmonic.

Franck-Condon Factors

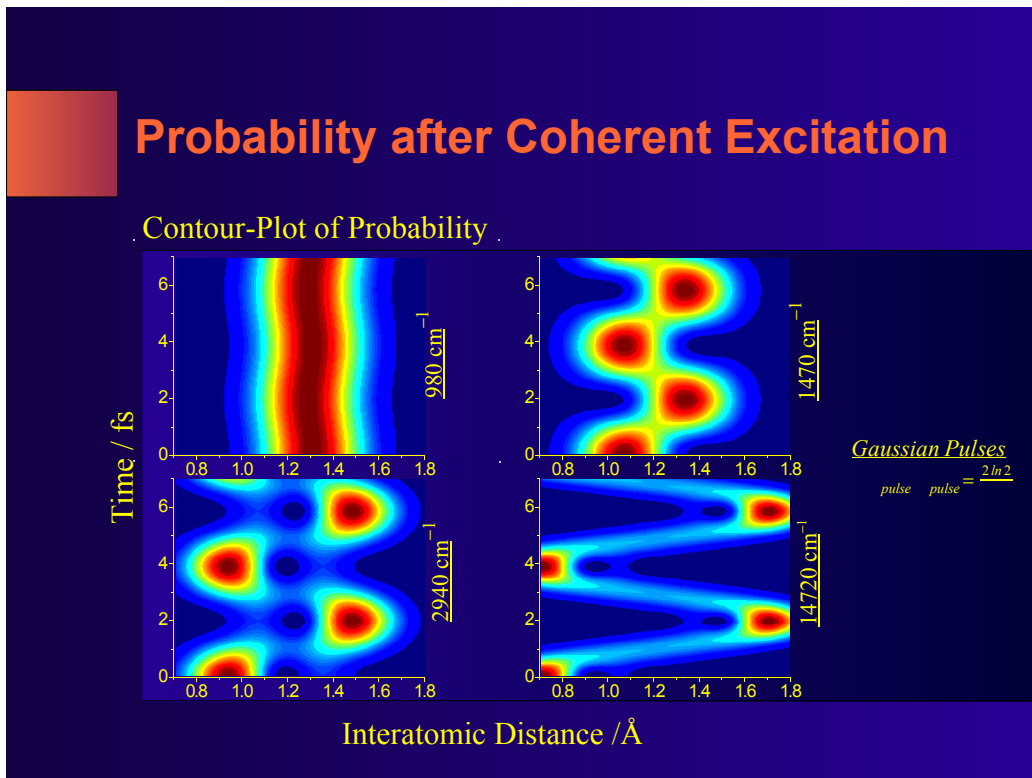


1. The Franck-Condon factors (**FC**) for the different vibronic transitions are calculated as the squared overlap integral extended to the whole space of the corresponding eigenfunctions of the harmonic oscillator .
2. On the *rhs* we show the experimental photoionization spectrum of the hydrogen molecule. The agreement between both pictures is reasonable.

