Problem Set 3 ***Molecules and radiative transitions***

Some questions require further reading or looking up of facts, but many answers can be found in the lecture notes. They should be written out nevertheless - important derivations and proofs need to be worked through. The questions have been chosen to cover the ground as economically as possible, so there is little repetition. Starred problems (*) are more challenging and may be omitted initially.

1. (a) Suppose that the valence electrons of the molecule are confined to a region of size a. Show that the electronic energy of the molecule will be of order,

$$E_{\mathrm{e}} = \frac{\hbar^2}{2ma^2}$$

where m is the electron mass.

(b) Show that the vibrational energy of the molecule will be of the order,

$$E_{\mathrm{v}} \approx \hbar\omega_{\mathrm{v}} \approx \sqrt{\frac{m}{\mu}} E_{\mathrm{e}},$$

where $\mu = M_1 M_2/(M_1 + M_2)$ is the reduced mass of the two nuclei. Find an expression for the vibrational frequency ω_{v} in terms of a and μ.

(c) Show that the rotational energy of the molecule will be of order,

$$E_{\mathrm{r}} = \frac{m}{\mu} E_{\mathrm{e}}.$$

(d) For the HCl molecule the equilibrium separation is $R_0 = 0.128\,\mathrm{nm}$. Construct a table giving the energy scale, characteristic frequency, and characteristic timescale of the electronic, vibrational, and rotational motions.

(e) A quantum treatment shows that the energy levels of diatomic molecules may be written in the form,

$$E = E_{\mathrm{e}} + (v + 1/2)\hbar\omega_{\mathrm{v}} + B_{\mathrm{r}} K(K+1).$$

Use your results to find approximate values for ω_{v} and B_{r}, and compare these with the measured values of $\tilde{\nu_{\mathrm{v}}} = \omega_{\mathrm{v}}/2\pi c = 2090\,\mathrm{cm}^{-1}$ and $B_{\mathrm{r}} = 20.8\,\mathrm{cm}^{-1}$.

2*. The interaction potential for a diatomic molecule is parametrized using the Morse potential:

$$V(r) = D\left[1 - \mathrm{e}^{-\beta(r-r_0)}\right]^2,$$

where r_0 is the equilibrium nuclear separation, and D and β are constants.

(a) Treating the diatomic molecule as a classical harmonic oscillator, derive the vibrational frequency, ω_{v}, in terms of the Morse potential parameters and the reduced mass of the system (μ).

(b) Now suppose the molecule is rotating. The induced perturbation in the interatomic potential can be modelled in terms of an effective potential

$$V_{eff}(r) = D\left[1 - \mathrm{e}^{-\beta(r-r_0)}\right]^2 + \frac{\hbar^2 K(K+1)}{2\mu r^2},$$

where K is the rotational quantum number. Determine the new equilibrium distance between the two atoms.

(c) Show that this change in separation leads to a new term in the molecular energy of the form $\Delta E = -B_1 K^2(K+1)^2$, where

$$B_1 = \frac{8}{\hbar^2\omega_{\mathrm{v}}^2}\left(\frac{\hbar^2}{2\mu r_0^2}\right)^3 .$$

3. (a) Assume that transitions between two levels in an atom occur only by radiative processes (namely stimulated emission or absorption, and spontaneous emission). Show that the ratio of the steady-state populations is

$$\frac{N_2}{N_1} = \frac{B_{12}\rho(\omega_{21})}{B_{21}\rho(\omega_{21}) + A_{21}}$$

where $\rho(\omega)$ is the energy density per unit (angular) frequency of the radiation field driving the stimulated processes, ω_{21} is the transition frequency, and A and B are the Einstein coefficients.

(b) What happens to the relative populations in the two levels as the energy density of the radiation is increased to very large values? Would it be possible to create a population inversion this way?

(c) In thermal equilibrium, the radiation density is given by the Planck black-body distribution. Show that this leads to the following relations between the Einstein coefficients:

$$B_{21} = \frac{g_1}{g_2} B_{12} \qquad\qquad A_{21} = \frac{\hbar\omega_{21}^3}{\pi^2 c^3} B_{21}$$

where g_1 and g_2 are the degeneracies of the lower and upper levels.

(d) Does the relation between A_{21} and B_{21} still hold if the radiation is *not* black-body? Is it necessary to assume that the atom has *only* two levels?

