Problem Set 2: Electric hyperfine structure for hydrogenic atoms

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Exercise 1: Isotope shift

In this exercise we investigate the influence of the nuclear charge distribution on the electronic energy levels. With the help of a simple model we derive the so called 'isotope shift' that emerges due to the finite extent of the nuclear charge distribution and interpret its dependencies.

Remark: This exercise is expected to be solved with pen and paper.

a) Model the nucleus as a sphere with radius R and assume a homogeneous charge distribution $\rho(\vec{r}) = \rho_0$ within the sphere. Show that the potential energy $V(\vec{r})$ experienced by an electron at position $\vec{r}$ takes the form:

$$V(\vec{r}) = \begin{cases} \frac{Ze^2}{8\pi\epsilon_0 R} \cdot (\frac{r^2}{R^2} - 3) & r \leq R \\ -\frac{Ze^2}{4\pi\epsilon_0 r} & r > R \end{cases} \tag{1}$$

Hint: To calculate the potential energy $V(\vec{r})$, we can first consider the electric field $\vec{E}(\vec{r})$ generated by the nucleus and then integrate from infinity to the position $\vec{r}$ to obtain the electrostatic potential $\phi(\vec{r})$, which is linked to the potential energy as $V(\vec{r}) = -e\phi(\vec{r})$. For the electric field, apply Gauss's law from classical electrodynamics and make use of the spherical symmetry of the problem.

As a reminder, Gauss's law relates the flux of an electric field through a closed surface to the total charge enclosed within it:

$$\iint_\Sigma \vec{E} \cdot \mathrm{d}\vec{S} = \frac{Q}{\epsilon_0}$$

where Σ is a closed surface and Q is the total charge inside the surface.

b) Start with the Hamiltonian of hydrogenic atoms. By making use of perturbation theory, derive the energy shift ΔE caused by the deviation of the potential energy $V(\vec{r})$ compared to the one originating from a point like charge distribution.
Hints: (i) Use the ansatz for hydrogenic wavefunctions $\psi_{nlm}(r,\theta,\phi) = R_{nl}(r) Y_{lm}(\theta,\phi)$ and assume $R_{nl}(r) \approx R_{nl}(0)$ for r within the spatial extent of the nucleus.
(ii) Recall and use the dependence of $R_{nl}(0)$ on the angular momentum quantum number l.

c) The quantity which is measured experimentally is the energy difference between isotopes δE, whose nuclear radii differ by δR.
Give the expression for δE dependent on δR.
Recall the property $|\psi_{n00}(0)|^2 = \frac{1}{4\pi}|R_{n0}(0)|^2 = \frac{Z^3}{\pi a_\mu^3 n^3}$ where $a_\mu = a_0 \frac{m}{\mu}$ is the modified Bohr radius, μ the reduced mass $\mu = \frac{mM}{m+M}$, m and M the mass of the electron and nucleus, respectively. For which electronic states and which atoms do you expect the isotope shift to be significant? Does a spherically symmetric charge distribution, as considered in this exercise, contribute to the hyperfine structure of the energy levels of atoms?

Exercise 2: Beyond spherical charge distributions: electric quadrupole interaction

We have seen that a classical, spherical nuclear charge distribution with a finite extent gives rise to an isotope shift. In this exercise we go one step further and consider all possible charge distributions of the nucleus (not only spherically symmetrical ones). We will see that such distributions can influence other levels than $l = 0$. We will also see how quantum mechanical properties of the nucleus can fundamentally determine this effect.

We start again with the potential energy $V(\vec{r}) = -\frac{Ze^2}{4\pi\epsilon_0} \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'$, where we denote with $n(\vec{r}')$ the charge density distribution, related to the charge distribution as $\rho(\vec{r}) = Qn(\vec{r})$ with Q the total charge of the nucleus. We make use of the so called multipole expansion:

$$\frac{1}{|\vec{r} - \vec{r}'|} = \frac{1}{\sqrt{r'^2 + r^2 - 2rr'\cos(\vartheta)}} = \frac{1}{r_>} \sum_{k=0}^{\infty} \left(\frac{r_<}{r_>}\right)^k P_k(\cos(\vartheta)) \tag{2}$$

Where $r_{<,>} = \min\{r, r'\}, \max\{r, r'\}$, ϑ is the angle enclosed by $\vec{r}$ and $\vec{r}'$ and the expansion coefficients P_k are Legendre polynomials of degree k. The subsequent terms of this expansion are referred to as the **monopole** ($k = 0$), **dipole** ($k = 1$), **quadrupole** ($k = 2$) and in general the $2k$ contribution to the expansion.

a) Use the multipole expansion to write the electrostatic potential arising from the nuclear charge distribution in the form:

$$V(\vec{r}) = \mathcal{H}_{\mathrm{EM}} + \mathcal{H}_{\mathrm{ED}} + \mathcal{H}_{\mathrm{EQ}} + \ldots$$

where the term $\mathcal{H}_{\mathrm{EM}}$ denotes the monopole interaction term, $\mathcal{H}_{\mathrm{ED}}$ denotes the electric dipole interaction term and $\mathcal{H}_{\mathrm{EQ}}$ the electric quadrupole interaction term.

Recall that the Legendre polynomials P_k can be related to the spherical harmonics Y_{lm} (see theorem (4)). Show that for electronic states with $l = 0$ (s-

waves) we expect a contribution to the energy shift ΔE originating from the monopole term only.

b) **Monopole term**: From the expansion in part a) it is directly visible that only the first term is spherically symmetric. Convince yourself that, assuming a sperically symmetric and constant charge distribution, indeed the potential arising from this term takes the same form as (1), which we had found in exercise 1 a).

c) **Dipole term**: Use the addition theorem (4) to separate the dependence on $\vec{r}$ and $\vec{r}'$. Show that this term equals zero.
Hint: You may assume that the parity of the nuclear charge distribution $\rho(\vec{r})$ is always even.

d) **Quadrupole term**:

1. Use the addition theorem (4) to separate the dependence on $\vec{r}$ and $\vec{r}'$ and express the quadrupole term of the potential in terms of the nuclear quadrupole tensor Q_{2q} defined for a classical charge distribution $\rho(\vec{r})$:

$$Q_{2q} := \int r^2 \sqrt{\frac{4\pi}{5}} Y_{2q}(\hat{r}) \rho(\vec{r}) \mathrm{d}\vec{r}.$$

3. Relate the nuclear quadrupol tensor component Q_{20} to the definition of the quadrupole moment of a classical distribution
$Q := \int r^2 (3\cos^2(\theta) - 1)\rho(\vec{r})\mathrm{d}\vec{r}$.

What do you expect Q_{20} to be for a spherically symmetric charge distribution?
From classical intuitions, give an example of a charge distribution $\rho(\vec{r})$ for which you expect a the quadrupole tensor to have non zero entries.
Note: In case you find it useful, you can use the cell below to define a constant charge distribution over an ellipsoid and compute its classical quadrupole moment.

In [1]:
```python
import scipy.integrate as integrate
from mpl_toolkits.mplot3d import Axes3D
import numpy as np
import matplotlib.pyplot as plt
```

In [2]:
```python
###################################################
# Define parameters of charge density ρ
# (for a = c = 1, we recover the case of a sphere)
###################################################

a = 1. # semi-axes a, c of ellipsoid
c = 1.

Z = 2. # Charge number
V = 4 * np.pi / 3 * a**2 *c # Volume of ellipsoid
rho = Z/V # Assume constant charge density over volume


###################################################
# Visualize charge density
###################################################

# Create meshgrid
theta = np.linspace(0, np.pi, 50)   # Polar angle
phi = np.linspace(0, 2*np.pi, 50)   # Azimuthal angle
theta, phi = np.meshgrid(theta, phi)

# Convert spherical to cartesian coordinates
x = a * np.sin(theta) * np.cos(phi)
y = a * np.sin(theta) * np.sin(phi)
z = c * np.cos(theta)

# Define figure
fig = plt.figure(figsize=(10, 8))
ax = fig.add_subplot(111, projection='3d')

# Plot ellipsoid
ax.plot_surface(x, y, z, color='c', edgecolor='k', alpha=0.5)
ax.set_xlabel('X')
ax.set_ylabel('Y')
ax.set_zlabel('Z')
ax.set_title('Charge distribution')
ax.set_xticks(np.linspace(-a, a, 5))
ax.set_yticks(np.linspace(-a, a, 5))
ax.set_zticks(np.linspace(-c, c, 5))
ax.set_box_aspect([a, a, c])
plt.show()

###################################################
# Compute classical quadrupole moment Q, given the
# charge density n(r) defined above
###################################################

def f_quadrupole(theta):
    ### Returns angular part of the integral to compute Q
    return rho * np.pi/3. * (a**2*c**2/(c**2*np.sin(theta)**2 + a**2*np.cos(theta)**2)**(5/2))*np.sin(theta) * (3*np.cos(theta)**2-1.)

result = integrate.quad(f_quadrupole, 0, np.pi)

print(r'Quadrupole moment of the classical charge distribution ρ(r): ', np.round(result[0],2))
```
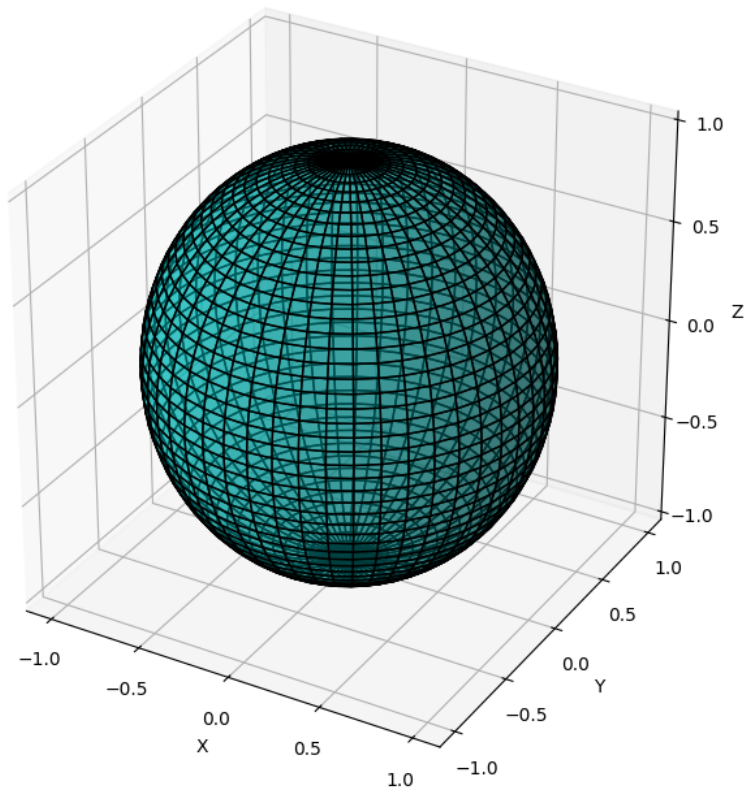
Charge distribution

