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Chapter 9

Two-Photon Excitation

9.1 Introduction

Every radiative process described so far has involved a single photon, whether it be a hyperfine transition in magnetic resonance, optical excitation, or spontaneous emission. However, processes can occur in which an atom *simultaneously* absorbs two or more photons. Such multi-photon processes can lead to ionization of atoms or dissociation of molecules in intense laser fields, and phenomena such as free-to-free transitions in which an electron absorbs successive quanta as it flies out from the field of an atom. The most frequently encountered multi-photon process is two-photon absorption or emission. Two-photon processes have become one of the standard tools in atomic physics for exciting atoms to states whose energies are too high to achieve with a single photon, and also to states of the same parity that would normally be inaccessible. In addition, a number of ultra-high resolution spectroscopic techniques are based on two-photon processes. Our approach will be to use second-order perturbation theory, extending the first order development used in earlier chapters in a straightforward fashion. An alternative approach involves solving the dynamical equations in the same manner as we analyzed the two-level system. However, the perturbation approach is appropriate in many cases, and is simpler than the dynamical approach.

The aim is to cause a transition $a \rightarrow b$ by applying two fields:

$$\vec{\mathcal{E}}(t) = \mathcal{E}_1 \hat{\mathbf{e}}_1 \cos \omega_1 t + \mathcal{E}_2 \hat{\mathbf{e}}_2 \cos \omega_2 t \quad (9.1)$$

where

$$\hbar(\omega_1 + \omega_2) = (E_b - E_a) \quad (9.2)$$

States $|a\rangle$ and $|b\rangle$ have the same parity, so a single photon transition is forbidden. The process is shown in Fig. 9.1, left. A more realistic view is shown in Fig. 9.1 right, where $|f\rangle$ represents some intermediate state of opposite parity. One way to describe the process is that photon ω_1 causes a transition from $|a\rangle$ to a “virtual” state near $|f\rangle$ and the second photon at ω_2 carries the system from the virtual state to the final state $|b\rangle$. As will be seen, however, the “virtual” state does not need to be interpreted literally, since the system will never be found in it. Alternatively, the virtual state can be thought of as a real state whose energy, for a sufficiently short interval, is broadened to the point that it can be excited by ω_1 . In reality, $|f\rangle$ represents one of a complete set of eigenstates which have non-vanishing dipole matrix elements with $|a\rangle$.

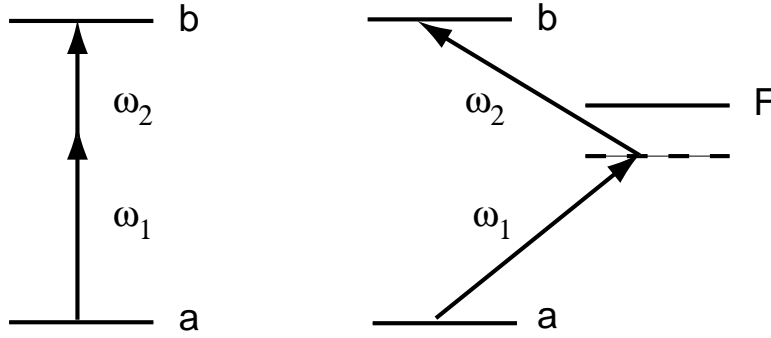


Figure 9.1. Two-photon absorption

9.2 Calculation of the Two-Photon Rate

The Hamiltonian is of the form $H = -\vec{\mathcal{E}} \cdot \mathbf{d}$, where $\mathbf{d} = -er$. With the field described by Eq. 9.1, we have

$$H = -\frac{1}{2}(e^{i\omega_1 t} + e^{-i\omega_1 t})\mathcal{E}_1\hat{\mathbf{e}}_1 \cdot \mathbf{d} - \frac{1}{2}(e^{i\omega_2 t} + e^{-i\omega_2 t})\mathcal{E}_2\hat{\mathbf{e}}_2 \cdot \mathbf{d}. \quad (9.3)$$

Defining

$$H_{fa,1} = -E_1\langle f|\hat{\mathbf{e}}_1 \cdot \mathbf{d}|a\rangle, \quad H_{fa,2} = -E_2\langle f|\hat{\mathbf{e}}_2 \cdot \mathbf{d}|a\rangle, \quad (9.4)$$

The matrix element $\langle f|H|a\rangle$ is

$$H_{fa} = \frac{H_{fa,1}}{2}e^{-i\omega_1 t} + \frac{H_{fa,2}}{2}e^{-i\omega_2 t}. \quad (9.5)$$

We have neglected the counter-rotating terms because their effect is usually negligible and we have dropped them for simplicity. Following the procedure used earlier, the first order solution for the amplitude a_f of $|f\rangle$ is

$$\begin{aligned} a_f^{[1]} &= \frac{1}{2i\hbar} \int_0^t \left[H_{fa,1}e^{-i(\omega_1 - \omega_{fa})t'} + H_{fa,2}e^{-i(\omega_2 - \omega_{fa})t'} \right] dt' \\ &= \frac{1}{2\hbar} \left[\frac{H_{fa,1}(e^{-i(\omega_1 - \omega_{fa})t} - 1)}{\omega_1 - \omega_{fa}} + \frac{H_{fa,2}(e^{-i(\omega_2 - \omega_{fa})t} - 1)}{\omega_2 - \omega_{fa}} \right]. \end{aligned} \quad (9.6)$$

The second order solution for the b state amplitude, $a_b^{[2]}$, is found from

$$i\hbar\dot{a}_b^{[2]} = \sum_k H_{bk}a_k^{[1]}e^{i\omega_{bk}t} \quad (9.7)$$

The contribution to the sum due to state f is

$$a_b^{[2]} = \frac{1}{i\hbar} \int_0^t \langle b|H|f\rangle e^{i\omega_{bf}t'} a_f^{[1]}(t') dt' \quad (9.8)$$

Introducing

$$H_{bf,1} = -\mathcal{E}E_1\langle b|\hat{\mathbf{e}}_1 \cdot \mathbf{d}|f\rangle, \quad H_{bf,2} = -\mathcal{E}E_2\langle b|\hat{\mathbf{e}}_2 \cdot \mathbf{d}|f\rangle. \quad (9.9)$$

and defining $\omega_0 \equiv \omega_{ba}$, we have,

$$\langle b|H|f\rangle = \frac{H_{bf,1}}{2}e^{-i\omega_1 t} + \frac{H_{bf,2}}{2}e^{-i\omega_2 t}. \quad (9.10)$$

Eq. 9.8 yields

$$a_b^{[2]} = \frac{1}{4\hbar^2} \sum_f \left[\frac{H_{bf,1}H_{fa,1}}{\omega_1 - \omega_{fa}} \frac{e^{i(\omega_0 - 2\omega_1)t} - 1}{\omega_0 - 2\omega_1} + \frac{H_{bf,2}H_{fa,2}}{\omega_2 - \omega_{fa}} \frac{e^{i(\omega_0 - \omega_2)t} - 1}{\omega_0 - 2\omega_2} \right. \\ \left. + \frac{H_{bf,2}H_{fa,1}}{\omega_1 - \omega_{fa}} \frac{e^{i(\omega_0 - \omega_1 - \omega_2)t} - 1}{\omega_0 - \omega_1 - \omega_2} + \frac{H_{bf,1}H_{fa,2}}{\omega_2 - \omega_{fa}} \frac{e^{i(\omega_0 - \omega_1 - \omega_2)t} - 1}{\omega_0 - \omega_1 - \omega_2} \right] \quad (9.11)$$

Note that the first two terms involve absorbing two photons from the same beam, while the last two involve absorbing one photon from each of the two beams. When two different frequencies are used, the first terms are invariably far from resonance and can be neglected. In the case of absorbing two photons at the same frequency, discussed below, all four terms contribute.

9.3 Cases of Two-Photon Absorption

Two cases are of particular interest: when one intermediate state makes the dominant contribution to the two-photon excitation rate, and when both photons come from a single radiation source.

9.3.1 Two-photon rate with a single intermediate state

Suppose that ω_1 is close to ω_{ka} where k is a particular intermediate state. In this case Eq. 9.11 becomes

$$a_b^{[2]} \approx \frac{1}{4\hbar^2} \frac{H_{bk,2}H_{ka,1}}{\omega_1 - \omega_{ka}} \frac{e^{i(\omega_0 - \omega_1 - \omega_2)t} - 1}{\omega_1 - \omega_1 - \omega_2} \quad (9.12)$$

We then obtain for the transition probability

$$W_{a \rightarrow b}^{[2]} = \frac{1}{(4\hbar^2)^2} \frac{|H_{bk,2}|^2 |H_{ka,1}|^2 \sin^2(\omega_0 - \omega_1 - \omega_2)t/2}{(\omega_1 - \omega_{ka})^2 [(\omega_0 - \omega_1 - \omega_2)/2]^2} \quad (9.13)$$

Integrating over the appropriate spectral distribution gives

$$\Gamma_{ab}^{(2)} = \frac{\pi}{8\hbar^4} \frac{|H_{bk,2}|^2 |H_{ka,1}|^2}{(\omega_1 - \omega_{ka})^2} f(\omega_0) \quad (9.14)$$

We can cast this into a more familiar form by introducing the usual Rabi frequencies

$$\omega_R^{(1)} = \frac{|H_{ka,1}|}{\hbar}, \quad \omega_R^{(2)} = \frac{|H_{ka,2}|}{\hbar} \quad (9.15)$$

Denoting the detuning of the intermediate state by

$$\Delta \equiv \omega_1 - \omega_{ka} \quad (9.16)$$

then we can define the two-photon Rabi frequency by

$$\omega_{R2} = \frac{\omega_R^{(1)}\omega_R^{(2)}}{2\Delta} \quad (9.17)$$

and we have

$$\Gamma_{ab} = \frac{\pi}{2}\omega_{R2}^2 f(\omega_0), \quad (9.18)$$

in analogy with the expression for one-photon transitions.

A more useful expression for the two-photon transition rate is in terms of the radiation intensity, I . Noting that $\mathcal{E}^2 = 8\pi I/c$ (cgs units), we have from Eq. 9.4

$$\begin{aligned} |H_{ka,1}|^2 &= \mathcal{E}_1^2 |\langle k|\hat{\mathbf{e}}_1 \cdot \mathbf{d}|a\rangle|^2 = 8\pi |d_{ka}^{(1)}|^2 I_1/c, \\ |H_{bk,2}|^2 &= \mathcal{E}_2^2 |\langle b|\hat{\mathbf{e}}_2 \cdot \mathbf{d}|k\rangle|^2 = 8\pi |d_{bk}^{(1)}|^2 I_2/c, \end{aligned} \quad (9.19)$$

Eq. 9.14 becomes

$$\Gamma_{ab}^{(2)} = \frac{8\pi^3}{\hbar^4 c^2} \frac{|D_{ka}^{(2)}|^2 |D_{bk}^{(2)}|^2}{\Delta^2} f(\omega_0) I_1 I_2. \quad (9.20)$$

9.3.2 Two-photon absorption from a single radiation source

In many cases, a two-photon transition is driven by a single radiation source—invariably a laser. However, the absorption can occur with two laser beams having different directions and polarizations. Denoting the polarizations by $\hat{\mathbf{e}}_1$ and $\hat{\mathbf{e}}_2$, Eq. 9.11 becomes

$$a_b^{[2]} = \frac{1}{4\hbar^2} \sum_f \left[\frac{H_{bf,1}H_{fa,1} + H_{bf,2}H_{fa,2} + H_{bf,2}H_{fa,1} + H_{bf,1}H_{fa,2}}{\omega - \omega_{fa}} \right] \frac{e^{i(\omega_0 - 2\omega)t} - 1}{\omega_0 - 2\omega} \quad (9.21)$$

Following the procedure of Sect. 9.3.1, we obtain the following expression for the two-photon absorption rate: (assuming that the process where two photons are absorbed from the same laser beam does not contribute.)

$$\Gamma_{ab} = \frac{8\pi^3}{\hbar^4 c^2} |A_{ba}|^2 f(\omega_0) I^2, \quad (9.22)$$

where the two-photon excitation operator is

$$A_{ba} = \sum_f \frac{\hat{\mathbf{e}}_1 \cdot \langle b|\mathbf{d}|f\rangle \langle f|\mathbf{d}|a\rangle \cdot \hat{\mathbf{e}}_2 + \hat{\mathbf{e}}_2 \cdot \langle b|\mathbf{d}|f\rangle \langle f|\mathbf{d}|a\rangle \cdot \hat{\mathbf{e}}_1}{\omega_{fa} - \omega} \quad (9.23)$$

If the laser is monochromatic, and the decay rate of state b is γ , then

$$f(\delta\omega) = \frac{2}{\pi} \frac{\gamma/2}{4(\delta\omega)^2 + \gamma^2/4} \quad (9.24)$$

where $\delta\omega = (\omega_0/2) - \omega$ is the detuning of the laser from its resonance value, $\omega_0/2$.

9.4 Two-Photon Doppler-Free Spectroscopy

The Doppler effect is the most common source of inhomogeneous line broadening. (Inhomogeneous broadening occurs because the resonance frequencies of different atoms are shifted by different amounts, giving a width to the ensemble. This is in contrast to homogeneous broadening, when the response of each atom is the same, as in the case of spontaneous decay.) If two-photon excitation involves absorption from two light beams with frequencies and wave vectors (ω_1, ω_2) and $(\mathbf{k}_1, \mathbf{k}_2)$, respectively, where $k = \omega/c$, then the frequencies “seen” by an atom moving with velocity \mathbf{v} are, to first order in v/c ,

$$\omega'_1 = \omega_1 - \mathbf{k}_1 \cdot \mathbf{v}, \quad \omega'_2 = \omega_2 - \mathbf{k}_2 \cdot \mathbf{v} \quad (9.25)$$

The line shape function for an atom moving with velocity \mathbf{v} is

$$\begin{aligned} f(\omega_1, \omega_2) &= \frac{2}{\pi} \frac{(\gamma/2)}{(\gamma/2)^2 + (\omega_0 - \omega'_1 - \omega'_2)^2} \\ &= \frac{2}{\pi} \frac{(\gamma/2)}{(\gamma/2)^2 + (\omega_0 - \omega_1 - \omega_2 + (\mathbf{k}_1 + \mathbf{k}_2) \cdot \mathbf{v})^2} \end{aligned} \quad (9.26)$$

The Doppler effect is minimized by taking $\hat{k}_1 = -\hat{k}_2$, in which case the shift is

$$\Delta\omega_D = (\omega_1 - \omega_2)v/c. \quad (9.27)$$

The ensemble line shape function is obtained by averaging over the distribution of velocities. Clearly, it is desirable to use frequencies as similar as possible. The ideal case is when $\mathbf{k}_1 = -\mathbf{k}_2$, which would occur in two photon-absorption from counter-propagating beams from the same laser. The simplest way to assure counter-propagating beams is to use a standing wave. Consequently, two-photon absorption in a standing wave displays no first-order Doppler broadening. Nevertheless, there is a residual second-order Doppler broadening. The second-order Doppler shift is given by

$$\frac{\delta\omega_{D2}}{\omega} = -\frac{1}{2} \frac{v^2}{c^2} = -\frac{Mv^2/2}{Mc^2}. \quad (9.28)$$

Taking $\frac{1}{2}M\overline{v^2} \simeq k_B T$, we have

$$\frac{\delta\omega_{D2}}{\omega} \approx \frac{-k_B T}{Mc^2}. \quad (9.29)$$

At room temperature, $k_B T = (1/40)$ eV. For hydrogen, $Mc^2 \approx 1\text{GeV}$. Consequently, the fractional second order Doppler shift is about 2×10^{-11} .

If one considers spectroscopy at a resolution of 1 part in 10^{13} or better, the second order Doppler shift can be a major source of systematic error. Fortunately, methods have been developed for cooling below a millikelvin, where the effect is unimportant, at least for the next few years. Also, in heavier atoms, the second order Doppler effect is correspondingly diminished.

A particularly important case is two-photon absorption on the $1S \rightarrow 2S$ transition in hydrogen. The 2S state is metastable and has a lifetime of 1/7 sec, yielding an extremely high Q for the transition and the possibility of ultra-high spectral resolution. The excitation operator has been calculated for hydrogen by [1]. The result yields

$$\Gamma_{1s,2s} = 84 \frac{I^2}{\gamma} s^{-1} \quad (9.30)$$

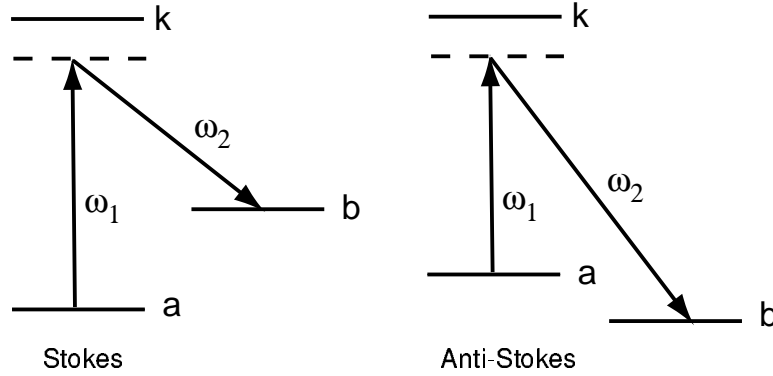


Figure 9.2. Raman emission. Photon ω_2 can be emitted spontaneously, or by stimulated emission.

where the intensity I is now expressed in $\text{W}\cdot\text{cm}^{-2}$. A transition becomes saturated when the transition rate equals the line width, or $\Gamma_{1s,2s} = \gamma$. The required power is only 0.6 W/cm^2 .

By using two-photon Doppler free excitation in hydrogen, Hänsch and his group have been able to achieve an experimental line width of about 30 kHz. The line width is dominated by the time of flight of the atoms across the laser beam. Although 30 kHz may seem large compared to the natural line width of 1 Hz, it is impressively narrow considering that the spectral line width was many MHz not many years ago. For developments, see Ref. [2].

9.5 Raman Processes

9.5.1 Stimulated Raman scattering

We have considered two-photon absorption processes, but stimulated emission can also occur as can be seen from Fig. 9.1.

In this case, the transition $a \rightarrow b$ occurs by absorbing a photon at frequency ω_1 , and emitting a photon at frequency ω_2 . If the transition is stimulated by two applied radiation fields, then the process is known as stimulated Raman scattering. If $\omega_2 < \omega_1$, the emission is called Stokes radiation. If $\omega_2 > \omega_1$, the emission is called anti-Stokes radiation. In either case, the frequencies are related by