4. A blob of matter is placed in a cavity and allowed to interact with blackbody radiation of temperature T. (a) Show that for a transition of angular frequency ω_{21}, the rate of stimulated emission becomes equal to that of spontaneous emission when

$$k_B T = \frac{\hbar\omega_{21}}{\ln 2}$$

(b) Calculate this temperature for the following transitions:

- radio frequencies of 50 MHz
- microwaves at 1 GHz
- visible light of wavelength 500 nm
- X-rays of energy 1 keV

5. (a) Atomic hydrogen is illuminated by light resonant with the $n = 1 \to n = 2$ Lyman-α transition, linearly polarized along the z-axis. Which upper state(s) can be excited?

(b) Calculate the electric dipole matrix element $\langle 1|ez|2\rangle$ for the transition, expressing your answer in units of ea_0 where a_0 is the Bohr radius. (Look up the relevant hydrogen wavefunctions.)

(c) Use your result to calculate the Einstein A coefficient for the transition, and hence the lifetime of the upper state.

(d) A laser capable of producing continuous wave Lyman-α radiation was recently developed, which yielded a power of 1 nW in a beam of 1 mm diameter. Estimate the Rabi frequency if the laser were tuned to resonance with this transition. Comment on the feasibility of observing Rabi oscillations in this system.

6. (a) A two-level atom has eigenstates $|1\rangle$ and $|2\rangle$ of a time-independent Hamiltonian $\hat{H}$ which are separated by an energy $\hbar\omega_0 = E_2 - E_1$. Monochromatic light of amplitude $\mathbf{E}_0$ and angular frequency $\omega = \omega_0 + \delta$ (where $\delta \ll \omega_0$) is incident on the atom. Writing the wavefunction as

$$|\Psi(t)\rangle = c_1(t)\exp(-\imath E_1 t/\hbar)|1\rangle + c_2(t)\exp(-\imath E_2 t/\hbar)|2\rangle$$

show by substitution into the time-dependent Schrödinger equation, with Hamiltonian $\hat{H}+\hat{V}(t)$, that the rate of change of the coefficient c_2 is

$$\dot{c}_2 = -\frac{1}{\hbar}V_{21}c_1\exp(\imath\omega_0 t)$$

where $V_{21} = V_{12} = \langle 1|\hat{V}|2\rangle = \langle 1|e\mathbf{r}.\mathbf{E}_0|2\rangle\cos\omega t$ and $V_{11} = V_{22} = 0$. What assumptions have you made about the "perturbation" $\hat{V}$?

(b) Explain what is meant by the *rotating wave approximation* and justify its use here. Make it, and show that this leads to the following coupled differential equations for the coefficients:

$$\begin{aligned}\dot{c}_2 &= -\tfrac{1}{2}\imath\Omega c_1\exp(-\imath t\delta)\\ \dot{c}_1 &= -\tfrac{1}{2}\imath\Omega c_2\exp(+\imath t\delta)\end{aligned}$$

where the Rabi frequency $\Omega = \langle 1|e\mathbf{r}.\mathbf{E}_0|2\rangle/\hbar$.

(c) Solve for $c_2(t)$ and hence show that, if the atom is in state $|1\rangle$ at $t = 0$, the probability of finding it in state $|2\rangle$ at later time t is given by

$$|c_2(t)|^2 = \frac{\Omega^2}{\Omega^2+\delta^2}\sin^2\left(\tfrac{1}{2}t\sqrt{\Omega^2+\delta^2}\right)$$

Sketch this probability as a function of time for the cases $\delta = 0$ and $\delta = \Omega$.

7*. (a) Find the solutions $c_1(t)$ and $c_2(t)$ to the differential equations in the previous question, with the same initial conditions, but for the case of resonant driving ($\delta = 0$).

(b) What is the state of the system after times given by $\Omega t = \pi/2, \pi, 2\pi$?

(c) Sketch the positions of the Bloch vector at these times, with the convention that the angular co-ordinates (θ, ϕ) on the Bloch sphere are defined by $c_1 = \sin\left(\frac{\theta}{2}\right)$ and $c_2 = \mathrm{e}^{\imath\phi}\cos\left(\frac{\theta}{2}\right)$. Which axis (x, y, z) is the rotation around?

(d) What happens to a general state at co-ordinates (θ, ϕ) after a π-pulse (that is, after a time $t = \pi/\Omega$)? Is this a rotation about the same axis? Is it possible to perform a rotation about an axis orthogonal to this one?

