Advanced Kinetics   Prof. Martin Quack   Spring Semester 2013

Exercise 2

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Return solution:	to secretary Ruth Schüpbach in E 237 by 24 May 2013
Discussion of solution:	To be announced

2.1. Read chapter 2 of the script Advanced Kinetics until the end of the chapter and ask questions (in writing) as necessary.

2.2. Read the article "Multiphoton Excitation" as distributed and ask questions as necessary. Check the equations (1) - (109) and correct where necessary.

2.3. Read chapter 1 of the Handbook of High Resolution Spectroscopy and ask questions and report possible corrections as necessary.

2.4. Try to derive the matrix elements of the evolution operator $\mathbf{U}$ in the basis $\{a\}$ for the two-level system (equations (83) to (89) in the article "Multiphoton Excitation"). Use the following effective hamiltonian:

$$\mathbf{H}_{\text{eff}} = \begin{bmatrix} 0 & 0 \\ 0 & D \end{bmatrix} + \frac{1}{2}\begin{bmatrix} 0 & V \\ V & 0 \end{bmatrix} = \begin{bmatrix} 0 & \frac{1}{2}V \\ \frac{1}{2}V & D \end{bmatrix}$$

2.5. Show that the solution of the Rabi-two-level problem for the upper state $p_2(t)$ can be described by

$$p_2(t) = |a_2(t)|^2 = \frac{V^2}{V^2 + D^2}\sin^2\left(\frac{t}{2}\sqrt{V^2 + D^2}\right)$$

if one uses the matrix elements given by the equations (83) to (89) and the initial conditions $p_1(0) = 1$ ($a_1(0) = 1$) and $p_2(0) = 0$ ($a_2(0) = 0$).

Chart a plot of $p_2(t)$ for several values of V and D.

2.6. Calculate the Einstein coefficient A_{fi} as well as the natural linewidth for a strong electric dipole-transition at 1100 cm^{-1} with a dipole moment of 0.5 Debye. Calculate the Doppler broadening for $m = 228\,\text{Da}$ and $T = 250\,\text{K}$ and the power broadening for a laser intensity of 100 MW cm^{-2} and 1 $\text{W}\,\text{cm}^{-2}$. All results should be given in cm^{-1} and Hz.

2.7. This exercise demonstrates the order of magnitude of the interaction energies. Solve the following exercise for the radiation of a NIR-diode laser at 10^4 cm^{-1} and of a microwave-maser at 1 cm^{-1} both having an intensity of 1 $\text{W}\,\text{cm}^{-2}$.

a) Calculate the wavelength λ and compare it to the dimension of a typical molecule.

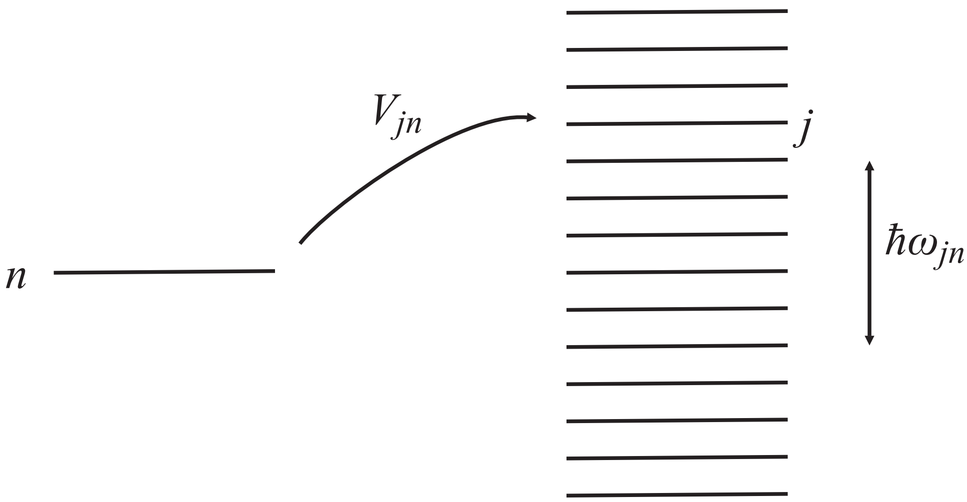
b) Calculate the electric and magnetic field strengths E_0 and B_0 in the plane wave approximation.

c) Calculate the dipole interaction energies for

- ^{15}NO with a electric dipole of 0.16 Debye
- a free unpaired electron with a magnetic dipole of $9.28482 \cdot 10^{-34}$ A m^2
- a free ^{15}N nucleus with a magnetic dipole of $-1.430326 \cdot 10^{-27}$ A m^2

2.8. Solve the problem at the end of chapter 2.7.1 in the Script (exact solution of the degenerate two level "quasi-Rabi" problem).

2.9. **Analysis of the perturbational treatment for transition probabilities**
Read at first chapter 2.4.3 of the Script and follow through every step of the derivation. Ask questions (in writing) where you see problems to follow the derivation. Instead of integrating (2.129) one can in principle evaluate (2.109) and (2.121) numerically for a real spectrum with corresponding couplings. We will use the following model assumptions for a general coupling scheme:



Calculate the expressions given by (2.109) as well as the sum in (2.121). Use the following assumptions on the spectral distribution and the coupling scheme and compare your results with the analytic expression gained from integration of (2.129):

a) The spectrum is equidistant with $\widetilde{\rho} = 10^4$ cm and a constant coupling matrix element $V_{jn} = 10^{-2}$ cm^{-1}. The state n with energy E_n lies in the middle between the next adjacent states j. Sum up a sufficiently high number of states until you reach convergence and plot your results for selected $P_{jn}(t)$ as well as $1 - p_n(t)$. Hint: You may want to sum up states with j ranging from 1 to N (and -1 to $-N$ respectively). The state n then lies symmetrically in the middle between states $j = -1$ and $j = +1$. This results in reducing the summations needed to evaluate (2.121) by a factor of 2!

b) The spectrum is the same as in a) with $\widetilde{\rho} = 10^4\,\mathrm{cm}$, but the coupling matrix elements are distributed statistically with a density $\rho(\widetilde{V}) = \mathrm{const}$ for $-\widetilde{V}_m \leq \widetilde{V} \leq +\widetilde{V}_m$ and zero elsewhere. The distribution should follow the constraint that $\langle|\widetilde{V}|^2\rangle^{\frac{1}{2}} = 10^{-2}\,\mathrm{cm}^{-1}$.
Note: You can use a random number generator to generate the matrix elements $\widetilde{V}_{jn}$. In principle one could use complex numbers of the form $\widetilde{V}_{jn} = \left|\widetilde{V}_{jn}\right| e^{i\alpha}$ with an arbitrary angle $0 \leq \alpha \leq 2\pi$. However the phase factor cancels out when taking $|\widetilde{V}_{jn}|^2$.

c) In a different coupling model one can make the same assumptions as in b) with $\widetilde{\rho} = 10^4\,\mathrm{cm}$, but this time $\widetilde{V}_{jn}$ follows a Gaussian distribution with $\langle|\widetilde{V}|^2\rangle^{\frac{1}{2}} = 10^{-2}\,\mathrm{cm}^{-1}$.

d) Eventually one can combine the assumptions for $\widetilde{V}_{jn}$ made in b) and c) with a statistically distributed spectrum with an average density of states of $\langle\widetilde{\rho}\rangle = 10^4\,\mathrm{cm}$. To get such a spectrum several assumptions are possible. In the easiest case, one would use a fixed interval for possible values of ω_{jk}, e.g. $-5 \cdot 10^4\langle|\widetilde{V}|^2\rangle^{\frac{1}{2}} \leq \dfrac{\omega_{jn}}{2\pi c} \leq 5 \cdot 10^4\langle|\widetilde{V}|^2\rangle^{\frac{1}{2}}$ and choose random values for ω_{jn}. This must be done for every term of the sum until the total number of states N in the defined interval equals the average density of states, i.e. $N = 10^5\langle\widetilde{\rho}\rangle\langle|\widetilde{V}|^2\rangle^{\frac{1}{2}}$ and $\langle\widetilde{\rho}\rangle = N/\left(10^5\langle|\widetilde{V}|^2\rangle^{\frac{1}{2}}\right)$ respectively.

2.10. (optional)
Instead of using perturbation theory and evaluating the expressions (2.109) and (2.121) one can solve the matrix representation of the Schrödinger equation directly. To do this, plug in the corresponding couplings and energies into the Hamiltonian matrix $\mathbf{H}(t)$ (eq. (2.93)) or better $\mathbf{H}^{(a)}$ (eq.(2.98)). Discuss this treatment and perform an examplary calculation. What do you notice and which numerical problems occur?
Hint: To get a solution in a reasonable time you will have to reduce the total number of states used in the diagonalization of the Hamiltonian matrix. One way would be to scale the values of $\widetilde{\rho}$ and $|\widetilde{V}|$ such that the product $\widetilde{\rho}\langle|\widetilde{V}|^2\rangle$ remains constant (i.e. $k = \mathrm{const}$).

2.11. Write equation (2.144) for the transmission coefficient γ in the form $\gamma(x) = 4x/(1+x)^2$ with $x = \pi\Gamma\rho/2$. Show that $\gamma(x)$ has a maximum $\gamma_{\max}(x) = 1$ for $x = 1$ and make a graph of the function $\gamma(x)$. Discuss the limits for k with $\gamma = \gamma_{\max}$, $\Gamma\rho \gg 1$ and $\Gamma\rho \ll 1$.

2.12. **Power broadening.**
Draw a suitable graph of the average excitation $\langle p_2(\omega)\rangle_{\mathrm{t}}$ in Eq. 2.177 and discuss the full width at half maximum in terms of power broadening. Write the equation in terms of a Lorentzian distribution explicitly. Discuss at which laser intensities with a typical transition dipole moment $\mu = 9.85 \cdot 10^{-2}\mathrm{D}$ for HF and a wavenumber $\tilde{\nu} = 3961\mathrm{cm}^{-1}$ becomes the power broadening equal to the Doppler broadening at 10 K and at 300 K for HF. Make the same estimates for the rotational transition

($J = 0 \rightarrow 1$) in the far infrared. So called "permanent" dipole moment of HF in the ground state is about 1.826 D. The rotational constant is $B_0 = 20.546$ cm^{-1}.

2.13. Discuss the power series mentioned in "1. Anmerkung" at the end of chapter 2.6. in detail, add some more terms and look for their behavior.

2.14. Try to solve the problem at the end of section 2.7.1.