

## Week 8

# The Hydrogen Atom

### 8.1 Hydrogen Atom II

2/19:     • Review of the hydrogen atom.

- The potential is given by

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$

- This is an important case of motion in a central potential in quantum mechanics.
- We go to polar coordinates because they are most convenient for motion in a central potential.
- We achieve separation of variables via

$$\psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r)Y_{\ell m}(\theta, \phi)$$

- This leads into the spherical harmonics

$$\begin{aligned}\hat{L}^2 Y_{\ell m}(\theta, \phi) &= \hbar^2 \ell(\ell + 1) Y_{\ell m}(\theta, \phi) \\ \hat{L}_z Y_{\ell m}(\theta, \phi) &= \hbar m Y_{\ell m}(\theta, \phi)\end{aligned}$$

- Additionally, the quantum number  $m$  satisfies  $-\ell \leq m \leq \ell$ , giving us  $2\ell + 1$  solutions for each  $\ell$ .
- With the spherical harmonics, the main question becomes how to find  $R_{n\ell}$ .
- We do this via the change of variables

$$U_{n\ell}(r) = r R_{n\ell}(r)$$

yielding a function that satisfies the analogous one-dimensional effective system

$$-\frac{\hbar^2}{2M} \frac{d^2}{dr^2} [U_{n\ell}(r)] + \underbrace{\left[ V(r) + \frac{\hbar^2 \ell(\ell + 1)}{2Mr^2} \right]}_{V_{\text{eff}}(r)} U_{n\ell}(r) = E_{n\ell} U_{n\ell}(r)$$

- We analyze such systems using their asymptotic behavior as  $r \rightarrow 0$  and  $r \rightarrow \infty$ .
- See Figure 7.2. We are looking for bound states  $E_{n\ell}$ .
- When the energy is positive, we have continuous solutions; it's only when the energy is negative that we have quantized bound states.
- Performing such analyses, we propose an ansatz

$$U_{n\ell}(r) = f_{n\ell}(r) r^{\ell+1} e^{-k_{n\ell} r}$$

where

$$E_{n\ell} = -\frac{\hbar^2 k_{n\ell}^2}{2M}$$

- We suppose that  $f$  is a polynomial function

$$f_{n\ell}(r) = \sum_j a_j r^j$$

and solve for it using the differential equation

$$f''_{n\ell}(r) + f'_{n\ell}(r) \left[ \frac{2(\ell+1)}{r} - 2k_{n\ell} \right] + f_{n\ell}(r) \left[ -\frac{2k_{n\ell}(\ell+1)}{r} + \frac{2}{a_B r} \right] = 0$$

- This analysis leads us to the recursion relation

$$a_{j+1} = \frac{2k_{n\ell}(j+\ell+1) - \frac{2}{a_B}}{(j+1)(j+2\ell+2)} a_j$$

- We then choose  $j_{\max} = N$ , yielding

$$k_{n\ell} = \frac{1}{a_B \underbrace{(N+\ell+1)}_n}$$

where we canonically call  $n$  the **principal quantum number**.

- This is a divergence from last time's notation, but one made for good reason, as we will see shortly.
- Note that we did not introduce this notation last time because we didn't want to have to discuss its subtleties then, as we will today.
- Thus, the energy depends only on this value  $n$  via

$$E_{n\ell} = -\frac{\hbar^2}{2m_e a_B^2 (N+\ell+1)^2} = -\frac{\text{Ry}}{n^2}$$

where Ry is the Rydberg constant defined last time.

- Essentially, the energy depends on this value  $n$  which in turn has a hidden dependence on  $\ell$ .
- We now begin on new content, continuing from above however.
- The energy spacing versus  $n$ .

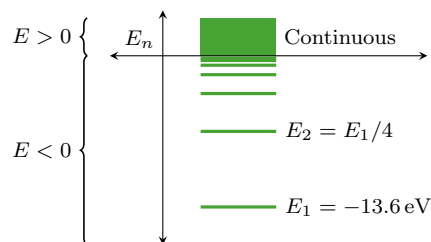


Figure 8.1:  $^1\text{H}$  energy spacing vs.  $n$ .

- The energies get closer and closer together as  $n$  increases until they become continuous for positive values of energy.
- The equations and figure imply that  $-E_1 = \text{Ry}$  is the minimum energy necessary to remove the electron from the hydrogen atom.
- If we don't have this much energy, a lesser amount will still affect the electron, just moving it to an **excited state**.