Problem Set 4 ***Light propagation through matter and lasers***

8. (a) Explain what is meant by the terms **homogeneous broadening** and **inhomogeneous broadening**. Give two examples of each class of broadening.

(b) Describe in outline how the natural linewidth of a transition is consistent with the Uncertainty Principle. What is the natural linewidth of a transition between two levels with radiative lifetimes of τ_1 and τ_2?

(c) Show that the full-width at half-maximum linewidth of a Doppler-broadened transition is given by

$$\Delta\nu_{\mathrm{D}} = \nu_0\sqrt{8\ln 2}\sqrt{\frac{k_B T}{Mc^2}},$$

where T is the temperature of the atoms, M their mass, and ν_0 the frequency emitted on the transition by a stationary atom.

9. Figure 1 shows data from measurements of the homogeneous linewidth of the D_1 ($6p\,^2\mathrm{P}_{1/2} \rightarrow 6\mathrm{s}\,^2\mathrm{S}_{1/2}$) and D_2 ($6p\,^2\mathrm{P}_{3/2} \rightarrow 6\mathrm{s}\,^2\mathrm{S}_{1/2}$) transitions in Cs at 894 and 852 nm respectively.

(a) Calculate the Doppler width in MHz of these transitions assuming that the temperature of the Cs vapour is 21 °C, and comment on the relative magnitudes of the inhomogeneous and homogeneous linewidths.

(b) The radiative lifetimes of the D_1 ($6p\,^2\mathrm{P}_{1/2}$ and D_2 ($6p\,^2\mathrm{P}_{3/2}$ levels are 34.75 and 30.41 ns respectively. What is the natural linewidth of the D_1 and D_2 transitions? Is your calculated value consistent with Fig. 1?

(c) Use the data presented to deduce the rate of increase in the homogeneous linewidth in units of $\mathrm{MHz\,Torr}^{-1}$ for each of the two transitions. Explain briefly the cause of this increase in homogenous linewidth with pressure.

(d) What is the mean collision time at a He pressure of 100 Torr for He-Cs collisions?

[The molar mass of Cs is 132.9 g.]

10. (a) The He-Ne laser operates on several $s \rightarrow p$ transitions in neon, including the $5s \rightarrow 3p$ transition at 632.8 nm. Under the operating conditions of the laser, the fluorescence lifetimes of the upper and lower levels are aproximately 100 ns and 10 ns respectively for this transition, and the Einstein-A coefficient is 10^7 s^{-1}. Taking the upper and lower laser levels to have equal degeneracies, determine whether or not it is possible, in principle, for continuous-wave laser oscillation to be observed on this transition.

(b) Repeat the calculation for the $3d^{10}4p\;^2\mathrm{P}_{3/2} \rightarrow 3d^94s^2\;^2\mathrm{D}_{5/2}$ transition at 510 nm in the copper-vapour laser, given that the Einstein A coefficient is 2×10^6 s^{-1} and the fluorescence lifetime of the lower laser level is approximately 10 μs.

11. (a) Show that the optical gain cross-section of a homogeneously broadened laser transition may be written as,

$$\sigma_{21}(\omega - \omega_0) = \frac{\pi^2 c^2}{\omega_0^2} A_{21} g_H(\omega - \omega_0),$$

where $g_H(\omega - \omega_0)$ is the lineshape function of the transition.

