4. (Quantum Mechanics)

In the standard approximation, the hydrogen atom consists of a heavy, essentially motionless proton of charge e, together with a ligher electron (charge -e) and mass m that orbits around it. We treat both the proton and the electron as point charges, and the hydrogen wave functions are given by $\psi_{n\ell m} = R_{n\ell}(r)Y_{\ell m}(\theta,\phi)$, with the quantum numbers n, ℓ , and m. We usually use 1s, 2s, 2p, etc. to represent the energy levels, which combine the quantum numbers $n\ell$. For example, we have n = 1 and $\ell = 0$ for the 1s state, while n = 2 and $\ell = 1$ for the 2p state.

In this problem, we instead take the proton to be a uniformly charged ball of radius R, with $R/a \ll 1$, where $a = 4\pi\epsilon_0\hbar^2/me^2$ is the "Bohr radius" for hydrogen.

(a) Compute the change in energies of the 2s and 2p states due to the fact that the proton is not point-like. Work to order $(R/a)^2$. In other words, compute $\Delta E_{2s} = E_{2s}(R) - E_{2s}(R=0)$ to order $(R/a)^2$ and do the same for the 2p state. Here, $E_{2s}(R)$ is the energy of the 2s state for the proton with finite size.

Compare the energies of the states 2s and 2p: E_{2s} and E_{2p} . Are they equal to each other?

(b) Show that the difference in energy of the 2s and 2p state, $E_{2s}(R) - E_{2p}(R)$, gives a measure of the proton radius R.

Useful formulas: for the hydrogen wave functions $\psi_{n\ell m} = R_{n\ell}(r)Y_{\ell m}(\theta, \phi)$, the expressions for the first few $R_{n\ell}(r)$ are given by

$$R_{10}(r) = 2a^{-3/2} \exp(-r/a),$$

$$R_{20}(r) = \frac{1}{\sqrt{2}}a^{-3/2} \left(1 - \frac{1}{2}\frac{r}{a}\right) \exp(-r/2a),$$

$$R_{21}(r) = \frac{1}{\sqrt{24}}a^{-3/2}\frac{r}{a}\exp(-r/2a).$$

Solution:

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There are three features of this problem that we should note before starting, which may not be immediately obvious from the description:

- This is a time-independent perturbation theory problem.
- The only effect of the taking the proton to be a uniformly charged ball of radius R (that we will consider) is to change the electric potential felt by the electron.
- (a) To start, we need to calculate the electric potential for a uniformly charged ball of total charge e and radius R. Let the charge density of the ball be $\rho \equiv \frac{e}{\frac{4}{3}\pi R^3}$. Use Gauss' law $\int \mathbf{E} \cdot d\mathbf{a} = Q_{\text{encl}}/\epsilon_0$ with a Gaussian sphere of radius r to find the electric field:

For
$$r < R$$
: $4\pi r^2 E = \int \mathbf{E} \cdot d\mathbf{a} = \frac{Q_{\text{encl}}}{\epsilon_0}$
= $\frac{\frac{4}{3}\pi r^3 \rho}{\epsilon_0}$
= $\frac{e}{\epsilon_0} \frac{r^3}{R^3}$ using $\rho \equiv \frac{e}{\frac{4}{3}\pi R^3}$

$$r \Longrightarrow \mathbf{E}(r) = \frac{e}{4\pi\epsilon_0} \frac{r}{R^3} \hat{\mathbf{r}} \quad \text{for } r < R$$
 (38)

For
$$r > R$$
: $4\pi r^2 E = \int \mathbf{E} \cdot d\mathbf{a} = \frac{Q_{\text{encl}}}{\epsilon_0}$
= $\frac{e}{\epsilon_0} \frac{r^3}{R^3}$

$$\implies \mathbf{E}(r) = \frac{e}{4\pi\epsilon_0} \frac{1}{r^2} \hat{\mathbf{r}} \quad \text{for } r > R \tag{39}$$

Setting the electric potential ϕ equal to zero at infinity and using $\phi(b) - \phi(a) = -\int_a^b \mathbf{E} \cdot d\boldsymbol{\ell}$, we can find the electric potential everywhere in space:

For
$$r > R$$
: $\phi(r) = \phi(r) - \phi(\infty)$ since $\phi(\infty) = 0$

$$= -\int_{\infty}^{r} \mathbf{E} \cdot d\boldsymbol{\ell}$$

$$= \int_{r}^{\infty} E(r')dr'$$

$$= \frac{e}{4\pi\epsilon_{0}} \int_{r}^{\infty} \frac{1}{(r')^{2}} dr'$$

$$= \frac{e}{4\pi\epsilon_{0}} \left[-\frac{1}{r'} \right]_{r}^{\infty}$$

$$= \frac{e}{4\pi\epsilon_{0}} \frac{1}{r}$$
(40)

For
$$r < R$$
: $\phi(r) = \phi(R) + (\phi(r) - \phi(R))$
 $= \phi(R) - \int_{R}^{r} \mathbf{E} \cdot d\ell$
 $= \phi(R) - \int_{R}^{r} E(r')dr'$
 $= \phi(R) - \frac{e}{4\pi\epsilon_{0}} \int_{R}^{r} \frac{r'}{R^{3}} dr'$
 $= \phi(R) - \frac{e}{4\pi\epsilon_{0}} \left[\frac{(r')^{2}}{2R^{3}} \right]_{R}^{r}$
 $= \phi(R) + \frac{e}{4\pi\epsilon_{0}} \left[\frac{1}{2R} - \frac{r^{2}}{2R^{3}} \right]$
 $= \phi(R) + \frac{e}{4\pi\epsilon_{0}} \frac{1}{2R} \left[1 - (r/R)^{2} \right]$
 $= \frac{e}{4\pi\epsilon_{0}} \frac{1}{R} + \frac{e}{4\pi\epsilon_{0}} \frac{1}{2R} \left[1 - (r/R)^{2} \right]$ using (40)
 $= \frac{e}{4\pi\epsilon_{0}} \frac{1}{2R} \left[3 - (r/R)^{2} \right]$ (41)

Thus, the electric potential everywhere in space is

$$\phi(r) = \begin{cases} \frac{e}{4\pi\epsilon_0} \frac{1}{2R} \left[3 - (r/R)^2 \right] & r < R \\ \frac{e}{4\pi\epsilon_0} \frac{1}{r} & r > R \end{cases}$$
(42)

Note that $\phi(r)$ is continuous at r = R, as it should be. The electric potential energy of the electron is equal to the charge of the electron (-e) times the electric potential:

$$V_{\text{proton ball}}(r) = \begin{cases} -\frac{e^2}{4\pi\epsilon_0} \frac{1}{2R} \left[3 - (r/R)^2 \right] & r < R \\ -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r} & r > R \end{cases}$$
(43)

This means that the Hamiltonian for the hydrogen atom where the proton is a uniformly charged ball is

$$H_{\text{proton ball}} = \frac{p^2}{2m} + V_{\text{proton ball}}(r)$$
(44)

where m is the mass of the electron. (Technically speaking, it is the reduced mass, but the proton is much more massive than the electron, so the reduced mass is approximately equal to the electron mass.)

To make this a time-independent perturbation theory problem, we should break this up into the unperturbed Hamiltonian and the small perturbation. Here, the unperturbed Hamiltonian should be the Hamiltonian for the hydrogen atom with a point proton. That's because we already know the energy levels for this Hamiltonian and want to find the change in energy from this Hamiltonian. That said, we should write

$$H_{\text{proton ball}} = \underbrace{\left(\frac{p^2}{2m} - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}\right)}_{\substack{H_{\text{pointlike proton}}\\\text{unperturbed Hamiltonian}}} + \underbrace{\left(V_{\text{proton ball}}(r) + \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}\right)}_{\substack{V(r)\\\text{small perturbation}}}$$
(45)

Using (43), we can write the perturbation Hamiltonian as

$$V(r) = V_{\text{proton ball}}(r) + \frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$$

$$= \begin{cases} -\frac{e^2}{4\pi\epsilon_0} \frac{1}{2R} \left[3 - (r/R)^2 \right] + \frac{e^2}{4\pi\epsilon_0} \frac{1}{r} & r < R \\ -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r} + \frac{e^2}{4\pi\epsilon_0} \frac{1}{r} & r > R \end{cases}$$

$$V(r) = \begin{cases} \frac{e^2}{4\pi\epsilon_0} \frac{1}{r} \left(1 - \frac{3}{2} \frac{r}{R} + \frac{1}{2} \left(\frac{r}{R} \right)^3 \right) & r < R \\ 0 & r > R \end{cases}$$
(46)

Technically speaking, this is a degenerate perturbation theory problem, since there are infinitely many degenerate energy eigenstates identified by angular momentum quantum number ℓ . Moreover, there are $2\ell + 1$ degenerate energy eigenstates with orbital angular momentum quantum number ℓ , and each of these states has degeneracy 2 because the electron is a spin-1/2 particle. However, the perturbation Hamiltonian V(r) does not depend on angular momentum or spin, so it does not lift the degeneracy. For that reason, we can treat this as a nondegenerate time-independent perturbation theory problem.

In nondegenerate time-independent perturbation theory, the first-order correction to the nth unperturbed energy level is

$$\Delta E^{(1)} = \langle n|V|n\rangle = \int d^3r \ V(\mathbf{r}) \ |\psi_n(\mathbf{r})|^2 \tag{47}$$

where $\psi_n(\mathbf{r})$ is the wave function of the *n*th unperturbed energy level. In this case, the problem tells us that the wave functions of the 2s state $(n = 2, \ell = 0, m = 0)$ and 2p state $(n = 2, \ell = 1, \text{ and some value of } m)$ are

$$\psi_{2s}(\mathbf{r}) = R_{20}(r)Y_{00}(\theta,\varphi) \tag{48}$$

$$\psi_{2p}(\mathbf{r}) = R_{21}(r)Y_{1m}(\theta,\varphi) \tag{49}$$

Here $Y_{\ell m}(\theta, \varphi)$ is one of the spherical harmonics. We don't need to know anything about them for this problem, other than that the spherical harmonics are properly normalized when we integrate over the solid angle:

$$\int d\Omega \left| Y_{\ell m}(\theta,\varphi) \right|^2 = 1 \tag{50}$$

With this information, we are ready to set up the integral for the energy shift to the 2s state:

$$\Delta E_{2s} = \int d^3 r V(r) |\psi_{2s}(\mathbf{r})|^2$$

$$= \int dr \, d\Omega \, r^2 V(r) \, |\psi_{2s}(\mathbf{r})|^2 \quad \text{using the spherical integration measure } d^3 r = r^2 dr d\Omega$$

$$= \int dr \, d\Omega \, r^2 V(r) \, |R_{20}(r) \, Y_{00}(\theta, \varphi)|^2$$

$$= \left(\int_0^\infty dr \, r^2 V(r) \, |R_{20}(r)|^2 \right) \left(\int d\Omega \, |Y_{00}(\theta, \varphi)|^2 \right)$$

$$= \int_0^\infty dr \, r^2 V(r) \, |R_{20}(r)|^2$$
(51)

Plugging in the provided formula for $R_{20}(r)$, we get

$$\Delta E_{2s} = \int_0^\infty dr \ r^2 V(r) \left[\frac{1}{\sqrt{2}} a^{-3/2} \left(1 - \frac{1}{2} \frac{r}{a} \right) \exp\left(-r/(2a)\right) \right]^2$$
$$= \int_0^\infty dr \ r^2 V(r) \left[\frac{1}{2} a^{-3} \left(1 - \frac{1}{2} \frac{r}{a} \right)^2 \exp\left(-r/a\right) \right]$$
$$= \frac{1}{2a^3} \int_0^\infty dr \ r^2 V(r) \left(1 - \frac{1}{2} \frac{r}{a} \right)^2 \exp(-r/a)$$
(52)

