PC Advanced Kinetics FS 2013

Martin Quack

Exercise 3 (holiday exercise)

Responsible:	Robert Prentner, Eduard Miloglyadov, Luboš Horný, Sieghard Albert
Return of solutions	in the office E 237 of the secretary until end of May
Date and place of discussion	will be announced on the website and by email

3.1. Read chapter 2 and 3 of Advanced Kinetics script as far as distributed and comment in writing, where you have questions or detect errors or inconsistencies. Read as a repetition also again Chapter 3 of PC II and make connections between experiments and Advanced Kinetics Theory. Work through chapter 3 of Advanced Kinetics course, even those parts, which have not been treated in details in the course.

3.2. Read the paper by Donley et al. *Mol. Phys.* (2001) **99**, 1275-1287 and make comments where something is not clear to you or appears wrong or misprinted.

3.3. Expressions (2.74) and (3.89) give an inequality for the recurrence time τ_{R} in spectra with average density of states $\langle \rho\,(\mathrm{E}) \rangle$

$$\tau_{\mathrm{R}} \geq h \langle \rho\,(\mathrm{E}) \rangle \tag{1}$$

where it is known that the recurrence time in an equidistant spectrum is given by the equation. Show that the inequality holds if the spectrum is non-equidistant.

3.4. Aufgabe 1 at the end of section 3.1 (Eqs. 3.18 and 3.12) (density of prime numbers).

3.5. Aufgabe 2 at the end of section 3.1 (Eqs. 3.2 and 3.4, Boltzmann equilibrium with Einstein kinetics).

3.6. (optional) Aufgabe 3 at the end of section 3.1 (logarithmic integral and prime numbers).

3.7. The radiative excitation scheme in Fig 2.24 can also be treated in terms of a Bixon-Jortner like situation presented on Fig. 1 where the excitation is a two level problem for a zero order hamiltonian, but there is intramolecular coupling V_{intra} in the field free molecule to many non-absorbing background levels leading to exponential decay of level 2.

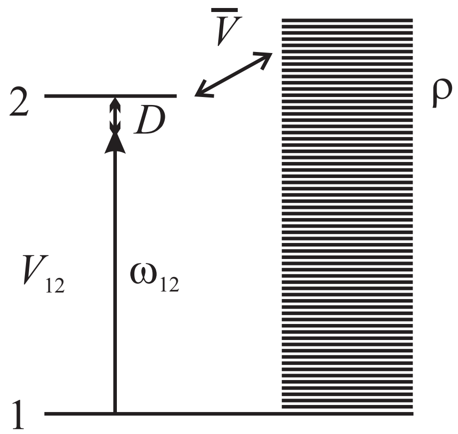

Figure 1: The radiative excitation scheme in terms of a Bixon-Jortner like situation.

This exponential decay is sometimes modeled with a complex energy eigenvalue for level 2

$$E_2 = \mathrm{Re}(E_2) - i\gamma_2/2, \tag{2}$$

where γ_2 is real and positive.

(a) Show that this corresponds to an exponentially decaying population of level 2, if the total wavefunction is given by

$$\Psi(t) = c_1\varphi_1 \exp(-2\pi i E_1 t/h) + c_2\varphi_2 \exp(-2\pi i E_2 t/h). \tag{3}$$

(b) Try to solve the two level problem in quasiresonant approximation by calculating the $\boldsymbol{U}^{(\mathrm{a})}$-matrix element for the time evolution.

(c) Solve for the population $p_2(t)$ of the level 2 with $p_2(0) = 1$ and the real coupling matrix elements $V_{12} = V_{21} = V$.

(d) Compare the result of b) and c) with the results of the Excercise 2 with real eigenvalues E_1 and E_2.

(e) Consider the special effective Hamiltonian matrix

$$\frac{\boldsymbol{H}_{\mathrm{eff}}}{\hbar}/\mathrm{s}^{-1} = (\boldsymbol{X} + \frac{1}{2}\boldsymbol{V})/\mathrm{s}^{-1} = \begin{pmatrix} 0 & 1 \\ 1 & -2i \end{pmatrix} \tag{4}$$

and discuss the solution of the time dependent Schrödinger equation for this case.

(f) Try to solve also for the general $\boldsymbol{U}^{(a)}$-matrix with $E_1 = \mathrm{Re}(E_1) - i\gamma_1/2$ and $E_2 = \mathrm{Re}(E_2) - i\gamma_2/2$ both being complex. γ_1 is real and positive.

3.8. Criticize the model in 3.7 and suggest a better model for such dynamics with radiative excitation and intramolecular dynamics.

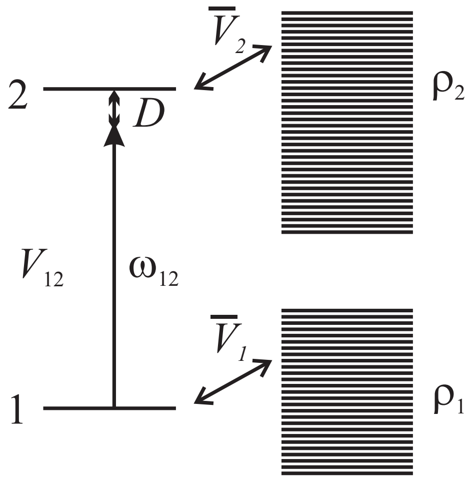

Figure 2: Graphical model

3.9. Try to solve an analogous model (see Fig. 2) with both a lower level and an upper level being coupled to a dense set of states and discuss the physical implications.

3.10. Treat the exercises given in chapter 3 of the script to the extent that you find time to do so (treat as many as you can accordingly to your own choice).

3.11. (Voluntary Reading) Read the chapter "Fundamental Symmetries and Symmetry Violations from High-resolution Spectroscopy" (v. 1, p. 659) of the Handbook of High Resolution Spectroscopy and formulate your questions, as they arise (in writing).

3.12. Try to work out in detail the solution to exercise 3 at the end of section 3.5 (on Laplace transformations).