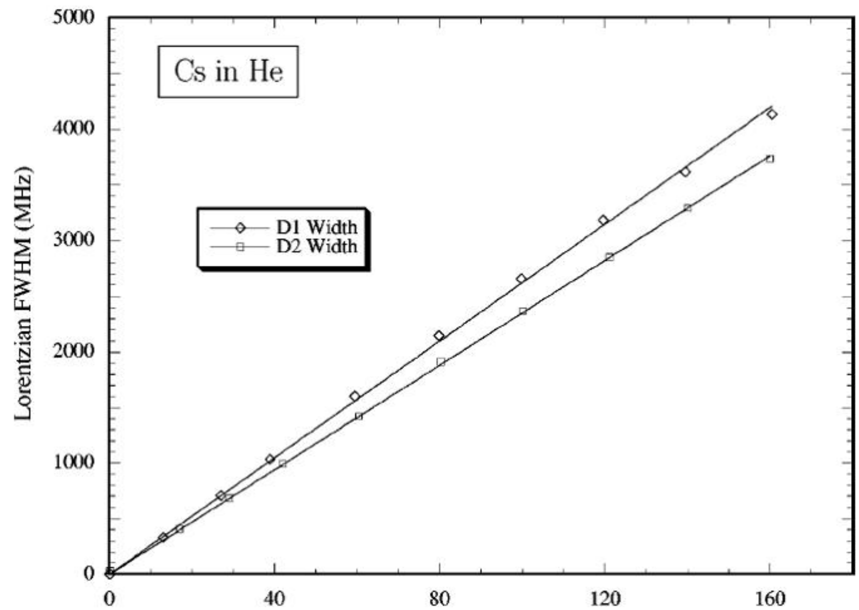

Figure 1: Measured full width at half maximum of the homogeneously broadened component of the D_1 and D_2 lines of Cs as a function of the pressure of helium (data from A. Andalkar and R. B. Warrington *Phys. Rev. A* **65** 032708 (2002)).

(b) Show that for the special case of a purely lifetime broadened transition from an upper level 2 which decays only radiatively to a long-lived lower level 1 the peak optical gain cross-section is given by:

$$\sigma_{21}(0) = \frac{\lambda_0^2}{2\pi},$$

where λ_0 is the vacuum wavelength of the transition.

(c) A laser operates on a transition from an excited electronic energy level of a diatomic molecule in which the two constituent atoms form a molecular bond with each other. This level has a lifetime of 10 ns against radiative decay which is entirely on the laser transition at 250 nm to the unstable ground electronic level, which has a lifetime of 3×10^{-14} s against dissociation into its constituent atoms.

- Calculate the peak optical gain cross-section of the laser transition, assuming that it is purely lifetime broadened.
- What upper level population density would be needed to provide a small signal gain of 0.1cm^{-1}?
- Assuming that 10% of the power input leads to formation of molecules in the upper laser level, calculate the minimum power input per unit volume required to sustain the population of the upper level at the value calculated above. Comment briefly on the implications of this result.

12*. (a) Use a rate equation analysis to show that the gain coefficient of a homogeneously broadened laser transition is modified by the presence of narrow-band radiation of total intensity I to,

$$\alpha_I(\omega - \omega_0) = \frac{\alpha_0(\omega - \omega_0)}{1 + I/I_s(\omega_L - \omega_0)},$$

where ω_L is the laser frequency. Give an expression for the saturation intensity I_s.

(b) Explain in physical terms why the saturation intensity depends on the detuning of the intense beam from the centre frequency of the transition.

(c) On the same graph plot the gain coefficient as a function of frequency ω:

- as measured by a weak probe beam in the absence of any other radiation;
- as measured by a weak probe beam in the presence of a narrow-band beam of intensity $I_s(\omega_L - \omega_0)$;
- as measured by an intense, narrow-band beam of constant intensity $I_s(0)$.

13. A saturated amplifier: A steady-state laser amplifier operates on the homogeneously broadened transition between two levels of equal degeneracy. Population is pumped exclusively into the upper level at a rate of 1.0×10^{18} s^{-1} cm^{-3}. The lifetimes of the upper and lower levels are 5 ns and 0.1 ns respectively. A collimated beam of radiation enters the 2 m long amplifier with an initial intensity $I(0)$. The gain cross section of the medium is 4×10^{-12} cm^2 at the 400 nm wavelength of the monochromatic beam. Calculate the intensity of the beam at the exit of the amplifier when:

- $I(0) = 0.1\,\mathrm{W\,cm^{-2}}$
- $I(0) = 500\,\mathrm{W\,cm^{-2}}$
- $I(0) = 50\,\mathrm{W\,cm^{-2}}$

[*Hint:* In the latter case guess a solution and proceed by iteration]

14. (a) Explain briefly what is meant by the terms **three-level** and **four-level laser**. Discuss why there is a large difference in the threshold power which is required to achieve laser oscillation in these two classes of laser.

(b) A laser cavity is formed by two mirrors of reflectivity 100% and 95%. Calculate the energy absorbed by the active ions which is necessary to achieve pulsed laser oscillation for rods of ruby and Nd:YAG each 50 mm long, 5 mm diameter, and each with an active ion concentration of 4×10^{19} cm^{-3}. Take the pump bands to be at 20 000 cm^{-1} and 12 000 cm^{-1} for the ruby and Nd:YAG laser respectively. For the Nd:YAG laser, you may assume that the peak optical gain cross-section is $\sigma_{21}(0) = 6 \times 10^{-19}$ cm^2.

(c) How will these values compare with the electrical energy which must be supplied to the laser?