By (46), V(r) is equal to zero for r > R, so we can change the upper limit of the integral to r = R. We can then plug in our result from (46) for r < R to get

$$\Delta E_{2s} = \frac{1}{2a^3} \int_0^R dr \ r^2 \left[\frac{e^2}{4\pi\epsilon_0} \frac{1}{r} \left(1 - \frac{3}{2} \frac{r}{R} + \frac{1}{2} \left(\frac{r}{R} \right)^3 \right) \right] \left[1 - \frac{1}{2} \frac{r}{a} \right]^2 \exp(-r/a)$$
$$= \frac{e^2}{4\pi\epsilon_0} \frac{1}{2a^3} \int_0^R dr \ r \left(1 - \frac{3}{2} \frac{r}{R} + \frac{1}{2} \left(\frac{r}{R} \right)^3 \right) \left[1 - \frac{1}{2} \frac{r}{a} \right]^2 \exp(-r/a)$$
(53)

We now follow an important guideline for keeping comp answers manageable:

Make approximations before taking integrals.

In this case, we can make the approximation $R/a \ll 1$. Within the integral, $r/a < R/a \ll 1$, so we can set all terms of the form r/a (but not r/R) to zero. This gets us

$$\Delta E_{2s} \approx \frac{e^2}{4\pi\epsilon_0} \frac{1}{2a^3} \int_0^R dr \ r \left(1 - \frac{3}{2} \frac{r}{R} + \frac{1}{2} \left(\frac{r}{R} \right)^3 \right)$$
$$= \frac{e^2}{4\pi\epsilon_0} \frac{1}{2a^3} \int_0^R dr \ \left(r - \frac{3}{2} \frac{r^2}{R} + \frac{1}{2} \frac{r^4}{R^3} \right)$$
(54)

We can now take the integral to get

$$\Delta E_{2s} \approx \frac{e^2}{4\pi\epsilon_0} \frac{1}{2a^3} \left(\frac{R^2}{2} - \frac{R^3}{2R} + \frac{R^5}{10R^3} \right) = \frac{e^2}{4\pi\epsilon_0} \frac{1}{2a^3} \left(\frac{R^2}{10} \right) = \frac{e^2}{4\pi\epsilon_0 a} \frac{1}{20} \left(\frac{R}{a} \right)^2 \quad \text{to order } (R/a)^2$$
(55)

Using the same logic as we used to get (51), we can set up the integral for the energy shift to the 2p state:

$$\Delta E_{2p} = \int dr \, d\Omega \, r^2 \, V(r) \, |R_{21}(r) \, Y_{1m}(\theta, \varphi)|^2 = \left(\int_0^\infty dr \, r^2 \, V(r) \, |R_{21}(r)|^2 \right) \left(\int d\Omega \, |Y_{1m}(\theta, \varphi)|^2 \right) = \int_0^\infty dr \, r^2 \, V(r) \, |R_{21}(r)|^2$$
(56)

Plugging in the provided formula for $R_{21}(r)$, we get

$$\Delta E_{2p} = \int_0^\infty dr \ r^2 V(r) \left[\frac{1}{\sqrt{24}} a^{-3/2} \frac{r}{a} \exp(-r/(2a)) \right]^2$$
$$= \frac{1}{24a^3} \int_0^\infty dr \ r^2 V(r) \left(\frac{r}{a}\right)^2 \exp(-r/a)$$

Using (46) and substituting in for V(r) for r < R, we get

$$\Delta E_{2p} = \frac{1}{24a^3} \int_0^R dr \ r^2 \left[\frac{e^2}{4\pi\epsilon_0} \frac{1}{r} \left(1 - \frac{3}{2} \frac{r}{R} + \frac{1}{2} \left(\frac{r}{R} \right)^3 \right) \right] \left(\frac{r}{a} \right)^2 \exp(-r/a)$$
$$= \frac{e^2}{4\pi\epsilon_0} \frac{1}{24a^3} \int_0^R dr \ r \left(1 - \frac{3}{2} \frac{r}{R} + \frac{1}{2} \left(\frac{r}{R} \right)^3 \right) \left(\frac{r}{a} \right)^2 \exp(-r/a)$$
(57)

