The Hydrogen Atom

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Lecture 25

Outline

- Mystery of the Hydrogen Atom
- The Bohr Model
- Ground-State Energy from Uncertainty Principle
- Solutions of Schroedinger's Equation

Mystery of the Hydrogen Atom

- By the early 1900s, scientists understood that matter came in tiny pieces called atoms and that an atom of hydrogen contained charge $+e$ proton at its center and charge $-e$ electron outside that center.

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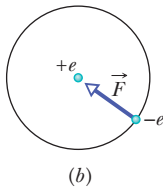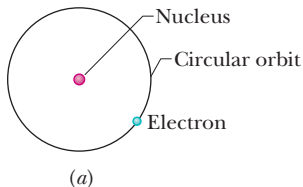
Bohr's model for hydrogen resembles the orbital model of a planet around a star.

- Because the proton's mass is much greater than the electron's mass, we shall assume that the proton is fixed in place. So, the atom is a fixed potential trap with the electron moving around inside it.
- A hydrogen atom contains an electron that is trapped by the Coulomb force it experiences from the proton, which is the nucleus of the atom.
- Under Newtonian laws, the electron would move around the proton, like planets around the Sun, i.e.,

$$\frac{1}{4\pi\epsilon_0}\frac{e^2}{r^2} = m\frac{v^2}{r}.$$

- Multiplying by $-r$, we obtain

$$E_C = -\frac{e^2}{4\pi\epsilon_0 r} = -mv^2 = -2E_K.$$

Alternatively, the total energy of the electron is

$$E = E_K + E_C = E_C/2 = -E_K.$$

- However, any charged particle which moves in a curved path will emit electromagnetic radiation, hence losing energy continuously. Why doesn't the electrical attraction between the electron and the positive charge simply cause the two to collapse together?

- One clue lies in the experimental fact that a hydrogen atom can emit and absorb only four wavelengths in the visible spectrum (656 nm, 486 nm, 434 nm, and 410 nm).

Hydrogen Spectrum
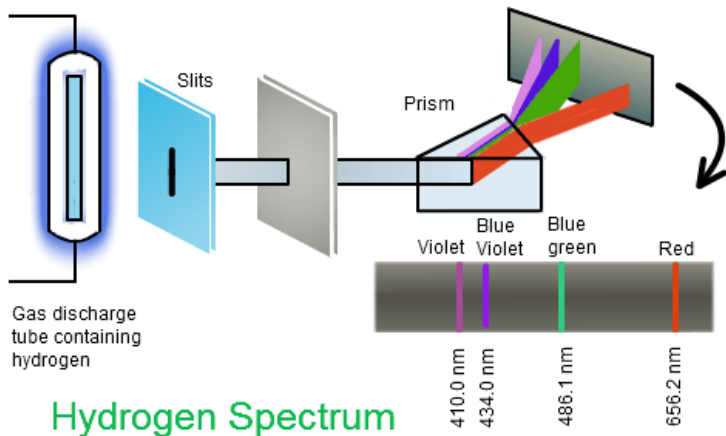
The Bohr Model of Hydrogen (1913)

- Bohr made two bold (and completely unjustified) assumptions:
    1. The electron in a hydrogen atom orbits the nucleus in a circle much like Earth orbits the Sun.
    2. The magnitude of the angular momentum $\vec{L}$ of the electron in its orbit is restricted (quantized) to the values

    $$L = n\hbar, \text{ for } n = 1, 2, 3, \ldots.$$

- However, as successful as his theory was on the four visible wavelengths and on why the atom did not simply collapse, it turned out to be quite wrong in almost every other aspect of the atom.

Physical meaning of the assumption, $L = n\hbar$

- The de Broglie wavelength λ of a free particle with momentum p is $\lambda = h/p = h/mv$.
- For an electron in a hydrogen atom whose orbital radius r, the above equation leads to

$$\lambda/r = h/rmv = h/L.$$

Therefore, we obtain

$$2\pi r/\lambda = L/\hbar.$$

$L = n\hbar$ means that the length of the orbit is an integer multiple of λ. Namely, the phase of the electron wave function returns to the initial value by moving for one cycle of the orbit.

Analysis based on Bohr's model

- We follow Bohr to quantize the electron orbit:

$$L = rmv = n\hbar,$$

from which we find $v = n\hbar/(mr)$.

