Quantum Mechanics I

Week 1 (Solutions)

Spring Semester 2025

1 Ionization Energy of Be^{3+}

In this exercise, we will calculate the ionization energy of the triply ionized beryllium atom Be^{3+}. Beryllium has an atomic number of $Z = 4$, and has four electrons orbiting its nucleus. Here, we consider the triply ionized state, where three of these electrons have been removed. As a result, only a single electron remains, orbiting the beryllium nucleus.

(a) How are the energies of the Bohr model modified for an electron orbiting around a nucleus with Z protons?

In the original Bohr model we have the energies

$$E_n = -\frac{ke^2}{2a_0}\frac{1}{n^2}, \quad n = 1, 2, 3, \dots, \tag{1.1}$$

where $a_0 = \hbar^2/(m_e ke^2)$ is the Bohr radius. This model applies to the case of a single electron orbiting around a nucleus comprised of one proton. If instead, the nucleus contained Z proton which is the case of the ionized elements He^+, Li^{2+} and Be^{3+}, the energies are modified as follows:

$$E_n = -\frac{ke^2}{2a_0}\frac{Z^2}{n^2}, \quad n = 1, 2, 3, \dots. \tag{1.2}$$

You may easily verify this by applying the assumptions of the Bohr model (as presented in the Lecture notes) to a system of an electron and a nucleus with Z protons. Thus, the energy of the system is

$$E = \frac{mv^2}{2} - k\frac{Ze^2}{r} = -k\frac{Ze^2}{2r} \tag{1.3}$$

where in the second equality we have used $mv^2/r = kZe^2/r^2$ (Newton's second law for a circular orbit). We express the latter as $L^2 = mkZe^2 r$ where $L = mvr$. Then we find, by using the angular momentum quantization condition $L_n = n\hbar$,

$$r_n = \frac{n^2\hbar^2}{mkZe^2}, \quad n = 1, 2, 3\dots. \tag{1.4}$$

We introduce this into Eq. (1.3), and we find Eq. (1.2).

(b) What is the ionization energy of the Hydrogen atom?

To obtain the ionization energy of the Hydrogen atom, i.e. the minimum energy required to remove an electron in the ground state of the atom, we take the $n = 1$, and we find that this energy is $E = -13.6\,eV$. This numerical value is obtained when we compute the constant $ke^2/(2a_0)$).

(c) Use the atomic number of the triply ionized Beryllium atom to find the ionization energy of this atom.

For the triply ionized Beryllium atom, we have $Z = 4$. Thus we find:

$$E_n = -13.6eV\frac{16}{n^2}\,. \tag{1.5}$$

For $n = 1$, the ionization energy is $E_1 = -217.6eV$.

2 Photoelectric effect

Caesium is an alkali metal, and has an extraction potential of approximately $V_s = 2.1$ V. Suppose to irradiate the metal with a lamp which emits light of wavelength $\lambda = 5000$Å.

(a) Calculate the maximum energy of a photoelectron.

The maximum energy of a photoelectron is given by $K_{max} = hf - \phi$ where ϕ is the work function. The work function can be obtained with the extraction potential. In eV, this is $\phi = qV = 2.1eV$. Then, we need to convert the given wavelength into energy in units of eV by using:

$$E = hf = \frac{hc}{\lambda}\,. \tag{2.1}$$

If we plug in λ in the above expression, we get 2.48 eV. Then, the maximum kinetic energy is found as $K_{max} = 2.48 \text{ eV} - 2.1 \text{ eV} = 0.38$ eV.

(b) Suppose to use a very weak lamp, with power 1 mW, located at a distance of 10 cm from a Cs sample. Suppose that the sample exposes a surface of 1 cm^2 to light, and that the intensity of the lamp is distributed in a spherically-symmetric way. The typical radius of an atom is assumed to be 10^{-8} cm. How many seconds of exposure would be necessary in the classical theory to absorb the energy necessary to emit a single electron at an energy equal to that computed in Question (a).

We start by computing the intensity of the source at a distance of $h = 10$ cm,

$$I = \frac{P}{4\pi h^2} = \frac{1mW}{4\pi 10^2 cm^2} = 7.96\cdot 10^{-7}\frac{W}{cm^2}\,. \tag{2.2}$$

Then, we need to compute to how much light each atom in the sample is exposed to. We do that by using the intensity of light times the are of exposure πR^2 where R is the radius of the atom,

$$P_{abs} = I \cdot \pi a^2 = 7.96 \cdot 10^{-7} \frac{W}{cm^2} \cdot \pi \cdot 10^{-16} cm^2 = 25 \cdot 10^{-23} W \,. \tag{2.3}$$

Now, we need to compute the time exposed to the radiation. The energy supplied to the atom is $hf = 2.48eV$, as found in the previous question.

$$t_{exp} = \frac{E}{P_{abs}} = \frac{2.48eV}{25 \cdot 10^{-23} W} = 1.58 \cdot 10^3 s \,. \tag{2.4}$$

However, the experiment shows that the extraction of an electron happens (almost) instantaneously. Thus a classical treatment fails to explain the observation.

