Dynamical Quantities: Visualization of Dynamics

Last time: absorption spectrum

\[ I_{\nu g}^{\nu} (\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp \left[ -i \left( \omega + \frac{E_{g,\nu''}}{\hbar} \right) t \right] \langle \Psi_i (t) | \Psi_i (0) \rangle \]

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 (\( F = ma = p \cdot V \)) that explains the qualitative features of the autocorrelation function.

Identifies the local features of the \( V'_{e} \) potential that account for the important features in the absorption spectrum.

Could we get the same information in a time domain 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:

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!


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

$\mu(Q)$ - usually slow variation with $Q$, but not when there is a qualitative change in geometry short pulse, centered at correct $\lambda$

negative wavepacket on ground state?
multiphoton processes
spatial and temporal distribution of molecules affected by laser pulse?

Dynamical Quantities

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

\[
\Psi_I(t) = \sum_i a_i \psi_i e^{-E_i t / \hbar}
\]

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 probability density

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

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

2. Density matrix

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

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 \( \rho(t) \) is separately time dependent, so there is too much information to look at here without some sort of magic filter.
\( \rho \) is very useful in helping us to design an experiment because

\[
\langle A \rangle = \text{Trace } \rho A = \text{Trace } (T^\dagger \rho TT^\dagger AT)
\]

trace is invariant to unitary transformation

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

Suppose \( A \) has simple structure in \( \{ \psi_i \} \) but not in the eigenbasis. This is a very common situation.

3. Autocorrelation function

\[
\langle \Psi_I(t) | \Psi_I(0) \rangle = \sum_i |\alpha_i|^2 e^{iE_i t/\hbar}
\]

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

dehasing, partial recurrences

4. Survival probability

\[
P_I(t) = \frac{|\langle \Psi_I(t) | \Psi_I(0) \rangle|^2}{|\langle \Psi_I(0) | \Psi_I(0) \rangle|^2} = \sum_i |\alpha_i|^2 + \sum_{j>i} 2|\alpha_i||\alpha_j|^2 \cos \omega_{ij} t
\]

even simpler. Real \( 0 \leq P_I(t) \leq 1 \)

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

\[
P_I(t) = \sum_i \left[ N^{-2} + \sum_{j>i} 2N^{-2} \cos \omega_{ij} t \right]
\]

\[
= N^{-1} + 2N^{-2} \sum_i \sum_{j>i} \cos \omega_{ij} t
\]

\[
= N^{-1} + \frac{2N(N-1)}{2N^2} = \frac{1}{N} \left[ 1 + (N-1) \right] = 1
\]

at \( t > 0 \) \( P_I(t) \to 0 \), if \( N \) is large
If \( N = 2 \)

\[ P(I(t)) = \frac{1}{2} + \frac{1}{2} \cos \omega_{12} t \]

2 limits

![dephasing](image1)

![beating](image2)

too simple — does not tell where system goes when it is not at \( I \).

5. \( I \rightarrow F \) transfer probability

\( F \) is some final or “target” state

\[ \psi_I = \sum_i a_i \psi_i \quad \psi_F = \sum_i b_i \psi_i \]

\[ P_{I \rightarrow F}(t) = \left| \langle \psi_I(t) | \psi_F(0) \rangle \right|^2 \]

\[ = \sum \left[ |a_i|^2 |b_i|^2 + \sum_{j>i} \left[ 2 \text{Re} \left( a_i^* a_j b_j b_i^* \cos \omega_{ij} t \right) - 2 \text{Im} \left( a_i^* a_j b_j b_i^* \sin \omega_{ij} t \right) \right] \right] \]

This is beginning to look like a mechanism, but it is necessary to know what to look for. How to choose a good \( \psi_F \)? 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 \( \langle Q \rangle \), \( \langle P \rangle \), \( \langle J \rangle \), \( \langle \text{Euler angles} \rangle \) or state space quantities \( N_i = a_i^* a_i \) number operator,

resonance operators \( a_i^* a_j a_j \) \( 1:2 \) 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

\[ \langle \psi_I(t) | \psi_I(0) \rangle = (\sin^2 \theta + \cos^2 \theta e^{i\omega_{12} t}) e^{iE_{2j}/\hbar} \]
\[ P_I(t) = 1 - \sin^2 2\theta \sin^2(\omega_{12}t/2) \]
\[ P_{I \to F}(t) = 1 - P_I(t) = \sin^2 2\theta \sin^2(\omega_{12}t/2) \]

**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 \( \theta = 0, \pi/8, \pi/4 \) (maximum amplitude), and \( \pi/2 \) (figure prepared by Kyle Bittinger).

Look at effect of varying mixing angle

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

\[ \theta = \pi/4 \text{ maximum } 0 \leftrightarrow 1 \text{ oscillation} \]
\[ \theta = \pi/8 \text{ reduced amplitude of oscillation} \]

More than 2 states? Complicated.

bright state, doorway state, dark state
state selective detection