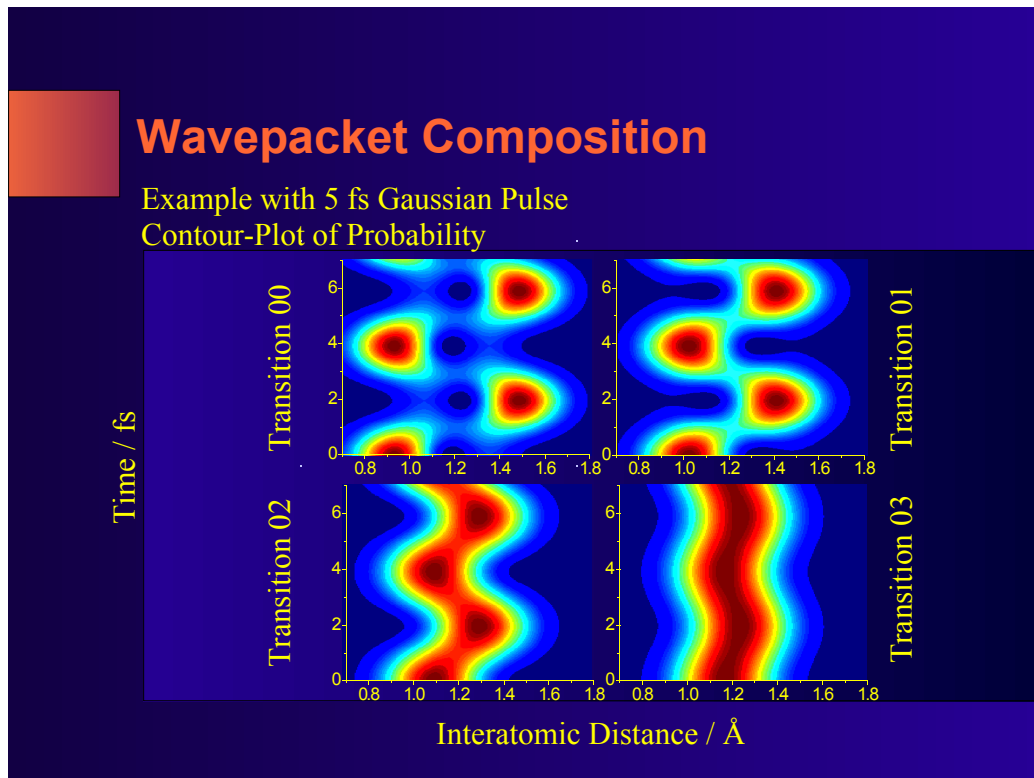
Superposition State



1. As mentioned before, following semiclassical theory of light-matter interaction and assuming the validity of the Franck-Condon approximation, the transition probability is proportional to the FC's, the transition dipole moment integral and the light intensity.
2. It could be assumed that the transition dipole moment integral is roughly constant for the different vibronic transitions. As a result, the excitation probability from the ground vibronic state to some given excited vibronic state is proportional to the product of the FC and the light intensity.
3. As excitation source we use a non-chirped gaussian pulse. This gaussian spectrum provides only an intensity distribution over the wavelengths but *excitation is done impulsively*. The resulting superposition state propagates according to the time-dependent Schrödinger equation.



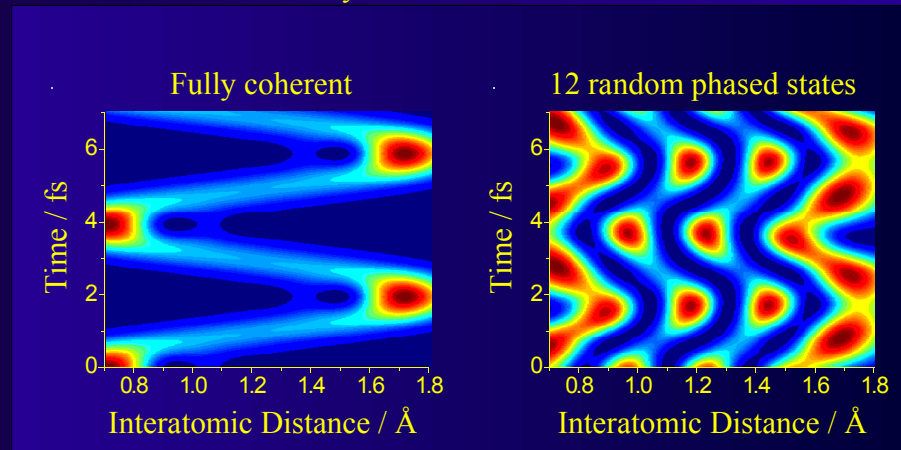
1. Here we plot the time evolution of the probability distribution, normalized, of the superposition state after excitation with fs pulses of different time-widths centered in the 0-0 vibronic transition. A decrease in the pulse duration increases the energy uncertainty.
2. Shorter pulses cover an increasing number of vibronic transitions. The higher is the number of vibronic states in the **WP**, the closer is the ensemble to the classical limit.
3. For 10 fs pulses we can clearly observe the interaction between the states, constructive only at given positions of the coordinate space and oscillating with a frequency equal to the oscillation frequency of the harmonic oscillator in the excited electronic state.



1. In the previous slide, we influenced or “controled” the composition of the **WP** by changing the pulse width. Here we show the influence of the peak position of the excitation pulse on the composition and ulterior evolution of the **WP**.
2. By centering the same pulse on different vibronic transtions we can change the contribution of different vibronic states to the superposition state.

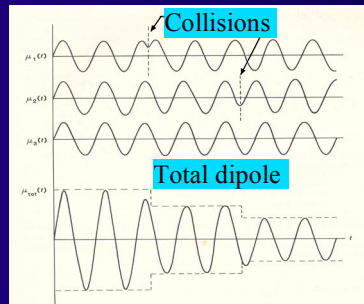
Non-Coherent Excitation

Example of excitation centered at the 00 transition with 1 fs pulses
Contour-Plot of Probability



1. In this picture we want to illustrate the influence of the phase on the **WP**. Here we compare impulsive excitation centered at the 0-0 transition with a non-chirped 1 fs gaussian pulse with the uncoherent excitation with an energy uncertainty equivalent to the former case.
2. In the *rhs* we propagate the **WP** in an ensemble of 12 systems excited with random phased pulses.
3. The picture shows clearly how the different phases are able to destroy the ability of interaction of the different states and washes the probability distribution out.
4. All the plots showed response functions, none of the plots was convoluted with the pulse shape.
5. Summarizing, we can use spectral shape and phase of our excitation pulses to “control” or “conditioning” the evolution of the ensemble in the excited potential energy surfaces.

Collisions Induce Dephasing

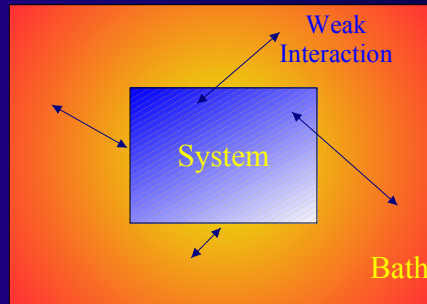


Decay of the total dipole moment resulting from random collisions in a collection of oscillating dipoles.

“Lasers”, Siegman, 1986 University Science Books.

1. Unfortunately, the examples shown before do not correspond exactly to reality. Even if we could prepare a highly coherent **WP**, the interactions of the ensemble of systems with the surrounding medium destroy the phase coherence.
2. All the effects which tend to destroy the coherence of the ensemble are called *collisions*. Collisions are responsible for dephasing. There are different kind of collisions, for instance, physical elastic or inelastic collisions with the bath molecules or against the walls of the reservoir. In solids another kind of collision is phonon broadening.
3. In general terms, a collision could imply an interchange of energy between the system and the environment, the energy relaxes and levels of lower energies are populated. As the collisions occur randomly, lower-energy levels are populated randomly introducing dephasing into the time-evolving superposition state. An elastic collision could also occur: the energy does not change, there is no population relaxation, but phase is shifted. The latter class of collisions contribute to dephasing but not to population relaxation.

System-Bath Interaction



The Redfield Relaxation Theory is a weak interaction theory. The time-dependent perturbation expansion is done to 2nd order.

1. In the following we will explain the principles of the Redfield theory of Relaxation. The Redfield theory of Relaxation is a weak interaction theory.
2. We want to describe the evolution of the ensemble (of the density matrix) in the presence of an weak interaction with the surrounding medium, the bath.
3. The time-dependent expansion of the elements of the desity matrix is done to second order.

The Reduced Density Matrix

The Reduced Density Matrix.

$$\rho_{ij} = \langle a_i a_j^* \rangle_{ensemble}$$

Liouville Equation in a NonB Perturbed System

$$\frac{d}{dt} \rho_{ij}(t) = -i(E_i - E_j) \rho_{ij}(t)$$

$$\rho_{ij}(t) = \rho_{ij}(0) \exp[-i(E_i - E_j)t]$$

1. In the following discussion we will consider the density matrix of our system of interest. All the degrees of freedom related to the bath are averaged over the ensemble. In order to emphasize this we substitute the symbol ρ by σ when referring to the density matrix.
2. In the absence of perturbation the time-evolution of the elements of the density matrix is given by the Liouville-Von Neumann equation of the system.
3. The formal solution of this equation says us that the populations of every basis state are time independent and the coherences oscillate around their time-zero value with a frequency given by the energy difference between the states.

