Photoionization

Objective: In this module, we will explore the process of the photoionization, in which a quantum system (atom, molecule, surface of a solid) is illuminated by an electromagnetic radiation (EM) and, as a result, emits an electron. Photoionization is one of the fundamental processes, described accurately only by quantum mechanical methods. Photoelectric effect, which leads to the early development of the quantum theory, could be considered as a particular case of the process. Here, we will consider atomic photoionization, more precisely, photoionization of an atom having, for simplicity, only one electron in the external shell, such as H, Li, Na, K, or similar. The module will focus on calculating (approximately) wave functions of the external electron of the atom. We consider the initial wave function (i.e. before ionization) and the final wave function (after ionization). Then, we apply the theory developed for photon absorption/emission to evaluate the transition probability from the initial to the final state of the system under the influence of the EM radiation. The transition probability is then used to computed the cross section of the photoionization. We consider an application of the developed python code to determination of photoelectric current in a gas subject of the EM radiation. Having studied the module, students will have an understanding of the process, will be familiar with possible applications and prepared to other advanced topics in quantum technology.

Problem:

In the last section of the "Photoionization" module (https://qtechedu.centralesupelec.fr/EN/ex1.html) the basic principles of operation of the photoionization detector (PID) were discussed (in the "Application" tab) .

Imagine that PID is used to measure the concentration of Na vapor in a room under standard condition:
- Pressure P = 101325 Pa;
- Temperature T = 298 K.

The detector uses an ultraviolet lamp with photon energy 10.6eV. Calculate the <u>*current*</u> generated in the detector if the detected concentration is 3.6 ppm.

Parameters for calculation:
- *Charge of an electron: e = 1.602 $\cdot$ 10^{-19} C;*
- *Volume of the ionization chamber: V = 10 x 10^{-6} m^3;*
- *Emitted power of the lamp: P_{lamp} = 20 x 10^{-3} W;*
- *Distance from the lamp's emitting surface (the UV window) to the center of the ionization volume in the PID: d = 3 x 10^{-3} m.*

Solution method:

The current in the PID is determined by the rate of ion production, which depends on:

- Concentration of gas (for example, benzene, sodium etc.) - the number of gas molecules present in the detector's gas stream.
- Photon flux of the UV lamp - the number of photons available to ionize the gas molecules.
- Photoionization cross section - the probability of a benzene molecule being ionized when hit by a photon.

Once ions are produced, they are collected at the electrodes. The current is proportional to the number of ions collected per unit time:

$$I = e \cdot N_i / t \quad,$$

where N_i is the number of ions produced per unit time. It is proportional to the volume density of the gas detected in the PID, the photoionization cross section and the photon flux (current density),

$$N_i = N_m \cdot \sigma \cdot \Phi_{ph}$$

where σ is photoionization cross section (units of area). The value of σ for photons of 10,6 eV (according to the problem statement) can be found from references or calculation.

The number of gaz molecules N_m inside the PID is

$$N_m = r_{gas} \cdot N_{all} = r_{gas} \cdot n_{all} \cdot V$$

where r_{gas} is the ratio of the number of gaz molecules to the total number of molecules (dimensionless), N_{all} and n_{all} are the total number of molecules (particles) and the volume density of all molecules in the PID ionization chamber (particles/m^3), respectively. V is the volume of the ionization chamber, which can be obtained from the technical documentation of the PID.

We can get n_{all} from Ideal Gas Law:

$$P = n \cdot k_B \cdot T \quad,$$

where k_B = 1.380649 × 10^{-23} JK^{-1} is the Boltzmann constant, and P is the total pressure of the gas in the chamber. Therefore,

$$N_m = \frac{r_{gas} \cdot P}{k_B T} \cdot V$$

where Φ_{ph} is photon flux, i.e. the number of photons received by the PID per unit time and per unit area (for example, in units of photons/(s · cm^2)). It determines how many UV photons are available to ionize gas molecules in the detector chamber. It is obtained from the intensity of radiation at PID as:

$$\Phi_{ph} = \frac{I_{rad}}{E_{ph}}$$

where E_{ph} is the photon energy. The radiation intensity I_{rad} can be obtained dividing the lamp radiation power P_{lamp} by $4\pi d^2$, where d is the distance from the lamp to the PID:

$$I_{rad} = \frac{\Phi_{ph}}{4\pi d^2}.$$

Combining all the above formulas together, we obtain

$$I = e\, r_{gas} \frac{PV}{k_B T} \sigma \frac{P_{lamp}}{4\pi d^2 E_{ph}}$$

To compute the current, the photoionization cross section σ *is* required. To obtain σ, use the "Quantum Technology" interface (https://qtechedu.centralesupelec.fr/EN/ex1.html) in the "Photoionization cross section" module.

