

## Coherent spectroscopy

In PC IV you have learnt about Bloch equations, Rabi oscillations and pulse sequences as an approach to extracting useful information on the structural and dynamical properties of matter based on the coherent interaction between nuclear or electronic spins and radio waves. In principle these approaches can be transferred to the domain of optical spectroscopy for the same purposes. Unfortunately, at optical frequencies one has to deal with different and much faster relaxation processes that destroy coherence. For example, in NMR, spontaneous emission is very slow, because of the  $\nu^3$  scaling (where  $\nu$  is the emitted frequency), such that its contribution to bringing the spin system into thermal equilibrium is negligible. On the contrary, at optical frequencies, spontaneous emission is one of the most important sources of decoherence. Nonetheless, progress in laser sources and techniques has provided a great deal of possibilities in the coherent manipulation of atoms and molecules that nowadays have important applications in areas as diverse as quantum information science and femtochemistry.

### 1 Rabi oscillations

Rabi oscillations are a fundamental consequence of coherent light-matter interaction. In this context the term “coherent” implies that the light field has a well-defined temporal phase  $\omega t + \phi$ . Nowadays this is most commonly realized using laser light sources. Being able to observe Rabi oscillations in an experiment is a clear signature of strong light-matter interaction.

- (a) Consider Eqs. (1.96) and (1.97) from the lecture notes. These equations describe the temporal behaviour of a driven quantum mechanical system. Show that the equations can be reformulated as

$$i \frac{dc_1}{dt} = \frac{V_{12}}{2} c_2 \quad \text{and} \quad (1)$$

$$i \frac{dc_2}{dt} = (\omega_2 - \omega) c_2 + \frac{V_{21}}{2} c_1. \quad (2)$$

Assume for simplicity that  $\phi = 0$ . It is also helpful to choose the ground-state energy to be  $E_1 = 0 \Rightarrow \omega_1 = 0$ . Use the ansatz

$$b_1 = c_1 \quad (3)$$

$$b_2 = c_2 \exp(-i\omega t) \quad (4)$$

where  $\omega$  represents the laser angular frequency. Further equations (1) and (2) are obtained by neglecting terms that oscillate with a frequency of  $2\omega$  and higher. This can be justified by the rotating wave approximation.

- (b) Consider the case of resonant driving, i. e.  $\omega = \omega_2$ . Solve the differential equation pair by differentiating (2) and substituting from (1).

- (c) Only the absolute square values of the coefficients  $c_i(t)$  have a physical meaning. Calculate  $|c_2(t)|^2$ . What is the characteristic oscillation frequency?

## 2 Ladder operator formalism

In general, the quantum mechanical Hamiltonian of a system can be derived by formulating its classical analogue and converting the observables into operators. *Example:* The quantum mechanical Hamiltonian for the well-known harmonic oscillator with resonance frequency  $\omega$  and mass  $m$  is given by

$$\mathcal{H} = \frac{\hat{P}^2}{2m} + \frac{m\omega^2 \hat{X}^2}{2}. \quad (5)$$

In the lecture on quantum mechanics (PC III), you have solved the time-independent Schrödinger equation for the harmonic oscillator in position space. Here, we will use a different approach to solve this problem. It involves the ladder operators

$$\hat{a} = \sqrt{\frac{m\omega}{2\hbar}} \left( \hat{X} + \frac{i\hat{P}}{m\omega} \right) \quad (6)$$

and

$$\hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}} \left( \hat{X} - \frac{i\hat{P}}{m\omega} \right). \quad (7)$$

- (a) Express the position operator  $\hat{X}$  and the momentum operator  $\hat{P}$  in terms of the two ladder operators (6) and (7).
- (b) Show that  $[\hat{a}, \hat{a}^\dagger] = 1$ . Use the fundamental commutator relationship  $[\hat{X}, \hat{P}] = i\hbar$ .
- (c) Express the Hamiltonian in terms of the operator  $\hat{a}^\dagger \hat{a}$  and show that the time-independent Schrödinger equation can be written as

$$\hbar\omega \left( \hat{a}^\dagger \hat{a} + \frac{1}{2} \right) |n\rangle = E_n |n\rangle \quad (8)$$

where  $E_n$  denotes the energy of eigenstate  $|n\rangle$ .

