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Atomic, molecular physics and optics
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Problem Set 11: Molecular spectroscopy

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Exercise 1: Rotational and vibrational modes

In this exercise we will study the rotational and vibrational modes of diatomic molecu

We start our analysis with the pure vibrational spectrum. The energies are given by the Schrödinger equation

$$\frac{\hbar^2}{2\mu R^2}\frac{d}{dR}\left(R^2\frac{d\psi}{dR}\right) - V(R)\psi(R) = E\psi(R)$$

where $\psi(R)$ is the radial part of the wavefunction, μ is the reduced mass and $V(R)$ is the energy of the system with fixed nuclei position. We have seen two approximations of $V(R)$ - the harmonic potential

$$V_{par}(R) = \frac{1}{2}k(R - R_e)^2$$

and the Morse potential

$$V_{mor}(R) = D_e\left(1 - e^{-a(R-R_e)}\right)^2$$

The spectrum is given by

$$E_{par,n} = \hbar\omega(n + \frac{1}{2}), \qquad \omega = \sqrt{\frac{k}{\mu}}$$
$$E_{mor,n} = \hbar\omega(n + \frac{1}{2}) - \hbar\omega x_e(n + \frac{1}{2})^2, \qquad \omega = a\sqrt{\frac{2D_e}{\mu}}, \quad x_e = \hbar a\sqrt{\frac{1}{8D_e\mu}}$$

a.) Show that $V_{mor}(R)$ is minimal at $R = R_e$. Expand the potential up to second order at the minimum and express k as a function of D_e and a. Show that this approximation recovers exactly the harmonic term of the Morse potential spectrum (i.e. the anharmonicity term with x_e is excluded).

b.) Taking $D_e \approx 1$ eV and $a \approx 1/$Ang and $\mu = 1u$ as typical orders of magnitudes, estimate the energy scale of the vibrational spectrum. Express the characteristic energy in the units of temperature, photon wavelength and photon frequency.

The rotational spectrum in the rigid rotor estimation is given by the series

$E_(J) = B_e J(J+1) = \frac{\hbar^2}{2\mu R_e^2} J(J+1)$

c.) Using that $R_e \approx 1$ Ang and $\mu \approx 1u$, estimate the energy scale of the rotational spectrum, as well as the corresponding temperature, photon wavelength and frequency.

Since the rotational energy scale is much smaller than the vibrational energy scale one might add the rotational energy as a first order perturbation in the full Hamiltonian:

$$H_{vib+rot} = \underbrace{\frac{\hbar^2}{2\mu R^2}\frac{d}{dR}\left(R^2\frac{d}{dR}\right) - V(R)}_{H_{vib}} + \underbrace{\frac{\hbar^2}{2\mu R^2}J(J+1)}_{H_{rot}}$$

d.) Show that the total energy can be written as

$$E(n,J) = E_{vib,n} + \underbrace{B_n J(J+1)}_{E_{rot,n}}$$

where $E_{vib,n}$ is the pure vibrational energy of the n-th state, and express B_n in terms of $\langle\psi_n|\frac{1}{R^2}|\psi_n\rangle$. Further express the emission spectrum of the $n = 1 \rightarrow 0$ transition in terms of $\Delta E_{vib} = E_{vib,1} - E_{vib,0}$ and B_1 and B_0.

Remark: Recall that only the $\Delta J = \pm 1$ transitions are allowed. This means that eve
mode is lower than the $n = 0$ vibrational mode) or the R-branch (where the angular m

We will now turn our attention to a qualitative analysis of B_e, B_0 and B_1.

e.) Which approximation of $\langle\psi_n|\frac{1}{R^2}|\psi_n\rangle$ was used in the rigid rotor assumption to get $B_e = B_0 = B_1$?

f.) Assume we go beyond the rigid rotor assumption, such that B_n is not only defined by the position of the potential minimum R_e but requires information of the entire potential $V(R)$. Order the energies B_e, B_0 and B_1 for a parabolic potential $V_{par}(R)$.

g.) Sketch a potential characterized by $B_e > B_0 > B_1$.

Hint: The Morse potentialfulfills this condition. Explain which characteristics of the

In the last part we address the information that can be obtained from the emission spectrum. This is often used in astrophysics e.g. to study the composition and temperature of interstallar medium (see Figure 1). The following spectrum (Figure 2) is obtained from a diatomic molecule in this cloud, and the transition in question is $n = 1 \rightarrow 0$. The rigid rotor approximation is used.

\newline

Figure 1: The interstellar medium (ISM) is the matter and radiation that exists in the space between the star systems in a galaxy. This matter includes gas in ionic, atomic, and molecular form, as well as dust and cosmic rays. It fills interstellar space and blends smoothly into the surrounding intergalactic medium.

