Spectroscopy and Control with Ultra-Short Laser Pulses

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Controlled coherent excitation

- The large bandwidth and high coherence of femtosecond pulses can be exploited for controlled excitation of quantum systems.
- The subsequent evolution of those systems results from the combination of the mixture of states coherently excited and the phase and amplitude pattern of the exciting field.
- This can be used to control system behaviour, or probe the system spectrum.
- Two examples:
  - Femtosecond adiabatic passage
  - Coherent Raman spectroscopy
Outline

Spectral Shaping of Ultra-short Pulses

1. Main tools
2. Quantum Control
   Control of adiabatic dynamics with non-adiabatic pulses
3. Spectroscopy
   Coherent spectroscopy with incoherent pulses

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We would like to modulate field on a *femtosecond time scale*

\[ E_{out}(t) = E_{in}(t) \times H(t) \]

Electro-optics too slow!

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Spectral Pulse Shaping. *Principle*

Amplitude & Phase mask for individual spectral components

\[ E_{in}(t) \xrightarrow{\text{Fourier Transform}} E_{in}(\omega) \]

\[ E_{out}(\omega) = E_{in}(\omega) \times H(\omega) \]

\[ H(\omega) = T(\omega)e^{i\varphi(\omega)} \]

\[ E_{out}(\omega) \xrightarrow{\text{Fourier Transform}} E_{out}(t) \]

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Spectral Pulse Shaping. *Implementation*

input pulse \[\rightarrow\] lens \[\rightarrow\] grating \[\rightarrow\] spatial light modulator \[\rightarrow\] lens \[\rightarrow\] shaped pulse

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Shaped pulses. Examples

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Application I. Quantum control

Non-adiabatic population transfer between two quantum states

\[ E(t)e^{i\omega_0 t + \varphi(t)} \]

\[ |\psi_2|^2 = \cos^2(\Omega t) \]
\[ \Omega = \mu_{12} E(t) / \hbar \]

Rabi oscillations:
- Fast
  - Sensitive to precise timing
  - Sensitive to exact frequency
  - Sensitive to phase coherence

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Application I. Quantum control

Adiabatic population transfer between two quantum states

\[ |2\rangle \]

\[ E(t)e^{i\omega_0 t + \varphi(t)} \]

\[ \omega(t) = \omega_0 + \frac{d}{dt}\varphi(t) \]

Adiabaticity: pulses are long on the time scale of system’s evolution

\[ \frac{d}{dt}\Delta(t) \ll (\Omega(t))^2 \]

Adiabatic passage:

- Slower but still fast
- Much more robust

\[ \varphi(t) \propto t^2 \rightarrow \omega(t) \propto t \]

Frequency chirping

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What if the dynamics is fast even on a picosecond scale?

We use pulse shaping to create a “Pulse train” with a piecewise quadratic phase or a “piecewise chirp”

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Dynamics of the state vector is a series of rotations:

\[
\hat{R} = \prod \hat{R}_{Rabi} \times \hat{R}_\varphi
\]

\[
\hat{R}_{Rabi} = \hat{R}_1 (\Omega \tau)
\]

\[
\hat{R}_\varphi = \hat{R}_3 (\Delta \varphi)
\]

\[
\hat{R}_{Rabi} \times \hat{R}_\varphi = \hat{R}_{(\theta, \phi)} (\alpha)
\]

\[
\begin{align*}
\alpha &= \sqrt{(\Omega \tau)^2 / 2 + (\Delta \varphi)^2 / 2} \\
\phi &= \pm \pi / 2 - \Delta \varphi / 2 \\
\tan(\theta) &= \pm \frac{\Omega \tau}{\Delta \varphi}
\end{align*}
\]

1. Start: \( \Omega \tau \ll \Delta \varphi \rightarrow \theta = 0 \)
2. Middle: \( \Omega \tau \gg \Delta \varphi \rightarrow \theta = \pi / 2 \)
3. End: \( \Omega \tau \ll \Delta \varphi \rightarrow \theta = \pi \)
Preliminary results: $^{85}\text{Rb} \ 5s \rightarrow 5p$ Piecewise Adiabatic Passage

Detection Scheme

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Very preliminary results

Rb 5p population as a function of chirp

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Stimulated Raman population transfer

- To reach optically inaccessible states, or to cool highly vibrationally excited molecules
  - Example: cooling ultracold molecules formed by photo-association
- Need to use Raman type transitions:
  \( \Omega_P \) connects \( \Psi_1 \) and \( \Psi_2 \) (pump)
  \( \Omega_S \) connects \( \Psi_2 \) and \( \Psi_3 \) (Stokes)
Stimulated Raman Adiabatic Passage: STIRAP

- Create a state that evolves from \( |1> \) to \( |2> \) without developing amplitude in \( |3> \)
- Do this by starting with \( \omega_{23} \), then applying \( \omega_{13} \): counter-intuitive ordering

\[
\psi(t) = a_1 e^{i\omega_{13}t} |1> + a_2 e^{i\omega_{23}t} |2> + a_3 e^{i\omega_{31}t} |3>
\]

\[
\hat{H} = \begin{pmatrix}
0 & \mu_{13} E_1 & 0 \\
\mu_{31} E_1^* & 0 & \mu_{32} E_2 \\
0 & \mu_{23} E_2^* & 0
\end{pmatrix}
\]

... By creating the Dark State with counter-intuitive pulse sequence...

\[
\psi_0(t) \propto \mu_{23} E_2 |1> - \mu_{31} E_1^* |2>
\]

\[
\hat{H} \psi_0(t) = 0
\]
Simulations for Na

Again, to avoid problems caused by longer pulses, can use a pulse sequence.

... And by using the \textit{Femtosecond Pulse Train}
**Piecewise Adiabatic Passage. Summary**

- Spectral pulse shaping enables creation of femtosecond pulse trains with predefined temporal amplitude and phase.
- Tailoring the amplitude and phase of the pulses in the train allows to mimic traditional (continuous) adiabatic passage in a piecewise manner.
- Piecewise adiabatic passage is as robust (vs intensity and timing) as the traditional adiabatic passage.
- Piecewise adiabatic passage offers new possibilities of controlling quantum dynamics of complex systems on a femtosecond time scale.
- Theory: accepted to *PRL*
- Experiment: underway

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Application II. **Ultrafast Spectroscopy**

Coherent anti-Stokes Raman Scattering

- Coherent (directional): easy to detect
- Non-resonant (electronic): low fluorescence background
- High efficiency: low average power, non-invasive imaging in bio-applications
- Low non-resonant background

Ultrafast CARS

- High time resolution (< 10^{-12} s)!
- Poor spectral resolution (>100 cm^{-1})

**But**

- Scan time delay, then do Fourier transform (too long…)
- Reduce bandwidth (waste of energy or too many lasers)
- **PULSE SHAPING!**
In time

\[ A(t) = C_{NR} + \sum C_n \exp(i\Omega_n t - \Gamma_n t) \]

\[ E_{as}(t) \propto P^{(3)}(t) \propto A(t)E_{pr}(t) \]

In frequency

\[ A(\Omega) = C_{NR} + \sum \frac{C_n}{\Omega - \Omega_n + i\Gamma_n} \]

\[ E_{as}(\omega) \propto P^{(3)}(\omega) \propto \int A(\Omega)E_{pr}(\omega - \Omega)d\Omega \]
CARS with shaped pulses

Vibration: \( \text{amplitude}; \quad \text{--- phase} \)

Probe field: \( \text{amplitude}; \quad \text{--- phase} \)

CARS spectrum \( I_{as}(\omega) \propto |E_{as}(\omega)|^2 \)

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CARS with shaped pulses. **Experiment**

**(a)**

- **Anti-Stokes wavelength (nm):** 720, 730, 740, 750
- **Probes time delay (ps):** -2, -1, 0, 1, 2
- **Shaping of Probe pulse**

**Raman spectrum of Toluene**

- **Raman shift (cm⁻¹):** 900, 1000, 1100, 1200, 1300
- **Raman spectrum of Toluene**

**Diagram:**
- **Stokes**
- **Probe**
- **Pump**
- **CARS**
- **Scan delay**
- **Sample**
- **Monochromator**
- **CCD**
- **Ti:Sapphire Amplifier (Spitfire)**
- **OPA (TOPAS)**
- **Shaping of Probe pulse**

**Mathematical Expression:**

\[ E_{pr}(\omega) \times S(\omega) \]
Good news and bad news

- Recovery technique analogous to cross-correlation frequency resolved optical gating (XFROG), standard technique used to measure femtosecond pulses.
- We recover full phase and amplitude information about the system – locations and decoherence times of all resonances.
- However, this technique requires knowledge of the probe field, and controlled phase coherence of that field.
- Also, requires a scan of the time delay, resolution determined by the maximum time delay.
- A “scan-less” method would be better.
- Complex media (i.e. cells) introduce incoherence in the probe that cannot be corrected for.
Correlations in CARS spectrum

Assuming two infinitely narrow resonances:

\[ E_{aS}(t) = E_{pr}(t) \times (e^{i\Omega_1 t} + e^{i\Omega_2 t}) \]

Intensity spectrum is the Fourier transform of the field correlation function:

\[ G_{E_{aS}}(\tau) = \int E_{aS}(t) E_{aS}^*(t - \tau) dt = G_{E_{pr}}(\tau) \times (e^{i\Omega_1 \tau} + e^{i\Omega_2 \tau}) \]

Applying Fourier transform:

\[ I_{aS}(\omega) = I_{pr}(\omega + \Omega_1) + I_{pr}(\omega + \Omega_2) \]

Thus, resonances introduce new correlations in the spectrum:

\[ G_{I_{aS}}(\Delta \omega) = 2G_{I_{pr}}(\Delta \omega) + G_{I_{pr}}(\Delta \omega + \delta \Omega) + G_{I_{pr}}(\Delta \omega - \delta \Omega) \]
CARS with noisy pulses. Calculations

$A(\Omega)$

$|E_{pr}(\omega)|$

$I_{as}(\omega)$

$G_{I_{as}}(\Delta \omega)$

one noise realization

$\delta \Omega$

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$\langle G_{I_{as}}(\Delta \omega) \rangle$ average over noise realizations

$\langle G_{I_{as}}(\Delta \omega) - 2G_{I_{pr}}(\Delta \omega) \rangle$
CARS with *noisy* pulses. *Experiment*

**Toluene**
\[ \Omega_n = (1000, 1027) \text{ cm}^{-1} \]

**Toluene + Ortho-xylene**
\[ \Omega_n = (982, 1000, 1027, 1049) \text{ cm}^{-1} \]

*Resolution* is determined by the granularity of noise (not by the pulse bandwidth)
What can we call this new method?

- Relies on Noise Autocorrelation
- It is a Spectroscopy
- Although general for non-linear spectroscopies, this realization is based on Coherent Anti-Stokes Raman Scattering

NASCARS
“Cheap” shaping for NASCARS

Toluene
Preliminary results

Temporal randomization (noise) by means of fiber mode dispersion

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Spectroscopy with Shaped Pulses. Summary

- Broad spectral bandwidth of ultra-short pulses offers new ways of “interference spectroscopy”
- Pulse shaping technology enables design of “spectrally incoherent” pulses with no correlation between separate spectral components of the pulse
- Interference of noise, coherently produced via CARS, results in the appearance of correlations in the Raman spectrum
- Identifying Raman resonances by the spectral correlations of interference noise offers quick and easy way of doing Raman spectroscopy with femtosecond pulses.

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Alternate formulation of dark state (1)

Hamiltonian for 3 states:

\[
C(t) = [C_1(t), C_2(t), C_3(t)]^T
\]

\[
H(t) = \hbar \begin{bmatrix}
0 & \frac{1}{2} \Omega_P(t) & 0 \\
\frac{1}{2} \Omega_P(t) & \Delta_P & \frac{1}{2} \Omega_S(t) \\
0 & \frac{1}{2} \Omega_S(t) & \Delta_P - \Delta_S
\end{bmatrix}.
\]

