Problem set 4: Rydberg atoms

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A Rydberg atom is an atom excited to a state of very high principal quantum number n. Typically, the valence electron of an alkali atom can be excited to $\mathrm{n} \sim 20-200$. There, it behaves (almost) like the electron of a Hydrogen atom. Let's explore a few of the properties of Rydberg atoms, their interactions and the phenomenon called Rydberg Blockade.

Exercise 1: Properties of Rydberg atoms

Rydberg atoms are one class of *hydrogen-like* atoms, meaning that a single electron dominates the atomic properties. As in the case of Hydrogen, the electronic wavefunctions, or "atomic orbitals", can be indexed by the quantum numbers n, l, j and m_j (taking into account the spin-orbit coupling) and can be separated into a radial term and an angular term $\psi_{n,l,j,mj}(r,\theta,\phi) = R_{n,l}(r)A_{l,j,m_j}(\theta,\phi)$. Here we denote with $R_{n,l}(r)$ the solutions of the radial part of the Schrödinger equation for Rydberg atoms, keeping in mind that they slightly differ from the functions we are familiar with from the case of Hydrogen[1]. We further denote by $A_{l,j,m_j}(\theta,\phi)$ the angular part of the wavefunction. It is constructed, as in the case of Hydrogen, using the spherical harmonics Y_{l,m_l}.[2]

The corresponding eigenenergies read:

$$E_{n,l,j} = -\frac{E_I}{(n-\delta_{nlj})^2}$$

where E_I is the ionization energy for the electron and δ_{nlj} denotes the the so called *quantum defect*.
We will now explore a few general properties of Rydberg atoms.

a) Write the matrix element of the position vector $\langle n,l,j,m_j \mid \hat{\vec{r}} \ \ |n',l',j',m_j'\rangle$ between two orbitals as a product of an angular term $\vec{\mathcal{A}}(l\ j\ m_j, l'\ j'\ m_j')$ and a radial term $\mathcal{R}(n\ l, n'\ l')$.

b) Write the mean value of the radius $\langle \hat{r} \rangle = \langle ||\hat{\vec{r}}|| \rangle$ for an atom in state $|n,l,j,m_j\rangle$.
*Hint: You can use that the angular part of the wavefunction $A_{l,j,m_j}(\theta,\phi)$ is normalized to 1.

c) Write as products of $\mathcal{R}$ and $\vec{\mathcal{A}}$ terms the matrix elements of the dipole operator $q\hat{\vec{r}}$, where q denotes charge, between:
(i) State $|n,l,j,m_j\rangle$ and state $|n',l',j',m_j'\rangle$. This is called the transition dipole moment between state $|n,l,j,m_j\rangle$ and state $|n',l',j',m_j'\rangle$.
(ii) State $|n,l,j,m_j\rangle$ and itself. What is the difference with the quantity calculated in question b)?

d) The radial part $\mathcal{R}$ of these integrations is a known mathematical problem. It can be solved numerically by a method known as Numerov integration. The main result we need to know here is that $\mathcal{R}(n\ l, n'\ l') \propto nn'$. How does the mean radius scale with n and how does this relate to the scaling of the mean radius of the Hydrogen wavefunctions that you have seen in the lecture?
How does the transition dipole moment between state $|n,l,j,m_j\rangle$ and state $|n',l',j',m_j'\rangle$ with similar quantum numbers $n' \approx n$, scale with n? We will use this result in the following exercise.

[1]: One approach to find the radial solutions of the Schrödinger equation in the case of Rydberg atoms is the quantum defect theory, as you have seen for alkali atoms in the lecture, taking into account the screening of the nuclear charge by the other electrons in the region close to the nucleus.

[2]: If we work in the coupled basis of l and s, we have to consider the different combinations of m_l and m_s that can lead to a specific m_j.
Explicitly written, the construction of the angular part of the wavefunction reads:

$$A_{l,j,m_j}(\theta,\phi) = \sum_{m_l,m_s} \langle l,m_l;1/2,m_s|j,m_j\rangle\ Y_{l,m_l}(\theta,\phi)\ \chi_{m_s}$$

where $\langle l,m_l;1/2,m_s|j,m_j\rangle$ denote the Clebsch-Gordan coefficients and we denote by χ_{m_s} the two spin eigenstates, given in vector form as:

$$\chi_{1/2} = \begin{pmatrix}1\\0\end{pmatrix}, \quad \chi_{-1/2} = \begin{pmatrix}0\\1\end{pmatrix}$$

Exercise 2: Rydberg-Rydberg Interaction

The scaling of the transition dipole moment with n between neighboring Rydberg levels makes them exceptional antennas for electromagnetic radiation at the transition frequencies. Just like in classical electromagnetism, dipoles can interact with an external field but also with each other. This will give rise to the Rydberg-Rydberg interactions that we will study here.