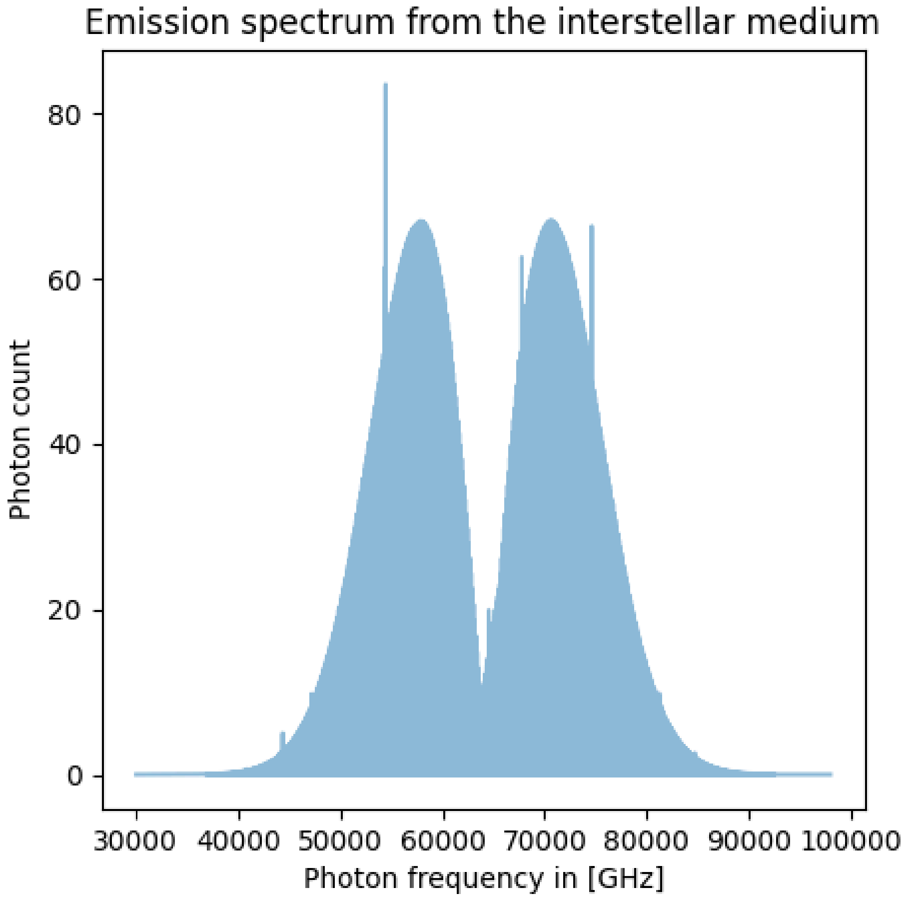


Figure 2: Model emission spectrum of a diatomic molecule in the ISM.

h) Plot the emission spectrum in the provided file 'fs.txt'. Use the provided code to plot its Fourier Transform.

Remark: Since the file is rather large, the operation can take 5-10 seconds.

Technical Remark on the numerical Fourier Transform:

Imagine we want to calculate $g(k) := \hat{f}\,(2\pi k) = \int e^{2\pi i k x} f(x) dx$, where $\hat{f}$ is the usual Fourier Transform of f. Numerically this is obtained as

$$g[m] = \sum_{n=0}^{N-1} e^{-\frac{2\pi i m n}{N}} f[n]$$

where we have dropped the normalization for the sake of simplicity. Writing $x[n] = ndv$ we see that defining $k[m] = \frac{m}{dvN}$ ensures consistency between the numerical and analytical result. Here N (the number of data points) was the length of the arrays f and g, and dv is the spacing between the x-values.

With regards to the following code we have:

f is written using the variable fs (the photon count)

x is written using the variable vs (the photon frequency in GHz)

g is written using the variable F (the numerical Fourier Transform of fs)

k is written using the variable freq

In [1]:

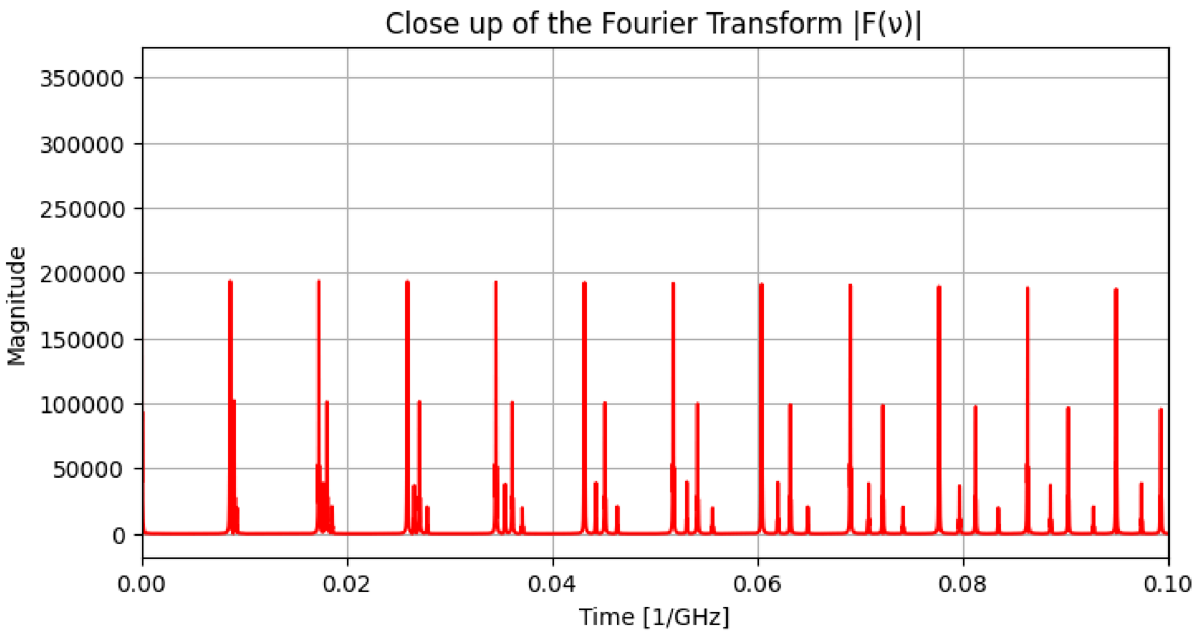
```
import numpy as np
import matplotlib.pyplot as plt
from scipy.fft import fft, fftfreq, fftshift

#Constants in SI units
hbar = 1.05457182*10**(-34) #hbar
u = 1.66054*10**(-27)       #unit mass
k_B =  1.380649*10**(-23)   #Boltzmann constant


#####################################################################

vs = np.linspace(30000, 98000, 2*680000)  #Photon frequencies in GHz
fs = np.loadtxt('fs.txt')  #emission spectrum

####################################################################
dv = vs[1] - vs[0]
N = len(vs)
# Compute FFT
F = fft(fs)
freq = fftfreq(N, dv)
# Shift zero freq to center
F_shifted = fftshift(F)          #fourier transform ready to plot (y-axis da
freq_shifted = fftshift(freq)    #x-axis data
```

i) A close up of the Fourier Transform shows 4 fundamental frequencies (all around 0.01 GHz^{-1}) corresponding to 4 dominant rotational modes. Determine their relative strength and the corresponding photon frequency.

Remark: We recommend analyzing the higher harmonics, where the signal is more sp

In [4]:

```
plt.figure(figsize=(8, 4))
plt.plot(freq_shifted, np.abs(F_shifted), 'r')
plt.title('Close up of the Fourier Transform |F(ν)|')
plt.xlabel('Time [1/GHz]')
plt.ylabel('Magnitude')
plt.xlim(0, 0.1)
plt.grid(True)
plt.show()
```



In [ ]:

```
data = np.abs(F_shifted)
h1 = np.max(data[(freq_shifted > 0.06)*(freq_shifted < 0.061)])     #The fir
h2 = np.max(data[(freq_shifted > 0.0615)*(freq_shifted < 0.0625)])  #The sec
h3 = np.max(data[(freq_shifted > ##)*(freq_shifted < ##)])          #The thi
h4 = np.max(data[(freq_shifted > ##)*(freq_shifted < ##)])          #The fou
hs = np.array([h1, h2, h3, h4])
print('The peak magnitudes are', h1, h2, h3, h4)



p1 = np.argmax(data[(freq_shifted > 0.06)*(freq_shifted < 0.061)])
p2 = np.argmax(data[(freq_shifted > 0.0615)*(freq_shifted < 0.0625)])
p3 = np.argmax(data[(freq_shifted > ##)*(freq_shifted < ##)])
p4 = np.argmax(data[(freq_shifted > ##)*(freq_shifted < ##)])

f1 = freq_shifted[p1+ len(freq_shifted[(freq_shifted < 0.06)])]          #Th
f2 = freq_shifted[p2+ len(freq_shifted[(freq_shifted < 0.0615)])]        #Th
f3 = freq_shifted[p3+ len(freq_shifted[(freq_shifted < ##)])]            #Th
f4 = freq_shifted[p4+ len(freq_shifted[(freq_shifted < ##)])]            #Th
rot_fs = np.array([7/f1, 7/f2, 7/f3, 7/f4])

print('The dominant photon frequencies are', 7/f1, 7/f2, 7/f3, 7/f4, 'GHz')
```

j) Assume that the interstellar medium only contains two of the four elements in the table. Deduce from the ratio of the photon frequencies in the emission spectrum what these two elements are. What are the relative abundances of the isotopes in the interstellar medium.

Hint: Use that in the rigid rotor approximation the reduced mass is proportional to th
of the (fundamental or) higher harmonics directly reflects the isotope abundance.

Element	Isotope Mass (u)
H	1
H	2
C	12
C	13
N	14
N	15
O	16
O	17

In [ ]:

```
import numpy as np
m_H = np.array([1, 2])     #hyrdogen atom mass in units
m_C = np.array([12, 13])   #carbon atom mass in units
m_N = np.array([14, 15])   #nitrogen atom mass in units
m_O = np.array([16, 17])   #oxygen atom mass in units


def redm(m_1s, m_2s):
    #formula that calculates the reduced masses
    return m_s


redms = redm(#, #)  #reduced masses for the 4 isotop combinations
ratio = np.average(redms*rot_fs)
#Compare np.sort(1/rot_fs) and np.sort(redms)/ratio with a method of your li

print('The abundance ratio of the first element is')  #Deduce using h1/h2, h
print('The abundance ratio of the second element is') #Deduce using h1/h2, h
```

k) Calculate the equilibrium bond length R_e of the diatomic molecule.

l) At last we are intersted in the temperature of the ISM. To deduce it we will concentrate solely on the R-branch of the diatomic molecule using the most abundant isotope combination.

In [ ]:

```
maxs = np.max(fs)
ys = fs[(fs > maxs/2)*(vs>##)]  #The factor 2 insures that only signals from
xs = vs[(fs > maxs/2)*(vs>##)]  #The factor 2 insures that only signals from


## Extracting solely the peaks of the signal
ymax = ys[0]
mys = []
mxs = []
for i in np.arange(len(ys)-2):
    if  ys[i+1] > ys[i] and ys[i+1] > ys[i+2]:
        mys.append(ys[i+1])
        mxs.append(xs[i+1])


def myT(xs, T, vm, A):
```

```
    # Fitting function
    #T is the temperature
    #vm is the pure vibrational energy
    #A is a normalization constant
    m = #Input reduced mass
    J = #input the J quantum number
    myexp = #Define the correct energy*T
    return A*(2*J+1)*np.e**(-myexp*J*(J+1)/T)

from scipy.optimize import curve_fit
coeffs = curve_fit(myT, mxs, mys, p0 = [1000, 60000, 1])[0]


plt.title('Emission spectrum')
plt.plot(mxs, mys, '.', label = 'data', color = 'k')
plt.plot(mxs, myT(mxs, coeffs[0], coeffs[1], coeffs[2]), label = 'fit', colo
plt.xlabel('photon frequency [GHz]')
plt.ylabel('Photon count')
plt.legend()

print('The temperature in the ISM is', coeffs[0], 'K')
```

m) Assuming a harmonic potential, calculate the spring constant k. Using the data from l.)

In [ ]:

```
k = ##
print('The spring constant k is', k, 'N/m')
```

The equilibrium distance R_e and the spring constant k used in this exercise are both r
Furthermore, while the temperature of the ISM is realistic, the isotope ratios are not,

Exercise 2: Raman spectroscopy

This exercise shows a semiclassical view on Raman spectroscopy

We start with a time dependent electrical field

$$E(t) = E_0 \cos(2\pi\nu t).$$

The induced dipole moment of the diatomic molecule can be written as

$$\mu(t) = \alpha E_0 \cos(2\pi\nu t)$$

where α is the polarizability. We furthermore assume that the interatomic distance oscillates like

$$x(t) = x_e + \Delta x \cos(2\pi\nu_{vib} t)$$

with the vibratonal frequency ν_{vib}.

a.) Assume that the polarizability $\alpha(x)$ is a function of the interatomic distance. Use a first order expansion and show that the dipole moment oscillates with 3 different frequencies, ν, $\nu + \nu_{vib}$ and $\nu - \nu_{vib}$.

Remark: Picking up these frequency using a detector allows the measurement of ν_{vib}.

We will now follow the same logic for the rotational spectrum.

b.) We write the polarizability matrix in the principle coordinates as

$$\alpha = \begin{pmatrix} \alpha_\perp & 0 & 0 \\ 0 & \alpha_\perp & 0 \\ 0 & 0 & \alpha_\parallel \end{pmatrix}$$

where the $\alpha_\parallel$ point along the axis connecting the two atoms. Express the induced dipole moment μ_E collinear to the incident electrical field. What is the corresponding α_E.

Use spherical coordinates and express everything in terms of θ*, defined as the angle b*

c.) Assume now that the molecule turns such that

$$\theta(t) = 2\pi\nu_{rot}t.$$

Show that μ_E oscillates with 3 different frequencies ν, $\nu + 2\nu_{vib}$ and $\nu - 2\nu_{vib}$.

In [ ]: