

# Ph125b Set

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# 1: Extension Note

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An extension was granted for an additional 24 hours.

## 2: Problem 9

### 2.1. Part A

From relativity, we know that:

$$E^2 = P^2 c^2 + m^2 c^4 \quad (1)$$

$$E = c\sqrt{P^2 + m^2 c^2} \quad (2)$$

Expanding in powers of  $P$ :

$$E = mc^2 + \frac{P^2}{2m} - \frac{3P^4}{4!c^2 m^3} \quad (3)$$

Ignoring the constant rest mass, quantizing, and putting this in a potential, we have:

$$\hat{H} = \frac{\hat{\mathbf{P}}^2}{2m} - \frac{\hat{\mathbf{P}}^4}{8c^2 m^3} + \hat{V} \quad (4)$$

Now we can use perturbation theory since  $\hat{H}_0 := \hat{H}_H$  is a well known problem. Thus we need only the  $\hat{\mathbf{P}}^4$  term. We can also write:

$$\hat{\mathbf{P}}^4 = \left( \frac{\hat{\mathbf{P}}^2}{2m} \right)^2 (2m)^2 = (2m)^2 (\hat{H}_0 - \hat{V})^2 \quad (5)$$

$$\langle \psi | \hat{\mathbf{P}}^4 | \psi \rangle = (2m)^2 \langle \psi | (\hat{H}_0 - \hat{V})^2 | \psi \rangle \quad (6)$$

$$= (2m)^2 \langle \psi | \hat{H}_0^2 - \hat{H}_0 \hat{V} - \hat{V} \hat{H}_0 + \hat{V}^2 | \psi \rangle \quad (7)$$

Letting  $\psi$  be an energy eigenket,

$$= (2m)^2 \langle \psi | \varepsilon_n^2 - \hat{H}_0 \hat{V} - \hat{V} \varepsilon_n + \hat{V}^2 | \psi \rangle \quad (8)$$

$$= (2m)^2 \left( \varepsilon_n^2 + \langle \psi | \hat{V}^2 - (\hat{H}_0 + \varepsilon_n) \hat{V} | \psi \rangle \right) \quad (9)$$

$$= (2m)^2 \left( \varepsilon_n^2 + \left\langle \frac{e^4}{r^2} \right\rangle_{nlm} - \langle \psi | (\hat{H}_0 + \varepsilon_n) \hat{V} | \psi \rangle \right) \quad (10)$$

$$= (2m)^2 \left( \varepsilon_n^2 + \left\langle \frac{e^4}{r^2} \right\rangle_{nlm} - \left\langle (\hat{H}_0 + \varepsilon_n)^\dagger \psi \middle| \hat{V} \middle| \psi \right\rangle \right) \quad (11)$$

$$= (2m)^2 \left( \varepsilon_n^2 + \left\langle \frac{e^4}{r^2} \right\rangle_{nlm} + 2\varepsilon_n \langle \psi | \hat{V} | \psi \rangle \right) \quad (12)$$

$$= (2m)^2 \left( \varepsilon_n^2 + 2\varepsilon_n \left\langle \frac{e^2}{r} \right\rangle_{nlm} + \left\langle \left( \frac{e^2}{r} \right)^2 \right\rangle_{nlm} \right) \quad (13)$$

Thus:

$$E_n^{(1)} = - \left\langle n \left| \frac{\hat{\mathbf{P}}^4}{8c^2m^3} \right| n \right\rangle \quad (14)$$

$$E_n^{(1)} = - \frac{(2m)^2}{8c^2m^3} \left( \varepsilon_n^2 + 2\varepsilon_n \left\langle \frac{e^2}{r} \right\rangle_{nlm} + \left\langle \left( \frac{e^2}{r} \right)^2 \right\rangle_{nlm} \right) \quad (15)$$

$$E_n^{(1)} = - \frac{1}{2mc^2} \left( \varepsilon_n^2 + 2\varepsilon_n \left\langle \frac{e^2}{r} \right\rangle_{nlm} + \left\langle \left( \frac{e^2}{r} \right)^2 \right\rangle_{nlm} \right) \quad (16)$$

