Quantum Mechanics II
Assignment I

Gabriel Balarezo

February 18, 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

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

(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

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

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:

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

i) $\lambda = \omega$

Compute the derivatives:

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

Aplying 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:

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

Aplying 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:

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

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 expresions in the right hand side can be written as

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

then, the theorem becomes

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

from here, we can derive the following expresion:

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

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)

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

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

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

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

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

This result agrees with that stated in Equation 6.55.

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 indefinilely, 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

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

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:

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

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

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

Pluggin $s = 2$

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

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

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

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

Pluggin $s = 3$

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

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

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

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

$$\boxed{\langle r^3 \rangle = \frac{n^2a_0^3}{8}\left[35n^4-30n^2l(l+1)+25n^2+3l^2(l+1)-6l(l+1)\right]}$$

Part b

Plugin $s=-1$

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

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

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

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

then

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

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

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:

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

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

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

We also know that

$$\langle \vec{S}_p \cdot \vec{S}_e \rangle = \frac{1}{2}\left(S^2_{tot} - S^2_e - S^2_d\right), \qquad S^2_n = \hbar^2 s_n(s_n+1)$$

here

$$S_d = 1 \Rightarrow S^2_d = \hbar^2 1(1+1) = 2\hbar^2$$

$$S_e = \frac{1}{2} \Rightarrow S^2_e = \hbar^2\frac{1}{2}\left(\frac{1}{2}+1\right) = \frac{3}{4}\hbar^2$$

for the total spin we will have to cases

$$S_{tot} = \begin{cases} \frac{3}{2}, & \text{when } s = \frac{1}{2} \\ \frac{3}{4}, & \text{when } s = -\frac{1}{2} \end{cases}$$

then

$$S^2_{tot} = \begin{cases} \frac{15}{4}\hbar^2, & \text{when } s = \frac{1}{2} \\ \frac{3}{4}\hbar^2, & \text{when } s = -\frac{1}{2} \end{cases}$$

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

Plugin this into the hyperfine splitting, we get

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

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

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

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

Now, using the energy gap of the hydrogen

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

we can rewrite as follows

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

The energy of a photon is given by

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

then

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

but

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

then,

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

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

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

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