$$\omega_1 = \omega_2 + \omega_{ba}. \quad (9.31)$$

Our treatment of the two-photon transition applies, except that one interaction step corresponds to emission, rather than absorption. The change is trivial: the counter-rotating term at frequency $-\omega_2$ in Eq. 9.3, which was dropped, is retained and the rotating term, at frequency ω_2 , is dropped in its place. This merely changes the sign of ω_2 in the ensuing steps, and Eq. 9.13 becomes

$$W_{a \rightarrow b}^{[2]} = \frac{1}{(4\hbar^2)^2} \frac{|H_{bk,2}|^2 |H_{ka,1}|^2 \sin^2(\omega_{ba} - \omega_1 + \omega_2)t/2}{(\omega_1 - \omega_{ka})^2 [(\omega_{ba} - \omega_1 + \omega_2)/2]^2} \quad (9.32)$$

and Eq. 9.14 becomes

$$\Gamma_{ab}^{(2)} = \frac{\pi}{8\hbar^4} \frac{|H_{bk,2}|^2 |H_{ka,1}|^2}{(\omega_1 - \omega_{ka})^2} f(\omega_1). \quad (9.33)$$

where, for a Lorentzian line with width γ , we have

$$f(\omega_1) = \frac{2}{\pi} \frac{\gamma/2}{\gamma^2/4 + (\omega_{ba} - \omega_1 + \omega_2)^2}. \quad (9.34)$$

In terms of the intensity of the two beams, we have, from Eq. 9.20,

$$\Gamma_{ab}^{(2)} = \frac{8\pi^3}{\hbar^4 c^2} \frac{|D_{ka}|^2 |D_{bk}|^2}{\Delta^2} f(\omega_1) I_1 I_2. \quad (9.35)$$

9.5.2 Spontaneous Raman scattering

An important aspect of Raman scattering that differentiates it from two-photon absorption is that the emission of the photon at frequency ω_2 can be spontaneous. Spontaneous emission is generally too slow to be useful at low frequencies but in the optical regime the spontaneous rate can be large enough to cause a sizeable scattering signal. Initially, spontaneous Raman scattering was the only important process: not until the advent of the laser did stimulated Raman scattering become useful.

We can estimate the rate of spontaneous Raman scattering by considering absorption at ω_1 and emission at ω_2 as separate processes, though strictly speaking only one process is involved. We start by evaluating the spontaneous emission at ω_2 . This takes place from a virtual intermediate state, which we shall denote as f . The spontaneous emission rate is given by the familiar expression

$$A_{fb} = \frac{4}{3} \alpha^3 \omega_2^3 |\langle f|r|b\rangle|^2 \quad (9.36)$$

Next, we consider the problem of ‘‘populating’’ the virtual state. The rate of exciting the state can be expressed in terms of the Rabi frequency

$$\omega_R = \mathcal{E}_1 |\langle f|\hat{\mathbf{e}}_1 \cdot \mathbf{d}|a\rangle|/\hbar \quad (9.37)$$

The detuning from state f is $\Delta = \omega_1 - \omega_{fa}$. The transition rate to the intermediate state is approximately

$$\Gamma_{af} \approx \frac{\omega_R^2}{\Delta} \quad (9.38)$$

The time τ the atom can occupy the state, however, is limited by the uncertainty principle to $\tau \approx 1/\Delta$. Hence the probability that state f is occupied is essentially $\Gamma_{af} \tau = \omega_R^2/\Delta^2$. Putting these together, we obtain the rate for spontaneous Raman scattering from a to b :

$$\Gamma_{ab}^{sr} \approx \frac{\omega_R^2}{\Delta^2} \cdot A_{fb}. \quad (9.39)$$

Since $\omega_R^2 \sim E^2 \sim I$, the spontaneous Raman rate depends linearly on the power. The absorption process can be continued, allowing multi-photon Raman transitions to a final state.

References for Chapter 9

- [1] Bassani *et al.*, PRL **39**, 1070 (1977).
- [2] Hänsch *et al.*, PRL **70**, 2261 (1993).