Let us consider two atoms 1 and 2 separated by a vector $\vec{r}$ and in states $|n_1, l_1, j_1, m_{j1}\rangle$ and $|n_2, l_2, j_2, m_{j2}\rangle$ respectively. We have to work in the Hilbert space that is the tensor product of the atomic states Hilbert space of each atom $\mathcal{S}_{12} = \mathcal{S}_1 \otimes \mathcal{S}_2$. For each atom, $\hat{\vec{r}}_{1,2}$ denotes the position operator of their valence electron, as represented in Fig. 1, and $\hat{\vec{d}}_{1,2} = q\hat{\vec{r}}_{1,2}$ the corresponding dipole operators.

The coupling between these two dipoles reads :

$$\hat{V}_{dd}(\vec{r}) = \frac{1}{4\pi\epsilon_0 r^3}\left(\hat{\vec{d}}_1 \cdot \hat{\vec{d}}_2 - 3(\hat{\vec{d}}_1 \cdot \frac{\vec{r}}{r})(\hat{\vec{d}}_2 \cdot \frac{\vec{r}}{r})\right) = \frac{q^2}{4\pi\epsilon_0 r^3}\left(\hat{\vec{r}}_1 \cdot \hat{\vec{r}}_2 - 3(\hat{\vec{r}}_1 \cdot \frac{\vec{r}}{r})(\hat{\vec{r}}_2 \cdot \frac{\vec{r}}{r})\right)$$

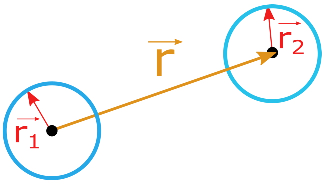

Figure 1: Two atoms separated by $\vec{r}$.

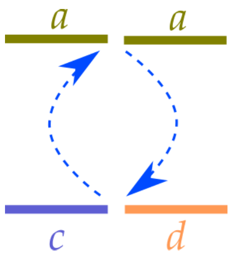

Figure 2: Diagram of the dipole-dipole second-order coupling between two atoms in the same Rydberg state $|a\rangle$

To carry on the calculation, we need to choose an axis to define coordinates. In the absence of any external field (electric or magnetic), which axis do you suggest to choose as a quantization axis?

a) Show that, in the right coordinate system, where the orbital for atom i will be described by (r_i, θ_i, ϕ_i), we can write

$$\hat{V}_{dd} = \frac{-q^2}{3\epsilon_0}\frac{\hat{r}_1\hat{r}_2}{r^3}f(\theta_1, \phi_1, \theta_2, \phi_2) = \frac{-q^2}{3\epsilon_0}\frac{\hat{r}_1\hat{r}_2}{r^3}(Y_{1,1}(\theta_1, \phi_1)Y_{1,-1}(\theta_2, \phi_2) + Y_{1,-1}(\theta_1, \phi_1)Y_{1,1}(\theta_2, \phi_2) + 2Y_{1,0}(\theta_1, \phi_1)Y_{1,0}(\theta_2, \phi_2))$$

where the spherical harmonics read: $Y_{1,0}(\theta, \phi) = \sqrt{3/4\pi}\cos\theta$ and $Y_{1,\pm1}(\theta, \phi) = \mp\sqrt{3/8\pi}\sin\theta e^{\pm i\phi}$ and we denote with $\hat{r}$ the absolute value of the position operator as in the previous exercise $\hat{r} = ||\hat{\vec{r}}||$. The form of f accounts for the angular part of the interaction and indicates that the $\hat{V}_{dd}$ operator conserves the total magnetic quantum number $m_{j_1} + m_{j_2}$ of the pair.

b) If the two atoms are in states with similar quantum numbers $n_1 \approx n_2$, what is the scaling of $\hat{V}_{dd}$ with n?

