PI-Na

June 19, 2023

Phtoionization cross section

We cosider the process of ionization of an atom. The origin of energy is chosen to be at energy of ionization E_{th}: $E_{th} = 0$. Therefore, the initial bound state $|i\rangle$ of the atom has a negative energy $E_i < E_{th}$, while after ionization, in the final state $|f\rangle$, when one of the electrons is at an infitite distance fromt the atom, the energy of the system is positive $E_f > E_{th}$.

For the simplicity of the discussion, it is assumed that only one electron in the outer electronic shell participates in the process. The assumption gives the exact result for one-electron systems (such as H or He^+). The assumption is a very good appoximation for alkali atoms and for many situations of excited states of other atoms. However, the approximation is not accurate for such atoms as He or Ne in their ground electronic state.

It is also assumed that the z axis of the laboratory reference frame is chosen along the axis of polarization of the incident light. In this situation, the photoionization cross section is given by the formula

$$\sigma_{PI} = \frac{4\pi^2 e^2}{c} \omega \left|\hat{z}_{fi}\right|^2 ,$$

where $\hat{z}$ is the z-coordinate of the active electron. In the general case, a sum over the z components of all electrons should be evaluated.

In the above expression $|i\rangle$ and $|i\rangle$ are initial and final states of the system. Because one-electron approximation is used, the wave functions of $|i\rangle$ and $|i\rangle$ are written as

$$|i\rangle = R_i(r) Y_{l_i m_i}(\theta, \phi)$$
$$|f\rangle = R_f(r) Y_{l_f m_f}(\theta, \phi)$$

and the z component of the electron is represented by spherical coordinates

$$\hat{z} = r\cos(\theta) = \sqrt{\frac{4\pi}{3}} r Y_{1,0}(\theta, \phi)$$

$$\hat{z}_{fi} = \langle R_f | r | R_i \rangle \sqrt{\frac{4\pi}{3}} \langle Y_{l_f m_f} | Y_{10} | Y_{l_i m_i} \rangle$$

The angular part of the integral in the matrix element $\hat{z}_{fi}$ is evaluated analytically

$$\langle Y_{l_f m_f} | Y_{10} | Y_{l_i m_i} \rangle = \sqrt{\frac{2l_i + 1}{2l_f + 1}} \sqrt{\frac{3}{4\pi}} C^{l_f 0}_{l_i 010} C^{l_f m_f}_{l_i m_i 10} .$$

Using the notation $r_{fi} = \langle R_f|r|R_i\rangle$, $\hat{z}_{fi}$ becomes

$$\hat{z}_{fi} = r_{fi}\sqrt{\frac{2l_i+1}{2l_f+1}}C^{l_f 0}_{l_i 0 1 0}C^{l_f m_i}_{l_i m_i 1 0}\delta_{m_i m_f}\,.$$

Radial functions $R_i = \frac{\chi_i}{r}$ and $R_f = \frac{\chi_f}{r}$ are obtained solving the radial Schrodinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\chi}{dr^2} + \left(\frac{\hbar^2 l(l+1)}{2mr^2} + V(r)\right)\chi = E\chi\,.$$

for the corresponding ($E_i < 0$ and $E_f > 0$) energies. The potential of interaction is a pure Coulomb potential $V(r) = -\frac{Ze^2}{r}$ if the atom has only one electron, such as H, He^+, etc. For multi-electron atoms, $V(r)$ behaves as $-\frac{Ze^2}{r}$ only for large distances r.

At large values of r, the bound-state wave function $\chi_i(r) \to 0$, while $\chi_f(r)$ oscillates. For pure Coulomn field, the asymptotic behavior of $\chi_f(r)$ is

$$\chi_f(r) \to \sqrt{\frac{2}{\pi k}}\sin(kr + \frac{\ln(r}{k} + \sigma_C)$$

Coulomb functions for negative enegies

The Schrodinger equation for the Coulomb potential

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dr^2} + \left(-E + \frac{\hbar^2 l(l+1)}{2mr^2} - \frac{Ze^2}{r}\right)\psi = 0$$

with $E < 0$. After the change $r = az$ and $\psi = bw$ is transformed to

$$\frac{\hbar^2 b}{2ma^2}\frac{d^2w}{dz^2} + \left(bE - \frac{\hbar^2 bl(l+1)}{2ma^2r^2} + \frac{Ze^2 b}{ar}\right)w = 0$$

with $bE = -1/4$ ($b > 0$) and $\frac{\hbar^2 b}{2ma^2} = 1$ the equation is brought to the top one

$$\frac{d^2w}{dz^2} + \left(-\frac{1}{4} + \frac{Ze^2}{\hbar}\sqrt{\frac{m}{-2E}}\frac{1}{z} - \frac{l(l+1)}{z^2}\right)w = 0$$

i.e.

$$k = \frac{Ze^2}{\hbar}\sqrt{\frac{m}{-2E}}$$

- effective quantum number and

$$m = \sqrt{l(l+1) + 1/4}.$$

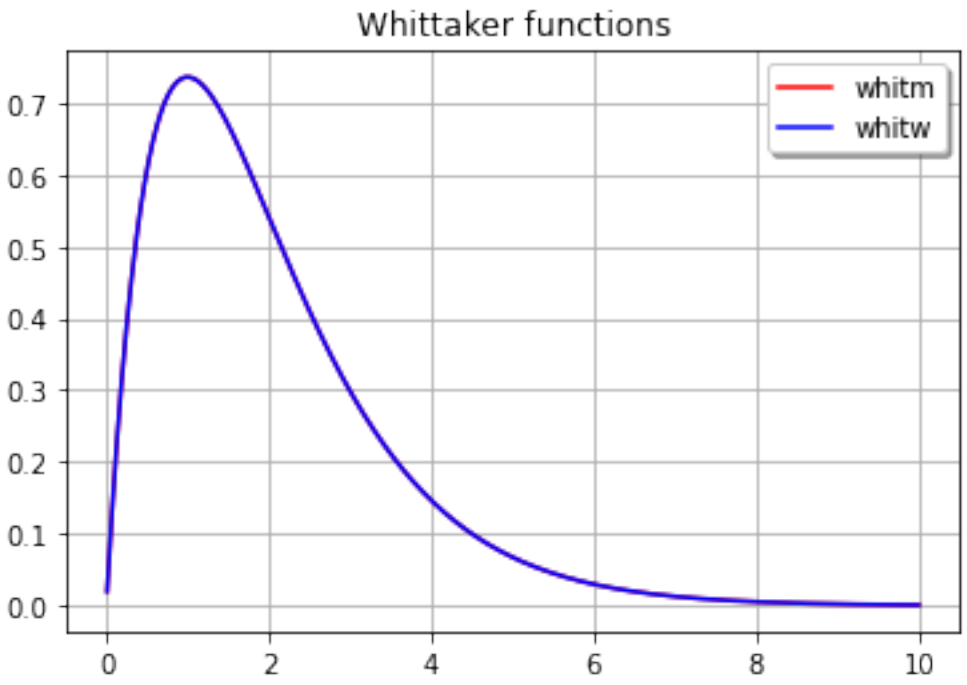
The scaling factor a for coordinate is

$$a = \frac{\hbar}{2}\sqrt{\frac{1}{-2mE}}$$

Below, Whittaker functions for E=energy are calculated and plotted. The norm is calculated.

[1]:
```
from mpmath import *
import matplotlib.pyplot as plt
import numpy


mp.dps = 15; #precision 25 digits
mp.pretty = True
energy_i=-1./2#+0.0001
l_partial_i=0.
k=sqrt(1./(-2*energy_i));
m=sqrt(l_partial_i*(l_partial_i+1)+0.25);
scale=sqrt(1./(-8.*energy_i));

npoints=1000
r_coor = numpy.linspace(0.01,10., npoints)
y1 = numpy.zeros( npoints)
y2 = numpy.zeros( npoints)
norm=0.
for i in range(npoints):
  z=r_coor[i]/scale
  y1[i]=whitm(k, m, z)
  y2[i]=whitw(k, m, z)
  norm=norm+y2[i]*y2[i]

norm=norm*(r_coor[2]-r_coor[1])
print('norm=',norm)
plt.title("Whittaker functions")
plt.plot(r_coor, y1, '-r', label='whitm')
plt.plot(r_coor, y2, '-b', label='whitw')
plt.legend(loc='best', fancybox=True, shadow=True)
plt.grid()
plt.show()
```

```
norm= 0.9999995479283429
```



Coulomb functions for positive enegies

mpmath.coulombf(l, eta, z) calculates the regular Coulomb wave function

$$F_l(\eta, z) = C_l(\eta) z^{l+1} e^{-iz} \, {}_1F_1(l + 1 - i\eta, 2l + 2, 2iz)$$

where the normalization constant $C_l(\eta)$ is as calculated by coulombc(). This function solves the differential equation

$$f''(z) + \left(1 - \frac{2\eta}{z} - \frac{l(l+1)}{z^2}\right) f(z) = 0.$$

A second linearly independent solution is given by the irregular Coulomb wave function $G_l(\eta, z)$ (see coulombg()). The Coulomb wave functions with real parameters are defined in Abramowitz & Stegun, section 14. However, all parameters are permitted to be complex in this implementation (see references).

The Schrodinger equation for the Coulomb potential

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dr^2} + \left(-E + \frac{\hbar^2 l(l+1)}{2mr^2} - \frac{Ze^2}{r}\right)\psi = 0$$

with $E > 0$. After the change $r = az$ and $\psi = bf$ is transformed to

$$\frac{\hbar^2 b}{2ma^2}\frac{d^2w}{dz^2} + \left(bE - \frac{\hbar^2 bl(l+1)}{2ma^2 z^2} + \frac{Ze^2 b}{az}\right) f = 0$$

with $bE = 1$ ($b > 0$) and $\frac{\hbar^2 b}{2ma^2} = 1$ the equation is brought to the top one

$$\frac{d^2f}{dz^2} - \left(1 + \frac{Ze^2}{\hbar}\sqrt{\frac{2m}{E}}\frac{1}{z} - \frac{l(l+1)}{z^2}\right) w = 0$$

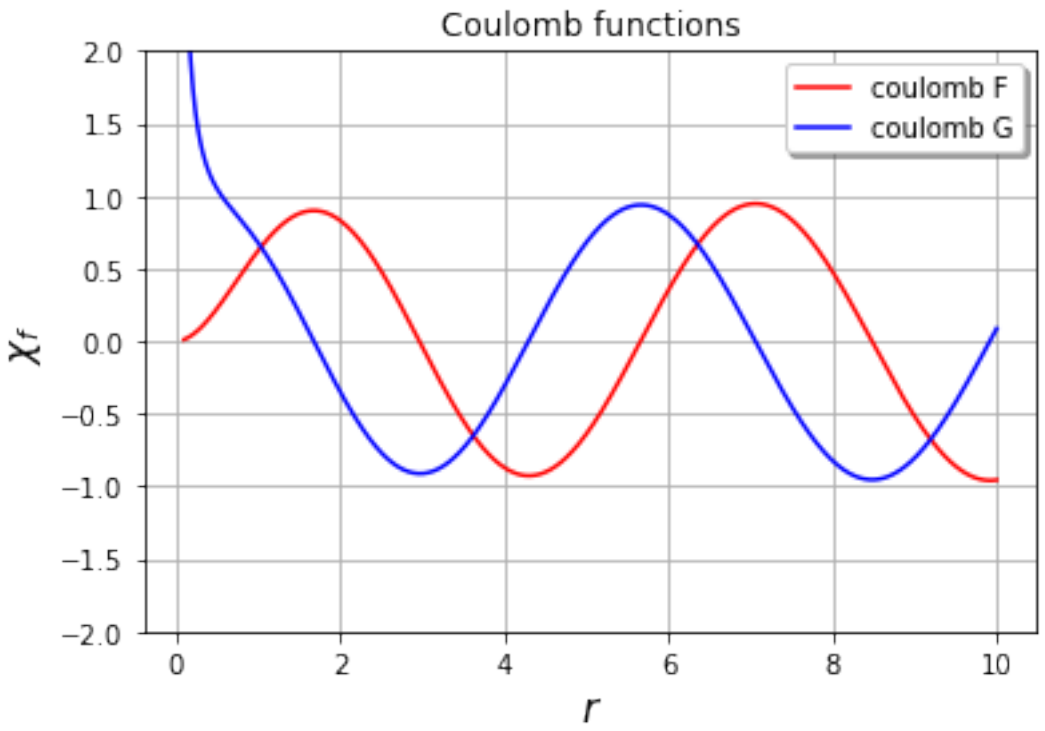
i.e.

$$\eta = -\frac{Ze^2}{\hbar}\sqrt{\frac{m}{2E}}.$$

It has the same form as the effective quantum number but with positive E. The scaling factor a for coordinate is

$$a = \frac{\hbar}{\sqrt{2mE}}$$

[4]:
```
from mpmath import *
import matplotlib.pyplot as plt
import numpy


energy_f=1./2
l_partial_f=1.
eta=-sqrt(1./(2*energy_f));
scale=sqrt(1./(2.*energy_f));

npoints=1000
r_coor = numpy.linspace(0.1,10., npoints)
chi_f1 = numpy.zeros( npoints,float)
chi_f2 = numpy.zeros( npoints,float)
norm=0.
for i in range(npoints):
  z=r_coor[i]/scale
  chi_f1[i]=coulombf(l_partial_f,eta, z)
  chi_f2[i]=coulombg(l_partial_f,eta, z)

plt.title("Coulomb functions")
plt.plot(r_coor,  chi_f1, '-r', label='coulomb F')
plt.plot(r_coor,  chi_f2, '-b', label='coulomb G')
plt.legend(loc='best', fancybox=True, shadow=True)
plt.grid()
plt.xlabel('$r$',size=15)
plt.ylabel('$\chi_f$',size=15)
plt.ylim(-2, 2)
plt.show()
```

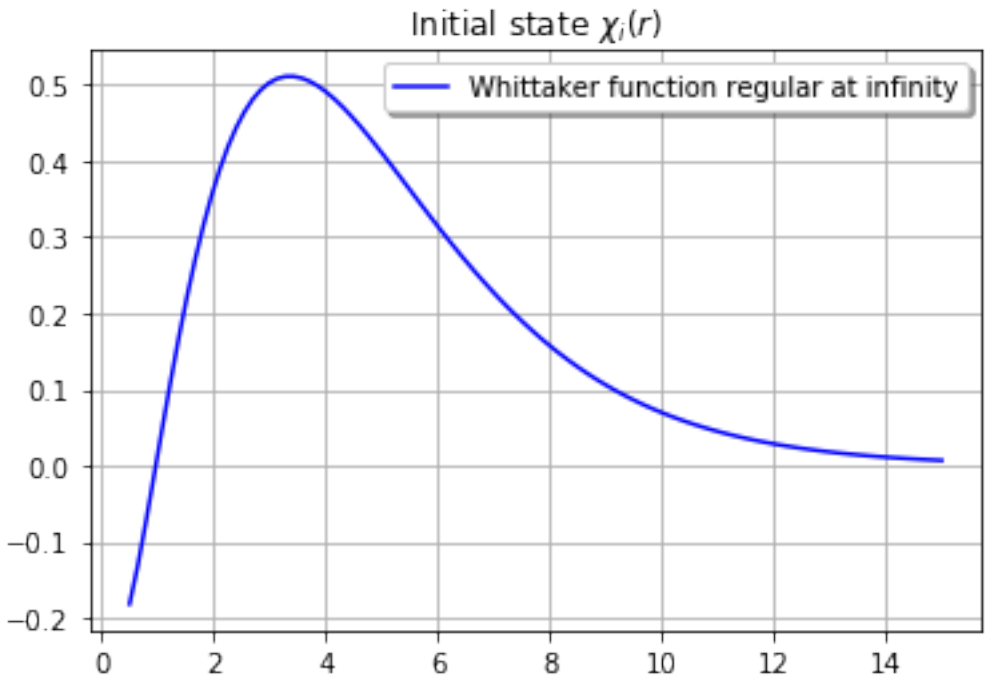


[6]:
```
from mpmath import *
import matplotlib.pyplot as plt
import numpy

# coordinate grid
npoints=100; rmax=15.
r_ini=0.5

# initial wave function
quan_def_i=1.3479;n_i=3
energy_i=-1./(2.*(n_i-quan_def_i)**2); l_partial_i=0 # energy and ang momentum
print ('initial energy is',energy_i)

k=sqrt(1./(-2*energy_i));
m=sqrt(l_partial_i*(l_partial_i+1)+0.25);
scale=sqrt(1./(-8.*energy_i));

r_coor = numpy.linspace(0.5,15., npoints)
dr=r_coor[2]-r_coor[1]
y1 = numpy.zeros( npoints)
chi_i = numpy.zeros( npoints)
norm=0.
for ip in range(npoints):
```

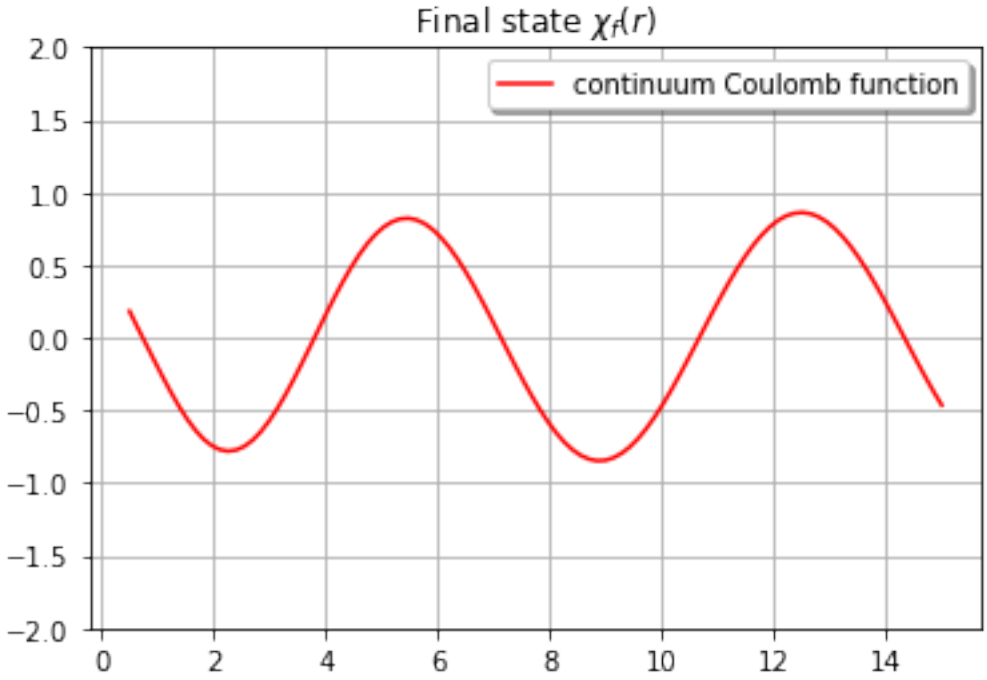
```
  z=r_coor[ip]/scale
  y1[ip]=whitm(k, m, z)
  chi_i[ip]=whitw(k, m, z)
  norm=norm+chi_i[ip]*chi_i[ip]


norm=norm*dr
chi_i=chi_i/sqrt(norm)

# plotting the initial wave function
plt.title("Initial state $\chi_i(r)$")
#plt.plot(r_coor, y1, '-g', label='whitm')  # regular at the origin
plt.plot(r_coor, chi_i, '-b', label='Whittaker function regular at infinity') ␣
 ↪# regular at infinity
plt.legend(loc='best', fancybox=True, shadow=True)
plt.grid()
plt.show()


# final wave functions
nE=50
chi_f=numpy.zeros([nE, npoints],dtype =float)
r_fi=numpy.zeros(nE,dtype =float)
energy_f=numpy.zeros(nE,dtype =float)
for i_energy in range(nE):
  energy_f[i_energy]=0.3/nE*(i_energy+1)
  l_partial_f=1
  eta=-sqrt(1./(2*energy_f[i_energy]));
  scale=sqrt(1./(2.*energy_f[i_energy]));


  for ip in range(npoints):
    z=r_coor[ip]/scale
    coul_f=coulombf(l_partial_f,eta, z)
    coul_g=coulombg(l_partial_f,eta, z)

    quan_def=0.8833
    chi_f[i_energy,ip]=coul_f*cos(pi*quan_def)+coul_g*sin(pi*quan_def)

    r_fi[i_energy]=r_fi[i_energy]+chi_f[i_energy,ip]*r_coor[ip]* chi_i[ip]*dr

# wave function should be energy-normalized
  wf_normalization_factor=sqrt(2./(pi*sqrt(2*energy_f[i_energy])))
  chi_f[i_energy,:]=chi_f[i_energy,:]*wf_normalization_factor
  r_fi[i_energy]=r_fi[i_energy]*wf_normalization_factor

# plotting one of the final wave functions
```

```
iE=nE-1
print('Energy-normalized final state for energy E=',energy_f[iE]*27.3,'eV')
plt.title('Final state $\chi_f(r)$')
plt.plot(r_coor, chi_f[iE-1,:], '-r', label='continuum Coulomb function')
plt.legend(loc='best', fancybox=True, shadow=True)
plt.ylim(-2, 2)
plt.grid()
plt.show()


# PI cross section
cross_section=numpy.zeros(nE,dtype =float)
for i_energy in range(nE):
  cross_section[i_energy]=abs(r_fi[i_energy])**2 /3. *4*pi**2 /137.
 ↪*(energy_f[i_energy]-energy_i)

print('Photoinization cross section for Na in the ground state 3S')
plt.plot(energy_f*27.3, cross_section, '-g', label='c.s.')
plt.legend(loc='best', fancybox=True, shadow=True)
#plt.ylim(-2, 2)
plt.grid()
plt.show()
```

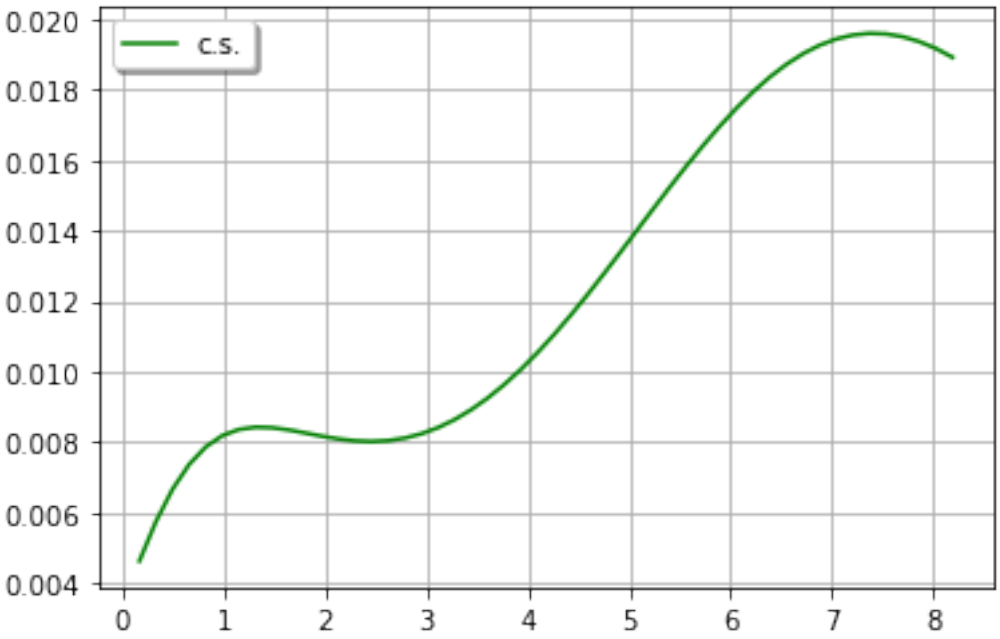
```
initial energy is -0.18318813530309383
```



Energy-normalized final state for energy E= 8.19 eV



Photoinization cross section for Na in the ground state 3S



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