## 2.2. Part B

Up to this point has been independent, but unfortunately I discovered pg. 467 on Shankar so I follow along from there:

Using Quantum Virial Theorem, we have:

$$\left\langle \frac{e^2}{r} \right\rangle = -2\varepsilon_n \quad (17)$$

And from problem 11, we'll find that

$$\left\langle \frac{e^4}{r^2} \right\rangle = \frac{e^4}{a_0^2 n^3 (l + \frac{1}{2})} = \frac{4\varepsilon_0^2 n}{l + \frac{1}{2}} \quad (18)$$

Therefore we have:

$$E_n^{(1)} = - \frac{1}{2mc^2} \left( \varepsilon_n^2 + 2\varepsilon_n (-2\varepsilon_n) + \frac{4\varepsilon_0^2 n}{l + \frac{1}{2}} \right) \quad (19)$$

$$E_n^{(1)} = - \frac{\varepsilon_n^2}{2mc^2} \left( 1 - 4 + \frac{4n}{l + \frac{1}{2}} \right) \quad (20)$$

$$E_n^{(1)} = - \frac{\varepsilon_n^2}{2mc^2} \left( -3 + \frac{4n}{l + \frac{1}{2}} \right) \quad (21)$$

$$E_n^{(1)} = - \frac{\frac{(mc^2\alpha^2)^2}{n^4}}{2mc^2} \left( -3 + \frac{4n}{l + \frac{1}{2}} \right) \quad (22)$$

$$E_n^{(1)} = - \frac{1}{2} mc^2 \alpha^4 \left( -\frac{3}{n^4} + \frac{4}{n^3 (l + \frac{1}{2})} \right) \quad (23)$$

# 3: Problem 10

## 3.1. Part A

$$\hat{H} = \hat{H}_H + \hat{V} \quad (1)$$

Consider a sphere of uniform charge. By Newton's Shell Theorem, it can be calculated that:

$$\Phi(r) = \begin{cases} \frac{KQ}{r} & ; \quad r \geq R \\ \frac{3KQ}{2R} \left(1 - \frac{r^2}{3R^2}\right) & ; \quad r \leq R \end{cases} \quad (2)$$

Thus the perturbation is

$$\hat{V} = \frac{3KQ}{2R} \left(1 - \frac{r^2}{3R^2}\right) - \frac{KQ}{r} \quad (3)$$

for  $r \leq R$ , and 0 otherwise.

## 3.2. Part B

We wish to know:

$$\langle \hat{V} \rangle = \langle \psi | \hat{V} | \psi \rangle = \iiint R_{nl}(r) Y_{lm}(\theta, \phi) \hat{V} R_{nl}(r) Y_{lm}(\theta, \phi) \quad (4)$$

Assume that  $R_{nl}$  is slowly varying and thus constant:

$$= R_{nl}(0)^2 \iiint Y_{lm}(\theta, \phi) \hat{V}(r) Y_{lm}(\theta, \phi) \quad (5)$$

$$= R_{nl}(0)^2 \iiint Y_{lm}(\theta, \phi) \hat{V}(r) Y_{lm}(\theta, \phi) \quad (6)$$

Recognize now that if  $l \neq 0$ , then  $R_{nl} = 0$ . So we may assume  $l = m = 0$  and therefore, with  $Y_{00} = \frac{1}{\sqrt{4\pi}}$

$$= \frac{R_{nl}(0)^2}{4\pi} \iiint \hat{V}(r) \quad (7)$$

$$= \frac{R_{nl}(0)^2}{4\pi} \iiint \frac{3KQ}{2R} \left(1 - \frac{r^2}{3R^2}\right) - \frac{KQ}{r} \quad (8)$$

$$= \frac{R_{nl}(0)^2}{4\pi} \int_0^R \int_0^\pi \int_0^{2\pi} \frac{3KQ}{2R} \left(1 - \frac{r^2}{3R^2}\right) - \frac{KQ}{r} d\theta \sin(\phi) d\phi r^2 dr \quad (9)$$

$$= (R_{nl}(0)^2) \int_0^R \frac{3KQ}{2R} \left(r^2 - \frac{r^4}{3R^2}\right) - KQr dr \quad (10)$$

$$= (R_{nl}(0)^2) \int_0^R \frac{3KQ}{2R} \left(r^2 - \frac{r^4}{3R^2} - \frac{2R}{3}r\right) dr \quad (11)$$

$$= \frac{3KQ}{2R} R_{nl}(0)^2 \left( -\frac{R^3}{15} \right) \quad (12)$$

$$= \frac{KQ}{2} R_{nl}(0)^2 \left( -\frac{R^2}{5} \right) \quad (13)$$

$$= -\frac{KQR^2}{10} R_{nl}(0)^2 \quad (14)$$

Using the results on the set:

$$R_{nl}(0) = \left( \frac{2Z}{na_0} \right)^{\frac{3}{2}} \sqrt{\frac{1}{2n^2}} L_{n-1}^1(0) \quad (15)$$

$$= \left( \frac{2Z}{na_0} \right)^{\frac{3}{2}} \sqrt{\frac{1}{2n^2}} \binom{n}{n-1} \quad (16)$$

$$= 2 \left( \frac{Z}{na_0} \right)^{\frac{3}{2}} \quad (17)$$

Thus:

$$\langle \hat{V} \rangle = -\frac{KQR^2}{10} \left( 2 \left( \frac{Z}{na_0} \right)^{\frac{3}{2}} \right)^2 \quad (18)$$

$$\langle \hat{V} \rangle = -\frac{KQR^2}{10} 4 \left( \frac{Z}{na_0} \right)^3 \quad (19)$$

$$\langle \hat{V} \rangle = -\frac{2KQR^2 Z^3}{5n^3 a_0^3} \quad (20)$$

### 3.3. Part C

We see that for  $l \geq 0$ , we find these states are unaffected and have 0 expected perturbation energy (to first order).  $s$ -orbitals however have:

$$\langle \hat{V} \rangle = -\frac{2KQR^2 Z^3}{5n^3 a_0^3} \quad (21)$$

Now recognize that for every  $n$ , we have  $n^2$  degeneracies (no spin). It's natural to wonder if we should be worried about our example such as in Example 5.2:1. **The answer is no.** The reason being that because  $\hat{V}$  is angularly-independent, that the inner product gives  $\delta_{mm'} \delta_{ll'}$  in the answer. Therefore to get a non-zero result, we must have  $l = 0$  and  $m = 0$ . This leaves us with  $n$ , but if  $n \neq n'$ , then they are not degenerate, showing we have nothing to worry about.

# 4: Problem 11

## 4.1. Part A

We follow along with pg 470 of Shankar. Observe that in the radial equation, we have:

$$\left[ \frac{d^2}{dr^2} + \left( 2\frac{\mu}{\hbar^2} \right) \left( E - \hat{V}(r) - \frac{l(l+1)\hbar^2}{2\mu r^2} \right) \right] U_{\text{el}} = 0 \quad (1)$$

But taking out the perturbation term from  $\hat{V}(r)$ , we may adjust the centrifugal term.

$$\left[ \frac{d^2}{dr^2} + \left( 2\frac{\mu}{\hbar^2} \right) \left( E - \hat{V}_0(r) - \frac{\lambda}{r^2} - \frac{l(l+1)\hbar^2}{2\mu r^2} \right) \right] U_{\text{el}} = 0 \quad (2)$$

$$\left[ \frac{d^2}{dr^2} + \left( 2\frac{\mu}{\hbar^2} \right) \left( E - \hat{V}_0(r) - \frac{l'(l'+1)\hbar^2}{2\mu r^2} \right) \right] U_{\text{el}} = 0 \quad (4.1:3)$$

Since we've only modified the differential equation, the energy from Shankar 13.1.14 must still hold:

$$E(l') = -\frac{me^4}{2\hbar^2(k+l'+1)^2} = E^{(0)} + E^{(1)} + \dots \quad (4)$$

Where now  $l'$  is derived from **Equation (3)**. We now simplify an equation for  $l'(\lambda)$  implicitly:

$$\frac{\hbar^2 l(l+1)}{2mr^2} + \frac{\lambda}{r^2} = \frac{\hbar^2 l'(l'+1)}{2mr^2} \quad (5)$$

$$l'(l'+1) = l(l+1) + \frac{2m\lambda}{\hbar^2} \quad (6)$$

$$l'(l'+1) = l(l+1) + \frac{2m\lambda}{\hbar^2} \quad (4.1:7)$$

But now remembering that (In the Professor's formulation, not Shankar's):

$$\left\langle \frac{1}{r^2} \right\rangle = E^{(1)} = \left[ \frac{dE}{d\lambda} \right]_{\lambda=0} = \left[ \frac{dE}{dl'} \frac{dl'}{d\lambda} \right]_{\lambda=0} \quad (8)$$

Differentiating:

$$\frac{dE}{dl'} = \frac{me^4}{\hbar^2(k+l'+1)^3} \quad (9)$$

$$2\left(l' + \frac{1}{2}\right)dl' = \frac{2m}{\hbar^2}d\lambda \quad (10)$$

$$\frac{dl'}{d\lambda} = \frac{m}{\hbar^2(l' + \frac{1}{2})} \quad (11)$$

Which if we evaluate **Equation (7)** with  $\lambda = 0$ , we see implies either:

$$l' = l \quad \text{or} \quad l' = -(l+1) \quad (12)$$

It is clear though that  $l' = -(l+1)$  is unphysical so we have:

$$\left[ \frac{dE}{dl'} \frac{dl'}{d\lambda} \right]_{\lambda=0} = \left( \frac{me^4}{\hbar^2(k+l'+1)^3} \frac{m}{\hbar^2(l'+\frac{1}{2})} \right) \quad (13)$$

$$\left\langle \frac{1}{r^2} \right\rangle = E^{(1)} = \frac{1}{a_0^2(k+l'+1)^3(l'+\frac{1}{2})} \quad (14)$$

$$\left\langle \frac{1}{r^2} \right\rangle = E^{(1)} = \frac{1}{a_0^2 n^3(l+\frac{1}{2})} \quad (15)$$

## 4.2. Part B

We know from 12.6:3 that the radial part of the Hamiltonian is

$$\frac{-\hbar^2}{2m} \left( \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \right) \quad (16)$$

Observe that with

$$\hat{P}_r := -i\hbar \left( \frac{\partial}{\partial r} + \frac{1}{r} \right) \quad (17)$$

we have

$$\frac{\hat{P}_r^2}{2m} = \frac{-\hbar^2}{2m} \left( \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \right) \quad (18)$$

Likewise, observe that for an eigenstate  $\psi$  and by Ehrenfest's Theorem, we have:

$$\frac{d\langle \hat{P}_r \rangle}{dt} = 0 = \langle [\hat{H}, \hat{P}_r] \rangle \quad (19)$$

Explicitly evaluating the commutator, we find, using the radial equation, that

$$[\hat{H}, \hat{P}_r] = \hat{H}\hat{P}_r - \hat{P}_r\hat{H} \quad (20)$$

$$= \left[ -\frac{\hbar^2}{2m} \left( \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{l(l+1)}{r^2} \right) + \hat{V} \right] \hat{P}_r - \hat{P}_r \left[ -\frac{\hbar^2}{2m} \left( \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{l(l+1)}{r^2} \right) + \hat{V} \right] \quad (21)$$

$$= \left[ -\frac{\hbar}{2m} \frac{l(l+1)}{r^2} + \hat{V} \right] \hat{P}_r - \hat{P}_r \left[ -\frac{l(l+1)}{r^2} + \hat{V} \right] \quad (22)$$

$$= -\frac{\hbar}{2m} \left[ \frac{l(l+1)}{r^2}, \hat{P}_r \right] + [\hat{V}, \hat{P}_r] \quad (23)$$

Breaking this up:

$$[\hat{V}, \hat{P}_r] \propto \left[ \frac{1}{r}, \frac{\partial}{\partial r} \right] = \frac{1}{r} \psi' - \frac{\partial}{\partial r} \frac{\psi}{r} = \frac{1}{r^2} \quad (24)$$

$$\left[ \frac{1}{r^2}, \hat{P}_r \right] \propto \left[ \frac{1}{r^2}, \frac{\partial}{\partial r} \right] = \frac{1}{r^2} \psi' - \frac{\partial}{\partial r} \frac{\psi}{r^2} = \frac{2}{r^3} \quad (25)$$

Therefore we have:



$$[\hat{H}, \hat{P}_r] = K \left( -\frac{\hbar^2}{2m} l(l+1) \left[ \frac{1}{r^2}, \frac{\partial}{\partial r} \right] + e^2 \left[ \frac{1}{r}, \frac{\partial}{\partial r} \right] \right) \quad (26)$$

$$[\hat{H}, \hat{P}_r] = K \left( -\frac{\hbar^2}{2m} \frac{2l(l+1)}{r^3} + \frac{e^2}{r^2} \right) \quad (27)$$

But now we see that we must have:

$$\left\langle -\frac{\hbar^2}{m} \frac{l(l+1)}{r^3} + \frac{e^2}{r^2} \right\rangle = 0 \quad (28)$$

$$\left\langle \frac{\hbar^2}{m} \frac{l(l+1)}{r^3} \right\rangle = \left\langle \frac{e^2}{r^2} \right\rangle \quad (29)$$

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{me^2}{\hbar^2 l(l+1)} \left\langle \frac{1}{r^2} \right\rangle \quad (30)$$

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{a_0 l(l+1)} \left\langle \frac{1}{r^2} \right\rangle \quad (31)$$

But combining our previous statement, we have:

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{a_0 l(l+1)} \frac{1}{a_0^2 n^3 (l + \frac{1}{2})} \quad (32)$$

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{a_0^3 n^3 (l + \frac{1}{2})(l+1)} \quad (33)$$

## 5: Problem 12

### 5.1. Part A

$$\hat{H}_0 = \frac{\hat{\mathbf{P}}^2}{2m} - \frac{\alpha}{r} \quad (1)$$

$$\hat{V} = -Eez \quad (2)$$

$$\hat{H} = \frac{\hat{\mathbf{P}}^2}{2m} - \frac{\alpha}{r} - Eez \quad (3)$$

It is clear that with a homogenous electric field, we need only consider the relative radius, as did the original Hamiltonian. Consider now in the  $\mathbf{r}$  basis:

$$[\hat{V}, \hat{L}_z] = \hat{V}(\hat{X}\hat{P}_y - \hat{Y}\hat{P}_x) - (\hat{X}\hat{P}_y - \hat{Y}\hat{P}_x)\hat{V} \quad (4)$$

$$= Ee(z(\hat{X}\hat{P}_y - \hat{Y}\hat{P}_x) - (\hat{X}\hat{P}_y - \hat{Y}\hat{P}_x)z) \quad (5)$$

But these commute so:

$$[\hat{V}, \hat{L}_z] = 0 \quad (6)$$

This gives us a selection rule in accordance with Eq 17.2.12 from Shankar. Namely, that the matrix elements between any states of different eigenvalues for  $\hat{L}_z$  will always be 0. Formally:

$$\langle \alpha_1 m_1 | \hat{V} | \alpha_2 m_2 \rangle = 0 \quad (7)$$

if  $m_1 \neq m_2$ .

### 5.2. Part B

Since we're ignoring spin, and since we've removed worry about any degeneracies between different eigenvalues of  $\hat{L}_z$ , we now only need to worry about when  $n_1 = n_2$ ,  $m_1 = m_2$ , but  $l_1 \neq l_2$ . Recalling that  $0 \leq m \leq l \leq n$ , this implies we have  $(n - m)$  degenerate states.

### 5.3. Part C

This leaves us with only 4 potentially non-zero elements for  $n = 2$ :

$$\langle 200 | \hat{V} | 200 \rangle \quad ; \quad \langle 210 | \hat{V} | 200 \rangle \quad ; \quad \langle 200 | \hat{V} | 210 \rangle \quad ; \quad \langle 210 | \hat{V} | 210 \rangle \quad (8)$$

We have:

$$|200\rangle = K_0 \left( 2 - \frac{r}{a_0} \right) e^{-\frac{r}{2a_0}} \quad (9)$$

$$|210\rangle = K_1 \cos(\theta) \frac{r}{a_0} e^{-\frac{r}{2a_0}} \quad (10)$$

To cut work for ourselves, first recognize that  $z = r \cos(\phi)$  is odd parity, while combining any two psi's, that is,  $\langle \psi | \psi \rangle$  is even. Thus  $\langle \psi | z | \psi \rangle$  is odd and the integral over it must cancel to 0. This gives  $\langle 200 | \hat{V} | 200 \rangle = \langle 210 | \hat{V} | 210 \rangle = 0$ . We can also recognize that  $\langle 200 | \hat{V} | 210 \rangle = \langle 210 | \hat{V} | 200 \rangle$  since  $\hat{V}$  commutes with all wave functions. Thus we have:

$$\langle 210 | z | 200 \rangle = \iiint K_0 \left( 2 - \frac{r}{a_0} \right) e^{-\frac{r}{2a_0}} r \cos(\phi) K_1 \cos(\phi) \frac{r}{a_0} e^{-\frac{r}{2a_0}} \quad (11)$$

$$= 4\pi K_0 K_1 \int_0^\infty \int_0^\pi \frac{r}{a_0} \left( 2 - \frac{r}{a_0} \right) r^3 \cos(\phi)^2 \sin(\phi) e^{-\frac{r}{a_0}} d\phi dr \quad (12)$$

$$= 4\pi K_0 K_1 \int_0^\infty \frac{r}{a_0} \left( 2 - \frac{r}{a_0} \right) r^3 e^{-\frac{r}{a_0}} \int_0^\pi \cos(\phi)^2 \sin(\phi) d\phi dr \quad (13)$$

$$= \frac{8\pi}{3} K_0 K_1 \int_0^\infty \frac{r}{a_0} \left( 2 - \frac{r}{a_0} \right) r^3 e^{-\frac{r}{a_0}} dr \quad (14)$$

$$= -\frac{8\pi}{3} K_0 K_1 (72a_0^4) \quad (15)$$

$$= -\frac{8\pi}{3} \left( \frac{3}{4\pi} \frac{\sqrt{3}}{8\sqrt{12}} \right) (72a_0) \quad (16)$$

$$= -3a_0 \quad (17)$$

Therefore:

$$\langle 210 | \hat{V} | 200 \rangle = 3Eea_0 \quad (18)$$

#### 5.4. Part D

For the constant electric field, we find:

$$\langle 210 | \hat{V} | 200 \rangle = 3Eea_0 = 1.5 \text{ meV} \quad (19)$$

For a Hydrogen atom, we find:  $E = 5 \cdot 10^{11} \frac{\text{N}}{\text{m}}$  so:

$$\langle 210 | \hat{V} | 200 \rangle = 3Eea_0 = 81.6 \text{ eV} \quad (20)$$

So we see that for  $E$  fields comparable to the hydrogen atom, it is unreasonable, but it is fine for fields comparable to  $E = 100 \frac{\text{kV}}{\text{cm}}$