Activity with the interface:

https://qtechedu.centralesupelec.fr/EN/ex1.html

Using the interface answer the following question and perform the suggested calculations.

1. <u>The Introductory part:</u>

- What is the physical interpretation of the photoionization cross section and what physical quantities determine its value?

- Compare the concept of cross section in classical and quantum mechanical approaches.

- Provide the formula used in this module to calculate the photoionization cross section of an atom?

- What physical assumptions and mathematical approximations are involved in the derivation?

- Why is the photoionization process often modeled by assuming that only one outer-shell electron participates? For which types of atoms is this one-electron approximation valid? Can you provide examples where this assumption is not valid?

- How are the initial and final states of an atom characterized in terms of energy and wave functions during the photoionization process?

2. <u>In Tab "Coulomb functions for Negative Energies"</u> explore the method for calculating the wave function of an electron in a bound state using Whittaker functions.

- What method is used to solve the radial Schrödinger equation for a bound electron in a Coulomb potential, and why is a variable transformation typically applied?

- What are the Whittaker functions?

- How are the Whittaker functions related to the solution of the Schrödinger equation for the Coulomb potential? What is the difference between the Whittaker functions $M_{\kappa,m_w}(z)$ and $W_{\kappa,m_w}(z)$ and which one is appropriate for describing bound electron states?

- How would you calculate these functions for a given energy E?

To visualize the wave function of an electron in bound state, use the interface. The necessary tools are located at the bottom of the tab <u>"Coulomb functions for negative energies" (as shown in the image below).</u>
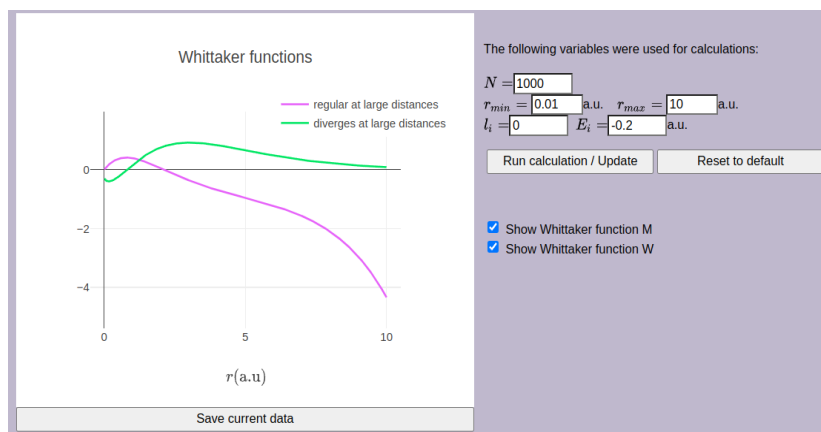
1. Use the following parameters:

$r_{\min} = 0.01$ a.u. (bohr)
$r_{\max} = 10$ a.u. (bohr)
$l_i = 0$
$E_i = -0.2$ a.u (hartree)
The mass is 1 a.u. (mass of electron, m_e)

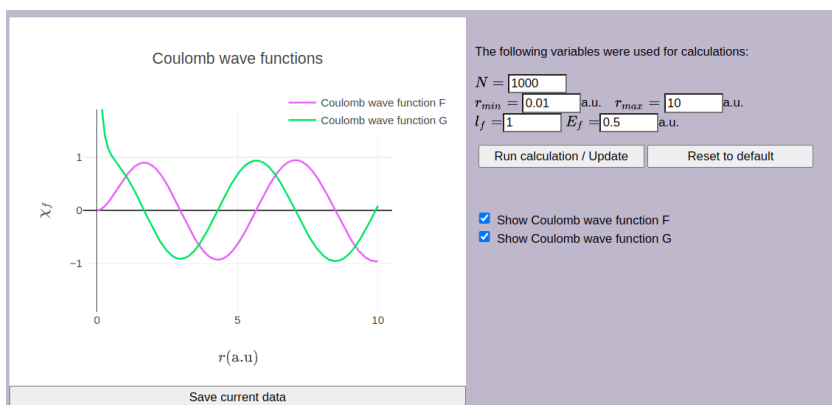Click button "Run calculation".