Making the approximation $r/a < R/a \ll 1$ within the integral, we get

$$\Delta E_{2p}^{(1)} \approx \frac{e^2}{4\pi\epsilon_0} \frac{1}{24a^3} \int_0^R dr \ r \left(1 - \frac{3}{2}\frac{r}{R} + \frac{1}{2}\left(\frac{r}{R}\right)^3\right) \left(\frac{r}{a}\right)^2$$
$$= \frac{e^2}{4\pi\epsilon_0} \frac{1}{24a^3} \int_0^R dr \ \left(\frac{r^3}{a^2} - \frac{3}{2}\frac{r^4}{Ra^2} + \frac{1}{2}\frac{r^6}{R^3a^2}\right)$$
(58)

We can take the integral to get

$$\Delta E_{2p} \approx \frac{e^2}{4\pi\epsilon_0} \frac{1}{24a^3} \left(\frac{1}{4} \frac{R^4}{a^2} - \frac{3}{10} \frac{R^5}{Ra^2} + \frac{1}{14} \frac{R^7}{R^3 a^2} \right)$$
$$= \frac{e^2}{4\pi\epsilon_0} \frac{1}{24a^3} \left(\frac{1}{4} \frac{R^4}{a^2} - \frac{3}{10} \frac{R^4}{a^2} + \frac{1}{14} \frac{R^4}{a^2} \right)$$
$$= \frac{e^2}{4\pi\epsilon_0 a} \frac{1}{24} \left(\frac{1}{4} - \frac{3}{10} + \frac{1}{14} \right) \left(\frac{R}{a} \right)^4$$
(59)

Since $\Delta E_{2p}^{(1)}$ is proportional to $(R/a)^4$, the energy change of the 2*p* state to order $(R/a)^2$ is zero:

$$\Delta E_{2p} = 0 \quad \text{to order } (R/a)^2 \tag{60}$$

Summarizing our results, we have

$$\Delta E_{2s} = \frac{e^2}{4\pi\epsilon_0 a} \frac{1}{20} \left(\frac{R}{a}\right)^2 \quad \text{and} \quad \Delta E_{2p} = 0 \quad \text{to order } (R/a)^2 \tag{61}$$

The unperturbed hydrogen atom eigenstates are

$$E_n = -\frac{me^4}{2(4\pi\epsilon_0)^2\hbar^2} \frac{1}{n^2} = -\frac{e^2}{8\pi\epsilon_0 a} \frac{1}{n^2}$$
(62)

Therefore, the perturbed 2s and 2p eigenstates are

$$E_{2s}(R) = -\frac{e^2}{32\pi\epsilon_0 a} + \frac{e^2}{4\pi\epsilon_0 a} \frac{1}{20} \left(\frac{R}{a}\right)^2 \quad \text{and} \quad E_{2p}(R) = -\frac{e^2}{32\pi\epsilon_0 a} \quad \text{to order } (R/a)^2$$
(63)

The energies are not the same; the perturbation lifts the energy degeneracy between the 2s and 2p states in the unperturbed Hamiltonian.

(b) Using the answer from part (a), the energy difference between the 2s and 2p states, to order $(R/a)^2$, is

$$E_{2s}(R) - E_{2p}(R) = \frac{e^2}{4\pi\epsilon_0 a} \frac{1}{20} \left(\frac{R}{a}\right)^2$$
(64)

Therefore, if we know the energy difference between the 2s and 2p states, the Bohr radius a, and the constants e and ϵ_0 , we can calculate an approximation of the proton radius R using this equation. (Note that there could be other perturbations that change the energy of the 2s state relative to the 2p state, like spin-orbit coupling.)