

Questions and Exercises

Chapter 2

1. A closed electronic shell of an atom becomes spherically symmetric. Why?
2. Discuss the two angular momentum coupling schemes, LS and jj coupling. How can it be determined experimentally which coupling scheme is relevant for a particular atomic configuration?
3. Why do rare-earth elements (lanthanides) have similar chemical properties and sharp spectral lines even when incorporated in a crystal matrix?
4. What can be learned from measurements of
 - a) Landé g_J factors,
 - b) Stark effect constants (polarizabilities),
 - c) Magnetic hyperfine structure constants,
 - d) Isotopic shifts,
 - e) Radiative lifetimes?
5. What characterizes the Zeeman and the Paschen–Back effects, respectively? What is the meaning of the non-crossing rule?
6. Explain why the Zeeman effect is linear in the applied magnetic field B while the (non-hydrogenic) Stark effect is quadratic in the electric field E .
7. Why are there magnetic sublevels which progress with a linear energy displacement as a function of the magnetic field? Discuss the fine-structure and the hyperfine-structure cases.
8. The Stark effect:
 - a) Write down the expression for the Stark shift of a fine-structure level with quantum numbers J and m_J .
 - b) Explain the particular dependence on the electric field strength for non-hydrogenic states.
 - c) Can you see any practical application of measurements of the Stark effect?
9. In a strong electric field an atom can be ionized. Discuss this phenomenon and under what conditions it can most easily be studied.

10. The atomic hyperfine structure is due to the interaction between the nucleus and the electronic shell. Discuss the origin of the interactions and what nuclear and electronic properties are being tested. Give some example of hyperfine splitting (e.g. for a state with electronic spin $J = 3/2$ and nuclear spin $I = 3/2$) with reference to the mathematics governing the structure.
11. Discuss electrical hyperfine structure. What is its origin? What can be learned from it? Under what circumstances (quantum numbers etc.) can it be observed?
12. Hyperfine structure:
 - a) What is the typical size of atomic hyperfine structures?
 - b) Which hyperfine structure quantum numbers F are possible for a $J = 3/2$ state in an $I = 5/2$ atom?
 - c) For what types of electrons does the Fermi contact interaction yield a large contribution to the hyperfine structure?
 - d) How can an inverted hyperfine-structure level sequence occur?
 - e) How does the electric hyperfine structure show up in high-resolution spectra?
 - f) What are the requirements for the I and J quantum numbers to make an electric quadrupole interaction possible?
13. When do the normal mass isotopic shift and the volume shift dominate?

Chapter 3

14. What is the essence of the Born–Oppenheimer approximation?
15. Discuss the vibrational energy of a diatomic molecule. How can the simplest quantum-mechanical model be extended for realistic molecules? Explain how observed deviations from the simplest model can be utilized for temperature measurements in molecular gases.
16. What information about a diatomic molecule can be obtained from the rotational constant B ?
17. Discuss how the vibrational spectrum is influenced in electronic transitions in diatomic molecules considering the Franck–Condon principle.
18. Why are electronic molecular transitions necessary in order to be able to observe band-heads (bent-over Fortrat parabolas)? What determines if a band is shaded to the red or to the violet?

Chapter 4

19. Discuss the energy-level diagram and the spectrum of the helium atom. Which types of emission lines are seen in the spectrum? The calcium atom

also has two electrons outside its closed shells. Discuss the differences between the calcium and helium spectra!

20. What is phosphorescence?
21. Discuss Rayleigh and Raman scattering.
22. When the sublevels of an excited state are statistically populated, the emitted light becomes isotropic and non-polarized. What does this mean in terms of the relation between π and σ radiation?

Chapter 5

23. Describe the physics behind the X-ray absorption spectroscopy method and discuss its refinement, EXAFS.
24. Discuss the PIXE method for chemical analysis.
25. What is common to XPS (ESCA) and Auger spectroscopy, and what is different? Discuss how the techniques can be used for identifying chemical compounds.
26. Discuss Auger electron spectroscopy. Why are the requirements for energy sharpness of the exciting X-ray radiation more relaxed than for normal electron spectroscopy (XPS)?

Chapter 6

27. What is the meaning of the two concepts homogeneous and inhomogeneous linewidths?
28. Electron synchrotrons provide radiation of great importance for spectroscopy. Describe briefly the generation process and the properties of the radiation.
29. What factors determine the resolution of the following spectroscopic instruments:
 - a) Grating spectrometer
 - b) Fabry-Pérot interferometer
 - c) Fourier transform spectrometer
30. What is the difference between an Ebert and a Czerny-Turner spectrometer?
31. Mention three different types of detectors for IR radiation.
32. Describe the construction and use of an optical multichannel analyser system with time-gating possibility.

33. How short-lived would an excited level have to be to exhibit a natural radiative width of the same order of magnitude as the Doppler width (visible light)? How does the Doppler broadening depend on the temperature and the mass of the gas particles?
34. What is the use of neutral density filters?
35. Transmission of media:
 - a) What window material is transparent at the shortest possible optical wavelengths, and what is the wavelength cut-off?
 - b) Below what wavelength can spectroscopic investigations not be performed without evacuating the air from the apparatus?
 - c) Below what wavelength can ground-based astronomers not observe the stars using optical techniques?
 - d) How far out into the IR spectral region can quartz be used as a lens material?
 - e) At what wavelength towards the UV region does the atmosphere cut off sunlight, and what molecule is responsible for the absorption?
 - f) Discuss the transmission of sea water.
36. Discuss the problems that occur when one wants to push optical spectroscopy from the visible region down towards shorter wavelengths (transmission in optical components, air etc.).
37. What practical problems might be encountered when performing satellite-based measurements of the reflectance of the Earth's surface in order to do Earth-resource inventories?
38. Spectroscopic lineshapes:
 - a) How does pressure influence the linewidth of a spectral absorption line?
 - b) Discuss briefly how a vertical atmospheric concentration profile can be obtained by satellite limb absorption measurements for a particular species?
39. Why are hollow-cathode lamps used in connection with atomic absorption spectrometry?
40. Describe the calibration procedure for atomic absorption spectrometry (establishing a calibration curve, or using the standard addition method).
41. Discuss satellite remote sensing of land and water areas using passive optical techniques.

Chapter 7

42. Precession:
 - a) Show that a quantum-mechanical magnetic moment precesses around a magnetic field.
 - b) Are there any clear manifestations of such a precession in any laser spectroscopic experiment?
 - c) The precession of a magnetic moment can be used for the detection of nuclear magnetic resonance signals. How?
43. Briefly explain the Atomic Beam Magnetic Resonance (ABMR) technique according to Rabi. Why can only certain types of magnetic resonance transitions be seen? What determines the linewidth of the transitions?
44. Briefly discuss the level-crossing spectroscopic method. The zero-field level-crossing effect is understandable also classically. How?
45. Level-crossing signals at certain magnetic fields can be used for determining hyperfine structure constants of excited states. Why is the number of detectable signals quite limited? Describe in general terms how hyperfine-structure information can be deduced from the experimental data.
46. When is it advantageous to use the level-crossing method instead of the optical double resonance technique?
47. What is the advantage of using the Fourier Transform NMR method instead of a scanning technique?
48. Discuss microwave radiometry, applied to environmental monitoring and to astronomy.
49. Discuss radio astronomy paying special attention to telescope resolution, aperture synthesis and microwave lineshapes.
50. How can a reasonable spatial resolution still be obtained when imaging in the microwave region (radar, radio astronomy)?

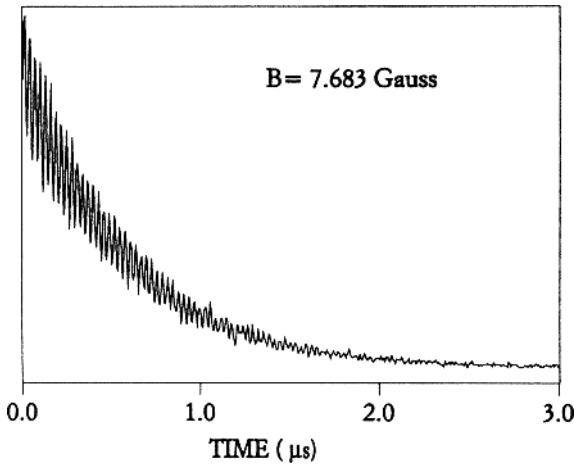
Chapter 8

51. Why is it easier to achieve a maser than an X-ray laser?
52. How does the laser process start?
53. Why is a combination of an oscillator and an amplifier preferred to a strongly pumped laser oscillator only?
54. Discuss the CO₂ laser: molecular basis, arrangement, and spectroscopic possibilities.

55. The dye laser and the titanium-doped sapphire ($\text{Ti} : \text{Al}_2\text{O}_3$) laser are both capable of generate pulsed or continuous tuneable radiation. Discuss the advantages (possibilities) and disadvantages (limitations) of the two different types.
56. Mode locking:
- Describe the generation of short laser pulses by mode locking.
 - What is the relation between mode locking and a spectroscopic grating in terms of interference?
57. Describe the general idea of chirped pulse amplification.

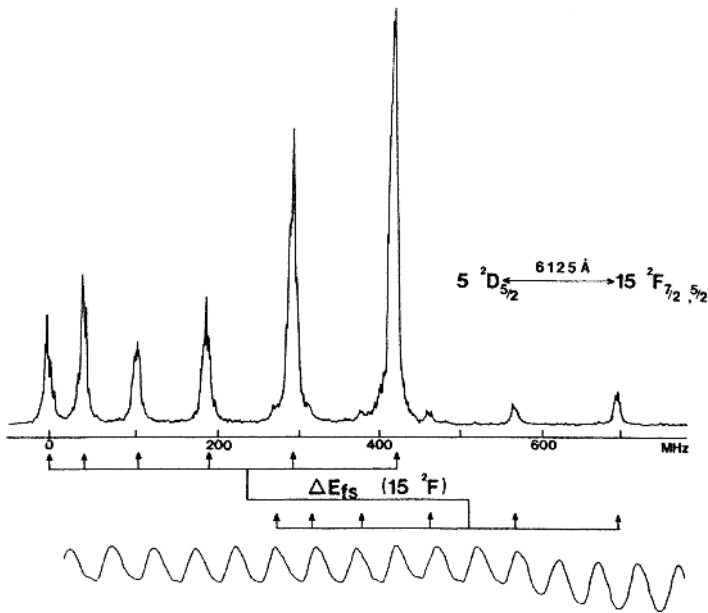
Chapter 9

58. Give some characteristics of Rydberg atoms.
59. Indicate some advantages of laser spectroscopic analytical techniques.
60. Laboratory trace gas monitoring: Discuss and compare the following methods: optoacoustic spectroscopy, cavity ring-down spectroscopy and frequency modulation spectroscopy.
61. Describe the Zeeman quantum beat method using laser excitation. If a Landé g factor of 1.500 is determined for an atomic state designated 3P_1 , how would you comment on such a result?
62. Discuss the relation between the Zeeman quantum beats and the Hanle effect.
63. In a Zeeman quantum-beat experiment of the $4p^35s \ ^5S_2$ state in the selenium atom the excitation was performed at 207 nm from the ground state $4p^4 \ ^3P_2$ using linearly polarised light from a pulsed laser. In the decay a signal curve in an external magnetic field as illustrated below was obtained.
- Comment on the fact that the selected transition can be used for the excitation. Is this expected?
 - Evaluate the natural radiative lifetime τ and the Landé g_J factor for the state from the recording.
 - Comment on the g_J factor result. Is the result expected?
64. In Zeeman quantum-beat measurements oscillations superimposed on an exponential decay of the fluorescence light intensity are observed. In experiments on ytterbium atoms with zero nuclear spin the beat frequency for the $6s19d \ ^1D_2$ state was 31.52 MHz for a fixed magnetic field, in which the beat frequency for the signal from the $6s6p \ ^3P_1$ state (with known g_J value = 1.493) was 46.05 MHz. What is the g_J value of the $6s19d \ ^1D_2$ state? Is the result expected? Discuss what can be learned from measurements of Landé g_J factors.



Qu. 63.

65. The spectrum below is recorded in fluorescence from a collimated cesium atomic beam, excited on the D–F transition by a single mode tunable dye laser. The D level is populated in cascade decay from the P state, which is excited with a broadband CW dye laser. The Fabry–Pérot fringes at the bottom correspond to a free spectral range of 50 MHz.



Qu. 65.

- a) How can it be seen from the spectrum that the magnetic dipole interaction constant (a) of the D-state is negative?
 - b) Give an approximate value for the a constant.
 - c) What is the nuclear spin of the single cesium isotope in the beam?
 - d) What is the fine-structure splitting of the F doublet (which has a negligible hyperfine structure)? Could this splitting be resolved using conventional Doppler-broadened spectroscopy?
66. Describe the saturation spectroscopy method. Why is the polarization spectroscopy version of the technique attractive? How can the technique be used to create a secondary standard for the metre unit?
 67. Describe the basic physics behind high-harmonic generation in gases. Discuss some applications of such radiation.
 68. Why is it interesting to study chemical reactions on the femtosecond timescale? How can such studies be achieved?
 69. Discuss how fundamental information on the hydrogen atom and basic atomic theories can be obtained by simultaneously performing two Doppler-free laser spectroscopic investigations on two different energy splittings in the atom.
 70. Why is it interesting from a spectroscopic point of view to be able to cool down atoms to very low translation energies (temperatures)?
 71. Discuss techniques to achieve laser cooling of atoms.
 72. How can a strongly forbidden atomic transition be used as a frequency standard with a strong spectroscopic signal in spite of the low transition probability (the shelving phenomenon)?
 73. What is the general idea behind Bose–Einstein condensation experiments?
 74. Discuss atomic optics and the concept of an atomic laser.

Chapter 10

75. Describe the CARS method and its application to combustion diagnostics.
76. How can the laser Doppler velocimetric method be used to measure flow velocities in particle-rich gas flows?
77. Describe air pollution measurements using the lidar method.
78. Why is it possible to obtain information on atmospheric gaseous pollutants using laser radar although elastic backscattering from particles is primarily observed?

79. Discuss the principles that allow laser-induced chemistry to be performed.
80. Discuss the penetration of laser light of different wavelengths into tissue and how this governs the medical applications of lasers.
81. Discuss the fluorescence diagnostics and photodynamic treatment of cancer tumours using tumour-seeking drugs and laser light.

Questions not pertaining to any special chapter

82. What spectroscopic method would you choose for the following tasks (explain)?
 - a) Determine the amount of cadmium in a blood sample from a patient.
 - b) Determine the amount of vanadium in a steel alloy.
 - c) Determine the average concentration of sulphur dioxide 5 m above street level.
 - d) Determine the amount of organic oil admixed in a sample of sea water after a tanker accident.
 - e) Determine the temperature of a welding torch flame.
 - f) Determine the water contents in newly harvested grain.
83. What spectroscopic method would you choose for the following tasks (explain)?
 - a) Determine the average concentration of atomic mercury in the smoke from a coal-fired power plant.
 - b) Determine the concentration of chlorophyll in leaves from a maple tree.
 - c) Monitor the growth of an oxide layer on a metal surface.
 - d) Determine the content of CO_2 in respiration air from a patient's lungs.
 - e) Determine if the ozone hole over Antarctica is increasing.
 - f) Determine if the red light from a piece of fireworks is due to strontium.
84. Suggest and explain (in a few words) a suitable spectroscopic method for the following tasks:
 - a) Determination of the absorption spectrum of a powder such as flour.
 - b) Measurement of the magnetic field in a Helmholtz coil system capable of producing a field strength of 0.1 Tesla.
 - c) Monitoring of thin oil films on metal surfaces.
 - d) Precision determination of the Rydberg constant.
 - e) Determination of the content of CO in the exhaust gases from a car at the car inspection station.
 - f) Determination of whether the black paints in two paintings, said to be by Rubens, are really of the same type.

85. What spectroscopic method would you choose for the following tasks (explain)?
- Determine the amount of mercury in the pikes in a lake in an industrial area.
 - Determine the concentration of sulphur dioxide 100 m above the top of the Big Ben Tower in London.
 - Determine if a sheet metal surface is really clean from press oil before it enters the painting stage at a car assembly plant.
 - Determine the amount of lead in the leaves of a tree standing close to a highway.
 - Determine if a metallic surface, prepared for fundamental surface physics research in an ultra-high vacuum system, is really clean.
 - Determine the concentration of carbon dioxide in indoor air.
86. Suggest, with a short explanation, a suitable spectroscopic method for the following tasks:
- Determination of the CO contents in car engine exhausts.
 - Determination of the total flux of SO₂ from a volcano.
 - Study of the start of corrosion/oxidation on a metal surface.
 - Determination of the Li contents in blood serum (this relates to certain psychiatric diseases).
 - Determination of the oil contents in sunflower seeds.
 - Determination of the average concentration of ozone in the stratosphere.
87. Suggest, with a short explanation, a suitable spectroscopic method for the following tasks:
- Calibration of the magnetic field in a coil designed for fields up to 0.001 Tesla (10 Gauss).
 - Determination of the gas temperature in the hot gas stream of a jet engine.
 - Detection of a major oil spill at sea.
 - Precision determination of the mass of an ion.
 - Study of the details of a molecular dissociation process.
 - Efficient detection of gas leaks in the petrochemical industry.
88. What factors determine the resolution obtainable using the following spectroscopic methods?
- Optical double resonance.
 - Optical pumping.
 - Laser saturation spectroscopy.
89. Discuss atomic clocks operating at microwave and optical frequencies (brief operating principles). Give examples of applications where a very high time precision is required.
90. Electron synchrotrons provide radiation of great importance for spectroscopy.

- a) Describe briefly the generation process and the properties of the radiation.
 - b) Compare synchrotron radiation with laser radiation and give some hints when one or the other is to be preferred.
91. Discuss the medical applications of X-rays. Recently, laser-produced X-rays have been generated. What are the possible future advantages in medicine using such X-rays?
92. In certain cases the energy levels of an atom are slightly modified by the environment, which can be utilized for chemical analysis and chemical structure determinations. Discuss the following cases:
- a) Electron spectroscopy.
 - b) Nuclear magnetic resonance spectroscopy.
93. How are picosecond laser pulses generated using mode locking? What parallels do you see between this process and the conditions for a diffraction grating, a Fabry–Pérot interferometer or a hologram?
94. Discuss hyperfine structure and isotopic shifts. What are the origins of these effects? What can be learned from these phenomena? Certain experimental techniques can be used for measuring hyperfine structures as well as isotopic shifts, while others are only useful for hyperfine-structure measurements. How does this arise?
95. Give approximate values for the following quantities (numbers without calculations are OK; numbers derived after calculations are also OK, but take more time!):
- a) Doppler broadening of spectral lines in the visible wavelength region.
 - b) Thermal velocities of atoms/molecules at room temperature.
 - c) kT at room temperature.
 - d) Frequency of visible light.
 - e) Energy in eV for visible light.
 - f) Number of atoms/molecules per cm^3 of gas at atmospheric pressure.
 - g) Distance light travels in 1 ns.
 - h) Size in eV of vibrational splittings in simple diatomic molecules.
 - i) Energy of X-rays in eV.
 - j) Cavity mode spacing in a normal laboratory He–Ne laser.
96. Laser mode locking:
- a) Describe the generation of short laser pulses by mode locking.
 - b) What is the relation between mode locking and a spectroscopic grating in terms of interference?
 - c) Is it possible to generate a 100 attosecond pulse (10^{-16} s) in the visible part of the spectrum?
97. Discuss the relation between the Hanle effect and Zeeman quantum beats following short laser light excitation of an ensemble of free atoms.

98. Mark with an (x) in the table below if the method listed is useful for the determination of the atomic physics properties indicated:

	Hyperfine coupling constants a, b	Scalar polarisability α_0	Natural lifetime τ
Level-crossing spectroscopy			
Doppler-free two-photon abs.			
Quantum-beat spectroscopy			
Saturation spectroscopy			

99. How can population differences be created between atomic sublevels to be used in resonance investigations of structures? Discuss three principally different methods.
100. Explain briefly why the optical Doppler effect is eliminated in the following types of experiments:
- Collimated thermal atomic-beam spectroscopy.
 - Accelerated ion-beam spectroscopy (irradiation along the beam).
 - Saturation spectroscopy.
 - Two-photon absorption spectroscopy.
 - Optical double resonance.
 - Spectroscopy on a sample of laser-cooled atoms.
101. Describe in a few words the meaning of the following concepts:
- Core polarization.
 - Bragg relation.
 - Hyperfine anomaly.
 - Equivalent width.
 - Magic angle.
 - Coherent detection.
102. Explain the meaning of the following abbreviations, and write one sentence describing each concept:
- QED
 - EXAFS
 - ESR
 - SAR
 - CARS
 - DIAL
 - NMR
 - MRI
 - DOAS
 - BEC
 - CPA
 - VLBI

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Chapter 1

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Chapter 2¹

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¹ Note that we make reference only to the European edition of Scientific American. The number following the slash gives the issue number. Page numbers for the American edition differ slightly.

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Chapter 7

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Chapter 8

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Chapter 10

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