Let us now consider a pair of Rydberg atoms in the same atomic state $|a\rangle = |n, l, j, m_j\rangle$ and consider $\hat{V}_{dd}$ as a perturbation in the total Hamiltonian.

c) Show that $\langle aa|\hat{V}_{dd}|aa\rangle = 0$. However, since there are neighboring Rydberg states with different quantum numbers, we need to consider the second order perturbation induced by $\hat{V}_{dd}$.

d) These neighboring states can be represented by pair states of the form $|cd\rangle = |n_c, l_c, j_c, m_{jc}\rangle \otimes |n_d, l_d, j_d, m_{jd}\rangle$. Write the contribution $\Delta E_{aa}(cd)$ of one pair state $|cd\rangle$ to the second order perturbation of the energy of $|aa\rangle$.

e) Summing over all these states $|cd\rangle$, write the explicit sum for the interaction energy $hC_{aa}(r)$ between two Rydberg atoms in state $|a\rangle$ given by second order perturbation theory.
What is the dependence on r of $hC_{aa}(r)$? Write it as $hC_{aa}(r) = \frac{hC_{\alpha,aa}}{r^\alpha}$ with the right integer value for α. Show that the terms in $C_{\alpha,aa}$ with $n_c \approx n_d \approx n_a = n$, scale as n^{11}.

From now on we focus on the case where $|a\rangle = |nS\rangle = |n, l = 0, j = 1/2, m_j = +1/2\rangle$.

f) Using the selection rules of dipole allowed transitions that you have seen in the lecure, as well as the properties of $f(\theta_{1,2}, \phi_{1,2})$, rewrite the sum $\sum_{|cd\rangle}$, mentioning explicitly all the combinations of $l_c, l_d, j_c, j_d, m_{j_c}, m_{j_d}$ that need to be considered.
Hint: The selection rules for dipole allowed transitions are $\Delta l = \pm1$; $\Delta j = 0, \pm1$ (except $j = j' = 0$);$\Delta m = 0, \pm1$.

g) Since the denominator $2E_a - E_c - E_d$ becomes very large when $|n - n_{c,d}|$ increases, a first rough approximation is to restrict the calculation to $n_{c,d} = n \pm 1$. With this restriction, and adding the constraint that $n_c + n_d = 2n$, write the list of states to take into account in the sum.

Note that **this approximation is too strong**, and and we should at least consider the terms where $n_c = n$ and $n_d = n \pm 1$ or the opposite. A better way to do the approximation is to set a limit on the denominator, such as for example $|2E_a - E_c - E_d| < h \times 25\mathrm{GHz}$.

Exercise 3: The Alkali Rydberg Calculator (ARC) and Rydberg Blockade

We have now treated the simplest case of Rydberg-Rydberg interaction. There are many more possible cases, including in particular the interaction between different Rydberg states |a⟩ and |b⟩, or cases where the choice of axis we made in exercise 2 is made invalid, for example by the presence of external fields. However, the case we just treated is sufficient to understand many phenomena of Rydberg atom physics, such as the **"Rydberg blockade"**, which will be treated in the following exercise.

To further explore the properties of Rydberg atoms and the phenomenon of the Rydberg blockade, we will use the Python library for alkali Rydberg atoms (ARC) that has been developed by the research group of Charles S. Adams at Durham University. It allows to calculate all the one- and two-atom properties of low-angular-momentum Rydberg states for any alkali atom.

Note: The detailed documentation of the ARC library can be found here:
https://arc-alkali-rydberg-calculator.readthedocs.io/en/latest/index.html.
Application examples are provided here:
https://arc-alkali-rydberg-calculator.readthedocs.io/en/latest/Rydberg_atoms_a_primer_notebook.html#Rydberg-atom-wavefunctions.

a) Use the cell below to plot the probability of presence of the electron as a function of the distance to the nucleus for states $10S$, $25S$ and $60S$ for $^{87}\mathrm{Rb}$. Comment the result, especially how does it compare to the expectation you have from exercise 1?

In [ ]:
```python
import matplotlib.pyplot as plt  # Import library for direct plotting functions
import numpy as np               # Import Numerical Python
from arc import *                # Import the Alkali Rydberg Calculator
```

In [ ]:
```python
atom=Rubidium87()

colors = ["b","r","g"]

### Todo: fill in the quantum numbers of the states of interest
pqn = [] # principle quantum numbers
l =           # L
j =          # J

plotLegend = []
for i in range(len(pqn)):
    n = pqn[i]
    step = 0.001
    a1,b1 = atom.radialWavefunction() ### Todo: complete
    legendInfo, = plt.plot(a1,(b1)*(b1),"-",lw=2,color = colors[i], label = ("n = %d" % n) )
    plotLegend.append(legendInfo)

plt.legend(handles=plotLegend)
plt.xlabel(r"Distance from nucleus $r$ ($a_0$)")
plt.ylabel(r"$\vert rR(r)\vert^2$")
plt.show()
```

b) Use the cell below to calculate the transition dipole moment between states $10S - 10P$ and between states $50S - 50P$ for $^{87}\mathrm{Rb}$.

