PHOT 222: Quantum Photonics

Final exam A: questions & solutions

Michaël Barbier, Spring semester (2024-2025)

General information on the exam

Grading: The final exam counts for 60% of your total grade.

Exam type: The exam consists of 6 open questions/problems. The exam is a written exam and all questions can be answered using only pen and paper. Calculators, mobile phones, laptops are not needed, and are not allowed to be used during the exam.

The duration of the exam is 3 hours.

Exam questions

Please fill in all questions listed below. Each of the questions is valued equally in the score calculation of the exam.

Please tell if any question is unclear or ambiguous.

This document contains both the problems and their solutions. Considering the scoring calculation:

- when you have to answer multiple subproblems each of the subtasks is given a score out of 5 points. For each question the sub-scores are then averaged.
- Answers should contain: The final formula/expression together with its derivation and a numerical approximate value with the **correct units**.

Question 1: Bohr model

A hydrogen atom is in state $n = 2$ and gets ionized by absorbing a photon.

(a) What is the minimum energy that the photon must have?
(b) What is the wavelength of the photon for that energy?

Solution (Q1)

For the hydrogen atom to get ionized (electron to escape) it should be brought from the initial state with $n = n_i = 2$ to a final state with $n_f \longrightarrow \infty$, i.e. the energy should become $E_{n_f \to \infty} = 0$.

(a) The photon should minimally have the energy ΔE:

$$\Delta E = E_{n\to\infty} - E_{n_i} = -\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \mathrm{Ry} = -\left(\frac{1}{\infty^2} - \frac{1}{2^2}\right) \mathrm{Ry} = 0 + \mathrm{Ry}/4 = 3.4\,\mathrm{eV}$$

(b) The maximum wavelength of the photon corresponding to this energy difference can be derived as:

$$\Delta E = hf = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{\Delta E} = \frac{1240\,\mathrm{eV\ nm}}{3.4\,\mathrm{eV}} \approx 365\,\mathrm{nm}$$

where the accuracy of the last approximation is not required for this exam, and an approximate numerical value using $\frac{124}{34} \lesssim 4$ is sufficient.

Question 2: Quantum Hydrogen Atom

The radial wave function of a hydrogen atom in the $2s$ state is given by:

$$R_{2,0}(r) = \frac{1}{\sqrt{2a_0^3}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$$

(a) Calculate the most likely radius for the particle to be found, i.e. where $|R_{2,0}(r)|^2 4\pi r^2$ attains its maximum value.
(b) Calculate the expectation value: $\langle r \rangle$. *Hint*: Integrating in spherical coordinates the volume element $dV = 4\pi r^2 dr$.

Solution (Q2)

(a) The most probable radius is where $|R_{2,0}(r)|^2 4\pi r^2$ attains its maximum value. Therefore we look where the derivative $4\pi \frac{d}{dr} |R_{2,0}(r)|^2 r^2$ becomes zero.

First, we simplify the condition $4\pi \frac{d}{dr} \left[r^2 \, |R_{2,0}(r)|^2\right] = 0$ by the following argument:

Set $f(r) = r\, R_{2,0}(r)$ then $\frac{df^2}{dr} = 2f\,\frac{df}{dr}$ which means that:

$$\frac{d}{dr}\left[r\, R_{2,0}(r)\right] = 0 \quad \Rightarrow \quad \frac{d}{dr}\left[r\, |R_{2,0}(r)|\right] = 0 \quad \Rightarrow \quad \frac{d}{dr}\left[|R_{2,0}(r)|^2 r^2\right] = 0$$

Using the first condition and substituting $\rho = r/a_0$ to simplify further calculations:

$$\begin{aligned}
\frac{d}{dr}\left[r\,R_{2,0}(r)\right] \propto \frac{d}{d\rho}\left[\rho\,(2-\rho)\;e^{-\rho/2}\right] \\
&= \frac{d}{d\rho}\left[\left(2\rho-\rho^2\right)\;e^{-\rho/2}\right] \\
&= e^{-\rho/2}\frac{d\;\left(2\rho-\rho^2\right)}{d\rho} + \left(2\rho-\rho^2\right)\frac{d\,e^{-\rho/2}}{d\rho} \\
&= e^{-\rho/2}\left[2-3\rho+\frac{\rho^2}{2}\right]
\end{aligned}$$

Since $e^{-\rho/2} \neq 0$ for finite ρ, this gives us a quadratic equation:

$$\frac{\rho^2}{2} - 3\rho + 2 = 0 \quad\Rightarrow\quad \rho_\pm = 3 \pm \sqrt{5} \approx 3 \pm 2.25$$

For the solution $\rho_- = r/a_0 \approx 0.75 < 1$, the radius is smaller than the "most likely radius" of the $1s$ orbital: $\rho_{1s} = 1$. The other solution $\rho_+ \approx 5.25$ is roughly comparable to 4, the radius calculated from the Bohr model, a better option.

To make sure we could sketch the function $g(\rho) = \rho^2\,(2-\rho)^2\;e^{-\rho}$.

An alternative solution is to start from the probability $4\pi r^2|R(r)|^2$:

$$\begin{aligned}
\frac{d}{dr}\left[\rho^2\,(2-\rho)^2\;e^{-\rho}\right] &= \frac{d\left[\rho^2\,(2-\rho)^2\right]}{dr}e^{-\rho} + \rho^2\,(2-\rho)^2\;\frac{de^{-\rho}}{dr} \\
&= \left[2\rho\,(2-\rho)^2 - 2\rho^2(2-\rho)\right]\;e^{-\rho} - \rho^2\,(2-\rho)^2\;e^{-\rho} \\
&= \rho\,(2-\rho)\;e^{-\rho}\;\left[2\,(2-\rho) - 2\rho - \rho\,(2-\rho)\right] \\
&= \rho\,(2-\rho)\;e^{-\rho}\;\left[4-6\rho+\rho^2\right]
\end{aligned}$$

The prefactor contains the roots in $\rho = 2$ and $\rho = 0$ and $e^{-\rho} \neq 0$. This brings us to the same 2nd order polynomial $4 - 6\rho - \rho^2 = 0$ as before with the same roots.

(b) The expectation value $\langle r\rangle$ is given by:

$$\langle r\rangle = \int_0^\infty |\psi(r)|^2 4\pi r^2\,dr = \int_0^\infty \frac{|R(r)|^2}{4\pi}4\pi r^2\,dr = \int_0^\infty |R(r)|^2 r^2\,dr = \frac{1}{2a_0^3}\int_0^\infty r^2\,(2-\rho)^2\;e^{-\rho}\,dr$$

And if we express r in units of the Bohr radius a_0:

$$
\begin{aligned}
\langle r\rangle/a_0 = \langle \rho\rangle &= \frac{1}{2}\int_0^\infty \rho^2\left(2-\rho\right)^2 e^{-\rho}\,d\rho \\
&= \frac{1}{2}\int_0^\infty \left[\rho^4 - 4\rho^3 + 4\rho^2\right] e^{-\rho}\,d\rho \\
&= \frac{1}{2}\left[\int_0^\infty \rho^4\, e^{-\rho}\,d\rho - 4\int_0^\infty \rho^3\, e^{-\rho}\,d\rho + 4\int_0^\infty \rho^2\, e^{-\rho}\,d\rho\right] \\
&= \frac{1}{2}\left[4! - 4\cdot 3! + 4\cdot 2!\right] \\
&= \frac{1}{2}\left[8\right] = 4
\end{aligned}
$$

This means that $\langle r\rangle = 4a_0$ with a_0 the Bohr radius.

Question 3: Angular momentum

A hydrogen atom has an angular momentum $L = 2.583\times 10^{-34}\,\mathrm{J\cdot s}$.

(a) What is the orbital quantum number l?
(b) What are the possible values for the magnetic quantum number m_l?

Solution (Q3)

(a) The angular momentum is quantized as $L = \sqrt{l(l+1)}\hbar$

$$L = \sqrt{l(l+1)}\hbar \quad\Rightarrow\quad \sqrt{l(l+1)} = \frac{L}{\hbar} = \frac{2.583\times 10^{-34}\mathrm{J\cdot s}}{1.055\times 10^{-34}\mathrm{J\cdot s}} \approx 2.5$$

l must be an integer $l = 0, 1, 2, 3, \cdots$, and for all l we have:

$$l^2 < l(l+1) < (l+1)^2 \quad\Rightarrow\quad l = \sqrt{l^2} < \sqrt{l(l+1)} < \sqrt{(l+1)^2} = l+1$$

Since $\sqrt{l(l+1)} \approx 2.5$ and $2 < 2.5 < 3$, the orbital quantum number $l = 2$.

(b) The options for m_l are $0, \pm 1, \ldots, \pm l$, and since $l = 2$ we obtain:

$$m_l = -2, -1, 0, 1, 2$$

Question 4: Shielding and effective nuclear charge

A Lithium atom in the ground state has configuration $1s^2\,2s^1$. Assume that the $Z_{\text{eff},2s} \approx 1.28$ and $Z_{\text{eff},2p} \approx 1$. Then suppose that the atom absorbs a photon and the electron in the ~~$1s$~~ $2s$ orbital gets excited to the $2p$ orbital.

(a) What is the wavelength of the photon assuming that the effective nuclear charges are good approximations.
(b) The real wavelength for the excitation from 2s to 2p is actually 670 nm. Assuming that our approximation for $Z_{\text{eff},2p} \approx 1$ is to blame, what would be correct energy level of the $2p$ orbital be (to compensate for the error in the wavelength)?

Solution (Q4)

For this question the numerical value is more important since we are looking for a possible small difference.

(a) The wavelength of the photon λ is determined by $\Delta E = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{\Delta E}$. The energy difference ΔE between the $2s$ and $2p$ levels is given by:

$$\Delta E = \left(\frac{Z^2_{\text{eff},2p}}{n^2_{2p}} - \frac{Z^2_{\text{eff},2s}}{n^2_{2s}}\right)\text{Ry} = \left(Z^2_{\text{eff},2p} - Z^2_{\text{eff},2s}\right)\frac{\text{Ry}}{4} = \left(1.28^2 - 1\right)\,3.4\,\text{eV} = 2.176\,\text{eV}$$

The last numerical value is calculated relatively accurate to understand the difference in wavelength afterwards in (b). The value can be obtained as follows:

$$\begin{aligned}
\left(1.28^2 - 1\right)\,3.4\,\text{eV} &= \left(1 + 0.56 + \frac{(28)^2}{10000} - 1\right)\,3.4\,\text{eV} = \left(0.56 + \frac{(30-2)^2}{10000}\right)\,3.4\,\text{eV} \\
&= \left(0.56 + \frac{784}{10000}\right)\,3.4\,\text{eV} = 0.6384 \cdot 3.4\,\text{eV} \\
&\approx (60+4)\cdot(30+4)\times 10^{-3}\,\text{eV} = (1800+360+16)\times 10^{-3}\,\text{eV} = 2.176\,\text{eV}
\end{aligned}$$

We can now obtain the wavelength:

$$\begin{aligned}
\lambda &= \frac{hc}{\Delta E} \approx \frac{1240\,\text{eV nm}}{64\cdot 34\,\text{eV}} \times 10^3 = \frac{155}{8\cdot 34} \times 10^3\,\text{nm} \\
&= \frac{155\cdot 125}{34}\text{nm} = \frac{(140+15)(140-15)}{34}\text{nm} = \frac{140^2 - 225}{34}\text{nm} \\
&\approx (4.1\cdot 140 - 7)\,\text{nm} = (560 + 14 - 7)\,\text{nm} = 567\,\text{nm}
\end{aligned}$$

Where we in the last approximation put more effort in the numerical value to see that it is different from the real wavelength $\lambda_{\text{real}} = 670\,\text{nm}$

(b) The real energy difference can be calculated as follows:

$$\Delta E_{\text{real}} = \frac{hc}{\lambda} = \frac{1240\,\text{eV nm}}{670\,\text{nm}} = \frac{124}{67}\,\text{eV} \approx 1.85\,\text{eV}$$

Where for the last more accurate approximate value we used:

$$\frac{124}{67} \Rightarrow 124 = (2-x)\,67 \Rightarrow x = 10/67 \approx 10/66.67 \approx 0.15$$

Therefore a better approximation for the $E_{\text{real},2p} = E_{2s} + \Delta E_{\text{real}}$ would be:

$$E_{\text{real},2p} = E_{2s} - \Delta E_{\text{real}} \approx -(3.4 + 1.85)\,\text{eV} = -5.25\,\text{eV}$$

which is different from $E_{\text{real},2p} = -(3.4 + 2.174)\,\text{eV} = -5.574\,\text{eV}$.

Question 5: Normal Zeeman effect

A hydrogen atom H is put in a magnetic field $\vec{B} = B\vec{e}_z$. Ignore spin and assume that the only contribution to the hydrogen atom energy levels is $U = m_l \mu_B B$ with μ_B the Bohr magneton.

(a) Calculate the energy levels of the $3d$ orbital if $B = 0.1$ Tesla.
(b) How strong does the magnetic field have to be for the $2p$ and $3d$ energy levels to overlap?

