

Quantum Mechanics II

Assignment I

Gabriel Balarezo

January 2, 2024

Problem 6.27

Suppose a Hamiltonian H , for a particular quantum system is a function of some parameter λ ; let $E_n(\lambda)$ and $\psi_n(\lambda)$ be the eigenvalues and eigenfunctions of $H(\lambda)$. The **Feynman-Hellmann theorem** states that

$$\frac{\partial E_n}{\partial \lambda} = \left\langle \psi_n \left| \frac{\partial H}{\partial \lambda} \right| \psi_n \right\rangle$$

(assuming either that E_n is nondegenerate, or if degenerate that ψ_n 's are the "good" linear combinations of the degenerate eigenfunctions).

- a) Prove the Feynman-Hellmann theorem. Hint: Use Equation 6.9.
- b) Apply it to the one-dimensional harmonic oscillator, (i) using $\lambda = \omega$ (this yields a formula for the expectation value of V), (ii) using $\lambda = \hbar$ (this yields $\langle T \rangle$), and (iii) using $\lambda = m$ (this yields a relation between $\langle T \rangle$ and $\langle V \rangle$). Compare your answers to Problem 2.37 and the virial theorem predictions (Problem 3.53).

Solution

Part a

Let's suppose H_λ a hamiltonian which depends on a parameter λ . Then let E_λ be the eigenenergies, and ψ_λ be the normalised eigenstates which also depend on λ .

Then we can write the following

$$H_\lambda |\psi_\lambda\rangle = E_\lambda |\psi_\lambda\rangle$$

and using Equation 6.9 as suggested, we can write the following equation

$$E_\lambda = \langle \psi_\lambda | H_\lambda | \psi_\lambda \rangle$$

Now let's differentiate w.r.t λ in both sides

$$\frac{\partial}{\partial \lambda} E_\lambda = \frac{\partial}{\partial \lambda} \langle \psi_\lambda | H_\lambda | \psi_\lambda \rangle$$

using chain rule

$$\frac{\partial E_\lambda}{\partial \lambda} = \left\langle \frac{\partial \psi_\lambda}{\partial \lambda} \middle| H_\lambda \middle| \psi_\lambda \right\rangle + \left\langle \psi_\lambda \middle| \frac{\partial H_\lambda}{\partial \lambda} \middle| \psi_\lambda \right\rangle + \left\langle \psi_\lambda \middle| H_\lambda \middle| \frac{\partial \psi_\lambda}{\partial \lambda} \right\rangle$$

we know that

$$H_\lambda | \psi_\lambda \rangle = E_\lambda | \psi_\lambda \rangle, \quad \text{and} \quad \langle \psi_\lambda | H_\lambda = E_\lambda \langle \psi_\lambda |$$

then

$$\begin{aligned} \frac{\partial E_\lambda}{\partial \lambda} &= E_\lambda \left\langle \frac{\partial \psi_\lambda}{\partial \lambda} \middle| \psi_\lambda \right\rangle + \left\langle \psi_\lambda \middle| \frac{\partial H_\lambda}{\partial \lambda} \middle| \psi_\lambda \right\rangle + E_\lambda \left\langle \psi_\lambda \middle| \frac{\partial \psi_\lambda}{\partial \lambda} \right\rangle \\ &= \left\langle \psi_\lambda \middle| \frac{\partial H_\lambda}{\partial \lambda} \middle| \psi_\lambda \right\rangle + E_\lambda \left(\left\langle \frac{\partial \psi_\lambda}{\partial \lambda} \middle| \psi_\lambda \right\rangle + \left\langle \psi_\lambda \middle| \frac{\partial \psi_\lambda}{\partial \lambda} \right\rangle \right) \\ &= \left\langle \psi_\lambda \middle| \frac{\partial H_\lambda}{\partial \lambda} \middle| \psi_\lambda \right\rangle + E_\lambda \left(\frac{\partial}{\partial \lambda} \langle \psi_\lambda | \psi_\lambda \rangle + \frac{\partial}{\partial \lambda} \langle \psi_\lambda | \psi_\lambda \rangle \right), \quad \langle \psi_\lambda | \psi_\lambda \rangle = 1 \\ &= \left\langle \psi_\lambda \middle| \frac{\partial H_\lambda}{\partial \lambda} \middle| \psi_\lambda \right\rangle + E_\lambda \left(\cancel{\frac{\partial}{\partial \lambda} (1)} + \cancel{\frac{\partial}{\partial \lambda} (1)} \right) \xrightarrow{0} \end{aligned}$$

Finally we have that:

$$\frac{\partial E_\lambda}{\partial \lambda} = \left\langle \psi_\lambda \middle| \frac{\partial H_\lambda}{\partial \lambda} \middle| \psi_\lambda \right\rangle$$

or

$$\frac{\partial E_n}{\partial \lambda} = \left\langle \psi_n \middle| \frac{\partial H_\lambda}{\partial \lambda} \middle| \psi_n \right\rangle$$

as stated in the problem.

Part b

For the 1D Harmonic oscillator:

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m \omega^2 x^2, \quad E_n = \hbar \omega \left(n + \frac{1}{2} \right), \quad n = 0, 1, 2, 3, \dots$$

i) $\lambda = \omega$

Compute the derivatives:

$$\begin{aligned} \frac{\partial E_n}{\partial \omega} &= \hbar \left(n + \frac{1}{2} \right) \\ \frac{\partial H}{\partial \omega} &= m \omega x^2 \end{aligned}$$

Applying the Feynman-Hellmann theorem:

$$\hbar \left(n + \frac{1}{2} \right) = \left\langle m\omega x^2 \right\rangle$$

we can notice that the right hand side can be written as

$$m\omega x^2 = \frac{2}{\omega} V$$

then

$$\hbar \left(n + \frac{1}{2} \right) = \frac{2}{\omega} \left\langle V \right\rangle$$

Finally we get

$$\boxed{\frac{\hbar\omega}{2} \left(n + \frac{1}{2} \right) = \left\langle V \right\rangle}$$

which is the expectation value of the potential energy for a 1D harmonic oscillator for any value of n .

ii) $\lambda = \hbar$

Compute the derivatives:

$$\begin{aligned} \frac{\partial E_n}{\partial \hbar} &= \omega \left(n + \frac{1}{2} \right) \\ \frac{\partial H}{\partial \omega} &= \frac{-\hbar}{m} \frac{d}{dx} \end{aligned}$$

Applying the Feynman-Hellmann theorem:

$$\omega \left(n + \frac{1}{2} \right) = \left\langle \frac{-\hbar}{m} \frac{d^2}{dx^2} \right\rangle$$

we can rewrite the right hand side as follows

$$\frac{-\hbar}{m} \frac{d^2}{dx^2} = \frac{2}{\hbar} T$$

then

$$\omega \left(n + \frac{1}{2} \right) = \frac{2}{\hbar} \left\langle T \right\rangle$$

from here we get

$$\boxed{\frac{\hbar\omega}{2} \left(n + \frac{1}{2} \right) = \left\langle T \right\rangle}$$

which is the expectation value of the kinetic energy for a 1D harmonic oscillator.

iii) $\lambda = m$

Get the derivatives:

$$\begin{aligned}\frac{\partial E_n}{\partial m} &= 0 \\ \frac{\partial H}{\partial m} &= \frac{\hbar^2}{2m^2} \frac{d^2}{dx^2} + \frac{1}{2} \omega^2 x^2\end{aligned}$$

Apply the Feynman-Hellmann theorem

$$0 = \left\langle \frac{\hbar^2}{2m^2} \frac{d^2}{dx^2} \right\rangle + \left\langle \frac{1}{2} \omega^2 x^2 \right\rangle$$

the expressions in the right hand side can be written as

$$\begin{aligned}\frac{\hbar^2}{2m^2} \frac{d^2}{dx^2} &= -\frac{1}{m} T \\ \frac{1}{2} \omega^2 x^2 &= \frac{1}{m} V\end{aligned}$$

then, the theorem becomes

$$0 = -\frac{1}{m} \langle T \rangle + \frac{1}{m} \langle V \rangle$$

from here, we can derive the following expression:

$$\boxed{\langle T \rangle = \langle V \rangle}$$

which is the relation proposed by the virial theorem.

Now, let's compare our results with those from Problem 2.37, and the virial theorem predictions in Problem 3.53.

The results from (i) and (ii) agree with those we obtained using the Feynman-Hellmann theorem, which seems to be a more efficient way to compute those expectation values.

In addition, the result from part (iii) effectively agree with the virial theorem predictions.

Problem 6.28

The Feynman-Hellmann theorem (Problem 6.27) can be used to determine the expectation values of $1/r$ and $1/r^2$ for hydrogen. The effective Hamiltonian for the radial wave functions is (Equation 4.53)

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r},$$

and the eigenvalues (expressed in terms of l) are (Equation 4.70)

$$E_n = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2 (j_{\max} + l + 1)^2}$$

- a) Use $\lambda = e$ in the Feynman-Hellmann theorem to obtain $\langle 1/r \rangle$. Check your result against Equation 6.54 .
- b) Use $\lambda = l$ to obtain $\langle 1/r^2 \rangle$. Check your answer with Equation 6.55.

Solution

Part a

First let's compute the necessary derivatives setting $\lambda = e$:

$$\begin{aligned}\frac{\partial E_n}{\partial e} &= -\frac{1}{8} \frac{me^3}{\pi^2 \epsilon_0^2 \hbar^2 (j_{max} + l + 1)^2} \\ \frac{\partial H}{\partial e} &= -\frac{e}{2\pi\epsilon_0} \frac{1}{r}\end{aligned}$$

then, using the Feynman-Hellmann theorem we have

$$\begin{aligned}-\frac{1}{8} \frac{me^3}{\pi^2 \epsilon_0^2 \hbar^2 (j_{max} + l + 1)^2} &= \left\langle -\frac{e}{2\pi\epsilon_0} \frac{1}{r} \right\rangle \\ &= -\frac{e}{2\pi\epsilon_0} \left\langle \frac{1}{r} \right\rangle\end{aligned}$$

Solving for $\left\langle \frac{1}{r} \right\rangle$

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{4} \frac{me^3}{\pi \epsilon_0 \hbar^2 (j_{max} + l + 1)^2}$$

we can rewrite this expresion using the Bohr radius:

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2}$$

then,

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{a_0 (j_{max} + l + 1)^2}$$

let $n = j_{max} + l + 1$

$$\boxed{\left\langle \frac{1}{r} \right\rangle = \frac{1}{a_0 n^2}}, \quad \text{this result agrees with that stated in Equation 6.54.}$$

Part b

Now we set $\lambda = l$, let's get the derivatives:

$$\begin{aligned}\frac{\partial E_n}{\partial l} &= \frac{2me^4}{32\pi^2 \epsilon_0^2 \hbar^2 (j_{max} + l + 1)^3} \\ \frac{\partial H}{\partial l} &= \frac{\hbar^2}{2m} \frac{2l + 1}{r^2}\end{aligned}$$

Now, using the Feynman-Hellmann theorem we get

$$\begin{aligned}\frac{2me^4}{32\pi^2\epsilon_0^2\hbar^2(j_{max} + l + 1)^3} &= \left\langle \frac{\hbar^2}{2m} \frac{2l + 1}{r^2} \right\rangle \\ &= \frac{\hbar^2(2l + 1)}{2m} \left\langle \frac{1}{r^2} \right\rangle\end{aligned}$$

solving for $\left\langle \frac{1}{r^2} \right\rangle$

$$\begin{aligned}\left\langle \frac{1}{r^2} \right\rangle &= \frac{2me^4}{32\pi^2\epsilon_0^2\hbar^2(j_{max} + l + 1)^3} \frac{2m}{\hbar^2(2l + 1)} \\ &= \frac{m^2e^4}{16\pi^2\epsilon_0^2\hbar^4(j_{max} + l + 1)^3} \frac{1}{(l + 1/2)}\end{aligned}$$

using Bohr radius and using $n = j_{max} + l + 1$ we have

$\left\langle \frac{1}{r^2} \right\rangle = \frac{1}{(l + 1/2)n^3a_0^2}$	This result agrees with that stated in Equation 6.55.
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Problem 6.30

- a) Plug $s = 0, s = 1, s = 2$, and $s = 3$ into Kramers' relation (Equation 6.96) to obtain formulas for $\langle r^{-1} \rangle, \langle r \rangle, \langle r^2 \rangle$, and $\langle r^3 \rangle$. Note that you could continue indefinitely, to find any positive power.
- b) In the other direction, however, you hit a snag. Put in $s = -1$, and show that all you get is a relation between $\langle r^{-2} \rangle$ and $\langle r^{-3} \rangle$.
- c) But if you can get $\langle r^{-2} \rangle$ by some other means, you can apply the Kramers' relation to obtain the rest of the negative powers. Use Equation 6.55 (which is derived in Problem 6.28) to determine $\langle r^{-3} \rangle$, and check your answer against Equation 6.63.

Kramers' relation

$$\frac{s+1}{n^2} \langle r^s \rangle - (2s+1)a_0 \langle r^{s-1} \rangle + \frac{s}{4} [(2l+1)^2 - s^2] a_0^2 \langle r^{s-2} \rangle = 0$$

Part a

Pluggin $s = 0$

With $s = 0$, Kramers' relation becomes

$$\frac{1}{n^2} - a_0 \langle r^{-1} \rangle = 0$$

which yields to:

$$\boxed{\left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2 a_0}}$$

Pluggin $s = 1$

with $s = 1$, Kramers' relation becomes:

$$\frac{2}{n^2} \langle r \rangle - 3a_0 + \frac{1}{4} [(2l+1)^2 - 1] a_0^2 \langle r^{-1} \rangle = 0$$

solve for $\langle r \rangle$, and use result obtained for $\left\langle \frac{1}{r} \right\rangle$

$$\begin{aligned} \langle r \rangle &= \frac{n^2}{2} \left[3a_0 - \frac{1}{4} [(2l+1)^2 - 1] a_0^2 \langle r^{-1} \rangle \right] \\ &= \frac{n^2}{2} \left[3a_0 - \frac{1}{4} [(2l+1)^2 - 1] a_0^2 \left(\frac{1}{a_0 n^2} \right) \right] \\ &= \frac{n^2}{2} \left[3a_0 - \frac{1}{4n^2} [(2l+1)^2 - 1] a_0 \right] \end{aligned}$$

$$\boxed{\langle r \rangle = \frac{a_0}{2} [3n^2 - l(l+1)]}$$

Pluggin $s = 2$

with $s = 2$, Kramers' relation becomes:

$$\frac{3}{n^2} \langle r^2 \rangle - 5a_0 \langle r \rangle + \frac{1}{2} [4l(l+1) - 3] a_0^2 = 0$$

solve for $\langle r^2 \rangle$ and use the result obtained for $\langle r \rangle$

$$\begin{aligned} \langle r^2 \rangle &= \frac{n^2}{3} \left[5a_0 \langle r \rangle - \frac{1}{2} [4l(l+1) - 3] a_0^2 \right] \\ &= \frac{n^2}{3} \left[5a_0 \left(\frac{a_0}{2} [3n^2 - l(l+1)] \right) - \frac{1}{2} [4l(l+1) - 3] a_0^2 \right] \\ &= \frac{n^2 a_0^2}{6} [15n^2 - 5l(l+1) - 4l(l+1) + 3] \end{aligned}$$

$$\boxed{\langle r^2 \rangle = \frac{n^2 a_0^2}{2} [5n^2 - 3l(l+1) + 1]}$$

Pluggin $s = 3$

with $s = 3$, Kramers' relation becomes:

$$\frac{4}{n^2} \langle r^3 \rangle - 7a_0 \langle r^2 \rangle + \frac{3}{4} [4l(l+1) - 8] a_0^2 \langle r \rangle = 0$$

solve for $\langle r^3 \rangle$. and use the results obtained for $\langle r \rangle$ and $\langle r^2 \rangle$

$$\begin{aligned}
\langle r^3 \rangle &= \frac{n^2}{4} \left[7a_0 \langle r^2 \rangle - \frac{3}{4} [4l(l+1) - 8] a_0^2 \langle r \rangle \right] \\
&= \frac{n^2}{4} \left[7a_0 \left[\frac{n^2 a_0^2}{2} (5n^2 - 3l(l+1) + 1) \right] - \frac{3}{4} (4l(l+1) - 8) a_0^2 \left[\frac{a_0}{2} (3n^2 - l(l+1)) \right] \right] \\
&= \frac{n^2 a_0^3}{4} \left[\frac{1}{2} (35n^4 - 21n^2 l(l+1) + 7n^2) - \frac{3}{8} [12n^2 l(l+1) - 4l^2(l+1)^2 - 24n^2 + 8l(l+1)] \right] \\
&= \frac{n^2 a_0^3}{8} [(35n^4 - 21n^2 l(l+1) + 7n^2) - (9n^2 l(l+1) - 3l^2(l+1) - 18n^2 + 6l(l+1))] \\
\boxed{\langle r^3 \rangle} &= \frac{n^2 a_0^3}{8} [35n^4 - 30n^2 l(l+1) + 25n^2 + 3l^2(l+1) - 6l(l+1)]
\end{aligned}$$

Part b

Plugin $s = -1$

with $s = -1$, Kramers' relation becomes:

$$a_0 \langle r^{-2} \rangle - \frac{1}{4} [4l(l+1)] a_0^2 \langle r^{-3} \rangle = 0$$

solve for $\langle r^{-3} \rangle$

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

Part c

Using the result for $\langle r^{-2} \rangle$ obtained in Problem 6.28, we get

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

then

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

$$\boxed{\langle r^{-3} \rangle = \frac{1}{l(l+1/2)(l+1)n^3 a_0^3}}$$

Finally, we can see that this result agrees with that stated in Equation 6.63.

Problem 6.33

Calculate the wavelength, in centimeters, of the photon emitted under a hyperfine transition in the ground state ($n = 1$) of deuterium. Deuterium is "heavy" hydrogen, with an extra

neutron in the nucleus. The proton and neutron bind together to form a deuteron, with spin 1 and magnetic moment

$$\vec{\mu}_d = \frac{g_d e}{2m_d} \vec{S}_d$$

the deuteron g-factor is 1.71.

Solution

We know that

$$\vec{\mu}_d = \frac{g_d e}{2m_d} \vec{S}_d \quad \text{and} \quad g_d = 1.71$$

The hyperfine splitting is given by:

$$E_{hf}^1 = \frac{\mu_0 g_p e^2}{3\pi m_p m_e a_0^3} \langle \vec{S}_p \cdot \vec{S}_e \rangle$$

, but in this case we are interested in deuterium, so we have that:

$$E_{hf}^1 = \frac{\mu_0 g_d e^2}{3\pi m_d m_e a_0^3} \langle \vec{S}_d \cdot \vec{S}_e \rangle$$

We also know that

$$\langle \vec{S}_p \cdot \vec{S}_e \rangle = \frac{1}{2} (S_{tot}^2 - S_e^2 - S_d^2), \quad S_n^2 = \hbar^2 s_n(s_n + 1)$$

here

$$\begin{aligned} S_d = 1 &\Rightarrow S_d^2 = \hbar^2 1(1 + 1) = 2\hbar^2 \\ S_e = \frac{1}{2} &\Rightarrow S_e^2 = \hbar^2 \frac{1}{2} \left(\frac{1}{2} + 1 \right) = \frac{3}{4}\hbar^2 \end{aligned}$$

for the total spin we will have to cases

$$S_{tot} = \begin{cases} \frac{3}{2}, & \text{when } s = \frac{1}{2} \\ \frac{1}{2}, & \text{when } s = -\frac{1}{2} \end{cases}$$

then

$$\begin{aligned} S_{tot}^2 &= \begin{cases} \frac{15}{4}\hbar^2, & \text{when } s = \frac{1}{2} \\ \frac{3}{4}\hbar^2, & \text{when } s = -\frac{1}{2} \end{cases} \\ \langle \vec{S}_p \cdot \vec{S}_e \rangle &= \begin{cases} \frac{1}{2} \left(\frac{15}{4}\hbar^2 - \frac{3}{4}\hbar^2 - 2\hbar^2 \right) &= \frac{1}{2}\hbar^2 \\ \frac{1}{2} \left(\frac{3}{4}\hbar^2 - \frac{3}{4}\hbar^2 - 2\hbar^2 \right) &= -\hbar^2 \end{cases} \end{aligned}$$

Plugin this into the hyperfine splitting, we get

$$E_{hf}^1 = \frac{\mu_0 g_d e^2}{3\pi m_d m_e a_0^3} \begin{cases} \frac{1}{2}\hbar^2 \\ -\hbar^2 \end{cases}$$

Now, let's compute ΔE

$$\Delta E = \frac{\mu_0 g_d e^2 \hbar^2}{2\pi m_d m_e a_0^3}$$

but

$$\mu_0 \epsilon_0 = \frac{1}{c^2} \Rightarrow \mu_0 = \frac{1}{\epsilon_0 c^2}$$

So,

$$\Delta E = \frac{g_d e^2 \hbar^2}{2\pi \epsilon_0 c^2 m_d m_e a_0^3}$$

Rewrite this using Bohr radius

$$a_0 = \frac{4\pi \epsilon_0 \hbar^2}{m_e e^2}$$

$$\Rightarrow \Delta E = \frac{2g_d \hbar^4}{m_d m_e^2 c^2 a_0^4}$$

Now, using the energy gap of the hydrogen

$$\Delta E_h = \frac{4g_p \hbar^4}{3m_p m_e^2 c^2 a_0^4} \quad (\text{Griffiths Equation 6.92})$$

we can rewrite as follows

$$\Delta E = \frac{3g_d m_p}{2g_p m_d} \Delta E_h$$

The energy of a photon is given by

$$E = h\nu = h \frac{c}{\lambda} \Rightarrow \lambda = \frac{hc}{E}$$

then

$$\lambda_d = \frac{2g_p m_d}{3g_d m_p} \frac{hc}{\Delta E_h}$$

but

$$\Delta E_h = \frac{hc}{\lambda_h} \Rightarrow \Delta E_h \lambda_h = hc$$

then,

$$\lambda_d = \frac{2g_p m_d}{3g_d m_p} \lambda_h$$

pluggin $g_p = 5.59, g_d = 1.71, m_d/m_p = 2, \lambda_h = 21 \text{ cm}$

$$\lambda_d = \frac{2(5.59)(2)}{3(1.71)} (21 \text{ cm})$$

$$\boxed{\lambda_d = 91.53 \text{ cm}}$$