The "Reset to default" button allows you to restore the default values.

If you need to save the result, click button "Save current data".

2. Perform calculations the Whittaker functions for different values of the initial energy, for example, -0.5 a.u., -0.25 a.u. Present the results of the calculation for the Whittaker $W_{\kappa, m_w}(z)$ functions and explain the obtained results.

3. <u>In the tab "Coulomb functions for Positive Energies"</u> a method for calculating the wave function of an electron in a free state after photoionization using Coulomb functions is presented.

- What are the regular (F_1 (η, z)) and irregular (G_1 (η, z)) Coulomb wave functions? How do they differ in their physical interpretations?

- How would you calculate the Coulomb wave functions F_l (η, z) and G_l (η, z) for a given positive energy E?

- What are the initial and final energy states of the atom during the ionization process? Describe the process of solving the radial Schrödinger equation for the case of a Coulomb potential for the bound and continuum states.

- Why the Schrödinger equation has to be transformed into a standard form?

1. Use the parameters in the cases:

$r_{\min}$ = 0.01 a.u. (bohr)
$r_{\max}$ = 10 a.u. (bohr)
l_i = 0
E_i = 0.5 a.u (hartree)
The mass is 1 a.u. (mass of electron, m_e)

Click button "Run calculation".

2. Perform calculations for different values of the final energy: 0.8 a.u., 1.2 a.u. Present the results of the calculation and explain the obtained results.

4. <u>In the **"Photoionization Cross Section"** tab</u>, it is proposed to calculate the PI cross section for different atoms and transition types. When an atom is selected from the drop-down menu, its corresponding quantum numbers are automatically set, or you can manually enter the quantum numbers into the designated fields.

Select the atom for which calculation will be carried out in this section Na ⌄ its initial state P ⌄ and final state D ⌄

The following variables were used for calculations:

$N = $ [100] $r_{min} = $ [0.5]   a.u. $r_{max} = $ [25]   a.u. $N_E = $ [50]

$n_i = $ [3] $l_i = $ [1] $l_f = $ [2] $m_i = $ [0]

For initial quantum defect $\mu_i = $ [0.8] $E_i = -\dfrac{1}{2(n_i - \mu_i)^2}$ = -0.10331 a.u.

For final quantum defect $\mu_f = $ [0.014897] $E_f = -\dfrac{1}{2(n_i - \mu_f)^2}$ = -0.05611 a.u.

[Run calculation / Update]   [Reset to default]

1. To find the PI cross section σ^{PI}:

- Select **Na** and the desired transition ($P \rightarrow D$) or enter the required values into the fillable boxes.
- The corresponding values of the quantities will automatically appear in the boxes.

2. Using the interface, complete the blanks below with each quantity and its corresponding description.

$N = $

$N_E = $

$r_{min} = $ a.u.*

$r_{max} = $ a.u.

$n_i = $

$l_i = $, $l_f = $

$m_i = $

$\mu_i = $, $\mu_i = $

Click button "Run calculation".

3. Look at the graphs, describe what they show and what you can learn from them.

The calculation results will be required to solve the problem described in the first paragraph, which involves determining the concentration of sodium vapor using a photoionization detector (PID). The basic principles of PID operation are discussed in the "**Application**" tab (https://qtechedu.centralesupelec.fr/EN/ex1.html). To solve this problem, answer the following questions:

- Using the resulting figures, determine the PI cross section for photons with energy 10,6 eV.
- Explain how the unit of concentration in [ppm] is converted to SI units [m^{-3}].
- Write the final formula for current I using the material from "Solution method". Use dimensional analysis to verify its correctness in SI units.
- Calculate the current that the PID shows, if the relative fraction of Na atoms is 3.6 ppm.

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* Atomic units are used https://en.wikipedia.org/wiki/Hartree_atomic_units that are defined as following:
$\hbar$=1 unit of angular momentum,
e=1 unit of charge,
mass of the electron m_e=1 unit of mass.
Units of all other quantities are derived from these three units. Atomic units are very convenient in quantum mechanics (atomic, molecular physics). If you see the symbols "a.u.", it means that one uses atomic units for this quantity.