

Quantum Non-linear Spectroscopy

Lecture 1 Notes

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Foreword

I have added some more steps and explanations so as to make the notes suit my needs.

1 Introduction

- This course assumes familiarity with quantum mechanics at the Quantum 2 level.
- We adopt a semiclassical framework: matter is treated quantum mechanically, while light is treated classically, appropriate for many nonlinear optics problems.
- Linear dielectrics obey $\mathbf{P} \propto \mathbf{E}$, but in nonlinear media, polarization has higher-order terms: $\mathbf{P} = \chi^{(1)}\mathbf{E} + \chi^{(2)}\mathbf{E}^2 + \chi^{(3)}\mathbf{E}^3 + \dots$.
- Materials interact with light via quantum transitions (e.g., $|0\rangle \leftrightarrow |1\rangle$), and linewidths arise from finite excited-state lifetimes via $\Delta E \cdot \tau \sim \hbar$.
- Linear spectroscopy provides limited insight for characterizing system-bath interactions, motivating nonlinear techniques that probe multi-time correlations. Third-order responses like $R^{(3)} \rightarrow P^{(3)} \rightarrow \chi^{(3)}$ reveal richer dynamics, but ensemble averaging complicates interpretation.
- A key reference is Mukamel's *Principles of Nonlinear Optical Spectroscopy*.

1.1 NOTE: Lorentzian Curve

The transition probability, absorption intensity, population of the excited state all depend on $|b_k|^2$, and all follow a Lorentzian distribution:

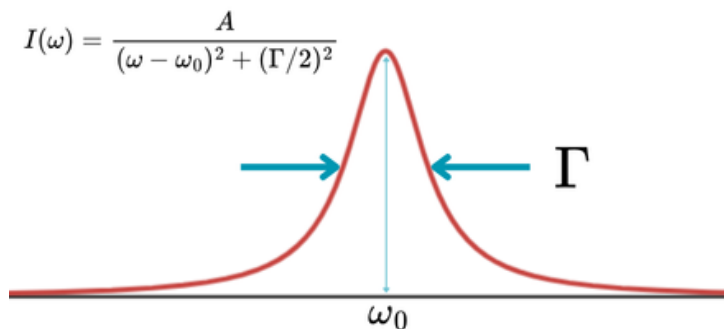


Figure: Lorentzian curve

2 Review of Time Dependent Quantum Mechanics

The time-dependent Schrödinger equation (TDSE) governs the evolution of quantum states:

$$i\hbar \frac{\partial}{\partial t} \psi(t) = \hat{H}(t) \psi(t)$$

For a single particle in a potential, the Hamiltonian takes the form:

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + \hat{V}(\mathbf{r}, t)$$

The expectation value of an operator \hat{A} at time t is given by:

$$\langle \hat{A} \rangle(t) = \langle \psi(t) | \hat{A} | \psi(t) \rangle = \int \psi^*(\mathbf{r}, t) \hat{A} \psi(\mathbf{r}, t) d^3\mathbf{r}$$

where \hat{A} is assumed Hermitian (i.e., observable).

Assume the time-independent Schrödinger equation (TISE) has eigenfunctions:

$$\hat{H}_0 \phi_n(\mathbf{r}) = E_n \phi_n(\mathbf{r})$$

Then, for a time-independent Hamiltonian, the TDSE has separable solutions:

$$\psi_n(\mathbf{r}, t) = \phi_n(\mathbf{r}) e^{-iE_n t/\hbar}$$

More generally, if the initial state is a linear combination of eigenstates:

$$\psi(\mathbf{r}, 0) = \sum_n C_n \phi_n(\mathbf{r})$$

then the full time-evolved wavefunction is:

$$\psi(\mathbf{r}, t) = \sum_n C_n e^{-iE_n t/\hbar} \phi_n(\mathbf{r})$$

For a two-level system (e.g., two eigenstates ϕ_1, ϕ_2), we may write:

$$\psi(\mathbf{r}, t) = C_1 \phi_1(\mathbf{r}) e^{-iE_1 t/\hbar} + C_2 \phi_2(\mathbf{r}) e^{-iE_2 t/\hbar}$$

The probability density is:

$$\begin{aligned} P(t) &= |\psi(\mathbf{r}, t)|^2 \\ &= |C_1|^2 + |C_2|^2 + 2\text{Re} [C_1^* C_2 \langle \phi_1 | \phi_2 \rangle e^{i(E_1 - E_2)t/\hbar}] \end{aligned}$$

Assuming orthonormality $\langle \phi_1 | \phi_2 \rangle = 0$ eliminates the interference term; if the eigenstates are not orthogonal or if the observable overlaps both states, the cross term contributes oscillations at frequency $\omega = (E_2 - E_1)/\hbar$.

3 Exponential Operators

$$\hat{T} = e^{\hat{A}}$$

Time evolution operator: $\hat{U} = e^{-i\hat{H}t/\hbar}$

- Since \hat{A} is Hermitian, $T^{-1} = T^\dagger$
- If $\hat{A}\psi = a_n\psi$, then $f(\hat{A})\psi = f(a_n)\psi$
- Spatial Displacement operator: D
- Angular displacement operator: R_n
- $\psi(t) = \hat{U}(t - t_0)\psi(t_0)$ and he derived it

We want the equation of motion of \hat{U} :

$$\lim_{\delta t \rightarrow 0} \hat{U}(t + \delta t, t) = 1$$

For small δt , $U(t)$ varies linearly:

$$U(t + \delta t) = U(t) - i\Omega(t)\delta t$$

Where does the complex i arise from?

previous form missed

$$i\hbar \frac{\partial U(t, t_0)}{\partial t} = HU(t, t_0)$$

where

$$\hat{\Omega} = \hat{H}/\hbar$$

expand the U , as an exponential Will only work if

$$[H(t'), H(t'')] = 0$$

$$U(t, t_0) = 1 - \frac{-i}{\hbar} \int_{t_0}^t d\tau H(\tau)U(\tau, t_0)$$

Implications: $U(t, t_0)$ depends on itself...

Lets keep expanding till the 3rd term

$$\begin{aligned} U(t, t_0) = & 1 - \frac{i}{\hbar} \int_{t_0}^t d\tau H(\tau) \\ & + \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^t d\tau \int_{t_0}^{\tau} d\tau' H(\tau)H(\tau') \\ & + \left(-\frac{i}{\hbar}\right)^3 \int_{t_0}^t d\tau \int_{t_0}^{\tau} d\tau' \int_{t_0}^{\tau'} d\tau'' H(\tau)H(\tau')H(\tau'')U(\tau'', t_0) \end{aligned} \quad (1)$$

Implications: lets say we have an $|i\rangle$ and $|f\rangle$

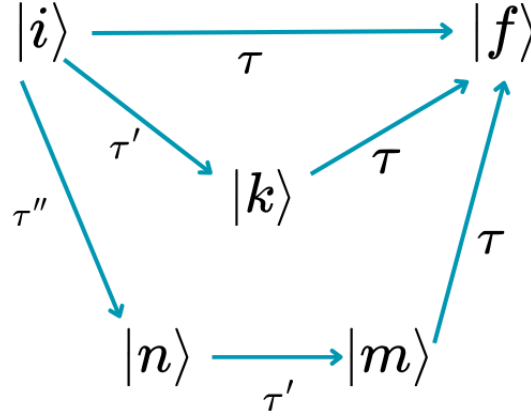


Figure: pictorial depiction of Dyson series

General form:

$$U(t, t_0) = 1 + \sum_{n=1}^{\infty} \left(\frac{-i}{\hbar}\right)^n \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \int_{t_0}^{\tau_{n-1}} d\tau_{n-2} \dots \int_{t_0}^{\tau_1} d\tau_1 H(\tau_n) \dots H(\tau_1)$$

$$\hat{T} = \left[\exp\left(\frac{-i}{\hbar} \int_{t_0}^t d\tau H(\tau)\right) \right]$$

\hat{T} is called the Dyson time-ordering operator.

4 Time dependent Hamiltonian

In Spectroscopy the Hamiltonian will look like:

$$H(t) = H_0 + V(t)$$

where $V(t) = -\mu * E$

$$H_0 |n\rangle = E_n |n\rangle$$

$$\psi(t) = \sum_n C_n(t) |n\rangle$$

*steps

$$\frac{\partial C_k}{\partial t} + \frac{i}{\hbar} E_k C_k(t) = \frac{-i}{\hbar} V_{kn} C_n(t)$$

now replace :

$$c_m(t) = b_m(t) e^{-iE_m t/\hbar}$$

1.add2lines

(2)

$$e^{-iE_k t/\hbar} \frac{\partial b_k}{\partial t} = \frac{-i}{\hbar} \sum_n V_{kn} e^{-iE_n t/\hbar} b_n(t)$$

5 Interaction Picture

Here he gave an explanation and mentioned that we will be working in the weak coupling regime (that is the system can be expressed in terms of the original basis states (like a perturbation across the original))

We begin by splitting the Hamiltonian into a time-independent part H_0 and a time-dependent perturbation $V(t)$:

$$H = H_0 + V(t)$$

The time evolution operator for $V(t) = 0$ satisfies

$$\frac{d}{dt}U_0(t, t_0) = -\frac{i}{\hbar}H_0(t)U_0(t, t_0)$$

so formally,

$$U_0(t, t_0) = \exp \left[-\frac{i}{\hbar} \int_{t_0}^t d\tau H_0(\tau) \right]$$

For a time-independent H_0 , we get

$$U_0(t, t_0) = e^{-iH_0(t-t_0)/\hbar}$$

The state in the interaction picture is defined as

$$|\psi_I(t)\rangle = U_0^\dagger(t, t_0)|\psi_S(t)\rangle$$

This transformation removes the accumulated phase due to H_0 .

Taking the time derivative:

$$i\hbar \frac{d}{dt}|\psi_S(t)\rangle = H(t)|\psi_S(t)\rangle$$

So,

$$\frac{d}{dt}U_0(t, t_0)|\psi_I(t)\rangle = -\frac{i}{\hbar}H_I(t)U_0(t, t_0)|\psi_I(t)\rangle$$

We define the interaction picture Hamiltonian as:

$$V_I(t) = U_0^\dagger(t, t_0)V(t)U_0(t, t_0)$$

Then the Schrödinger equation in the interaction picture becomes:

$$i\hbar \frac{d}{dt}|\psi_I(t)\rangle = V_I(t)|\psi_I(t)\rangle$$

The time evolution operator in the interaction picture satisfies:

$$U_I(t, t_0) = \mathcal{T} \exp \left[-\frac{i}{\hbar} \int_{t_0}^t d\tau V_I(\tau) \right]$$

The full time evolution operator in the Schrödinger picture can be factorized as:

$$U(t, t_0) = U_0(t, t_0)U_I(t, t_0)$$

To extract coefficients in the interaction picture, recall the expansion:

$$\begin{aligned} c_k(t) &= \langle k|\psi(t)\rangle = \langle k|U(t, t_0)|\psi(t_0)\rangle \\ &= \langle k|U_0(t, t_0)U_I(t, t_0)|\psi(t_0)\rangle \\ &= e^{-iE_k t/\hbar} \langle k|\psi_I(t)\rangle \\ &= e^{-iE_k t/\hbar} b_k(t) \end{aligned} \tag{3}$$

where $b_k(t)$ are the expansion coefficients of the wavefunction in the interaction picture.

6 Density Matrix

We are going to only deal with the density matrix from now on definition:

$$P(t) \equiv |\psi(t)\rangle \langle \psi(t)|$$

$\langle n| P |n\rangle$ gives the probability of finding a particle in $|n\rangle$ Also $\langle n| \hat{A} |n\rangle = Tr[\hat{A}\hat{P}]$

- Proof of the previous
- Diagonal elements: probabilities
- Off Diagonal elements: coherence

6.1 Properties of density Matrices

1. ρ is Hermitian
2. $Tr[\rho] = 1$ for pure states and < 1 for mixed states

6.2 Time Evolution of Density Matrix

$$\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial t} [|\psi(t)\rangle \langle \psi(t)|]$$

from here he derived the Liouville Von-Neumann eq

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

2 eqs:(missed first)

$$\rho(t) = U\rho(0)U^\dagger$$

Density Matrix in Interaction Picture:

$$\frac{\partial \rho_I}{\partial t} = \frac{-i}{\hbar} [\hat{V}_I, \hat{\rho}_I]$$

$$\rho_I(t) = \rho_I(0) - \frac{i}{\hbar} \int_{t_0}^t dt [V_I(t), \rho_0]$$

we can write this as a perturbative expansion till the 3rd order which looks like:

$$\begin{aligned} \rho_I(t) = & \rho_0 - \frac{i}{\hbar} \int_{t_0}^t d\tau [V_I(t), \rho_0] \\ & + \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^t d\tau \int_{t_0}^{\tau} d\tau' [V_I(t_2), [V_I(t), \rho_0]] \\ & + \left(-\frac{i}{\hbar}\right)^3 \int_{t_0}^t d\tau \int_{t_0}^{\tau} d\tau' \int_{t_0}^{\tau'} d\tau'' [V_I(t_3), [V_I(t_2), [V_I(t), \rho_0]]] \end{aligned} \quad (4)$$