Beyond the Bloch Model

The Bloch Model, Secular Approximation

$$i \frac{d}{dt} \hat{\rho} = [\hat{\mathcal{H}}(t), \hat{\rho}(t)]$$

$$\frac{d}{dt} \rho_{ij}(t) = B \frac{i}{t} (E_i B E_j) \rho_{ij}(t) A - \rho_{ij}(t) \frac{1}{T_1} + \rho_{ii}(0) B \frac{i}{t} (E_i B E_j) \rho_{jj}(t) \frac{1}{T_1} - \rho_{ij}(t) \frac{1}{T_2}$$

The Redfield Relaxation Model

$$\frac{d}{dt} \rho_{ij}(t) = B \frac{i}{t} (E_i B E_j) \rho_{ij}(t) A + \sum_{i',j'} R_{ij,i'j'} \rho_{i'j'}(t)$$

1. However, when we have an interaction with the environment, we need to consider a time-dependent hamiltonian. The commutator containing the time-dependent part of the hamiltonian adds to the Liouville-Von Neumann term and it is called the **Relaxation** term. If we would have some other time-dependent interactions (oscillatory excitation, for instance) they would also appear.
2. In the phenomenological Bloch model the complex nature of the interaction with the bath is not considered and it is proposed that the decay of the populations and coherences is exponential with characteristic times T_1 and T_2 , the longitudinal and transverse times, respectively. The latter is also known as the **dephasing time**.
3. It would be good for us to find a relaxation term linear in σ . If this were the case, computational treatment of the problem will be highly simplified.

The Relaxation Matrix

$R_{ij,ij}$ are the elements of the Relaxation Matrix
The elements of \mathbf{R} are RATE CONSTANTS

$$R_{ii,jj}$$

$$R_{ii,jj} \text{ and } R_{jj,ii}$$

$$\sum_j R_{ii,jj} = R_{jj,ii}$$

1. It is important to underline now the physical meaning of the elements of the relaxation matrix (\mathbf{R}). The elements of \mathbf{R} are rate constants in correspondence with the Bloch time constants.
2. Some of these rate constants have a simple physical meaning. For example:

$R_{ii,jj}$ is the rate constant for the transference of population from the basis state ϕ_j to the state ϕ_i .

$R_{jj,ii}$ are related by a Boltzmann factor which ensures us that no evolution takes place in the system once the equilibrium is achieved.

The sum over j of the $R_{jj,ii}$ elements is the total rate of population depletion from the level i to all the other levels j .

Time-Dependent Perturbation Theory

Time-Dependent Hamiltonian

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t)$$

$\hat{V}(t)$ is a fast, hermitian and random perturbation

Wavefunction

$$| \psi(t) \rangle = \sum_i a_i(t) e^{i E_i t} | \psi_i \rangle$$

$$a_i(t) = \sum_n a_i^{(n)}(t)$$

$$a_i^{(0)}(t) = a_i(t)$$

$$a_i^{(n)}(t) = \frac{i}{\hbar} \int_{t_0}^t dt' \sum_j a_j^{(n-1)}(t') V_{ij}(t') e^{i(E_i - E_j)t'}$$

1. $V(t)$ is an hermitian perturbation, random in time which is responsible for the relaxation. It is assumed to be different for each member of the ensemble.
2. In order to expand the elements of the density matrix at some given time t , we first express the **WF** as a linear combination of basis states. The coefficients of these basis states are afterwards expanded as usual in time-dependent perturbation theory. Once we know the coefficients at some given time $t + \Delta t$ in terms of those at time t , we can expand the density matrix elements at time $t + \Delta t$ in terms of those density matrix elements at time t .
3. The integration interval Δt has to be greater than τ_c (the collisions period) but smaller compared with the rate of change of the contribution coefficients $\{a_i\}$.