Quadrupole moment of the classical charge distribution ρ(r): 0.0

In [ ]:

Nuclear quadrupole moment in quantum mechanics

Now we make the link to quantum mechanics. The quadrupole term of the electrostatic potential is governed through the quadrupole operator Q_2, a spherical tensor operator of rank 2 with components Q_{2q}. We denote with I the total angular momentum of the nucleus and with m_I the quantum number representing its projection on the quantization axis. α represents all other quantum numbers of the nucleus.

In analogy to the classical calse, we can define the nuclar quadrupole moment Q:

$$\frac{1}{2}Q := \langle \alpha,\ I,\ m_I = I\ |Q_{20}|\ \alpha,\ I,\ m_I = I \rangle,$$

where Q_{20} is defined as $Q_{20} := \sqrt{\frac{4\pi}{5}} r^2 Y_{20}(\hat{r})$ in the quantum mechanical case.

The components of such a tensor obey the so called Wigner-Eckart theorem, which will be covered in upcoming lectures. In this exercise we will illustrate an example of how this theorem can be used to draw conclusions on physical quantities.

In case of the nuclear quadrupole moment Q, it follows from the Wigner-Eckart theorem that:

$$\frac{1}{2}Q := \langle \alpha,\ I,\ m_I = I\ |Q_{2,0}|\ \alpha,\ I,\ m_I = I \rangle \propto \langle I\,I; 2\,0\,|\,I\,I \rangle, \tag{3}$$

where $\langle I\,I; 2\,0\,|\,I\,I \rangle$ denotes the Clebsch-Gordan coefficient.

e) Argue why in general the Clebsch-Gordan coefficient $\langle I\,m_I; 2\,q\,|\,I\,m_I \rangle$ is zero if $I < 1$. Using equation (3), what follows for Q? Can you make a more general statement about the full quadrupole term including $Q_{2\pm1}$ and $Q_{2\pm2}$ in this case?

Note that, whereas for the isotope shift we found no dependency of ΔE on the quantum number m, for the quadrupole term it can be shown that there is a dependence on both, l and m. Therefore, the quadrupole term lifts the degeneracy of the fine-structure electronic levels and contributes, besides the magnetic hyperfine term, to the hyperfine structure of atoms.

f) According to what you learned in the previous two exercises, for which energy levels of which atomic species do you expect a level splitting due to the electric hyperfine interaction?

(i) ^{6}Li, ^{2}S$_{1/2}$
(ii) ^{87}Rb, ^{2}P$_{3/2}$
*(iii) ^{87}Rb, ^{2}P$_{1/2}$

Useful theorems:

$$P_k(\cos(\vartheta)) = \frac{4\pi}{2k+1} \sum_{q=-k}^{k} (-1)^q\, Y_{k\,-q}(\hat{r})\, Y_{kq}(\hat{r}') \tag{4}$$

where ϑ is the angle between $\hat{r}$ and $\hat{r}'$ and we denote with $\hat{r}$ the absolute direction $\hat{r} = \frac{\vec{r}}{r}$.

In [ ]: