Exercise 1. ***Feynman-Hellman theorem for the hydrogen atom***

The aim of this exercise is to prove a simple yet powerful result by Feynman and Hellman, which was used in class to evaluate the expectation value of $1/r$, $1/r^2$ and $1/r^3$ on the eigenstates of the Coulomb potential.

(a) Let H_λ be a Hamiltonian operator depending on a continuous parameter λ, with eigenvectors $|\psi\rangle$ and eigenfunctions E_λ. Prove the relation

$$\langle\psi| \frac{dH_\lambda}{d\lambda} |\psi\rangle = \frac{dE_\lambda}{d\lambda} \,.$$

This result is known as the Feynman-Hellmann theorem.

(b) Using the Feynman-Hellmann theorem show that

$$\begin{aligned}
\langle\psi_{nlm}| \;\frac{1}{r}\; |\psi_{nlm}\rangle &= \frac{Z}{a\,n^2}, \\
\langle\psi_{nlm}| \;\frac{1}{r^2}\; |\psi_{nlm}\rangle &= \frac{Z^2}{a^2(l+1/2)\,n^3}, \\
\langle\psi_{nlm}| \;\frac{1}{r^3}\; |\psi_{nlm}\rangle &= \frac{Z^3}{a^3 l(l+1/2)(l+1)\,n^3},
\end{aligned}$$

where ψ_{nlm} are the eigenfunctions of the Coulomb problem.
Hint: apply the Feynman-Hellmann theorem with a suitable choice of λ to the time-independent Schrödinger equation for the rescaled radial function $u(r)$, $\mathcal{H}u(r) = Eu(r)$, where

$$\mathcal{H} = -\frac{\hbar^2}{2m}\left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2}\right) - \frac{Ze^2}{r}$$

and the eigenvalues of $\mathcal{H}$ read

$$E_n = -\frac{(Ze^2)^2}{\hbar^2}\frac{m}{2\,n^2} = -\frac{(Ze^2)^2}{\hbar^2}\frac{m}{2(N+l+1)^2} \,.$$

Exercise 2. ***Zeeman effect***

The aim of this exercise is to study the splitting in the energy levels of a hydrogen atom placed in an external magnetic field, a phenomenon known as *Zeeman effect.* Consider a hydrogen atom placed in a uniform magnetic field $\vec{B}_{ext}$; the modification to the Hamiltonian of the system is

$$H_Z = -(\vec{\mu}_l + \vec{\mu}_s) \cdot \vec{B}_{ext} \,,$$

where $\vec{\mu}_s$ and $\vec{\mu}_l$ are the magnetic dipole moments associated with the spin and the orbital momentum of the electron, defined as

$$\vec{\mu}_s = -\frac{e}{m}\vec{S} \qquad\qquad \vec{\mu}_l = -\frac{e}{2m}\vec{L}\,.$$

Depending on the relative strength of the external magnetic field in comparison with the internal magnetic field of the atom, we identify two different regimes for the Zeeman effect.

Case 1: Weak-field

Suppose that B_{ext} is much weaker than the internal magnetic field of the atom; in this case fine structure dominates and H_Z can be treated as a small, time-independent perturbation.

(a) Identify the unperturbed eigenstate basis. Why are m_l and m_s "bad" quantum numbers in this case?

(b) Compute the expectation value of $\vec{S}$ on a generic unperturbed eigenstate.
Hint: use the Wigner-Eckart theorem, namely

$$\langle \vec{S} \rangle = \langle \frac{\vec{S} \cdot \vec{J}}{J^2} \vec{J} \rangle$$

and express the scalar product $\vec{S} \cdot \vec{J}$ in terms of the quantum numbers j, s and l.

(c) Use the result you just derived to compute the first order correction to the hydrogen energy levels. Show that it amounts to

$$E_Z^{(1)} = \frac{e}{2m} g_J \vec{B}_{ext} \cdot \langle \vec{J} \rangle$$

where the Landé g-factor g_J is given by

$$g_J = \left[1 + \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)} \right]$$

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(d) Choose the z-axis to lie along $\vec{B}_{ext}$. How does the first excited state ($n = 2$) split due to the combined effect of fine structure and weak Zeeman effect? Draw the energy-splitting.

Case 2: Strong-field (Paschen-Back effect)

Now consider the opposite situation and suppose that the external magnetic field is so strong that the effect of H_Z is far more important than the fine structure, which can be now treated as a perturbation. Again, take $\vec{B}_{ext} = (0, 0, B_z)$.

(e) Identify a good eigenstate basis for the unperturbed Hamiltonian. Why are m_l and m_s "good" quantum numbers in this case?

(f) Identify the unperturbed Hamiltonian and compute the unperturbed energy levels.

(g) Use first order perturbation theory to compute the fine structure correction to these levels for $l \neq 0$. Show that it is given by

$$E_{fs}^{(1)} = \frac{2nE_n^2}{mc^2} \left[\frac{3}{4n} - \frac{l(l+1) - m_l m_s}{l(l+\frac{1}{2})(l+1)} \right]$$

(h) Determine the energy splitting of the first excited state ($n = 2$) under strong-field Zeeman effect and compare the result with the one obtained in the weak field limit.