Solution (Q5)

(a) For the $3d$ orbital $n = 3$ and $l = 2$, therefore $m_l = 0, \pm 1, \pm 2$ and the energy levels are given by:

$$\begin{aligned} E_{n,m_l} &= E_n + U_{m_l} = -\frac{\text{Ry}}{n^2}\,\text{eV/T} + m_l \mu_B B = -\frac{13.6}{3^2} + m_l (5.8 \times 10^{-5}\,\text{eV/T}) \cdot (0.1\,\text{T}) \\ &= \left[-\frac{10 + 3.6}{9} + m_l 5.8 \times 10^{-6} \right] \text{eV} = -\left[1.411111\cdots + m_l\, 5.8 \times 10^{-6} \right] \text{eV} \end{aligned}$$

So the 5 levels are close to 1.411111 eV and split over an interval of 23.2 meV.

(b) The energy difference between the $2p$ and $3d$ orbitals of hydrogen is given by:

$$\Delta E = |E_2 - E_3| = -\left(\frac{1}{4} - \frac{1}{9}\right) \text{Ry} = (3.4 - 1.4111)\,\text{eV} = 2.9899\,\text{eV}$$

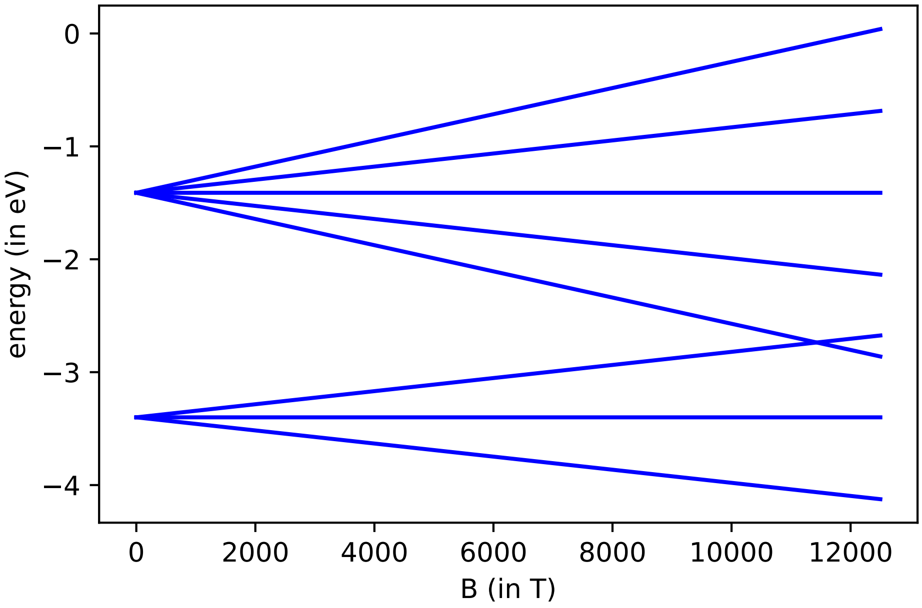
If energy levels are splitted this energy difference reduces with increasing magnetic field B. The $2p$ orbital has $l = 1$ and largest $m_l = 1$, while the $3d$ orbital has $l = 2$ and largest negative $m_l = -2$ leading to:

$$\Delta E = \max(|U_{2p}|) + \max(|U_{3d}|) = (1+2)\,\mu_B B$$

Extracting B we get:

$$B = \frac{\Delta E}{3\mu_B B} = \frac{2.9899\,\text{eV}}{3 \cdot 5.8 \times 10^{-5}\,\text{eV / T}} = \frac{2.9899\,\text{eV}}{3 \cdot 5.8 \times 10^{-5}\,\text{eV / T}} = \frac{1}{5.8} \times 10^{5}\,\text{T} \approx 1.5 \times 10^{4}\,\text{T}$$

Notice that the resulting magnetic field is not feasible in reality: the magnetic field strength is huge (found in certain neutron stars but not feasible in a lab). Further, these large magnetic fields actually require to take into account spin, nonlinear effects, and using the relativistic Dirac equation (our model is not appropriate here).



Question 6: Molecular spectra

Assume you have a NO molecule existing of an oxygen and a nitrogen atom with a separation distance $r_0 = 0.115$ nm.

(a) Calculate the reduced mass μ and the moment of inertia I of the molecule. Remember that nitrogen has an atomic mass of approximately 14 and oxygen 16 atomic mass units (or Dalton, see formulas/values).
(b) Suppose the molecule is in state with rotational quantum number $l = 3$, and transitions to $l = 4$ thereby absorbing a photon. Calculate the wavelength of the photon.

Solution (Q6)

(a) The reduced mass μ is given by:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{14 \cdot 16}{14 + 16}\mathrm{Da} = \frac{225 - 1}{30} \cdot \frac{5}{3} \times 10^{-27}\,\mathrm{kg} \approx 1.25 \times 10^{-26}\,\mathrm{kg}$$

The moment of inertia $I = \mu r_0^2$. The numerical value is approximately:

$$\begin{aligned} I = \mu r_0^2 &= (1.25 \times 10^{-26}) \cdot (1.15)^2 \times 10^{-20}\,\mathrm{kg\ m}^2 \\ &= \frac{5}{4}(1 + 0.3 + 0.225) \times 10^{-46}\,\mathrm{kg\ m}^2 \approx \frac{5}{4} \cdot \frac{4}{3} \times 10^{-46}\,\mathrm{kg\ m}^2 \\ &\approx 1.66 \times 10^{-46}\,\mathrm{kg\ m}^2 \end{aligned}$$

(b) The wavelength of the photon can be derived from $\lambda = \frac{hc}{\Delta E}$ where the difference between the rotational energy ΔE is given by

$$\Delta E = E_{\mathrm{rot},4} - E_{\mathrm{rot},3} = [4(4+1) - 3(3+1)]\,\frac{\hbar^2}{2I} = \frac{4\,\hbar^2}{I}$$

and the approximate numerical value is given by:

$$\begin{aligned} \lambda = \frac{hc}{\Delta E} = hc \cdot \frac{I}{4\,\hbar^2} &\approx \frac{(1240\,\mathrm{eV\ nm}) \cdot (5/3 \times 10^{-46}\,\mathrm{kg\ m}^2)}{4 \cdot (10^{-68}\,\mathrm{J}^2\,\mathrm{s}^2) \cdot (10/16 \times 10^{19}\,\mathrm{eV/J})} \\ &\approx 1240 \cdot \frac{5}{3} \cdot \frac{16}{4 \cdot 10} \times 10^3\,\mathrm{nm} \\ &= 0.827\,\mathrm{mm} \end{aligned}$$

A wavelength roughly about a millimeter.

Values and formulas:

Mass of an electron: $m_e = 9.11 \times 10^{-31}$ kg
Mass of a proton: $m_p \approx 1836\ m_e$
1 eV $= 1.602 \times 10^{-19}$ J
An atomic mass unit: $1\,\mathrm{Dalton} = 1.66 \times 10^{-27}\,\mathrm{kg} \approx \frac{5}{3} \times 10^{-27}\,\mathrm{kg}$
Bohr magneton: $\mu_B = 9.3 \times 10^{-24}$ J/T $= 5.8 \times 10^{-5}$ eV/T
Joule in SI units: $[\mathrm{J} = \mathrm{kg\ m^2/s^2}]$
$h = 6.63 \times 10^{-34}$ J s $= 4.14 \times 10^{-15}$ eV s
$\hbar = \frac{h}{2\pi} = 1.055 \times 10^{-34}$ J s $= 6.582 \times 10^{-16}$ eV s
$c = 3 \times 10^8$ m/s
$hc = 1240$ eV nm
Rydberg energy unit: $\mathrm{Ry} = 13.6\,\mathrm{eV}$
Rydberg constant for hydrogen: $R_H = 1.0968 \times 10^7\mathrm{m}^{-1} \approx 1.1 \times 10^7\mathrm{m}^{-1}$
Rydberg constant for heavy atoms: $R_\infty = 1.0974 \times 10^7\mathrm{m}^{-1} \approx 1.1 \times 10^7\mathrm{m}^{-1}$
$m_e c^2 = 0.511$ MeV

For a wave function $\psi(x)$ with $x \in [a, b]$, the expectation value of a function $f(x)$ is:

$$\langle f(x) \rangle = \int_a^b f(x)\,|\psi(x)|^2\,dx.$$

You can also make use of following definite integrals:

Definite integrals:

$$\int_0^\infty x^n e^{-ax}\,dx = \frac{n!}{a^{n+1}}$$
$$\int_0^\infty e^{-ax^2}\,dx = \frac{\sqrt{\pi}}{2\sqrt{a}}$$
$$\int_0^\infty x^2 e^{-ax^2}\,dx = \frac{\sqrt{\pi}}{4a^{3/2}}$$
$$\int_0^\infty x^4 e^{-ax^2}\,dx = \frac{3\sqrt{\pi}}{8a^{5/2}}$$