- Combining with the Newtonian result, we find

$$r_n = n^2 a_B,$$

where the characteristic length

$$a_B = \frac{\hbar^2}{me^2/(4\pi\epsilon_0)} = 0.529 \text{ Å}.$$

- In the Bohr model of the hydrogen atom, the electron's orbital radius r is quantized and the smallest possible orbital radius (for $n = 1$) is a_B, which is called the **Bohr radius**.
  - Can you obtain the length scale, alternatively, from dimension analysis?

- In order that the attraction between electron and nucleus does not simply collapse them together in the Bohr model, the electron should not get any closer to the nucleus than orbital radius a_B by taking $n = 0$.

- The energy of the hydrogen atom, according to the Bohr model, is then

$$E_n = \frac{1}{2}mv^2 - \frac{1}{4\pi\epsilon_0}\frac{e^2}{r} = -\frac{E_R}{n^2},$$

where the characteristic energy (known as the **Rydberg**)

$$E_R = \frac{me^4/(4\pi\epsilon_0)^2}{2\hbar^2} = 13.6 \text{ eV}.$$

- Note that we still have, for each orbit,

$$E = E_K + E_C = E_C/2 = -E_K.$$

The Hydrogen Spectrum

- The energy of a hydrogen atom (or, equivalently, of its electron) changes when the atom emits or absorbs light. Emission and absorption involve a quantum of light according to

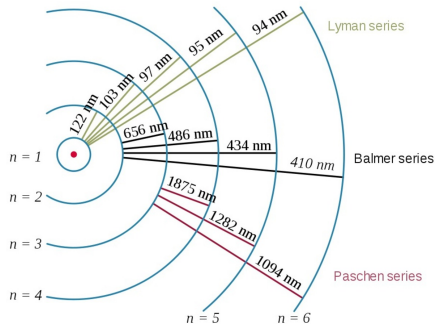$$\hbar\omega_{nm} = E_R \left(\frac{1}{n^2} - \frac{1}{m^2} \right)$$

  for integers $m > n$.

- The wavelengths of the emitted or absorbed light are given by

$$\frac{1}{\lambda} = \frac{E_R}{hc} \left(\frac{1}{n^2} - \frac{1}{m^2} \right).$$

- The collection of such lines (or wavelengths), such as in those in the visible range, is called a *spectrum* of the hydrogen atom.

- For convenience, we often quote the value of the combination $hc = 12400$ eV·Å.

- Hence, we have

$$\frac{hc}{E_R} = 912 \text{ Å}.$$

- Please verify the first four wavelengths in the Balmer series.

Combinations of Physical Constants

- As a side remark, it is often convenient to remember and use combinations of physical constants. Some examples are
  - $hc = 12400$ eV·Å
  - $\hbar c = hc/(2\pi) = 1973$ eV·Å
  - $e^2/(4\pi\epsilon_0) = 14.4$ eV·Å
  - $k_B T_{\text{room}} = 1/40$ eV
  - $m_e c^2 = 511000$ eV $= 0.511$ MeV
  - $m_p/m_e = 1836$
- For example, we calculate the Bohr radius as

$$a_B = \frac{(\hbar c)^2}{(m_e c^2)[e^2/(4\pi\epsilon_0)]} = \frac{1973^2}{511000 \times 14.4} = 0.529 \text{ Å}.$$

GS Energy from Uncertainty Principle

- The ground-state energy is the lowest energy allowed by Heisenberg's uncertainty principle.
- For a hydrogen atom, the size of the wave function, Δr, is the uncertainty in position.
- The uncertainty in momentum is, roughly speaking, $\Delta p \sim \hbar/\Delta r$, by the uncertainty principle.
- The energy of the electron can be estimated to be

$$E \sim \frac{(\Delta p)^2}{2m} - \frac{e^2}{4\pi\epsilon_0 \Delta r} = \frac{\hbar^2}{2m(\Delta r)^2} - \frac{e^2}{4\pi\epsilon_0 \Delta r}.$$

- To find the minimal energy, we solve, for Δr,

$$\frac{dE}{d(\Delta r)} = 0.$$

- After some algebra, we find

$$\Delta r = \frac{\hbar^2}{me^2/(4\pi\epsilon_0)} \equiv a_B,$$

and

$$E = -\frac{me^4/(4\pi\epsilon_0)^2}{2\hbar^2} \equiv -E_R.$$

Comments

- The energy of the ground state (or any stationary state) is uniquely determined. This is because of the energy-time uncertainty principle,
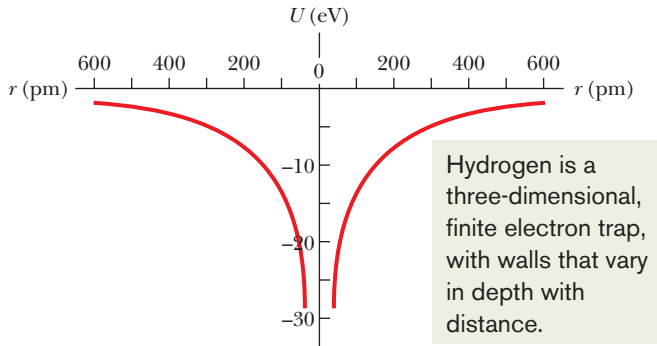
$$\Delta t \cdot \Delta E \geq \hbar/2.$$

In the extreme case of a stationary state, $\Delta t = \infty$, so we have $\Delta E = 0$.

- Note, however, both kinetic energy and potential energy have uncertainties, due to the uncertainties of position and momentum.

Schroedinger's Equation for the H-Atom

- In Schroedinger's model of the hydrogen atom, the electron (charge $-e$) is in a potential energy trap due to its electrical attraction to the proton (charge $+e$) at the center of the atom.

Hydrogen is a three-dimensional, finite electron trap, with walls that vary in depth with distance.

- With the central potential, we can use separation of variables and assume

$$\Psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi),$$

which breaks the equation into three separate differential equations for $R(r)$, $\Theta(\theta)$ and $\Phi(\phi)$.
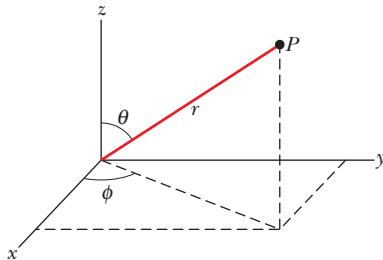
- The Φ function is found to have the quantum number m_ℓ, where

$$\Phi_{m_\ell}(\phi) \sim e^{im_\ell\phi}, \ \ m_\ell = 0, \pm 1, \pm 2, \ldots.$$

- The Θ function is known as *Legendre polynomials*, which have quantum number m_ℓ and ℓ. When Θ and Φ are multiplied together, the product is known as **spherical harmonics**

$$Y_\ell^{m_\ell}(\theta, \phi) = \Theta_\ell^{m_\ell}(\theta)\Phi_{m_\ell}(\phi).$$

- The radial wave function $R_{n\ell}(r)$ has quantum number n and ℓ.

Hydrogen Wave Functions

- The solution for the energy levels is exactly what Bohr found by using the *incorrect* planetary model of the atom.
- The corresponding wave function of a particular quantum state of the hydrogen atom can be labeled by a set of quantum numbers (n, ℓ, m_ℓ).
  - The corresponding energy only depends on the **principal quantum number** $n = 1, 2, 3, \ldots$.
  - The **orbital quantum number** $\ell = 0, 1, 2, \ldots, n-1$ is a measure of the magnitude of the angular momentum of the quantum state. States with $\ell = 0, 1, 2, 3$ are called *s*, *p*, *d*, *f*.
  - The **orbital magnetic quantum number** $m_\ell = -\ell, -\ell + 1, \ldots, \ell - 1, \ell$ is related to the space orientation of this angular momentum vector.

Ground State Wave Function

- The wave function for the ground state of the hydrogen atom, as obtained by solving the three-dimensional Schroedinger equation and normalizing the result, is

$$\psi_{100}(\vec{r}) = R_{10}(r) = \frac{1}{\sqrt{\pi}\, a_B^{3/2}} e^{-r/a_B}.$$

- Note that the hydrogen atom in its ground state has zero angular momentum ($l = 0$; more details will be discussed in the next lecture), which is *not* predicted in the Bohr model.
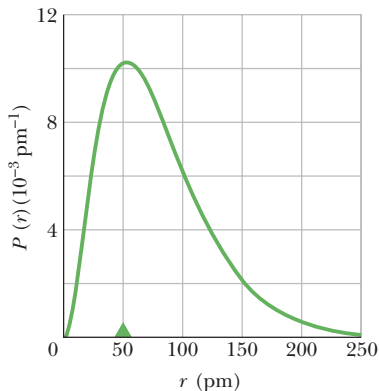
- The probability that the electron can be detected in any given (infinitesimal) volume element dV located at radius r from the center of the atom is $|\psi_{100}(\vec{r})|^2 dV$.

- With spherical symmetry, we have

$$dV = 4\pi r^2 dr.$$

- We define **radial probability density** $P(r)$ such that

$$P(r)dr = |\psi_{100}(\vec{r})|^2 dV.$$

$P(r)$ takes a maximum at $r = a_B$.

- The popular view that electrons in atoms follow well-defined orbits like planets moving around the Sun is incorrect.
- All that we can ever know about the location of the electron in the ground state of the hydrogen atom is the radial probability density.
- We can show the probabilistic nature of the wave function by a dot plot: The density of dots represents the probability density of detection of the electron with the hydrogen atom in its ground state.
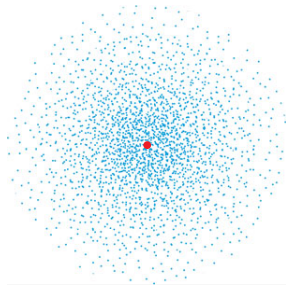
Quiz 25-1

1. What is the average position $\bar{x}$ of an electron in the ground state of a hydrogen atom?
2. What is the average momentum $\overline{p_x}$ of the electron?
3. What is the uncertainty in position $\Delta x = \sqrt{\overline{(x - \bar{x})^2}}$ of the electron? Notice $(\Delta x)^2 = \overline{x^2} - \bar{x}^2$.

$$\overline{x^\alpha} = \iiint x^\alpha |\psi(x, y, z)|^2 dxdydz$$

4. Now, can you calculate the uncertainty in momentum $\Delta p_x = \sqrt{\overline{(p_x - \overline{p_x})^2}}$ of the electron?

Excited States of the Hydrogen Atom

The $n = 2$ shell:

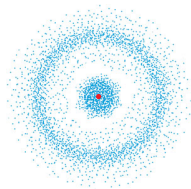Figure 1: All quantum states (such as 2s) with $l = 0$ have spherically symmetric wave functions, which have no preferred axis of symmetry.
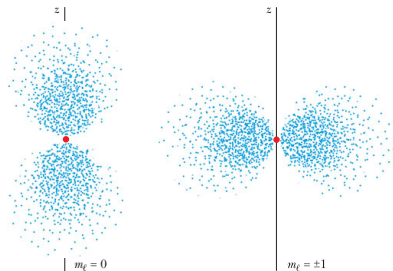

Figure 2: The other states with a definite value of m_l (i.e., 2p with $m_l = -1$, 0, and 1) are symmetric about the z axis, but not spherically symmetric.

- We can write down these wave functions more explicitly as

$$
\begin{aligned}
s &: \ f(r) \\
p_x &: \ g(r)x = \tilde{g}(r)\sin\theta\cos\phi \\
p_y &: \ g(r)y = \tilde{g}(r)\sin\theta\sin\phi \\
p_z &: \ g(r)z = \tilde{g}(r)\cos\theta
\end{aligned}
$$

  where $f(r)$ and $g(r)$ are radial wavefunctions, which depends on the principal quantum number. The angular dependence is the same for other atoms.

- In fact, the wave functions for $m_\ell = \pm 1$ are $g(r)(x \pm iy)$ or $g(r)\sin\theta e^{\pm i\phi}$, linear combinations of p_x and p_y.

Bohr's Correspondence Principle

- The probability density for a hydrogen atom state with a relatively high *n* and the highest $\ell = n - 1$ forms a ring that indeed look like a de Broglie wave.

- The resemblance of the probability density to the electron orbit of classical physics is another illustration of Bohr's **correspondence principle** — namely, that at large quantum numbers the predictions of quantum mechanics merge smoothly with those of classical physics.
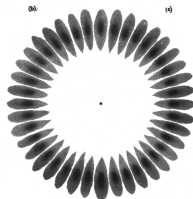
Summary

- Understand hydrogen atom in quantum physics.
  - Classical picture: Coulomb interaction, uniform circular motion, optical spectrum.
  - How did Bohr quantized the hydrogen atom?
  - How did Bohr solve the puzzle of the visible spectrum?
  - How to obtain the length and energy scale in the quantum hydrogen atom?
  - How to label the hydrogen wave functions? What is the probability density for the lowest few?

Reading

Halliday, Resnick & Krane:

- Chapter 48: Properties of Atoms