3 The Ground State of an Electron-Positron Pair

Consider an electron of mass m and charge $-e$ and a positron of mass m and charge $+e$. Due to the Coulomb attraction between the two charges, the two particles form a bound pair (known as "positronium"). The goal of this exercise is to calculate the ground state energy of positronium using the quantization condition.

(a) Derive an expression for the velocity and the radius of the orbit for the electron and the positron, in the frame of reference of the center of mass. In the calculations, assume that the orbits are circular, and assume a description in terms of classical mechanics.

In the frame of reference of the center of mass, the vectors specifying the coordinates and the momenta of the electron and the positron are always related by $\mathbf{r}_e = -\mathbf{r}_p$, $\mathbf{p}_e = -\mathbf{p}_p$.

These relations are a consequence of the fact that the masses of the electron and the positron are equal to each other, and is true not only for circular orbits but, more generally, even for the elliptical, parabolic or hyperbolic orbits (which are the possible solutions to the classical Coulomb or Kepler two-body problem)[1].

It follows that the angular momenta of the two particles are $\mathbf{L}_e = \mathbf{r}_e \times \mathbf{p}_e = \mathbf{L}_p = \mathbf{r}_p \times \mathbf{p}_p = \mathbf{L}_{tot}/2$, where $\mathbf{L}_{tot}$ is the total angular momentum. Using Newton's second law gives then for the absolute values:

$$mv_e^2/r_e = \frac{2mv^2}{r} = \frac{ke^2}{r^2} \,, \tag{3.1}$$

where v_e is the modulus of the electron's velocity, and $r = 2r_e$ is the distance between the electron and the positron.

[1] If the two masses were different, one would have $\mathbf{p}_e = -\mathbf{p}_p$ and $(m_e \mathbf{r}_e + m_p \mathbf{r}_p) m_{tot}^{-1} = \mathbf{r}_{com} = 0$ in the frame of reference of the center of mass.

(b) Assuming as a quantization condition that the total angular momentum of the bound pair is $L = n\hbar$ and assuming $n = 1$ find an expression for the ground-state energy of positronium.

The quantization condition on the total angular momentum gives $L_{tot} = mvr_e + mvr_p = 2 \times mv(r/2) = mvr = n\hbar$, since the velocities of the particles are equal and opposite in the center of mass frame. Combining these relations with those found from Newton's second law gives

$$v = \frac{ke^2}{2n\hbar} \qquad r = \frac{2n^2\hbar^2}{kme^2} = 2n^2 a_0 \,. \tag{3.2}$$

The total energy is, then,

$$E = 2 \times \frac{1}{2}mv^2 - \frac{ke^2}{r} = \frac{ke^2}{4n^2 a_0} - \frac{ke^2}{2n^2 a_0} = -\frac{ke^2}{4n^2 a_0} \,. \tag{3.3}$$

The ground state energy corresponds to $n = 1$ and gives

$$E = -\frac{ke^2}{4a_0} \,. \tag{3.4}$$

The energy is thus, twice smaller than that of a hydrogen atom. The ionization energy needed to break free a positronium pair starting from the ground state is approximately $E_0 \simeq -13.6/2eV = -6.8eV$.

As a remark, note that the two-body problem considered here can be reduced to an effective one-body problem. The effective problem is equivalent in form to the problem of the hydrogen atom, however with the mass replaced by the "reduced mass" $\mu = (1/m_e + 1/m_p)^{-1}$. In the case of positronium, μ is simply $\mu = (2/m)^{-1} = m/2$. The Bohr formula for the ground state energy, $E_0 = -k^2 me^4/(2\hbar^2)$, shows that E_0 is proportional to the mass (at fixed charge). We thus recover that the positronium energy is half of that of the hydrogen atom.

The same argument can be used to calculate the spectrum of the hydrogen atom taking into account the motion of the proton (which performs a small orbit around the center of mass). However since the proton is much heavier than the electron ($m_e/m_p \simeq 1/2000$), the reduced mass μ is to an excellent approximation equal to the electron mass: $\mu \simeq m_e$. This shows that for the hydrogen atom the motion of the proton can be neglected.

