MIT Department of Chemistry
5.74, Spring 2004: Introductory Quantum Mechanics II
Instructor: Prof. Robert Field

Dynamical Quantities: Visualization of Dynamics

Last time: absorption spectrum

$$I_{v_g''}(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt \exp\left[-i\left(\omega + E_{g,v_g''}/\hbar\right)t\right] \underbrace{\left\langle \overset{\boxed{\text{contains } \exp\left[iE_{e,v_e'}t/\hbar\right]}}{\Psi_i(t)} \middle| \Psi_i(0)\right\rangle}_{\text{initial state formed by a photon pluck}}$$

The autocorrelation function of the wavepacket created by a short pulse at $t = 0$ generates the absorption spectrum. Our picture is usually in coordinate space only. What is missing?

We get a microscopic, particle-like picture ($F = ma = \dot{p}$) that explains the qualitative features of the autocorrelation function.

Identifies the <u>local features</u> of the V'_e potential that account for the important features in the absorption spectrum.

Could we get the same information in a <u>time domain</u> experiment? Certainly. Short pulse pump/probe. We need to create the wavepacket and thus monitor its time evolving overlap with its $t = 0$ self.

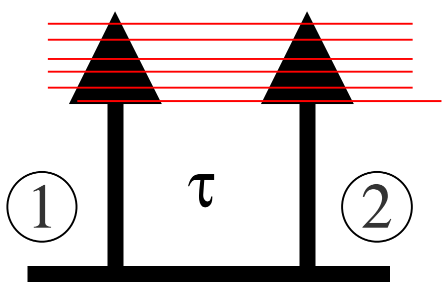
How would we do such an experiment?
What would we observe?
Would there be additional effects that might complicate the picture?

One color pump/probe? What do we detect? fluorescence? ionization? absorption?
Two color pump/probe?

Let's discuss experimental schemes.

Discussion of observation of $|\langle\Psi(t)|\Psi(0)\rangle|^2$ directly in a time domain experiment:

1. One-color pump-probe:



signal (either absorption or stimulated emission) observed by pulse 2

2. One-color pump-probe with polarization selectivity.

   * first pulse is circularly polarized
   * second pulse is linearly polarized. It is incident on a crossed polarizer. The spatial anisotropy written into the sample by the first pulse alters the polarization state of the second pulse, permitting some radiation to leak through the blocking polarizer.

3. One color pump-probe with fluorescence or ionization detection.

   * time resolution does not permit discrimination against signal produced by first pulse. Total signal results from two pulses as a function of delay between pulses. How does this work? Problem set!

4. two-color pump-probe with fluorescence-dip or ionizaiton detection. Stimulated Emission Pumping. Zewail experiment.

   If we try to make the wavepacket envisioned in the Heller picture, how do we deal with non-idealities?

   $\mu(\mathbf{Q})$ - usually slow variation with **Q**, but not when there is a qualitative change in geometry
   short pulse, centered at correct λ
   negative wavepacket on ground state?
   multiphoton processes
   spatial and temporal distribution of molecules affected by laser pulse?

<u>Dynamical Quantities</u>

eigenstates are stationary: no motion

to get motion you need coherent superposition of at least 2 eigenstates belonging to different E.

How do $\{\psi_i\}$ and $\{E_i\}$ encode understandable motion?

There is a huge amount of information in a coherent superposition state prepared by a short excitation pulse

$$\Psi_{\underset{\boxed{\text{initial}}}{I}}(t) = \sum_i a_i \psi_i e^{-E_i t/\hbar}$$

How do we reduce this information into something we can view and understand? Especially when **H** is not simple.

1. We can't observe $\Psi(t)$ but we can observe <u>probability density</u>

$$\Psi_I^*(t)\Psi_I(t) = \sum_i \left[|a_i|^2|\psi_i|^2 + \sum_{j>i}\left(a_i a_j^* \psi_i \psi_j^* e^{i(E_j - E_i)t/\hbar} + c.c.\right)\right]$$
$$= \sum_i |a_i|^2|\psi_i|^2 + \sum_{j>i}\left[2\mathrm{Re}\left(a_i a_j^* \psi_i \psi_j^* \cos\omega_{ji} t\right) - 2\mathrm{Im}\left(a_i a_j^* \psi_i \psi_j^* \sin\omega_{ji} t\right)\right]$$

Contains both spatial and temporal information. This is hopelessly complicated. Need to get rid of the wavefunctions.

2. <u>density matrix</u>

$$\rho_I(t) = |\Psi_I(t)\rangle\langle\Psi_I(t)| = \sum_i \left\{|a_i|^2|\psi_i\rangle\langle\psi_i| + \sum_{j>i}\left[a_i a_j^* e^{-i\omega_{ij}t}|\psi_i\rangle\langle\psi_j| + c.c.\right]\right\}$$

This is much better because we have implicitly integrated over the wavefunctions. It is a matrix of numbers. Populations (time independent) along the diagonal and coherences (time dependent) off-diagonal.

Every element of $\boldsymbol{\rho}(t)$ is separately time dependent, so there is too much information to look at here without some sort of magic filter.

ρ is very useful in helping us to design an experiment because

$$\langle \mathbf{A} \rangle = \overbrace{\text{Trace }\boldsymbol{\rho}\mathbf{A}}^{\text{trace is invariant to unitary transformation}} = \text{Trace}\left(\mathbf{T}^{\dagger}\boldsymbol{\rho}\underbrace{\mathbf{T}\mathbf{T}^{\dagger}}_{\mathbb{1}}\mathbf{A}\mathbf{T}\right)$$

write **ρA** in zero order basis, use $\mathbf{T}^{\dagger}\mathbf{H}\mathbf{T}$ to transform to eigen basis

We can design **A** (a detection scheme) to pick out only a few elements in **ρ**.

Suppose **A** has simple structure in $\{\psi_i^\circ\}$ but not in the eigenbasis. This is a very common situation.

3. <u>autocorrelation function</u>

$$\langle \Psi_I(t) | \Psi_I(0) \rangle = \sum_i |a_i|^2 e^{iE_i t/\hbar}$$

This is almost too simple. It tells us how a wavepacket moves away from and returns to its $t = 0$ self. Real and Imaginary parts.

dephasing, partial recurrences

4. <u>Survival probability</u>

$$\begin{aligned} P_I(t) &= \left|\langle \Psi_I(t) | \Psi_I(0) \rangle\right|^2 \\ &= \sum_i \left[|a_i|^2 + \sum_{j>i} 2|a_i|^2 |a_j|^2 \cos\omega_{ij} t \right] \end{aligned}$$

even simpler. Real $0 \le P_I(t) \le 1$

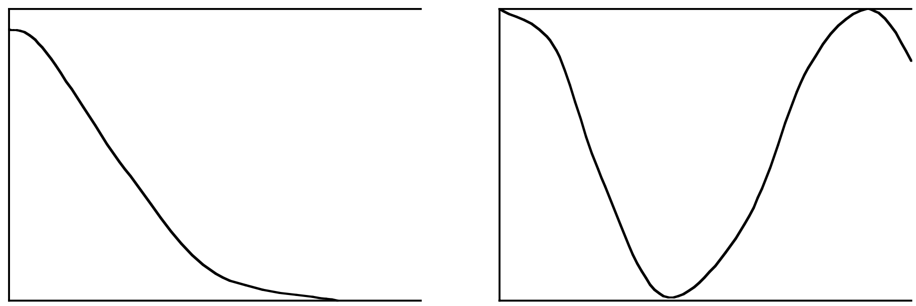
suppose we have N states in superposition with equal amplitude, $N^{-1/2}$

$$\begin{aligned} P_I(t) &= \sum_i \left[N^{-2} + \sum_{j>i} 2N^{-2} \cos\omega_{ij} t \right] \\ &= N^{-1} + 2N^{-2} \underbrace{\sum_i \sum_{j>i} \cos\omega_{ij} t}_{\substack{\frac{N(N-1)}{2} \text{ terms} \\ \text{at } t=0 \text{ all } = 1}} \\ &= N^{-1} + \frac{2N(N-1)}{2N^2} = \frac{1}{N}\left[1 + (N-1)\right] = 1 \end{aligned}$$

at $t > 0$ $\quad P_I(t) \to 0,\quad$ if N is large

If N = 2 $\quad P_I(t) = \frac{1}{2} + \frac{1}{2}\cos\omega_{12}t$

2 limits



dephasing beating

too simple — does not tell where system goes when it is not at *I*.

5. $I \to F$ transfer probability

F is some final or "target" state

$$\Psi_I = \sum_i a_i\psi_i \qquad \Psi_F = \sum_i b_i\psi_i$$

$$\begin{aligned} P_{I\to F}(t) &= \left|\langle\Psi_I(t)|\Psi_F(0)\rangle\right|^2 \\ &= \sum\left[|a_i|^2|b_i|^2 + \sum_{j>i}\left[2\,\mathrm{Re}\left(a_i^* a_j b_i b_j^* \cos\omega_{ij}t\right) - 2\,\mathrm{Im}\left(a_i^* a_j b_i b_j^* \sin\omega_{ij}t\right)\right]\right]. \end{aligned}$$

This is beginning to look like a mechanism, but it is necessary to know what to look for. How to choose a good ψ_F? This is always a serious problem. Things look simple only when you have found the right way to look at them!