The Perturbed Density Matrix

The Expansion of the Density Matrix up to Second Order

$$\rho_{ij}^*(t) = \rho_{ij}^*(t) A \left[a_j^{(1)*}(t) a_i(t) A a_j^*(t) a_i^{(1)}(t) A \right]$$

$$a_j^{(1)*}(t) a_i^{(1)}(t) A a_j^*(t) a_i^{(2)}(t) A a_j^{(2)*}(t) a_i(t)$$

$$\rho_{ij}^{*(2)}(t) = \int_{t'} e^{i(E_j - E_i) t} \rho_{i'j'}^*(t') \times$$

$$\left\{ \begin{matrix} ij, i'j' A & j'j, ji B & j'j' & i'i B & ii' & j'j \end{matrix} \right\}$$

1. To obtain σ , we simply multiply the expansion coefficients obtained in the previous slide. As the rate of change of the coefficients a is much smaller than the period of the perturbations, it can be shown that the mean values of the a 's at time t are statistically independent of the mean value of the perturbation at times t' between t and $t+\Delta t$. Therefore, it can be concluded that the first order term in the perturbation expansion vanishes since the mean value of the perturbation is zero.
2. In the limit when Δt tends to zero, but it is still large enough as compared with the bath correlation time: $[\sigma(t+\Delta t) - \sigma(t)] / \Delta t \sim d\sigma(t)/dt \sim \sigma^{(2)}(t) / \Delta t$
3. As we wanted, the time-derivative of the elements of σ depends linearly on σ itself. The linear coefficients are the elements of the Redfield Relaxation matrix. In the next slide we will analyze their meaning.

The Perturbation Correlation Function

$$\Gamma_{ij,ij'} = \int_0^\infty dt e^{i(E_j - E_{j'})t} P_{ij,ij'}(t)$$

$1/R_{ij,ij'} \gg t \gg \tau_c$

Factorization of the System-Bath Coupling

$$\hat{V} = \hat{V}_{system} \hat{V}_{bath}(t)$$

$$\Gamma_{ij,ij'} = \int_0^\infty dt \hat{V}_{ii'} \hat{V}_{jj'} e^{i(E_j - E_{j'})t} \hat{\rho}(0) \hat{\rho}(t) =$$

$\hat{V}_{ii'} \hat{V}_{jj'} \bar{A} \{ \hat{\rho}(0) \hat{\rho}(t) \}$

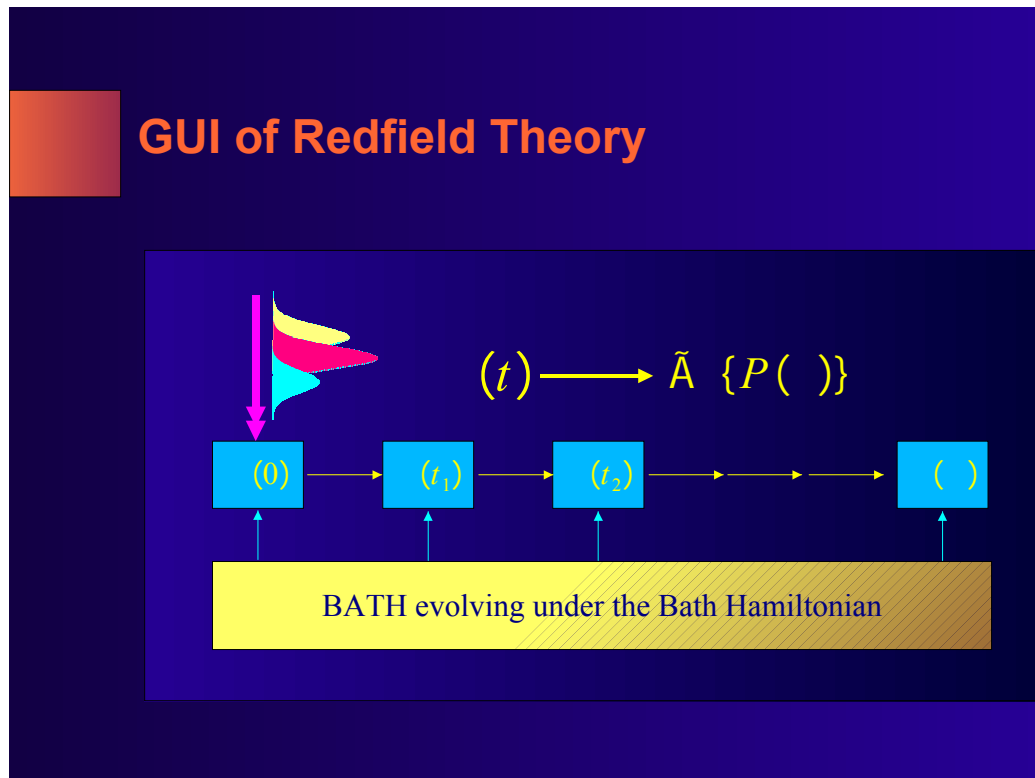
1. Γ 's in the Redfield relaxation matrix are the Fourier transforms of the time-correlation functions of the perturbation.