4 The Blackbody Radiation Formula

Consider the energy density per unit volume per frequency of a black body as conceived by Max Planck

$$u_f(f, T) = \frac{8\pi h f^3}{c^3} \frac{1}{e^{hf/k_B T} - 1} \,. \tag{4.1}$$

(a) Show that for large f, the energy density is reduced to

$$u_f(f,T) \approx \frac{8\pi h f^3}{c^3} e^{-hf/k_BT} \,. \tag{4.2}$$

This is the Wien's exponential law.

In this limit, the exponent of the exponential function in the denominator will be very large, i.e. $e^{hf/k_BT} \gg 1$. Thus, we have in this limit:

$$u_f(f,T) \approx \frac{8\pi h f^3}{c^3} \frac{1}{e^{hf/k_BT}} = \frac{8\pi h f^3}{c^3} e^{-hf/k_BT} \,, \tag{4.3}$$

which gives us the desired result.

(b) Show that for small f, the energy density is reduced to

$$u_f(f,T) \approx \frac{8\pi f^2}{c^3} k_B T \,. \tag{4.4}$$

Hint: You may use the Taylor expansion of the exponential function $e^x \approx 1 + x$ for small x.

In the limit of small f, we expand the exponential function in the denominator for small hf/k_BT using the Taylor expansion:

$$e^{hf/k_BT} \approx 1 + hf/k_BT \,. \tag{4.5}$$

Using this result in Eq. (4.1), we find

$$u_f(f,T) \approx \frac{8\pi h f^3}{c^3} \frac{1}{1 + hf/k_BT - 1} = \frac{8\pi f^2}{c^3} k_B T \,. \tag{4.6}$$

(c) Set $x = hf/k_BT$ in Eq. (4.1). Find an expression for the value x_{max} that maximizes the energy density $u_f(f,T)$.

By setting $x = hf/k_BT$ in Eq. (4.1), we obtain

$$u(x,T) = \frac{8\pi x^3 k_B^3 T^3}{h^2 c^3} \frac{1}{e^x - 1} \,. \tag{4.7}$$

Now, we take a derivative with respect to x

$$\frac{\mathrm{d}u(x,T)}{\mathrm{d}x} = \frac{8\pi k_B^3 T^3}{h^2 c^3} \left[\frac{3x^2}{e^x - 1} - \frac{x^3 e^x}{(e^x - 1)^2} \right] \tag{4.8}$$

We set this to zero, and we obtain the following equation:

$$\frac{3x_{max}^2}{e^{x_{max}}-1} - \frac{x_{max}^3 e^{x_{max}}}{(e^{x_{max}}-1)^2} = 0 \quad \Rightarrow \quad 3x_{max}^2 e^{x_{max}} - 3x_{max}^2 - x_{max}^3 e^{x_{max}} = 0 \quad (4.9)$$

We eliminate the solution of $x = 0$ as the trivial solution, thus

$$3e^{x_{max}} - 3 - x_{max}e^{x_{max}} = 0\,, \quad (4.10)$$

which we can re-write as

$$(3 - x_{max}) = 3e^{-x_{max}}\,. \quad (4.11)$$

(d) Find an approximate numerical value of x_{max} by solving the equations found in question (c) under the approximation $e^{-x} \ll 1$.

Using this approximation for Eq. (4.11), the RHS will tend to zero, and thus

$$x_{max} \approx 3\,. \quad (4.12)$$

(e) Show that the corresponding wavelength at the maximum takes the form of:

$$\lambda_{max}T = C\,. \quad (4.13)$$

Find the constant C and its value. This is the so-called Wien's displacement law for the maximum wavelength.

Using the latter result and the definition of x, we find

$$x_{max} = \frac{hf_{max}}{k_B T} = \frac{hc}{k_B\lambda_{max}T} = 3 \quad \Rightarrow \quad \lambda_{max}T = \frac{hc}{3k_B}\,. \quad (4.14)$$

Thus the constant C is equal to $hc/(3k_B)$. Evaluating C using the numerical values of all fundamental constants in SI units, we find $C \approx 4.8 \cdot 10^{-3} mK$. The value measured from the experiments is $C_{exp} \approx 2.9 \cdot 10^{-3} mK$. A significant discrepancy is observed which we address in the next question.