- In particular,  $E_m - E_1$  is the amount of energy necessary to move the electron to an excited state  $E_m$  of higher energy than  $E_1$ .
- What is also interesting is that if the electron is in an excited state of energy  $E_m$ , then it will *not* stay there forever.
  - Experimentally, even in this time independent potential, the electron can jump back down to a lower state by emitting electromagnetic radiation of energy  $E_\gamma = E_m - E_1$ .
  - This is evidence that the vacuum in which we assume the hydrogen atom lies is not really *vacuum*! Rather, the vacuum contains something called the EM field, and there are fluctuations in this EM field that can push the electron down energy states.
  - This is discussed more in Quantum Mechanics II, but is ignored in our present formalism of the hydrogen atom.
- Now for every fixed  $n$ , the equation  $n = N + \ell + 1$  implies that  $\ell = 0, 1, \dots, n - 1$ .
  - But for every  $\ell$ , there are  $2\ell + 1$  solutions with the same energy.
  - Thus, for every  $n$ , there are

$$\sum_{\ell=0}^{n-1} (2\ell + 1) = 2 \sum_{\ell=0}^{n-1} \ell + \sum_{\ell=0}^{n-1} 1 = 2 \cdot \frac{n(n-1)}{2} + n = n^2$$

different states with the same energy.

- Aside: A fun application of this stuff to cosmology.
  - The universe started as a hot plasma that cooled down as the universe expanded.
  - The early universe contained a lot of crap, including photons.
  - When early protons and electrons tried to combine at hot temperatures, the huge amount of EM radiation would kick the electrons out.
  - Thus, stable atoms could not form.
  - The specific temperatures at which this would occur were

$$k_B T > 13.6 \text{ eV}$$

- At temperatures  $k_B T < 13.6 \text{ eV}$ , protons and electrons bind together, and the universe becomes transparent to radiation.
  - Evidence that this happened: Cosmic microwave background.
    - When the universe became transparent, it was at microwave temperatures.
    - This was when the universe was about 13 000 years old.
- Now back to math.
- Since we now have an explicit definition for  $k_{n\ell}$ , we may rewrite the solutions as

$$U_{n\ell}(r) = f_{n\ell}(r) r^{\ell+1} e^{-r/a_B n}$$

- Notationally, do remember that  $n$  gives energy,  $\ell$  gives angular momentum, and  $N = n - \ell - 1$  gives the polynomial degree of  $f_{n\ell}(r)$ .
- Thus, if  $N = 0$ , then  $n = \ell + 1$  and the radial probability density of finding the particle at a given  $r$  is
 
$$r^2 |R_{n\ell}(r)|^2 = |U_{n\ell}(r)|^2 = r^{2n} e^{-2r/a_B n}$$
- What is the maximum, i.e., the most probable distance from the nucleus?

- Differentiate the probability density with respect to  $r$  and determine where it equals zero.

$$0 = 2nr^{2n-1}e^{-2r/a_B n} - \frac{2r^{2n}}{a_B n}e^{-2r/a_B n}$$

$$\frac{2r^{2n}}{a_B n} = 2nr^{2n-1}$$

$$r_{\max} = a_B n^2$$

- What happens if you have an ion of charge  $Ze$ ?

- Then

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

- Thus,

$$E_n = -\frac{\text{Ry } Z^2}{n^2}$$

and the Bohr radius halves.

## 8.2 Office Hours (Yunjia)

2/20:

- PSet 6, Q1a: Can I leave the solutions in terms of  $U_{n\ell}$ , or do I need to further manipulate them?
  - Since  $U_{n\ell}$  is defined in the question, it's perfectly fine to leave the answer in terms of it.
- PSet 6, Q1a: Do I need to do anything for the “observe...” part of the question? It almost sounds like I need to consider some nonzero values of  $\ell$  here; if not, what else could “each value of  $\ell$ ” refer to?
  - $\ell = 0$  is the only value of  $\ell$  we need to discuss in this part of this problem.
- PSet 6, Q1c: Is all we have to do start with the radial equation, turn it into the spherical Bessel equation, and do the variable substitution?
  - Yes.
- PSet 6, Q1d: Can you differentiate with respect to  $k_{n1}r$ , or do we need to do a  $u$ -substitution type thing and introduce a  $du/dr$  term?
  - We can differentiate with respect to  $k_{n1}r$ .
  - This yields the function we see on Wikipedia.
- PSet 6, Q1d: Do I need to do anything else with the boundary condition other than just commenting on it?
  - No.
- PSet 6, Q1e: Do I need to do anything else here?
  - Say something about the probability density getting larger at the origin vs. going to zero at the origin.
- PSet 6, Q2a: Do you want the  $\bar{n} = 0$  solutions or what else?
  - Give the first few examples ( $\bar{n} = 0, 1, 2$ ) and then say that the pattern continues.
  - There is a proof that the pattern continues for all  $\bar{n}$ , but we are neither expected to produce it nor research/learn it.
- PSet 6, Q2b: Just copy what he wrote on 2/14 for the  $\bar{n} = 1$  case and do a bit of algebra to prove linear combinations?

- Yes.
- PSet 6, Q2c: Just describe quantitatively the shape of the functions in 3D?
  - Yes.
- PSet 6, Q3b: What is this variable  $z$  and why does the  $n\ell$  subscript on  $f$  sometimes disappear?
  - $z := k_{n\ell}r$  is a variable defined to be unitless. It rigorously justifies the fact that we can do all of our differential equation manipulations abstractly in the context of pure mathematics without having to worry about units.
  - The  $n\ell$  subscript's occasional disappearance is just an abuse of notation (and another indication that we can treat  $f$  purely as a mathematical function).
- PSet 6, Q3c: How do I “demonstrate that  $q - w - 1 = n$  must be a positive integer (or zero)” and how does this help imply the final energy equation?
  - The relevant note is included in the problem statement purely to make it clear that the group of numbers  $n + w + 1$  can be treated as a single quantity and does not have to be binomially expanded.
  - Include some note about this in your answer, and you'll be all good to go!

## 8.3 Spin

- 2/21:
- We've probably all heard of spin, but today, we'll give it the mathematical treatment that it deserves.
  - What is spin?
    - Spin is an *intrinsic* property.
    - It is possessed by every particle in nature save one.
    - We may think of it as rotation about a characteristic axis, even though this is not a proper description for a point particle.
  - Since spin is an observable, we want to associate it with a Hermitian operator.
    - Call this operator  $\hat{\vec{S}}$ .
    - Since spin is intuitively associated with rotation, we demand that  $\hat{\vec{S}}$  satisfies the angular momentum algebra.
    - In particular, this means that the operator has three components.

$$\hat{\vec{S}} = \hat{S}_x \hat{x} + \hat{S}_y \hat{y} + \hat{S}_z \hat{z}$$

- We also expect that this operator obeys the following analogous commutativity relations

$$[\hat{S}_x, \hat{S}_y] = i\hbar \hat{S}_z \qquad [\hat{S}_y, \hat{S}_z] = i\hbar \hat{S}_x \qquad [\hat{S}_z, \hat{S}_x] = i\hbar \hat{S}_y$$

- Now recall that the angular momentum operator had the property that

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$$

- This meant that

$$\hat{L}_z Y_{\ell m}(\theta, \phi) = \hat{L}_z |\ell, m\rangle = \hbar m |\ell, m\rangle$$

- Additionally, we knew that the form of the spherical harmonics was  $P_{\ell m}(\theta)e^{im\phi}$ . Substituting into the above equality, this meant that

$$\hat{L}_z P_{\ell m}(\theta)e^{im\phi} = \hbar m P_{\ell m}(\theta)e^{im\phi}$$

- It followed by the boundary condition

$$e^{im(\phi+2\pi)} = e^{im\phi}$$

$$e^{2\pi im} = 1$$

that  $m$  is an integer.

- Later today, we will put an analogous constraint on a quantum number, but in a different way since we don't have such a convenient definition of  $\hat{S}_z$ .

- Let the eigenvalues of  $\hat{S}^2, \hat{S}_z$  be given by

$$\hat{S}^2 |s, m_s\rangle = \hbar^2 s(s+1) |s, m_s\rangle \quad \hat{S}_z |s, m_s\rangle = \hbar m_s |s, m_s\rangle$$

- Similarly to the angular momentum case, we can define ladder operators

$$\hat{S}_{\pm} = \hat{S}_x \pm i\hat{S}_y$$

- We inherit the commutativity relation

$$\begin{aligned} [\hat{S}_z, \hat{S}_{\pm}] &= [\hat{S}_z, \hat{S}_x \pm i\hat{S}_y] \\ &= [\hat{S}_z, \hat{S}_x] \pm i[\hat{S}_z, \hat{S}_y] \\ &= i\hbar\hat{S}_y \pm i(-i\hbar\hat{S}_x) \\ &= \pm\hbar(\hat{S}_x \pm i\hat{S}_y) \\ &= \pm\hbar\hat{S}_{\pm} \end{aligned} \quad \text{Rule 4}$$

- We can also demonstrate that  $\hat{S}_+$  is a *raising* operator.

- First, observe that

$$\begin{aligned} \hat{S}_z \hat{S}_+ |s, m_s\rangle &= (\hat{S}_z \hat{S}_+ - \hat{S}_+ \hat{S}_z) |s, m_s\rangle + \hat{S}_+ \hat{S}_z |s, m_s\rangle \\ &= \hbar\hat{S}_+ |s, m_s\rangle + \hbar m_s \hat{S}_+ |s, m_s\rangle \\ &= \hbar(m_s + 1) \hat{S}_+ |s, m_s\rangle \end{aligned}$$

- Then it follows that

$$\hat{S}_+ |s, m_s\rangle \propto |s, m_s + 1\rangle$$

- Analogously for  $\hat{S}_-$ ,

$$\hat{S}_- |s, m_s\rangle \propto |s, m_s - 1\rangle$$

- We now build up to proving that there are maximum and minimum values of  $m_s$ .

- First off, notice that

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$$

- It is also useful to (re)state here that

$$\hat{S}^2 |s, m_s\rangle = \hbar^2 s(s+1) |s, m_s\rangle \quad \hat{S}_z^2 |s, m_s\rangle = \hbar^2 m_s^2 |s, m_s\rangle$$

- Observe that the value of  $\hat{S}_z^2$  cannot exceed that of  $\hat{S}^2$  because of the first equality above, even though the ladder operator appears to be able to keep raising it indefinitely.

- Thus, there must exist an  $m_s^{\max}$  such that

$$\hat{S}_+ |s, m_s^{\max}\rangle = 0$$

- Separately, observe that

$$\begin{aligned}\hat{S}_- \hat{S}_+ &= (\hat{S}_x - i\hat{S}_y)(\hat{S}_x + i\hat{S}_y) \\ &= \hat{S}_x^2 + \hat{S}_y^2 + i(\underbrace{\hat{S}_x \hat{S}_y - \hat{S}_y \hat{S}_x}_{i\hbar \hat{S}_z}) \\ &= \hat{S}_x^2 + \hat{S}_y^2 - \hbar \hat{S}_z + \hat{S}_z^2 - \hat{S}_z^2 \\ &= \hat{S}^2 - \hbar \hat{S}_z - \hat{S}_z^2\end{aligned}$$

- Combining the last two results, we obtain that

$$\begin{aligned}\hbar^2 s(s+1) - \hbar^2 m_s^{\max} - \hbar^2 (m_s^{\max})^2 &= 0 \\ \hbar^2 m_s^{\max} + \hbar^2 (m_s^{\max})^2 &= \hbar^2 s(s+1) \\ \hbar^2 m_s^{\max} (m_s^{\max} + 1) &= \hbar^2 s(s+1) \\ m_s^{\max} &= s\end{aligned}$$

- Similarly, we have that

$$\hat{S}_- |s, m_s^{\min}\rangle = 0$$

- Thus,

$$\begin{aligned}\hat{S}_+ \hat{S}_- |s, m_s^{\min}\rangle &= (\hat{S}^2 + \hbar \hat{S}_z - \hat{S}_z^2) |s, m_s^{\min}\rangle \\ &= \hbar^2 [s(s+1) - (m_s^{\min})^2 + m_s^{\min}] |s, m_s^{\min}\rangle \\ &= 0\end{aligned}$$

- We conclude from this that

$$m_s^{\min} = -s$$

- Taken together, these two results mean that the ladder stops at both ends, i.e.,

$$-s \leq m_s \leq s$$

- It follows that there are  $2s + 1$  possible solutions/states for each  $s$ .
- But since there will clearly be a natural/positive integer number of solutions/states for  $\hat{S}^2$ , this means that

$$\begin{aligned}2s + 1 &= 1, 2, 3, \dots \\ 2s &= 0, 1, 2, 3, \dots \\ s &= 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \dots\end{aligned}$$

- Implication: Spin can take half-integer values!

- Aside: Spins of some elementary particles.
  - Photons have spin 1.
  - Gravitons have spin 2.
  - A particle discovered in 2012 has spin 0.

- Electron, proton, neutron all have spin 1/2.
- For now, we will concentrate on spin 1/2 particles.
- **Dirac equation:** The relativistic equation for spin 1/2 particles.
- We have that

$$\hat{S}_z \left| \frac{1}{2}, \pm \frac{1}{2} \right\rangle = \pm \frac{\hbar}{2} \left| \frac{1}{2}, \pm \frac{1}{2} \right\rangle$$

- A mathematical representation of this spin uses matrices.
  - We say that

$$\hat{S}_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

- We map

$$\left| \frac{1}{2}, \pm \frac{1}{2} \right\rangle \mapsto \left\{ \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \end{pmatrix} \right\}$$

so that

$$\left| \frac{1}{2}, \frac{1}{2} \right\rangle \mapsto \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \mapsto \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

- Thus, we can see that the relations among the matrices exactly match the properties of the spin operator:

$$\frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = -\frac{\hbar}{2} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

- Other operators have matrix representations, too.
  - Let's investigate  $\hat{S}_{\pm}$ , starting with  $\hat{S}_+$ .
  - Since  $\hat{S}_+ |s, m_s\rangle \propto |s, m_s + 1\rangle$ , we have in the particular case of spin 1/2 particles that

$$\hat{S}_+ \left| s, -\frac{1}{2} \right\rangle \propto \left| s, -\frac{1}{2} + 1 \right\rangle = \left| s, \frac{1}{2} \right\rangle \qquad \hat{S}_+ \left| s, \frac{1}{2} \right\rangle = \hat{S}_+ |s, m_s^{\max}\rangle = 0$$

- To determine the normalization constant, first observe that since  $\hat{S}_- \hat{S}_+ = \hat{S}^2 - \hbar \hat{S}_z - \hat{S}_z^2$ , we have that

$$\langle s, m_s | \hat{S}_- \hat{S}_+ | s, m_s \rangle = \hbar^2 [s(s+1) - m_s^2 - m_s]$$

- Thus, in the specific case that  $s = 1/2$  and  $m_s = -1/2$ , we have that

$$\left\langle \frac{1}{2}, -\frac{1}{2} \right| \hat{S}_- \hat{S}_+ \left| \frac{1}{2}, -\frac{1}{2} \right\rangle = \hbar^2 \left[ \frac{1}{2} \left( \frac{1}{2} + 1 \right) - \left( -\frac{1}{2} \right)^2 - \left( -\frac{1}{2} \right) \right] = \hbar^2$$

- Additionally, if  $N_+ \in \mathbb{C}$  and

$$\hat{S}_+ |s, m_s\rangle = N_+ |s, m_s + 1\rangle$$

then we have that

$$\begin{aligned} \langle s, m_s | \hat{S}_- \hat{S}_+ | s, m_s \rangle &= N_+ \langle s, m_s | \hat{S}_- | s, m_s + 1 \rangle \\ &= N_+ \langle \hat{S}_-^\dagger s, m_s | s, m_s + 1 \rangle \\ &= N_+ \langle \hat{S}_+ s, m_s | s, m_s + 1 \rangle \\ &= N_+^2 \langle s, m_s + 1 | s, m_s + 1 \rangle \\ &= N_+^2 \end{aligned}$$



- Combining the last two results by transitivity, we have that

$$N_+^2 = \hbar^2 N_+ = \hbar$$

- Hence,

$$\hat{S}_+ \left| \frac{1}{2}, -\frac{1}{2} \right\rangle = \hbar \left| \frac{1}{2}, \frac{1}{2} \right\rangle$$

- Therefore, altogether, we have that

$$\hat{S}_+ \left| \frac{1}{2}, -\frac{1}{2} \right\rangle = \hbar \left| \frac{1}{2}, \frac{1}{2} \right\rangle \quad \hat{S}_+ \left| \frac{1}{2}, \frac{1}{2} \right\rangle = 0$$

so we must define

$$\hat{S}_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

- Analogously, we can derive that

$$\hat{S}_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

- This means that the ladder operators act on the spins as follows.

$$\hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \hbar \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \hbar \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

- Now since

$$\hat{S}_+ = \hat{S}_x + i\hat{S}_y \quad \hat{S}_- = \hat{S}_x - i\hat{S}_y$$

we have that

$$\begin{aligned} \hat{S}_x &= \frac{\hat{S}_+ + \hat{S}_-}{2} & \hat{S}_y &= -i \frac{\hat{S}_+ - \hat{S}_-}{2} \\ &= \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} & &= \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \end{aligned}$$

- **Pauli matrices:** The three matrices associated with the components of  $\hat{\vec{S}}$ . Denoted by  $\sigma_1, \sigma_2, \sigma_3$ . Given by

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

- Related to the generators of the group  $SU(2)$ .

- Based on the above, we can compute that that

$$\langle s, m_s | \hat{S}_x | s, m_s \rangle = \langle s, m_s | \hat{S}_y | s, m_s \rangle = 0$$

- We also have

$$\langle s, m_s | \hat{S}_x^2 | s, m_s \rangle = \langle s, m_s | \hat{S}_y^2 | s, m_s \rangle = \langle s, m_s | \hat{S}_z^2 | s, m_s \rangle = \frac{\hbar^2}{4}$$

- We'll continue next time.