Validity Conditions of the Theory:

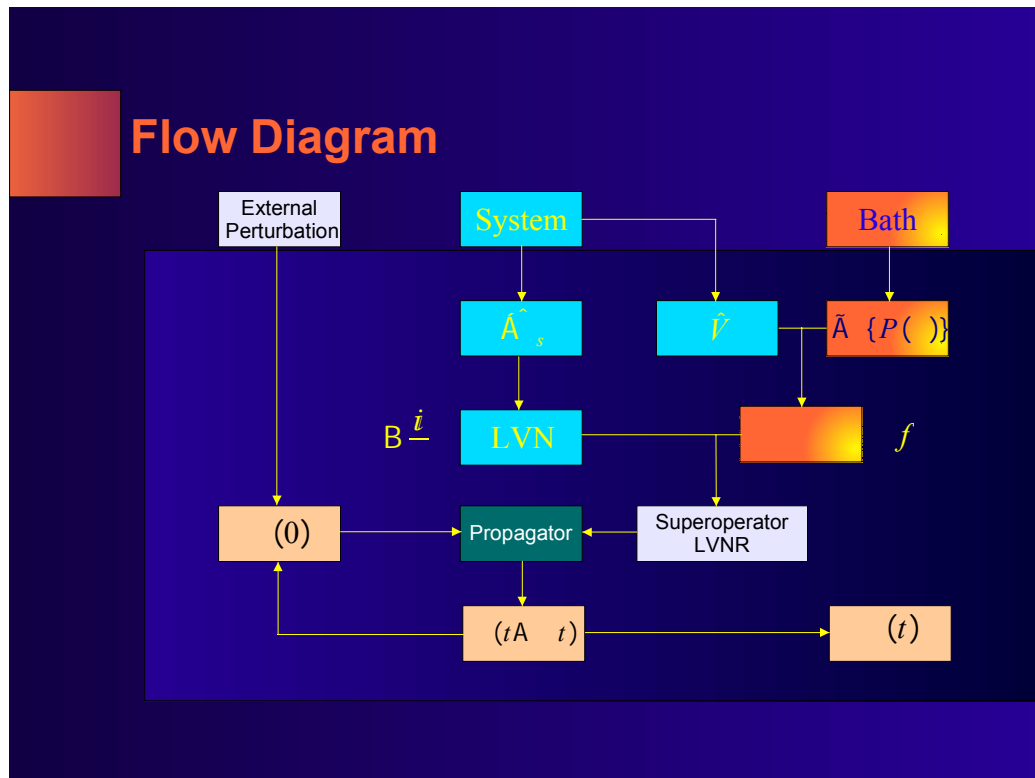
It is implicit in some of the assumptions made before and in the disregarding of the first order correction of the expansion of σ that the characteristic time of the transition between two states has to be much slower than the integration time Δt and this has to be itself much slower than the correlation time of the bath.

The Fourier components of the matrix elements of $V(t)$ at the various resonance frequencies of the system are responsible for the relaxation.

2. If we could decompose the interaction hamiltonian into a product of operators each one of which depends either on the variables of the system or the bath then, the elements of the Relaxation Tensor are a sum-of-products of coupling terms dependent only on the variables of the system and the Fourier transform of the correlation function of some bath variable.