- (d) Given an arbitrary eigenstate  $|n\rangle$  with energy  $E_n$ , calculate the energy of the state  $\hat{a}|n\rangle$ . Show that  $\hat{a}|n\rangle$  is also an eigenstate with energy  $E_n - \hbar\omega$ . *Hint:* Use  $[\hat{a}, \hat{a}^\dagger] = 1$ .

What you have just shown is that  $\hat{a}$  acting on an energy eigenstate produces another eigenstate the energy of which has been decreased by one quantum  $\hbar\omega$ . This is why  $\hat{a}$  is called the *lowering operator*. Likewise,  $\hat{a}^\dagger$  is called the *raising operator*; it produces an eigenstate the energy of which has been increased by one energy quantum.

An eigenstate's energy is thus nothing but the sum of several single energy quanta (excitations). The number  $n$  of quanta can be used to characterize an eigenstate, which is why we denoted the eigenstates  $|n\rangle$ .

- (e) We will now explore the limits for the eigenvalues of the number operator. Show that the expectation value for  $\hat{n}$  is always positive or zero. *Hint:* Consider the (arbitrary) state  $\hat{a}|\psi\rangle$ .

Combining the findings of problem 2 (e) with Equation (8) we see that there is a minimum energy

$$E_0 = \frac{\hbar\omega}{2} \quad (9)$$

corresponding to the *ground state*  $|0\rangle$ . In the language of ladder operators this reads

$$\hat{a}|0\rangle = 0, \quad (10)$$

i. e. there is no lower lying state below the ground state.

- (f) Assuming that all the energy eigenstates are normalized,  $\langle n|n\rangle = 1$ , find a general expression for  $\hat{a}|n\rangle$ . With that result, verify that  $\hat{a}|0\rangle = 0$ .

### 3 Probing and controlling vibrational wave packets

Rabi oscillations require a strong and steady laser source that drives the system faster than the decoherence time. Here we discuss a different approach, which is based on femtosecond ( $1 \text{ fs} = 10^{-15} \text{ s}$ ) laser pulses. The idea is to observe and control coherent dynamics via the preparation of a coherent superposition of vibrational states using broadband pulsed excitation. In particular, we look at the situation where a train of fs pulses excites a fluorescent molecule [1].

As shown in Fig. 1, each pulse creates a wave packet  $|\psi(0)\rangle$  in the vibrational levels of the first excited electronic state. We assume that the wave packet  $|\psi(t)\rangle$  evolves according to the Hamiltonian  $\hat{H}$  of a one-dimensional (1D) harmonic oscillator. At the same time, the wave packet loses quantum coherence due to vibrational relaxation at a rate  $\Gamma$ . If the next fs pulse in the train arrives before coherence has been completely destroyed by relaxation, it creates a copy of the initial wave packet  $|\psi(0)\rangle$  that interferes with the previous one  $|\psi(t)\rangle$ . By adjusting the time delay  $\Delta t$  and the relative phase  $\varphi$  between two pulses, one can coherently manipulate the wave function of the excited state manifold:

$$|\Psi(\Delta t, \varphi)\rangle = \exp(i\varphi)|\psi(0)\rangle + |\psi(\Delta t)\rangle. \quad (11)$$

This event can be observed by measuring the fluorescence signal, which is proportional to the population in the first excited electronic state  $|\Psi(\Delta t, \varphi)|^2$ . Hence, by observing a slow process (fluorescence), we have access to the fast coherent dynamics in the excited state, which are manipulated using ultrafast laser pulses (excitation).

- (a) The temporal evolution of a quantum mechanical system can be expressed in terms of time-dependent state coefficients. For our vibrational system this can be written as

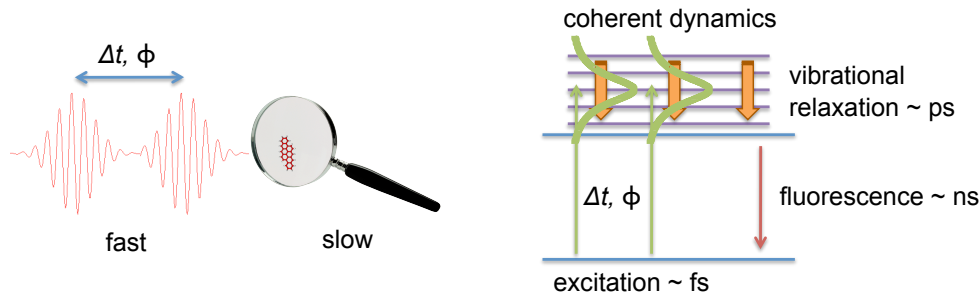


Figure 1: (left panel) Schematics of the experiment. A train of fs pulses with a controlled delay and phase excites a single molecule. Its fluorescence signal is observed using a standard epi-fluorescence microscope, sketched as a magnifying glass. (right panel) Level scheme, with pump sequences, evolution, vibrational relaxation and fluorescence transition. Each fs pulse creates a coherent wave packet that evolves and, at the same time, undergoes vibrational relaxation.

$$|\psi(t, q)\rangle = \sum_n c_n(t) \cdot \phi_n(q) \quad (12)$$

where  $q$  denotes the vibrational coordinate.

Show that the resulting wavefunction is of Gaussian shape for  $t = 0$ . Assume 1-D harmonic oscillator wavefunctions and coefficients  $c_n(0) = 1/\sqrt{2^n n!}$ .

*Hint:* The 1-D harmonic oscillator wavefunctions are given in Eq. (1.103) in the lecture notes. The exponential generating function of Hermite polynomials is  $H_n$ :

$$\exp(2xw - w^2) = \sum_n H_n(x)w^n/n!.$$

- (b) The generated wave packet  $|\psi(0)\rangle$  is a coherent superposition of vibrational levels. Use the time evolution operator

$$|\psi(t)\rangle = U(t_0, t)|\psi(t_0)\rangle \quad (13)$$

to describe the motion of the center of the wave packet.

*Hint:* For a time-independent Hamiltonian as the 1-D harmonic oscillator  $U(t_0, t) = \exp(-i\frac{H}{\hbar}(t - t_0))$ . Recall that  $\phi_n(q)$  are energy eigenstates of the harmonic oscillator Hamiltonian with eigen values given in Eq. (1.102) in the lecture notes.

- (c) Ignore vibrational relaxation and consider a second fs pulse that excites the molecule with a time delay  $\Delta t$  and a phase difference  $\varphi$ . Find an expression for  $|\Psi(\Delta t, \varphi)\rangle$ , i.e. the interference between the previous and the new wave packet.

*Hint:* Use equation (11) together with the results from a) and b). In Eq. (11)  $|\psi(0)\rangle$  represents the wave packet created by the second laser pulse and  $|\psi(\Delta t)\rangle = U(0, \Delta t)|\psi(0)\rangle$  the wave packet created by the first laser pulse.

- (d) The fluorescence signal is proportional to  $|\Psi(\Delta t, \varphi)|^2$ . Find a simple expression for this quantity.

*Hint:* You can simplify the expression for  $\Psi(\Delta t, \varphi)$  by approximating  $e^{i\omega\Delta t}$  in a power series expansion and by assuming that  $\omega\Delta t \ll 1$ .

## References

- [1] D. Brinks, F.D. Stefani, F. Kulzer, R. Hildner, T.H. Taminiau, Y. Avlasevich, K. Müllen, and N.F. van Hulst, *Nature* **465**, 905 (2010).