6. Expectation values of real (coordinate or phase) space quantities, such as $\langle Q\rangle$, $\langle P\rangle$, $\langle J_i\rangle$, ⟨Euler angles⟩ or state space quantities $\mathbf{N}_i = \mathbf{a}_i^\dagger\mathbf{a}_i$ number operator,

resonance operators $a_i^\dagger a_j a_j$ $\qquad$ 1:2 resonance.

These are really useful!

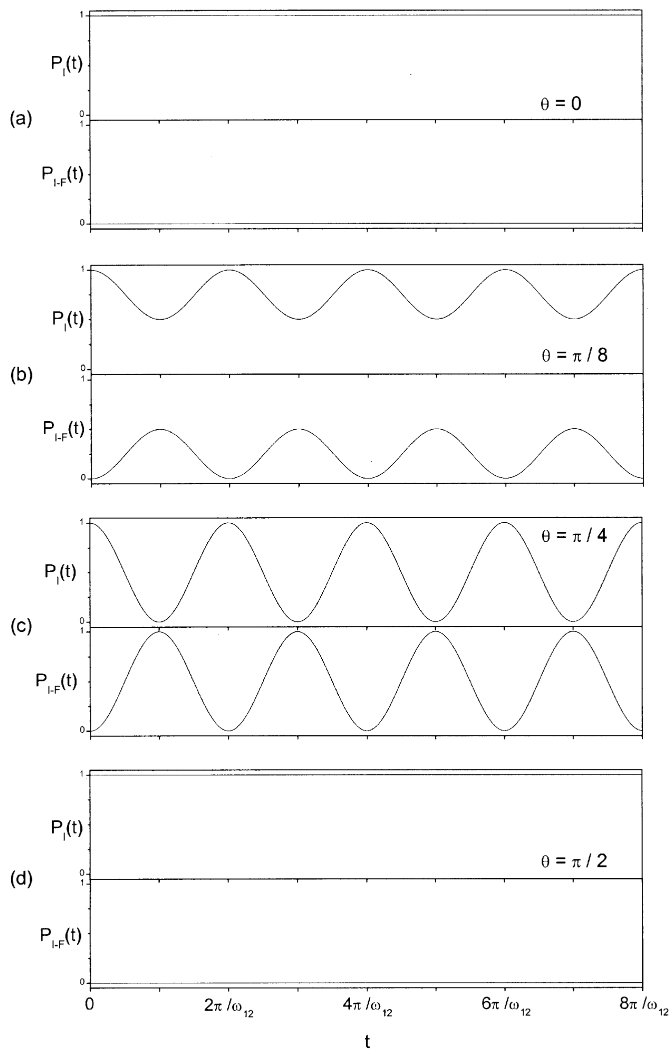
Example — simplest dynamics in state space

$$\Psi_I(0) = \cos\theta\psi_1 + \sin\theta\psi_2$$
$$\Psi_F(0) = -\sin\theta\psi_1 + \cos\theta\psi_2$$

skipped steps

$$\langle\Psi_I(t)|\Psi_I(0)\rangle = \left(\sin^2\theta + \cos^2\theta e^{i\omega_{12}t}\right)e^{iE_2t/\hbar}$$

$$P_I(t) = 1 - \sin^2 2\theta \sin^2(\omega_{12} t/2)$$
$$P_{I\to F}(t) = 1 - P_I(t) = \sin^2 2\theta \sin^2(\omega_{12} t/2)$$



Courtesy of Kyle Bittinger. Used with permission.

FIGURE 9.4. Dependence of the amplitude and phase of the survival and transfer probability on mixing angle in $\Psi_I(0)$ (see 9.1.46, 9.1.47, 9.1.49 and 9.1.50). $P_I(t)$ and $P_{I\to F}(t)$ are shown for mixing angles θ=0, π/8, π/4 (maximum amplitude), and π/2 (figure prepared by Kyle Bittinger).

Look at effect of varying mixing angle

$\theta = 0, \pi/2$ gives $P_I(t) = 1$, $P_{I\to F}(t) = 0$

$\theta = \pi/4$ maximum $0 \leftrightarrow 1$ oscillation

$\theta = \pi/8$ reduced amplitude of oscillation

More than 2 states? Complicated.

bright state, doorway state, dark state

state selective detection