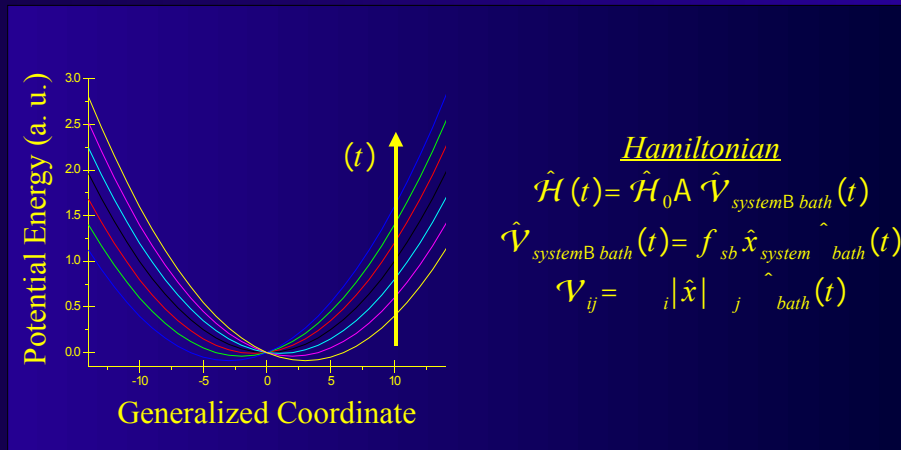


1. The following picture explains how we want to model the system in order to have a tractable expression which allows us to quantify and understand system evolution.
2. A superposition state is created by multicolor excitation. This state is continuously perturbed by the bath. Bath fluctuations are very fast and independent of the state of the system. This means that the bath evolves independently under its own Hamiltonian.
3. In these conditions it is possible to extract from the time-dependence of σ , through the relaxation tensor \mathbf{R} , the Fourier transform of the time-correlation function of some given variable of the bath. The concrete nature of this variable will depend on the concrete coupling mechanism between the system and the bath.



1. We prepared a short script to illustrate these ideas. Before going into the demonstration it is convenient to have a look to its flow diagram and to explain the different possibilities that we may have.
2. The interaction with the bath is modelled by means of the Fourier transform of the time-correlation function of the bath and some operator depending only on the system variables. With this two quantities we build the Relaxation tensor.
3. We build also the Liouville Von-Neumann operator for the unperturbed system in Liouville Space. The Liouville-Von Neumann matrix is diagonal and its elements are energy differences between the different basis states of the system.
4. With the Liouville-Von Neumann and Redfield operators we build the Liouville-Von Neumann-Redfield Superoperator which traces the evolution of σ . Compare with Bloch model here.
5. Some external perturbation, our pulse, creates an initial state. This state evolves under the influence of the LVNR superoperator. By using a propagation algorithm we can follow the evolution of the density matrix, the evolution of the populations and coherences.
6. We could work in the opposite way also. We could extract the density matrix from our signal and go back to $\tilde{A} \{P(\tau)\}$.

Linear System-Bath Coupling in the Harmonic Oscillator



1. It only rests to describe the coupling mechanism. Here we will assume a linear coupling between a stochastic bath variable (delta correlation function) and the coordinate of the unidimensional linear harmonic oscillator. The coupling is weighted by some coupling constant f . It is easy to show now that the coupling matrix element is the product of some coupling term depending only on system variables and the stochastic bath variable.
2. The stochastic bath variable could be figured out, for instance, as the fluctuating nearest-neighbour distance. A fluctuation in this variable will make swing the harmonic potential curve back and forth around the equilibrium position corresponding to the mean value of the stochastic variable.
3. For the proposed example, the coupling term of the system is the matrix element x_{ij} , where x is the generalized coordinate.

Summary

Advantages

- Non-phenomenological Generalization of the Bloch Model
- Allows for Studing Phenomena such as IVR, Dephasing and Cooling
- Bath Dynamics Obtained from System Evolution

To Overcome

- We Need to Go from σ to the Signal and Viceversa
- 2nd Order Perturbation Theory
- Experimental Limitations of the Signal

References

“The Redfield Equation in Condensed Phase Quantum Dynamics”,
W. Thomas Pollard, Anthony K. Felts, and Richard A. Friesner
Advances in Chemical Physics **1996**, *Volume XCIII*, 77.

“The Theory of Relaxation Processes”, A. G. Redfield
Advan. Mag. Reson. **1965**, *1*, 1.

“Lasers”, Siegman, **1986** *University Science Books*.

“Density Matrix Theory and Applications”, Karl Blum,
Plenum Press **1981**.

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