(f) Eq. (4.1) gives the energy density per unit volume and per unit frequency. Calculate, by a change of variables, the energy density per unit wavelengths $u_\lambda(\lambda, T)$ (such that the energy density of the electromagnetic waves within a range of wavelengths (λ_1, λ_2) is $\int_{\lambda_1}^{\lambda_2} d\lambda\ u_\lambda(\lambda, T)$). As shown in Questions (d,e), the maximum of $u(f,T)$ occurs at $f_{\rm max} = x_{max}k_B T/h \simeq 3k_{\rm B}T/h$. Show that instead the maximum of $u_\lambda(\lambda, T)$ is at $\lambda_{\rm max} T \simeq hc/(5k_{\rm B})$. Why is there a discrepancy?

Switching from λ to f, we find

$$\int df\, u_f(f,T) = \int d\lambda \left|\frac{\mathrm{d}f}{\mathrm{d}\lambda}\right| u_f(f(\lambda),T) = \int d\lambda\, u_\lambda(\lambda,T) \tag{4.15}$$

Thus, the spectral energy density is

$$u_\lambda(\lambda,T) = \left|\frac{\mathrm{d}f}{\mathrm{d}\lambda}\right| u_f(f(\lambda),T)\,. \tag{4.16}$$

Using $f = c/\lambda$ and $df = -c/\lambda^2 d\lambda$, we find:

$$u_\lambda(\lambda,T) = \frac{c}{\lambda^2}\frac{8\pi h c^3}{c^3\lambda^3}\frac{1}{e^{hc/\lambda k_B T}-1} = \frac{8\pi hc}{\lambda^5}\frac{1}{e^{hc/\lambda k_B T}-1}\,. \tag{4.17}$$

Now we set $x = hc/\lambda k_B T$, and we have

$$u_x(x,T) = \frac{8\pi (k_B T)^5}{(hc)^5}\frac{x^5}{e^x - 1}\,. \tag{4.18}$$

We take the derivative with respect to x and we set it to zero to obtain

$$5 - x_{max} = 5e^{-x_{max}}\,, \tag{4.19}$$

where we have discarded the trivial solution $x = 0$. We again use the approximation $e^{-x_{max}} \ll 1$, and thus obtain:

$$x_{max} \approx 5\,. \tag{4.20}$$

Using the definition of x, we obtain the Wien's displacement law

$$\lambda_{max} T = B, \quad B = \frac{hc}{5k_B}\,. \tag{4.21}$$

Evaluating the constant B yields $2.88 \cdot 10^{-3} mK$, which is much closer to the experimental value! Hence, in order to obtain the correct constant, we must appropriately map the energy density $u_f(f,T)$ to the spectral energy density $u_\lambda(\lambda,T)$.

(g) What are the characteristic temperatures for which the maximum of $u_\lambda(\lambda,T)$ corresponds to visible light with yellow color? ($\lambda \simeq 580$ nm).

We use the Wien's displacement law, as we have obtained it in the previous Question,

$$\lambda_{max} T = 2.88 \cdot 10^{-3} mK\,. \tag{4.22}$$

By using $\lambda_{max} = 580$ nm, we find $T = 4966$ K.

(h) Compute the total energy density by integrating over the frequency domain. This corresponds to the area under the energy density curve. Show that:

$$\frac{c}{4}\int_0^\infty df\, u_f(f,T) = \sigma T^4, \quad \sigma = \frac{2\pi^5 k_B^4}{15 h^3 c^2}\,, \tag{4.23}$$

and σ is the Stefan-Boltzmann constant. Hint: Use $\int_0^\infty dx\, x^3/(e^x - 1) = \pi^4/15$.

We simply integrate over the energy density as follows:

$$I = \frac{c}{4}\int_0^\infty df\, u(f,T) = \frac{c}{4}\frac{8\pi h}{c^3}\int_0^\infty df\, \frac{f^3}{e^{hf/k_B T} - 1}\,. \tag{4.24}$$

We change variables according to $x = hf/k_B T$, and our expression becomes:

$$I = \frac{2\pi h}{c^2}\frac{(k_B T)^4}{h^4}\int_0^\infty dx\, \frac{x^3}{e^x - 1} \tag{4.25}$$

By using what is given, i.e. $\int_0^\infty dx\, x^3/(e^x - 1) = \pi^4/15$, we find:

$$I = \frac{2\pi h}{c^2}\frac{(k_B T)^4}{h^4}\frac{\pi^4}{15} = \frac{2\pi^5 k_B^4}{15 h^3 c^2} T^4 = \sigma T^4\,. \tag{4.26}$$

The Stefan-Boltzmann law describes the intensity of the thermal radiation emitted in terms of the body's temperature. This relation was derived empirically by Josef Stefan, while proved theoretically by Ludwig Boltzmann.