In [ ]:
```python
atom=Rubidium87()

### Todo: fill in the quantum numbers of the states of interest
n1=
l1=
j1=
mj1=
n2=
l2=
j2=
mj2=
q=+1
```

```
print("Rb 87 Transition 10S_{1/2}-->10P_{3/2}")
print("==============================")
#Angular Coupling
print("<nljmj|er|n'l'j'mj'> = %.3f ea_0\n" %\
        atom.getDipoleMatrixElement(n1,l1,j1,mj1,n2,l2,j2,mj2,q))


### Todo: fill in the quantum numbers of the states of interest
n1=
l1=
j1=
mj1=
n2=
l2=
j2=
mj2=
q=+1

print("Rb 87 Transition 50S_{1/2}-->50P_{3/2}")
print("====================================")
#Angular Coupling
print("<nljmj|er|n'l'j'mj'> = %.3f ea_0\n" % \
        atom.getDipoleMatrixElement(n1,l1,j1,mj1,n2,l2,j2,mj2,q))
```

c) Using the functions of ARC, extract the value of the C_6 coefficient perturbatively for the state $60S$ of $^{87}\mathrm{Rb}$ that we have focused on in exercise 2. What is the interaction energy in MHz for a distance of 5 μm and 7 μm?
Plot the interaction energy as a function of distance between 5 μm and 20 μm.

In [ ]:

```
# ToDo: define quantum numbers of state
n0 =
l0 =
j0 =
mj0 =

theta = 0 # Polar Angle [0-pi w.r.t. quantization axis (0 in our case)
phi = 0 # Azimuthal Angle [0-2pi] w.r.t. quantization axis (0 in our case)
dn = 5 # Range of n to consider (n0-dn:n0+dn)
deltaMax = 25e9  # Max pair-state energy difference [Hz]

# Set target-state and extract value
calculation = PairStateInteractions(Rubidium87(), n0, l0, j0, n0, l0, j0, mj0, mj0)
C6 = calculation.getC6perturbatively(theta, phi, dn, deltaMax)
print("C6 [%s] = %.2f GHz (mum)^6" % (printStateString(n0, l0, j0), C6))

### Todo: complete
atom_distance =
int_energy =
print(r'Interaction energy at {} mum = '.format(atom_distance), int_energy, 'MHz')
```

d) We learned in the previous exercises that the interaction energy, and therefore the total energy of the two-atom state, can depend on the relative distance between the two atoms.
Given what you learned in the exercises before, sketch (qualitatively) the energy diagram you expect for a two-atom state as a function of r in the following cases:
(i) both atoms in the ground state
(ii) one atom excited to the Rydberg state $|a\rangle = |S\rangle = |n, l = 0, j = 1/2, m_j = +1/2\rangle$ as we considered before
(iii) both atoms excited to this Rydberg state
Hint: You only have to consider a dependence on r in case (iii).

e) Now imagine we shine a laser resonant with the transition from the ground state to a Rydberg state $|a\rangle$. Why is it not possible to excite both atoms to the Rydberg state in this situation?
Hint: The topic of light-matter interaction will be treated in detail towards the end of this course. For now, you can assume that there is a term in the Hamiltonian H' coupling state $|g\rangle$ to $|a\rangle$ if the difference in energy $|E_a - E_g|$ equals the energy of one photon $\hbar\omega$.

f) The natural linewidth of a Rydberg state is typically in the few kHz range. Assuming an infinitely narrow laser and given a linewidth $\Gamma/2\pi = \gamma = 4\mathrm{kHz}$ for the $60S$ state of $^{87}\mathrm{Rb}$, what is the minimal distance at which two atoms can be excited by the scheme mentioned above? This distance is called the “blockade radius”.

Remark: In the scope of this exercise we used basic functions of ARC. Don't hesitate to dive further into the documentation and try out more of its functionalities!

In [ ]: