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A collection of exercises for the course on Atomic and Molecular Physics Q3 + MN1 (English version)

A collection of exercises for the course Atomic- and molecular physics MN1+Q3

(answers are given directly after each problem in parentheses)

Chapter 1. Atoms, electrons and photons

The photoelectric effect.

1. The maximum wavelength that can be used in photoemission of electrons from a calcium surface is 462 nm. Suppose that you illuminate a surface of this kind with radiation having a wavelength of 280 nm. What would be the maximum kinetic energy and speed of the electrons leaving the material? ($E_{kin}(max)$ = 1.74 eV)

2.

a) Calculate the maximum energy of photoelectrons expelled from an aluminium surface by photons with a wavelength of 200 nm. The work function for aluminium is 4.2 eV. ($E_{kin}(max)$ = 2.0 eV)

b) How large would the stopping voltage be for these electrons? Make a schematic drawing of an arrangement that could be used to measure the stopping voltage and also Planck's constant. Show in the figure the electric connections and voltage supplies that would be necessary to carry out the experiment. (V = 2.0 V)

c) Would it be possible for photoelectrons to leave the surface with lower energy than the maximum energy? Explain your answer briefly. (Yes, the photoelectrons may become scattered and lose energy on their way through the material)

d) If the intensity of the incident radiation is 2,0 W/m^2, how many photons hit the surface per time unit? ($2.0 \cdot 10^{18}$ /s)

3. A calcium surface is irradiated with light and the stopping potential of the electrons emitted from the material is measured. The measurements were carried out for some different wavelengths and the result is tabulated below. Use the data to construct a graph which can be used to derive both

a) the work function of calcium and (ϕ = 2.69 eV)

b) a value of Planck's constant. ($h = 6.597 \cdot 10^{-34}$Js)

You may preferably use a computer program like Kaleida Graph to do the analysis.

Wave-length	415	387	368	352	345	325	315	290

Stopping voltage	0,28	0,46	0,67	0,81	0,94	1,11	1,25	1,53

Photon emission

1. The wavelengths of the visible light cover only a very small part of the electromagnetic spectrum and we know the wavelength range. In atomic physics we often use the unit electron volts (eV). Which are the limits of the visible light expressed in this unit?

2. Visible light can be emitted when atoms lower their energy by de-excitations. The radiation from hydrogen atoms forms Rydberg series. The question is if any of these is located in the visible region? Your answer should be supported by simple calculations, whatever the result. If you find a series, what is the name of it?

Answers:
(The Balmer series $n \rightarrow 2$)

Transition	ΔE (eV)	Wavelength (nm)	Colour
3->2	1.89	656.4	Red
4->2	2.55	486.2	Blue
5->2	2.86	434.1	Violet

The Bohr atom

1. In the Bohr model the electron is supposed to move in circular stable orbits around the nucleus. Show that in this motion the kinetic energy E_{kin} multiplied by two is equal to half the potential energy V with opposite sign, i.e.

$$E_{kin} = -\frac{1}{2}V$$

Answer:
($V=-ke^2/r$ $\quad F=ke^2/r^2=mv^2/r$ --> $E_{kin} = 1/2mv^2 = 1/2ke^2/r$)

2. Bohr postulated that the orbital angular momentum L of the electron is quantised and that it is a integer multiple of $h/2\pi$, that is

$$L = mvr = n\hbar$$

where n = 1, 2, 3, ... Alternatively stated, only such orbitals which fulfil this relationship are stable.

Show that this expression can be obtained from the de Broglie relationship for the wave-particle duality if one assumes that the wavelength is an integer number of the circumference.

Answer:
($n\lambda = nh/(mv) = 2\pi r$ → $nh/2\pi = mvr$)

3.

a. Show that if you use the relationships of problem 2 above along with the equations that are obtained from ordinary classical mechanics and electricity the following expressions are obtained for the radius r_n of the orbit and the speed v_n of the electron,

$$r_n = \varepsilon_0 \frac{n^2 h^2}{\pi m e^2}$$

$$\upsilon_n = \frac{1}{\varepsilon_0} \frac{e^2}{2nh}$$

where m is the mass of the electron and e is the electronic charge.

b. The above expressions are obtained under the assumption that the mass of the nucleus is infinite. Show that a more correct expression incorporates the reduced mass rather than the mass of the electron.

4. The Bohr radius is defined as

$$a_0 = \varepsilon_0 \frac{h^2}{\pi m e^2}$$

a. Calculate the value of the Bohr radius. (0.529 Å)

b. Calculate the radius of the orbits with the main quantum number n = 1, 2, 3 and 4.

Answer:

n	1	2	3	4
Radius	a_0	$4a_0$	$9a_0$	$16a_0$

5. Use the expression of problem 3 to calculate the speed of the electron in the orbits described by n = 1, 2, 3 and 4. The equations were derived for a non-relativistic system. Is this assumption reasonable?

Answer:

n	1	2	3	4
v (m/s)	$2.19 \cdot 10^6$	$1.09 \cdot 10^6$	$7.29 \cdot 10^5$	$5.47 \cdot 10^5$

6.

a. Show that in the Bohr model the kinetic, potential and total energies can be written as

$$E_{kin} = \frac{1}{\varepsilon_0^2} \frac{me^4}{8n^2 h^2}$$

$$V = -\frac{1}{\varepsilon_0^2}\frac{me^4}{4n^2h^2}$$

$$E = -\frac{1}{\varepsilon_0^2}\frac{me^4}{8n^2h^2}$$

Notice that the total energy is negative, which corresponds to bound states, and that there are obviously an infinite number of such states.

b. Calculate the energy of the five lowest energy states of the hydrogen atom in the eV unit. The lowest state is called the ground state. Remember its energy, it will appear in many different connections.

Answer:

n	1	2	3	4	5
E_n(eV)	-13.6	-3.40	-1.51	-0.85	-0.54

c. The ionisation energy, or binding energy, is the energy required for the removal of an electron entirely from the atom in the ground state. What is the ionisation energy of hydrogen?
(13.6 eV)

7.

a. In the lecture notes we have written the hydrogen energy levels as

$$E_n = -\frac{hcR}{n^2}$$

where n = 1, 2, 3,…. Also, c is the speed of light and R is the Rydberg constant.

Use the other expression for the energy levels obtained in problem 6 to derive an expression which can be used to calculate the value of the Rydberg constant R from general physical constants. Which value of R do you obtain? Compare with handbook data.

8.
a. Show that the energy levels of a hydrogen-like system, like He^+, can be obtained from the following expression where a_0 is the Bohr radius.

$$E_n = -\frac{Z^2}{2a_0n^2}$$

b. Calculate the energy levels of He^+ and compare with the corresponding results for the hydrogen atom. Are there any similarities?

9.
a. Calculate the value of the Rydberg constant using the reduced mass. What is the difference in % between this value and the value you obtain using simply the electron mass? (0.054 %)

b. Harold Urey discovered the deuterium (D) atom in 1932 by observing the difference in wavelength of radiation obtained from D atoms and ordinary hydrogen (H) atoms due to the mass difference. Calculate the energy shift between D and H radiation. ($\Delta E = 0.51$ meV)

10. The energies calculated for the $n = 2$ and $n = 3$ energy levels of hydrogen are the same as the $n = 4$ and $n = 6$ levels of helium if the masses of the nuclei are neglected. Assuming that the transitions between these energy levels were observed in an optical spectrum from a sample containing both H and He atoms, which energy difference should be expected between the lines? (1.03 meV)

Continuous radiation

1. Suppose that the average wavelength emitted by a 60 W light bulb is 580 nm. Calculate the number of photons produced per second if 10% of the power is transferred into light emission. ($1.69 \cdot 10^{20}$ /s)

2. Use Planck's radiation law to construct a diagram that shows the effect as a function of the wavelength of the emitted radiation from the sun (surface temperature = 6000 °C) and from the star Sirius (surface temperature = 20000 °C). You may use a computer along with for example a spreadsheet program to reduce the time consumption.

3. Use the Wien displacement law to calculate the wavelength for maximum emitted power for the two stars of problem 2. Compare your result with the curves obtained in problem 2.
Answer:

T(K)	6000	20000
λ_{max}(nm)	483	145

Compton scattering

1. A photon with wavelength 0.063 nm undergoes Compton scattering changing its motional direction by 90°.

a) Calculate the wavelength of the scattered photon. (0.0654 nm)

b) Calculate the energy of the scattered electron. (729.8 eV)

2. A photon having a wavelength of 0,125 nm is Compton scattered through an angle of 90°. Calculate under the assumption that the electron was initially at rest

a) the wavelength of the scattered photon (0.1274 nm)

b) the energy and direction of the electron after the collision. (E = 188.9 eV, angle =44,5°)

3. Consider a beam of photons each having a wavelength of 0,15 nm hitting a material. Calculate the maximum kinetic energy of electrons produced by Compton scattering and the energy of photoelectrons emitted from the valence shell ($E_B \approx 0$). Would it be appropriate to calculate the speed of the photoelectrons using non-relativistic equations?
($E_{kin}(max)$ = 259 eV $E_{photoelectron}$ = 8265 eV (rel))

4. The expression for Compton scattering given in problem 1 has been derived from relativistic expressions assuming energy and momentum conservation in the collision. The energy conservation gives the following relation

$$pc + mc^2 = p'c + E$$

Here pc is the momentum of the incident photon, mc^2 is the initial electron energy, $p'c$ is the momentum of the scattered photon and E is the total energy of the recoiling electron.

Use this relationship along with the conservation of the momentum to show the expression for Compton scattering given in problem 1.

The wave-particle duality.

1. X-rays having a wavelength of 0,0496 nm hit a crystal and are Bragg reflected in first order. In the second experiment the same crystal are exposed to a beam of neutrons at the same angle of incidence. Which energy should these neutrons have to become reflected?
($E_{neutron}$ = 0.333 eV)

2. For relativistic particles the de Broglie relation is still valid, however, the momentum p is related to the total energy by the equation

$$E = (pc)^2 + (mc^2)^2$$

a. Calculate the de Broglie wavelength for an electron with a total energy of 2,20 GeV.

b. Calculate the de Broglie wavelength for a proton with a total energy of 2,20 GeV.

3. The kinetic energy of neutrons in thermal equilibrium with the environment is on average 3/2 kT, where T is the absolute temperature and k is Boltzmann's constant. Suppose that we manage to create such neutrons (the best device is a nuclear reactor) in the course lab.

a) Calculate the wavelength of these neutrons. (0.1127 nm)

b) Suppose we want to detect these neutrons with one of the X-ray spectrometers of the course lab using a LiF crystal with a grating constant of d = 4.03 Å. At which angle towards the incoming neutron beam should the detector (Geiger-Müller tube) be set in order to read maximum intensity? Only even orders are reflected by the LiF crystal.
(32.5°)

The uncertainty relationship.

1. If ΔE is the uncertainty in the energy E of an excited system that decays by emission of radiation with the wavelength λ, show that the uncertainty in the wavelength of the radiation is given by the formula (if $\Delta\lambda$ is small compared to the value of λ):

$$\left|\frac{\Delta E}{E}\right| = \left|\frac{\Delta\lambda}{\lambda}\right|$$

2. The excited states of sodium which give rise to the yellow lines when the atom returns to the ground state have a lifetime of $1.8\cdot10^{-8}$ s.

a. Determine the uncertainty in the energy of these levels. ($3.66\cdot10^{-8}$)

b. Calculate the wavelength spread of the photons emitted in these transitions.
($\Delta\lambda$ = ($1.02\cdot10^{-14}$eV)

c. What is the relative uncertainty in the photon wavelength of 589 nm?
($1.74\cdot10^{-6}$)

A collection of exercises for the course Atomic- and molecular physics MN1 and Q3

Chapter 2. Quantum mechanics

1. A particle is in the ground state of an infinite one-dimensional square well potential of size L. Find the probability of finding the particle in an interval $\Delta x = 0.0015L$ at
a) $x = 0$ **b**) $x = L/2$ **c**) $x = 3/4\ L$ **d**) $x = L$

2. A particle is in the ground state of an infinite one-dimensional square well potential. Calculate the energy if the particle is a
a) proton and $L = 0.12$ nm which is typical for the internuclear distance of a molecule.
b) proton and $L = 1$ fm which is typical for the nucleus.

3. The wavelength of a ruby laser is 694.3 nm. Assume that this radiation is obtained in transitions from the first excited state to the ground state of an infinite square well system and calculate the value of L.

4. What's the derivative of Ψ_n' at the nodes for $n = 2$, 3 and 4 of an infinite one-dimensional square well potential?

5. The outermost electrons in conjugated hydrocarbons can be considered approximately to be in an infinite one-dimensional square well potential. In the butadiene molecule they may move over distances of about 7 Å.
a) Calculate the energy of the two lowest energy levels.
b) Normally the electrons are in the lowest energy level. What wavelength would an incoming photon have to cause an excitation to the next lowest level?

6. Calculate the separation between the lowest and next lowest electronic energy levels of an aromatic molecule assuming that the electrons are in an infinite one-dimensional square well potential with a width of 1 mm.

7. Where would the electron density be largest for the two levels in problem 4?

8. Use the energy relationship given in section 2.5 of the text to determine the number of bound energy levels of a potential well where $V_0 = 15\ E_{inf}$.

9. Sketch the wave function and the probability density for the $n = 3$ level of a one-dimensional potential well with depth V_0.

10. An electron in a rectangular box with sides of 3 Å, 4 Å and 6 Å returns from the next lowest to the lowest energy level by the emission of a photon. Which frequency would you expect for the photon?

11. Are the wave functions for the standing waves of a cube eigenfunctions of
a) $\hat{x}$?
b) $\hat{p}_x$?
c) $\hat{p}_x^2$?

Motivate your answer briefly.

12. Calculate for the $n = 3$ state of an infinite square well the expectation values $\langle x \rangle$ and $\langle x^2 \rangle$.

13. Derive the expectation value $\langle x \rangle$ for the harmonic oscillator in a state characterised by the vibrational quantum number $v = 1$.

14. Which range is allowed for a coordinate x of a classical harmonic oscillator?

15. Calculate for the ground state of an harmonic oscillator the expectation values $\langle x \rangle$ and $\langle x^2 \rangle$.

16. Calculate the most probable position for a quantum mechanical harmonic oscillator in a state with the vibrational quantum number $v = 1$.

17. Calculate $\langle E_{kin} \rangle$ and $\langle V \rangle$ for the ground state of a quantum mechanical harmonic oscillator. Show that these expectation values are equal.

18. A three-dimensional quantum mechanical harmonic oscillator has a potential function V that is

$$V = \frac{1}{2} k_x x^2 + \frac{1}{2} k_y y^2 + \frac{1}{2} k_z z^2$$

a) Calculate the energy eigenvalues by solving the Schrödinger equation.

b) Derive the degree of degeneracy assuming that all force constants are equal.

A collection of exercises for the course Atomic and molecular physics MN1 and Q3

(answers are given directly after each problem)

Chapter 3. Hydrogen and hydrogen-like atoms

b. Give the quantum numbers for all possible wavefunctions of an electron in the *L* shell.
Answer: (2,0,0,±1/2), (2,1,1,±1/2), (2,1,0,±1/2), (2,1,-1,±1/2)

c. Which states are accessible through spontaneous electric dipole transitions from the *3d* state of hydrogen?
Answer: 3*d*->2*p*; 2*p*->1*s*.
That is; 2*p*and 1*s* are accessible. 3*p*, 3*s* and 2*s* are accessible if QED effects are considered.

3. Show that if the electronic spin is neglected the number of degenerate states in each shell is equal to n^2.

4. Calculate the three longest wavelengths of the Balmer series of hydrogen. Is the radiation in the visible regime?
Answer: 656,4 nm (red), 486,2 nm (blue), 434,1 nm (violet)

5. **a**). Calculate the average distance of the electron from the nucleus in a hydrogen atom
in its ground state i.e. determine the value of the integral

$$\langle r\rangle = \int \Psi^* r\,\Psi\, dv$$

Compare the result with the radius obtained using the Bohr model. Answer: $3/2a_0$

b) Determine the distance from the nucleus for which there is maximum probability of finding the electron. Answer: a_0

6. Calculate the probability of finding a hydrogen 1*s* electron outside the classically allowed region, i.e. at distances *r* larger than $2a_0$. Show that the value $2a_0$ corresponds to the classical limit. Answer: 0.238

7. Determine the probability of finding a hydrogen 1*s* electron inside the nucleus, that is, inside a sphere with radius $1.2\cdot10^{-15}$ m.

8. Determine the probability of finding a hydrogen 1*s* electron inside the volume defined by $1.1a_0 \leq r \leq 1.105a_0$.
Hint. Calculate $P \approx \Psi^* \Psi r^2 \Delta r 4\pi$ where $\Delta r = 0.005\ a_0$

9. Determine the probability of finding a hydrogen $2p_z$ electron inside the volume defined by $1.1a_0 \leq r \leq 1.105a_0$.
Answer: $9.2 \cdot 10^{-11}$

10. Calculate the boundary surface of the electron in a hydrogen atom in its ground state. Let the boundary surface correspond to a sphere inside which there is a 90% probability of finding the electron.
Answer: $\approx 2.6\ a_0$

11.
a) Determine the maximum probability of the radial wavefunction of a hydrogen atom in the $n = 2$, $l = 1$ state. Answer: $4\ a_0$

b) Calculate the expectation value of the distance between the nucleus and the electron in this state.

c) Which is the physical difference between the two values you obtained in a) and b)?

12.
a) Calculate the expectation value $< E_{pot} >$ of the potential energy in the ground state of the hydrogen atom.

b) Show that for the total energy E in the ground state the value is $E = 1/2 < E_{pot}>$.

c) Use the relationship $E = E_{kin} + E_{pot}$ to calculate the expectation value of the kinetic energy in the ground state and show that $E_{kin} = - 1/2 < E_{pot} >$. The relationships are obtained generally for systems described by a potential function of the form $V(r) \sim 1/r$ and are known as the virial theorem.

13. Evaluate the probability density function for an electron in the $n = 2$ shell. Is the function spherically symmetric or not? Answer: symmetric

14. For a certain electronic state the j quantum number can be either 5/2 or 7/2. What is l?
Is it an *s*-orbital, *p*-orbital, or …..

15. Considering the electron being a classical particle with a spherical shape with radius 10^{-15} m and uniform mass density, use the magnitude of the spin angular momentum $\sqrt{s(s+1)}\ \hbar$ to compute the speed of rotation at the electron's equator. How does the result compare with the speed of light?

16. Calculate the spin-orbit splitting of a helium ion in the $2p\ ^2P$ state using

a) The ordinary formula for spin-orbit coupling Answer: 0.725 meV

b) The relativistic formula

Draw an energy level diagram for each case.

16. The fine structure levels of the of the LiIII ion in the $n = 2$ state are observed at 740731.2, 740733.6 and 740760.8 cm^{-1}. Use these data to draw an energy level diagram and to calculate a value of the spin-orbit coupling constant.

17. The angular momentum quantum number j of an yttrium atom in its ground state is equal to 3/2. How many lines would you expect to find in a Stern-Gerlach experiment on such atoms?

18. Calculate the Zeeman splitting of the fine structure levels of the $2p\ ^2P_{1/2}$ state of the helium ion if the magnetic field is 0.7 T.
Answer: 0.027 meV = 0.218 cm^{-1}

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(answer is given directly after each problem)

Chapter 4. Many-electron atoms

1.
Calculate the total energy of a boron atom neglecting electron-electron interaction.

2.
Write down the set of quantum numbers (n, l, m_l, m_s) for all the spin-orbitals of a boron atom in its neutral ground state.

3.
Calculate the total energy of a lithium atom using Slater's screening constants. Compare with the energy you obtain by employing the experimental value of the first and second ionisation energies and the calculated value of the third ionisation energy.
Answer: E_{Slater} = - 204 eV E_{exp} = -5.4 – 75.6 – 122.4 = -203.4 eV

4.
Calculate the binding energy of a 2*p* electron in the fluorine atom using Slater's screening constants. Compare with the experimental value.
Answer: 15.2 eV E_{exp} = 17.4 eV

5.
Use Slater's screening constants to determine the radius of the 2*p* orbital in the second row atoms B, C, N, O, F and Ne atom in the ground state configuration.
Answer: 0.81, 0.65, 0.54, 0.47, 0.41, 0.36

6.
Use Slater's screening constants to determine the following quantities for the carbon atom:

a) The first and second ionisation energy.

b) The radius of CI and CII in their respective ground state.

7.

a) Explain what is meant by autoionisation.

b) Calculate the kinetic energy of an electron produced by autoionisation of a helium atom in the state 2*s* 4*d*. The electron-electron interaction may be approximated by assuming that the 4*d* electron is completely shielded by the 2*s* electron.

8.

Excitation of the helium atom to the $2p^2$ ^{3}P state requires the energy 59.6744 eV. Suppose that an atom in this state undergoes autoionisation. At what kinetic energy would you expect to detect the outgoing electron?

Answer: 35.07 eV

9.

Consider photoionisation of a neutral Be atom in its ground state where one of the 1*s* electrons is expelled. Is it possible for this state to become de-excited via the emission of a second electron (so-called Auger decay)? If your answer happens to be yes, what is then the kinetic energy of the emitted electron and what is the configuration of the remaining cation?

Answer: Yes. E_{Auger} = 84.5 eV. Configuration of BeIII: $1s^2$

10.

Use Slater determinants to write down the wave functions that correspond to the terms which can be formed out of the 1*s* 2*s* configuration of the helium atom. Associate to each wave function a specific term symbol.

11.

Show that the helium ground state wavefunction

$$\Psi(1,2) = \frac{1}{\sqrt{2}} 1s(1)\,1s(2)\left[\alpha(1)\,\beta(2) - \beta(1)\,\alpha(2)\right]$$

is normalised, that is, show that

$$\iint \left[\Psi(1,2)\right] d\tau_1\, d\tau_2 = 1$$

The integration variable $d\tau$ is a product of the volume dv and spin $d\gamma$ variables.

12.

For the helium atom the excited states $1s2p$ ^{3}P and $1s2p$ ^{1}P are observed at 169081 cm^{-1} and 171129 cm^{-1}, respectively. Applying perturbation theory, the energies of these states can be calculated using the formula

$E = E^0 + J \pm K$

where E^0 is the total energy excluding electron-electron interaction, J is the Coulomb integral and K is the exchange integral.

Estimate the three terms E^0, J and K using the observed energies wherever needed.
Answer: E^0 = - 68 eV, J = 10.1 eV, K = 1024 cm^{-1}.

13.
Write down the Slater determinants for the singlet and triplet states obtained from the $1s2p$ configuration.

14.
For the helium atom in the excited state $1s3p$ ^1P some different states at lower energy can be reached through electric dipole transitions. Which?

15.
Derive the terms that can be obtained for a nitrogen atom in its ground state electron configuration.
Answer: ^4S, ^2D, ^2P

16.
d. Write down the wave function for the $2p$ sub-shell of the nitrogen atom as a Slater determinant using hydrogen-like orbitals and spin functions.
Answer: $|2p_1\alpha\ \ 2p_0\alpha\ 2p_{-1}\ \alpha|$

b) Calculate the probability density $P(1)$ of finding a single electron irrespective of the position of the other two. What is the angular dependence of of $P(1)$?
Answer: $P(1) = const/3*\alpha^2(1)$

17.
a) Which terms and fine structure levels are possible for an atom with a *pd*-configuration outside filled subshells?

b) Give the parity for each term.

18.
Verify that the following configurations give rise to the indicated terms:
a) *ns np*: ^3P, ^1P

b) *np n'd* or *np nd*: ^3P, ^3D, ^3F, ^1P, ^1D, ^1F.

e. Give the parity for each term.
Answer: a) odd; b) odd

19.

Which terms can be formed out of the following configurations?

a) *np n'p* Answer: $^{1,3}D$, $^{1,3}P$, $^{1,3}S$

b) np^2 Answer: ^3P, ^1D, ^1S

c) d^2 Answer: ^3P, ^3F, ^1S, ^1D, ^1G

d) p^3 Answer: ^4S, ^2D, ^2P

20.

Which terms are possible for an atom with three non-equivalent s-electrons outside filled subshells?

Answer: ^4S, ^2S

21.

Determine the possible values for the *J* quantum number in the terms ^4S, ^4P, ^4D and ^4F in the sodium atom.

Answer: $^4S_{3/2}$, $^4P_{1/2,\ 3/2,\ 5/2}$, $^4D_{1/2,\ 3/2,\ 5/2,\ 7/2}$, and $^4F_{3/2,\ 5/2,\ 7/2,\ 9/2}$

22.

Give the quantum numbers for the states that are given the following term symbols: $^2S_{3/2}$, $^3D_2$, $^5P_3$. Are all these states allowed? Explain.

Answer: $^2S_{3/2}$ forbidden

23.

The $^3D_3$ och $^4F_{3/2}$ fine structure levels appear within separate multiplets.

a) What other levels are there in these multiplets?

Answer: $^3D_{1,2}$ and $^4F_{5/2,\ 7/2,\ 9/2}$

b) Determine the degeneracy for the given levels.

Answer: Deg = $2J+1$. The deg are 3,5 and 6, 8, 10, respectively.

24.

a) Derive the terms and fine structure levels that the electron configuration $1s^2\ 2s^2\ 2p\ 3p\ 4s$ may generate.

Answer: $^2D_{3/2,5/2}$, $^4D_{1/2,\ 3/2,\ 5/2,\ 7/2}$, $^2P_{1/2,3/2}$, $^4P_{1/2,\ 3/2,\ 5/2}$, $^2S_{1/2}$, $^4S_{3/2}$

b) Give the parity for each term.

Answer: odd

25.

In the term scheme for neutral calcium there are three fine structure levels at 42 171.00 cm^{-1}, 42 170.53 cm^{-1} and 42 170.18 cm^{-1} above the ground state $4s^2\ ^1S_0$. Suggest a conceivable configuration for these levels and give the term symbol for each one of these.

26.

A low lying configuration for a singly charged titanium atom is d^3. In this configuration a multiplet with the energy separations 75, 104 and 130 cm^{-1} has been found.

a) Suggest a term to which these levels might belong.

Answer: ^4F

b) Is it probable that this term forms the ground state of the configuration?

Answer: Yes, because it gives the highest S and L for the configuration.

27.

In strontium there is a triplet with energy levels found at 31608, 31421 and 31027 cm^{-1} below the ionisation limit.

a) Give the labels for the three levels.

Answer: $5p\ ^3P_{0,1,2}$

b) Calculate the spin-orbit interaction parameter provided that *LS*-coupling holds.

Answer: $A \approx 192$ cm^{-1}

28.

The *D*-line of sodium corresponds to the transition $3p \rightarrow 3s$ for the valence electron. The wavelengths of the two components are 588,995 nm and 589,592 nm. Calculate the spin-orbit interaction constant for the ^2P term.

Answer: 1.42 meV ≈ 11.46 cm^{-1}

29.

The electron configuration of Europium ($Z = 63$) in the ground state is $4f^7\ 6s^2$. Which ground state term would you obtain from Hund's rules?

Answer: $^8S_{7/2}$

30.

The lowest excited term in Ca is ^3P.

a) Give the electron configuration.

Answer: Ar 4*s* 4*p*

b) In the table below the energy below the first ionisation limit is given for $^3P_0$ and $^3P_1$. Where do you expect to observe the $^3P_2$ term if *LS*-coupling is justified.

Level	Position
$^3P_0$	34147 cm^{-1}
$^3P_1$	34095 cm^{-1}

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Chapter 5. Atoms and spectroscopy

The quantum defect

1.

In the spectrum of the lithium atom the excited states $3s\ ^2S^o$, $3p\ ^2P^o$ and $3d\ ^2D^o$ are observed at 27206, 30925 och 31283 cm^{-1}, respectively. Calculate the quantum defect for the terms of the corresponding Rydberg series. The binding energy is 43487.19 cm^{-1}.

Answer: 0.4, 0.04, 0.03

Helium

2. Helium atoms in a gas cell gas were excited using a mono-energetic electron beam with the electron energy 22.95 eV. The radiation subsequently emitted from the sample was studied with an optical spectrometer sensitive to radiation both in the UV, visible and IR regions. Which wavelengths should be observed in the spectrum? Use Moore's table to find the excited states of helium.

Answer: $3s\ ^3S \rightarrow 2p\ ^3P$, 707,4 nm; $2p\ ^1P \rightarrow 2s\ ^1S$, 2057.75 nm; $2p\ ^1P \rightarrow 1s^2\ ^1S$, 58.4 nm; $2p\ ^3P \rightarrow 2s\ ^3S$, 1083.7 nm

3.

a) Write down the terms that can be formed for a helium atom in various electronic states defined by the electron configuration written $1s\ nl$, where n = 1, 2, 3 and l is the angular momentum quantum number. The answer should include term symbols and a brief explanation of the result.

Answer: $1s^2$ (^1S); $1s2s$ and $1s3s$ ($^{1,3}S$); $1s2p$ and $1s3p$ ($^{1,3}P$); $1s3d$ ($^{1,3}D$)

b) Draw a schematic Grotrian diagram where these terms are included as well as transitions pathways between them.

4. Estimate the energy needed to excite a helium atom to the $2p^2$ configuration using Slater's rules.

Answer: 60,3 eV (exp. 59.7 eV)

5. To take electron correlation into account, different configurations are mixed into the wavefunction. Would p^2 configurations be appropriate for mixing with the ground state configuration of the helium atom? Explain the answer briefly.

Answer: p^2 conf -> ^{3}P, ^{1}D, ^{1}S: Yes, the latter has the right symmetry to mix.

Wavefunction: $\Psi = a1s^2(^1S) + b2s^2(^1S) + c2p^2\ (^1S) + \ldots\ldots$

X-ray spectra.

6. Suppose we try to observe *X*-rays from anode of ^{89}Y using one of the *X*-ray spectrometers in the course laboratory. It employs a LiF-crystal with a grating constant of 4,03 Å and only even orders of reflection are detected?

a) At which angles should the characteristic radiation be observed in the second order spectrum ($m = 2$)?

Answer: $K_{\alpha II} = 23.9°$, $K_{\alpha I} = 23.7°$, $K_{\beta II} = 21.2°$, $K_{\beta I} = 21.1°$, $K\gamma = 20.8°$.

b) What is the lowest acceleration voltage that could be used in the *X*-ray tube in order to induce the *K* emission?

Answer: $V_{acc} > 17$ kV

7. An *X*-ray spectrometer using a crystal with a grating constant of 2,814 Å was used to study the radiation from an *X*-ray tube containing a molybdenum anode.

a. Determine the energy for the characteristic lines.

Answer: $E(K_{\alpha II}) = 17375$ eV, $E(K_{\alpha I}) = 17480$ eV, $E(K_{\beta II}) = 19590$ eV, $E(K_{\beta I}) = 19607$ eV, $E(K_\gamma) = 19965$ eV

b. The acceleration voltage was equal to 35 keV. What is the minimum angle with respect to the incoming beam at which intensity can be observed in this experiment?

Answer: Min angle 14.5°.

c. At which angles towards the incident X-rays should you adjust the crystal and the detector in order to observe the characteristic radiation in first order?

Answer: $K_{\alpha II} = 29.4°$, $K_{\alpha I} = 29.2°$, $K_{\beta II} = 26.0°$, $K_{\beta I} = 26.0°$, $K\gamma = 25.5°$.

Photoelectron spectroscopy.

8. The first ionisation energy of the CO molecule is 14.014 eV. Calculate the kinetic energy for the electrons emitted if the photon energy is

a) 21.2173 eV (Heα)

b) 23.087 eV (Heβ)

9. Photoionisation from the outermost orbital of the rare gases Ne, Ar, Kr and Xe leads to a spectrum showing two lines, provided the resolution of the instrument is sufficient.

a) What final state terms do these lines correspond to?

b) The intensity ratio between the lines is approximately 1:2. Explain this observation in statistical terms.

10. Gas phase UV photoelectron spectroscopy is often carried out using resonance radiation from a discharge in helium for the photoionisation. The by far highest intensity is obtained as HeIα radiation, which is generated in the transition $2p \rightarrow 1s$ in neutral helium atoms. Another component that is important is called HeIIα. It is emitted in the same transition but in singly ionised He (which is labelled HeII). Calculate the energy of the HeIIα radiation.
Answer: 40.8 eV

11. Gas phase UV photoelectron spectroscopy usually employs HeIα and HeIIα radiation at the wavelengths 58.433 nm and 30.378 nm, respectively, for ionisation. The radiation components are created in a discharge of helium and enter simultaneously into the gas cell where ionisation takes place. However, the HeI line is much stronger than the HeII line, so when HeII excited spectra are recorded, there is a point when the overlap from the HeI excited spectrum gets overwhelming. In fact, there is a Rydberg series in the HeI radiation going all the way up to the ionisation limit at 24.587 eV for helium, where overlap with the HeI radiation prevents studies of the HeII excited spectrum. Suppose that the lowest binding energy of a given sample is 10.51 eV. What is the highest binding energy that can be observed without the troublesome overlap with the HeI excited lines?
Answer: 26.7 eV

12. In UV photoelectron spectroscopy the radiation is usually obtained from a discharge in helium gas and it is common that some of this gas leaks into the gas cell where it is ionised with the hard HeIIα component. The photoelectrons from this process give rise to sharp line in spectra, which is very useful for calibration purposes. According to the results of optical spectroscopy, the ionisation energy of helium is 24.587 eV. However, in the photoelectron experiment there is also a recoil energy. What energy would you associate with this He 1*s* line taking the recoil energy into account?
Answer: 24.589 eV

The Zeeman effect

13. The transition $4\ ^1D_2 \rightarrow 4\ ^1P_1$ in calcium gives a line at 643,907 nm. Which wavelengths should be observed if the sample was located in a magnet field of 0,1 T?
Answer: λ = 643.895 nm, 643.907 nm, 643.919 nm.

14. The $4d\ ^2D_{3/2} \rightarrow 4p\ ^2P_{1/2}$ transition in carbon II gives rise to a line at 1784,051 nm. If the radiation source is exposed to a magnetic field, the energy levels are split which in turn leads to a splitting of the observed spectral line into several components.

a) Illustrate in a schematic diagram the energy levels and transitions you expect to observe.

b) What wavelengths would be observed if the magnetic field strength B is 0.95 T ?

Answer: λ = 1669.559 nm, 1686.207 nm, 1774.689 nm, 1793.512 nm, 1893.949 nm, 1915.402 nm.

A collection of exercises for the course Atomic- and molecular physics MN1+Q3

(answers are given directly after each problem)

Chapter 6. Electronic structure of diatomic molecules

1.

a) Write down the MO wave function Ψ(MO) for the ground state and the first excited state of the hydrogen molecule (H_2) under the assumption that the overlap integral is 0.20. The wave functions should include proper spin functions.

b) Give the term symbol for the electronic states.

2.

Use the simple MO method to show that the He_2^+ ion is bound.

3.

Consider two orbitals ϕ_s and ϕ_a where the first is symmetric and the second antisymmetric with respect to exchange of the coordinate *z* with -*z*, i.e.

$$\phi_s(x,y,z) = \phi_s(x,y,-z)$$
$$\phi_a(x,y,z) = -\phi_a(x,y,-z)$$

Show that the overlap integral *S* is zero i.e.

$$S = \int \phi_s \, \phi_a \, dv = 0$$

4.

Let ϕ_+ be an orbital that is symmetric with respect to reflection in a certain plane and let ϕ_- be a function that is antisymmetric with respect to reflection in the same plane.

a) Show that the overlap integral *S* is zero i.e.

$$S = \int \phi_+ \, \phi_- \, dv = 0$$

b) Show that if h_e is an effective Hamilton operator that is invariant with respect to reflection in the plane, the matrix element H_{+-} is zero, i.e.

$$H_{+-} = \int \phi_+ \, h_e \, \phi_- \, dv = 0$$

5.
The wave function for a two-electron system, for example the hydrogen molecule, must be antisymmetric with respect to exchange of co-ordinates for the electrons. Show that with this demand on the simple MO wave function the ground state of the hydrogen molecule must be a singlet.

6.
a) Use the simple molecular orbital model to explain the fact that rare gas molecules are not observed at room temperature.

b) Use the same qualitative arguments to find out which of the second row homonuclear diatomic molecules (Li_2, Be_2, ...) has the highest stability.

7.
The He_2 molecule could in principle be formed as an ionic complex where one electron is transferred to from one of the He atoms to the other. This would give the molecule He^+ + He^- that would be bound by the electrostatic attraction. The electrostatic repulsion between two helium atoms can be approximately calculated by B/R^5 where B = 3.5 $Å^5$ and R is the equilibrium bond distance.

a) Determine the value of R for which the energy of the molecule He^++He^- has a minimum. Calculate also the energy at this distance under the assumption that the zero energy level corresponds to the two helium atoms separated by a large distance.

b) Will the suggested ionic bonding mechanism give a stable helium molecule? One may assume that the electron affinity for a helium atom is much lower than the electron binding energy.

8.
Consider the diatomic molecule O_2, which has the electronic ground state configuration $2p\pi^2$ outside filled shells.

a) Which electronic terms may this configuration give rise to?
b) Give the energy ordering between the terms according to Hund's rules.

9.
For the molecular quantum numbers Λ and Σ the following relations applies
$\Lambda = 0, 1, 2, ..., L$
$\Sigma = -S, -S+1, ..., S-1, S$

The total angular momentum is determined by a quantum number Ω given by $\Omega = |\Lambda+\Sigma|$. If this quantum number is included, the term is written

$$^{2S+1}\Lambda_{\Omega}$$

Give the fine structure levels that can arise for a molecule for which $S = 1$ and $\Lambda = 2$ along with their mutual energy ordering according to Hund's rules.

10.
A certain diatomic molecule has the following electron configuration in the neutral ground state:

$$(1\sigma_g)^2 (1\sigma_u)^2 (2\sigma_g)^2 (2\sigma_u)^2 (3\sigma_g)^2 (1\pi_u)^4 (1\pi_g)^2$$

a) Which is the molecule? Explain the answer briefly.

b) Give the term symbol for the ground state. Explain the answer briefly.

c) Suppose that an electron is removed from the $1\pi_g$ orbital, for example by photoionisation. How would that influence the dissociation energy and the equilibrium bond distance? Give the dissociation energy for both the neutral and the ionised ground states using proper resonance integrals.

d) Suppose that an electron is instead removed from the $1\pi_u$ orbital by photoionisation. Give the electron configuration for the ionic state created by this process and, in addition, the terms that may arise from this process. Assume that the molecules to be ionised are all in the neutral ground state and that the coupling of the two outermost electrons does not change as a result of the ionisation. Order the terms energetically according to Hund's ru les.

11.
Describe briefly the Franck-Condon principle and its application for the interpretation of photoelectron spectra.

12.
The figure below shows a photoelectron spectrum of the CO molecule induced by *Al K*α radiation with a photon energy of 1485 eV. The main lines correspond to ionisation from the various molecular orbitals. Construct an energy level diagram based on the single particle model and atomic basis orbitals that is appropriate to interpret the spectrum by associating with each line a specific molecular orbital and term.

13.
a) Construct an electron configuration for the neutral ground state of the HCl molecule and give the term.
b) Construct an electron configuration for the ground state of the HCl cation and give the term.
c) Which fine structure levels can be expected for the ground state of the cation and which is their energy ordering according to Hund's rules?
d) The energy of fine structure levels is given by $E_{S\text{-}O} = E_0 + A\Lambda\Sigma$, where A is the spin-orbit coupling constant. Calculate the value of A for the ionic ground state of HCl from the experimental value of the spin-orbit splitting of 83 meV.

14.
A low energy excited configuration of the O_2 molecule is $(2p\pi_u)^3$ $(2p\pi_g)^3$. Determine the terms that may arise from this configuration and their relative order according to Hund's rules.

15.
Determine the electronic ground state of the following molecules by giving their electron configuration and term symbol including spin as well as total angular momentum:

a) NO **b**) O_2 **c**) P_2^- .

16.
Determine the ground state term for the hydrides of the elements from Li through F.

17.

For the B_2 molecule the following two different electronic configurations are conceivable for the ground state

$$KK(\sigma_g 2s)^2 (\sigma_u 2s)^2 (\pi_u 2p)^2$$
$$KK(\sigma_g 2s)^2 (\sigma_u 2s)^2 (\sigma_g 2p)^2$$

Experimentally, the lowest electronic excitation is from a $^3\Sigma_g^-$ ground state to an excited $^3\Sigma_u^-$ state.

a) Which ground state configuration seems to be experimentally favoured?
b) Suggest a configuration for the excited state.

A collection of exercises for the course Atomic- and molecular physics MN1+Q3

(answers are given directly after each problem)

Chapter 7.
Vibrational and rotational structure of diatomic molecules

1.

a) Show that for a diatomic molecule the angular frequency ω of the vibrational motion in the harmonic approximation is

$$\omega = \sqrt{\frac{k}{\mu}}$$

where μ is the reduced mass of the molecule and k is the force constant.

b) Calculate the reduced mass of the hydrogen molecule and the hydrogen halogenides HX (X=F, Cl, Br, I).

2.

It is often found that the vibrational energy of excited molecular states is lower than of the ground state. How may such observations be understood? Explain.

3.

The vibrational frequency of H_2, HD and D_2 is 4395.2, 3817.09 and 3118.4 cm^{-1}, respectively. Explain the difference quantitatively and try using these data to estimate the corresponding frequencies for the molecules $H\text{-}H^3$ and $H^3\text{-}H^3$ where H^3 is a tritium atom.

4.

Calculate the difference in dissociation energy between the H_2 and D_2 molecules.

5.

In gas phase (high temperature) the NaBr molecule has the vibrational constants ω_e = 315 cm^{-1} och $\omega_e x_e$ = 1.15 cm^{-1}. Use these values to calculate the dissociation energy of the molecule.

6.
The observed rotational line splitting in the rotational spectrum of $H^{19}F$ is 20,939 cm^{-1}.
a) Use this value to determine the equilibrium bond distance R_e of the molecule.
b) Which rotational line splitting would you expect for the $^{2}H^{19}F$ molecule?

7.
The observed rotational line splitting in the rotational spectrum of the $H^{35}Cl$ molecule is 20.7 cm^{-1}.
a) Use this value to determine the equilibrium bond distance R_e of the molecule.
b) Which rotational line splitting would you expect for the $H^{37}Cl$ molecule?

8.
The microwave spectrum of the HI molecule consists of a series of lines separated by 12.7 cm^{-1}. Calculate the equilibrium bond distance of the molecule.

9.
Calculate the energy of the four lowest rotational levels of the hydrogen molecule (H_2).

10.
The rotational constants of the oxygen molecule are B_e = 1.44566 cm-1 and α_e = 0.01579 cm^{-1}. Calculate the equilibrium bond distance r_e as well as the average internuclear distance of the four lowest excited vibrational levels.

11.
The figure below shows a photoabsorption spectrum in the IR-regime of a gaseous sample of the HBr molecule. A number of lines are observed that correspond to transitions between rotational levels of the $v = 0$ and v = 1 vibrational states.
a. Make an interpretation of the spectrum by assigning to each line in the spectrum a specific transition.
b. Use the spectrum to determine the rotational constant B of HBr.
c. Use the value you obtained for B to determine the equilibrium bond distance for the HBr molecule. (The handbook value is 1.414435 Å)
d. Explain qualitatively the fact that the line separations gradually decrease on the high frequency side of the spectrum.