Here \(\Omega_P(t)\) and \(\Omega_S(t)\) are the Rabi frequencies of the pump and Stokes pulses, respectively, and \(\Delta_P\) and \(\Delta_S\) are the single-photon detunings of the pump and Stokes lasers from their respective transitions. \(\hbar \Delta_P = E_2 - E_1 - \hbar \omega_P\), \(\hbar \Delta_S = E_2 - E_3 - \hbar \omega_S\). An essential condition for STIRAP is the two-photon resonance between states \(\psi_1\) and \(\psi_3\), \(\Delta_P = \Delta_S = \Delta\). Then the three instantaneous eigenstates of \(H(t)\) (the adiabatic states) are given by

\[
\Phi_+(t) = \psi_1 \sin \vartheta(t) \sin \varphi(t) + \psi_2 \cos \varphi(t) + \psi_3 \cos \vartheta(t) \sin \varphi(t), \quad \text{20.}
\]

\[
\Phi_0(t) = \psi_1 \cos \vartheta(t) - \psi_3 \sin \vartheta(t), \quad \text{21.}
\]

\[
\Phi_-(t) = \psi_1 \sin \vartheta(t) \cos \varphi(t) - \psi_2 \sin \varphi(t) + \psi_3 \cos \vartheta(t) \cos \varphi(t), \quad \text{22.}
\]

where the mixing angles \(\vartheta(t)\) and \(\varphi(t)\) are defined (modulo \(\pi\)) as \(\vartheta(t) = \arctan [\Omega_P(t)/\Omega_S(t)]\), \(\varphi(t) = \frac{1}{2} \arctan[\sqrt{\Omega_P^2(t) + \Omega_S^2(t)}/\Delta]\). These eigen states have the following eigen frequencies:

\[
\varepsilon_0(t) = 0, \quad \varepsilon_{\pm}(t) = \frac{1}{2} \Delta \pm \frac{1}{2} \sqrt{\Delta^2 + \Omega_P^2(t) + \Omega_S^2(t)}. \quad \text{23.}
\]
Alternate formulation (2)

STIRAP is based on the zero-eigenvalue adiabatic state $\Phi_0(t)$, which is a coherent superposition of the initial state $\psi_1$ and the final state $\psi_3$ only. This adiabatic state has no component of the excited state $\psi_2$, and hence it has no possibility of radiatively decaying; it is a trapped state (of population) or a radiatively dark state (85–89). For the counterintuitive pulse ordering the relations $\Omega_P(t)/\Omega_S(t) \rightarrow 0$ and $\Omega_P(t)/\Omega_S(t) \rightarrow \infty$ apply; hence, as time progresses from $-\infty$ to $+\infty$, the mixing angle $\vartheta(t)$ rises from 0 to $\pi/2$. Consequently, the adiabatic state $\Phi_0(t)$ evolves from the bare state $\psi_1$ to a superposition of states $\psi_1$ and $\psi_2$ at intermediate times and finally to the target state $\psi_3$ at the end of the interaction; thus, state $\Phi_0(t)$ links adiabatically the initial state $\psi_1$ to the target state $\psi_3$. Because the Hamiltonian is explicitly time dependent, diabatic transitions between the adiabatic states will occur. The goal is to reduce the diabatic transition rates to negligibly small values. When the system can be forced to stay in the dark state at all times, a complete population transfer from $\psi_1$ to $\psi_3$ will be achieved, as shown in Figure 9. This can be realized by ensuring adiabatic evolution: then no transitions between the adiabatic states can take place. The adiabatic condition requires that the coupling between each pair of adiabatic states is negligible compared with the difference between the energies of these states. With respect to the dark state $\Phi_0(t)$, the adiabatic condition reads (5, 6)

\[ |\varepsilon_0 - \varepsilon_\pm| \gg |\langle \Phi_0 | \Phi_\pm \rangle|, \]

On one-photon resonance ($\Delta = 0$) the adiabaticity condition simplifies and becomes (81)

\[ \sqrt{\Omega_P^2 + \Omega_S^2} \gg |\dot{\vartheta}| \propto T^{-1}, \]

where $T$ is the pulse width. Assuming that the pump and Stokes pulses have the same peak Rabi frequency $\Omega_0$, this condition can be written as $\Omega_0 T \gg 1$. Hence,
Experimental NASCARS spectrum of a mixture of toluene (782cm$^{-1}$, 1000cm$^{-1}$, 1027cm$^{-1}$) with ortho-xylene (982cm$^{-1}$, 1049cm$^{-1}$) mixture. Noise is introduced using spectral pulse shaper. Result is averaged over 100 noise realizations. Red curve is autocorrelation of Raman spectrum as reference.
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