Hydrogen Atom F2016

Problem 2: Hydrogen Atom (10 pts)

In this problem you will calculate the relativistic correction to the energies of the hydrogen atom. The hydrogen atom Hamiltonian is in terms of its electron in the field of the positively charged nucleus

$$H_0 = \frac{p^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0 r}$$

where p is the electrons momentum, r its position, m_e its mass, and e the charge. This Hamiltonian is nonrelativistic $(p/(mc) \ll 1)$. The correct relativistic expression to use for the kinetic energy is

$$T = \sqrt{p^2c^2 + m_e^2c^4} - m_ec^2$$

recall that

$$\langle r \rangle_{nl} = n^2 a_0\{1 + \frac{1}{2}[1 - \frac{l(l+1)}{n^2}]\}$$

$$\langle r^2 \rangle_{nl} = n^4 a_0^2\{1 + \frac{3}{2}[1 - \frac{l(l+1) - 1/3}{n^2}]\}$$

$$\langle \frac{1}{r} \rangle_{nl} = \frac{1}{a_0 n^2}$$

$$\langle \frac{1}{r^2} \rangle_{nl} = \frac{1}{a_0^2 n^3}\frac{1}{l + 1/2}$$

$$\langle \frac{1}{r^3} \rangle_{nl} = \frac{1}{a_0^3 n^3}\frac{1}{l(l+1/2)(l+1)}$$

a. Use this information to find the first non-zero order correction to the Hamiltonian due to the relativistic motion of the electron. **(2 Points)**

b. Show that this correction is diagonal in the $|nlm\rangle$ basis by proving that it commutes with the angular momentum operator $\vec{L}$. Why is it sufficient to prove that the perturbation commutes with $\vec{L}$ to show that the perturbation is diagonal in the $|nlm\rangle$ basis? **(4 Points)**

c. Using the fact that

$$\frac{p^2}{2m_e} = H_0 + \frac{e^2}{4\pi\epsilon_0 r}$$

find the relativistic energy correction to the energy levels of the Hydrogen atom. **(4 Points)**

Problem 2

(a)

Assume pc is much smaller than rest mass, then expand the kinetic energy.

$$T = mc^2 \sqrt{\frac{p^2c^2}{m^2c^4} + 1} - mc^2$$

$$= mc^2 \left(\sqrt{\left(\frac{p}{mc}\right)^2 + 1} - 1 \right)$$

Expand, letting $x = p/mc$.

$$(x^2+1)^{1/2} \approx f(0) + f'(0)(x-0) + \frac{f''(0)(x-0)^2}{2!} + \frac{f'''(0)(x-0)^3}{3!} + \frac{f^{(4)}(0)(x-0)^4}{4!} + \dots$$

$f(0) = 1$

$$f'(x) = \frac{1}{2}(x^2+1)^{-1/2} \cdot 2x = x(x^2+1)^{-1/2} \Rightarrow f'(0) = 0$$

$$f''(x) = (x^2+1)^{-1/2} - \frac{1}{2}x(x^2+1)^{-3/2} \cdot 2x$$
$$= (x^2+1)^{-1/2} - x^2(x^2+1)^{-3/2} \Rightarrow f''(0) = 1$$

$$f'''(x) = -\frac{1}{2}(x^2+1)^{-3/2} \cdot 2x + \frac{3}{2}x^2(x^2+1)^{-5/2} \cdot 2x - 2x(x^2+1)^{-3/2}$$
$$= -x(x^2+1)^{-3/2} + 3x^3(x^2+1)^{-5/2} - 2x(x^2+1)^{-3/2} \Rightarrow f'''(0) = 0$$

$$f^{(4)}(x) = \frac{3}{2}x(x^2+1)^{-5/2} \cdot 2x - (x^2+1)^{-3/2} - \frac{15}{2}x^3(x^2+1)^{-7/2} \cdot 2x + 9x^2(x^2+1)^{-5/2}$$
$$+ 3x(x^2+1)^{-5/2} \cdot 2x - 2(x^2+1)^{-3/2} \Rightarrow f^{(4)} = -3$$

$$(x^2+1)^{1/2} \approx 1 + 0 + \frac{x^2}{2!} + 0 - \frac{3x^4}{4!} \approx 1 + \frac{p^2}{2m^2c^2} - \frac{1}{8}\left(\frac{p^4}{m^4c^4}\right)$$

$$T \approx m\cancel{c^2}\left(\cancel{1} + \frac{p^2}{2m^2\cancel{c^2}} - \frac{p^4}{8m^{\cancel{4}}c^{\cancel{4}2}} \cancel{-1}\right)$$

$$\approx \underbrace{\frac{p^2}{2m}}_{\text{non-relativistic}} \underbrace{- \frac{p^4}{8m^3c^2}}_{\text{relativistic}}$$

$$\boxed{T' = -\frac{p^4}{8m^3c^2}}$$

(b)

$$p^2 = -\hbar^2 \nabla^2$$

$$= -\hbar^2\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2\hbar^2}L^2\right)$$

$$= -\frac{\hbar^2}{r}\frac{\partial^2}{\partial r^2}r - \frac{1}{r^2}L^2$$

$$[p^4, L^2] = [p^2 \cdot p^2, L^2] = p^2[p^2, L^2] + [p^2, L^2]p^2$$

want to show $[p^2, L^2] = 0$.

$$[p^2, L^2] = \left[-\frac{\hbar^2}{r}\frac{\partial^2}{\partial r^2}r - \frac{1}{r^2}L^2, L^2\right]$$

$[AB, C]$
$= A[B, C]$
$+ [A, C]B$

$$= \left[-\frac{\hbar^2}{r}\frac{\partial^2}{\partial r^2}r, L^2\right] + \left[-\frac{1}{r^2}L^2, L^2\right]$$

But L depends only on θ, ϕ, and partial derivatives of them. So

$$\left[-\frac{\hbar^2}{r}\frac{\partial^2}{\partial r^2}r, L^2\right] = 0$$

Also,

$$\left[-\frac{1}{r^2}L^2, L^2\right] = -\frac{1}{r^2}\underbrace{[L^2, L^2]}_{0} + \underbrace{\left[-\frac{1}{r^2}, L^2\right]}_{0 \text{ since } L = L(\theta,\phi)}$$

So perturbation commutes with L^2. For L_z (L_x, L_y):

$$L_z = -i\hbar\frac{\partial}{\partial\phi}$$

$$L_x = i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$$

$$L_y = i\hbar\left(-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$

$$[p^2, L_z] = \left[-\frac{\hbar^2}{r}\frac{\partial^2}{\partial r^2} r - \frac{1}{r^2}L^2, L_z\right]$$

$$= \left[-\frac{\hbar^2}{r}\frac{\partial^2}{\partial r^2} r, L_z\right] - \left[\frac{1}{r^2}L^2, L_z\right]$$

$$= \underbrace{\left[-\frac{\hbar^2}{r}\frac{\partial^2}{\partial r^2} r, L_z\right]}_{0 \text{ because}} - \frac{1}{r^2}\underbrace{\left[L^2, L_z\right]}_{0} - \underbrace{\left[\frac{1}{r^2}, L_z\right]}_{0 \text{ for same reason}} L^2$$

can move partials around & one in terms of spatial, other in terms of θ, ϕ

Likewise for L_x and L_y.

So we know $\{H_1, L^2, L_z\}$ is a CSCO since $H_1 = H_0 + T$ and $\{H_0, L^2, L_z\}$ is a CSCO in $|n\,l\,m\rangle$ basis.

Want

$$E^{(1)} = \langle n l m | T' | n l m \rangle$$

$$E^{(1)} \approx \langle n l m | p^4 | n l m \rangle$$

$$\langle n l m | p^2 \cdot p^2 | n l m \rangle$$

Know

our potential was negative!

$$\frac{p^2}{2m} = H_0 - V$$

unperturbed

$$\frac{p^2}{2m} | n l m \rangle = (H_0 - V) | n l m \rangle$$

$$\frac{p^2}{2m} | n l m \rangle = (E^{(0)} - V) | n l m \rangle$$

$$p^2 | n l m \rangle = 2m (E^{(0)} - V) | n l m \rangle$$

$$\langle n l m | p^2 \cdot p^2 | n l m \rangle = \langle n l m | 4m^2 (E^{(0)} - V)^2 | n l m \rangle$$

$$\langle n l m | p^4 | n l m \rangle = 4m^2 \langle n l m | E^{(0)2} - 2E_0 V + V^2 | n l m \rangle$$

Plug in $E^{(1)}$

$$E^{(1)} \approx 4m^2 \langle n l m | E^{(0)2} - 2E^{(0)} V + V^2 | n l m \rangle$$

$$E^{(1)} \approx E^{(0)2} - 2E^{(0)}\langle V\rangle + \langle V^2\rangle$$

Want to find $\langle V\rangle$ and $\langle V^2\rangle$, $V = -\frac{e^2}{4\pi\varepsilon_0 r}$

$$\langle V\rangle = -\frac{e^2}{4\pi\varepsilon_0}\left\langle \frac{1}{r}\right\rangle = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{a_0 n^2}$$

$$\langle V^2\rangle = \left(\frac{-e^2}{4\pi\varepsilon_0}\right)^2\left\langle\frac{1}{r^2}\right\rangle = \left(-\frac{e^2}{4\pi\varepsilon_0}\right)^2\frac{1}{a_0^2 n^3}\frac{1}{l+1/2}$$

but from Virial Theorem, know

$$\langle V\rangle = 2E^{(0)}$$

$$\cancel{E^{(0)} = \frac{1}{2}\langle V\rangle}$$

so

$$E^{(1)} \approx E^{(0)2} - 2E^{(0)}(2E^{(0)}) + \langle V^2\rangle$$

$$\approx E^{(0)2} - 4E^{(0)2} + \left(-\frac{e^2}{4\pi\varepsilon_0}\right)^2\frac{1}{a_0^2 n^3}\frac{1}{l+1/2}.$$

We also have

$$\langle V\rangle = \frac{-e^2}{4\pi\varepsilon_0}\frac{1}{a_0 n^2} = 2E^{(0)}$$

So

$$-\frac{e^2}{4\pi\varepsilon_0} = 2a_0 n^2 E^{(0)}$$

$$\left(-\frac{e^2}{4\pi\varepsilon_0}\right)^2 = 4a_0^2 n^4 E^{(0)^2}$$

$$E^{(1)} \approx E^{(0)^2} - 4E^{(0)^2} + 4\cancel{a_0^2} n^4 E^{(0)^2} \cdot \frac{1}{\cancel{a_0^2} n^3} \frac{1}{l+1/2}$$

$$\approx E^{(0)^2} - 4E^{(0)^2} + \frac{4n}{l+1/2} E^{(0)^2}$$

So

$$E^{(1)} \approx E^{(0)^2}\left(\frac{4n}{l+1/2} - 3\right)$$

with some
negative constants