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Problem 13.1: Relativistic corrections for the hydrogen atom

[**Written** | 4 (+1 bonus) pt(s)]

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Learning objective

In this problem, you examine the relativistic corrections to the hydrogen atom and derive the energy levels including relativistic effects like spin-orbit coupling and quantum fluctuations in the electron's position. These effects give rise to the fine structure of the hydrogen energy levels and can also be derived directly from the Dirac equation.

We examine the corrections after an expansion of the relativistic theory in powers of v/c for a single hydrogen atom. The expansion reads

$$H = mc^2 + \underbrace{\frac{\boldsymbol{p}^2}{2m} + V(r)}_{H_0} \underbrace{- \frac{\boldsymbol{p}^4}{8m^3c^2}}_{H_{\text{kin}}} + \underbrace{\frac{1}{2m^2c^2}\frac{1}{r}\frac{\mathrm{d}V(r)}{\mathrm{d}r}\,\boldsymbol{L}\cdot\boldsymbol{S}}_{H_{\text{SO}}} + \underbrace{\frac{\hbar^2}{8m^2c^2}\Delta V(r)}_{H_{\text{D}}} + \dots, \tag{1}$$

where H_0 is the Hamiltonian of the non-relativistic hydrogen atom with eigenstates $|n, l, m_l\rangle$ and $V(r) = -e^2/r$ is the Coulomb potential. The first term is given by the rest mass of the electron and plays no role in the dynamics.

a) We start with the relativistic correction of the kinetic energy H_{kin}. Calculate the energy corrections in first order perturbation theory. 1pt(s)

Hints:

- Rewrite the kinetic energy in the form

$$H_{\text{kin}} = -\frac{1}{2mc^2}\left[H_0^2 + e^2 H_0 \frac{1}{r} + e^2 \frac{1}{r} H_0 + e^4 \frac{1}{r^2}\right]. \tag{2}$$

- Note, that despite the degenracy of the states $|n, l, m_l\rangle$, the perturbation H_{kin} can be treated by non-degenerate perturbation theory. Why?
- Show that the occurring matrix elements $\langle r^{-s}\rangle_{nl}$ can be written in the form

$$\left\langle r^{-s}\right\rangle_{nl} = \int_0^\infty \mathrm{d}r\, r^{2-s} \left|R_{nl}(r)\right|^2. \tag{3}$$

- Convince yourself that the following identities hold true by either calculating the integrals explicitly for $1s$ and $2p$ or doing subtask (e).

$$\left\langle r^{-1}\right\rangle_{nl} = \frac{1}{a_0}\frac{1}{n^2}, \tag{4a}$$

$$\left\langle r^{-2}\right\rangle_{nl} = \frac{2}{a_0^2}\frac{1}{(1+2l)}\frac{1}{n^3}. \tag{4b}$$

b) The term H_{SO} is known as *spin-orbit coupling*. What are the good quantum numbers for this Hamiltonian? Derive the first order corrections due to this term. **1pt(s)**

Hints: Use

$$\left\langle r^{-3}\right\rangle_{nl} = \frac{4}{a_0^3}\frac{1}{n^3}\frac{2(2l-1)!}{(2l+2)!} \text{ for } 1 \leq l \leq n-1. \tag{5}$$

c) Calculate the energy corrections for the *Darwin term* H_{D}. **1pt(s)**

d) After having taken into account all the corrections to the lowest order, write down the energy $E = E_0 + E_{\text{kin}} + E_{\text{SO}} + E_{\text{D}}$ as a function of $\alpha = e^2/\hbar c$ and the rest energy mc^2 for the considered energy levels and show, that the total correction is independent of l and m_l. Determine the corrections for the $1s$, $2s$ and $2p$ orbitals explicitly and sketch how the energy levels change when taking into account more and more corrections. (Start with the unperturbed energy E_0, then add the kinetic energy correction E_{kin}, then the spin-orbit coupling E_{SO} and finally the Darwin term E_{D}). **1pt(s)**

*e) Derive the relations in equations 4 and 5. **+1pt(s)**

Hints:

- Bring the integrals to the form

$$\int_0^\infty dx\, x^{\alpha+1-s} e^{-x} L_k^\alpha(x) L_k^\alpha(x) \tag{6}$$

- Replace one Laguerre polynomial by

$$L_k^\alpha(x) = \frac{x^{-\alpha}e^x}{k!}\frac{d^k}{dx^k}\left(e^{-x}x^{k+\alpha}\right) \tag{7}$$

and one by

$$L_k^\alpha(x) = \sum_{j=0}^{k} \binom{k+\alpha}{k-j}\frac{(-x)^j}{j!} \tag{8}$$

- You should now arrive at integrals of the form

$$\int_0^\infty dx\, x^{j+1-s}\frac{d^k}{dx^k}\left(e^{-x}x^{k+\alpha}\right), \tag{9}$$

with $s = 1, 2, 3$. The integral can be solved using integration by parts and

$$\int_0^\infty dx\, x^m e^{-x} = m!. \tag{10}$$