Quantum Mechanics and Atomic Physics

Lecture 16:

The Coulomb Potential

http://www.physics.rutgers.edu/ugrad/361

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Last time

- Solved radial equation:

$$-\frac{\hbar^2}{2\mu}\left\{\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \ell(\ell+1)\right\} + V(r)r^2 = Er^2$$

- For two simple cases: *infinite and finite spherical wells*
  - Spherical analogs of 1D wells
- We introduced auxiliary function

$$u(r) = r\,R(r)$$

- And radial equation became:

$$\frac{d^2}{dr^2}u + \frac{2\mu}{\hbar^2}\left[E - V(r) - \frac{\ell(\ell+1)}{r^2}\cdot\frac{\hbar^2}{2\mu}\right]u = 0$$

- Today: we will find radial solutions for Coulomb Potential!

The Hydrogen Atom

- Model for hydrogen
  - Electron: charge Q_1 = -e, mass = m_e
  - Nucleus (proton): charge Q_2 = Ze = +e, mass = m_p
- Coulomb Potential:

$$V(r) = \frac{1}{4\pi\varepsilon_0}\frac{Q_1 Q_2}{r} = \frac{-e^2}{4\pi\varepsilon_0 r}$$

- Reduced Mass:

$$\mu = \frac{m_e m_p}{m_e + m_p} = \frac{m_e m_p}{M} \qquad M = m_e + m_p$$

- Two particles orbiting around each other is mathematically identical to one particle of the reduced mass orbiting around the other infinitely massive particle located at the center of mass.
- For hydrogen atom, practically $m_p \gg m_e \Rightarrow \mu \approx m_e$

Revisit the Radial Equation

$$\frac{d^2}{dr^2}u(r) + \frac{2\mu}{\hbar^2}\left[E - V(r) - \frac{l(l+1)}{r^2}\cdot\frac{\hbar^2}{2\mu}\right]u(r) = 0$$

where $u(r) = r\,R(r)$

Recall $\psi(r,\theta,\varphi) = R(r)\,Y(\theta,\varphi)$

For $V(r) = \frac{-e^2}{4\pi\varepsilon_0 r}$

$$\frac{d^2}{dr^2}u(r) + \frac{2\mu}{\hbar^2}\left[E + \frac{e^2}{4\pi\varepsilon_0 r} - \frac{l(l+1)}{r^2}\frac{\hbar^2}{2\mu}\right]u(r) = 0$$

Asymptotic Behavior r → 0

$r \to 0$

term that dominates is $\frac{1}{r^2}$ term so,

$$\frac{d^2}{dr^2}u - \frac{\ell(\ell+1)}{r^2}u \approx 0 \qquad U(r) = A r^k$$

$$k(k-1) A r^{k-2} = \ell(\ell+1) A r^{k-2}$$

$$k(k-1) = \ell(\ell+1)$$

$k = -\ell$ or $k = \ell+1$

But $\ell \geq 0$ so, $\underline{k = \ell+1}$

$U(r) \propto r^{\ell+1}$

or

$R(r) \propto r^{\ell}$ as $r \to 0$

Asymptotic Behavior r → ∞

$r \to \infty$

$\frac{1}{r}$ and $\frac{1}{r^2}$ terms $\to 0$

$$\frac{d^2}{dr^2} u \approx -\frac{2\mu}{\hbar^2} E \cdot u$$

So,

$$u(r) \propto e^{-\sqrt{-\frac{2\mu}{\hbar^2} E}\, r} \qquad \text{as } r \to \infty$$

$$\Rightarrow u(r) \propto r^{\ell+1} e^{-\sqrt{-\frac{2\mu}{\hbar^2} E}\, r}$$

or

$$R(r) \propto r^{\ell} e^{-\sqrt{-\frac{2\mu}{\hbar^2} E}\, r}$$

Look at term in exponential

$$\sqrt{-\frac{2\mu}{\hbar^2}E}$$

- This has units of $1/r$
- Let's call it $1/a_0$
- And let's note that we expect $E \propto 1/n^2$, according to Bohr's result.
- So, $\sqrt{-\frac{2\mu}{\hbar^2}E} = \frac{1}{a_0 \cdot n} \Rightarrow R(r) \propto r^l e^{-r/a_0 n}$

$$\Rightarrow R_{nl}(r) = r^l e^{-r/a_0 n} \underbrace{L_{nl}(r)}_{\text{polynomial to be found}}$$

- See your book for full derivation for $L_{n,l}(r)$ using a power series method

Simplest case: Ground state

- Let's try a solution to S.E. for the ground state n=1 and zero angular momentum $\ell = 0$ (Note: $Y_0^0(\theta,\varphi) = \frac{1}{\sqrt{4\pi}}$)
- Therefore, we can assume the ground state is spherically symmetric so: $\Psi(r,\theta,\phi) = \Psi(r)$
- So, let's try this solution: $R(r) = C e^{-r/a_0} \Rightarrow u(r) = C r e^{-r/a_0}$

$$\frac{d^2 u(r)}{dr^2} + \frac{2\mu}{\hbar^2}\left[E + \frac{e^2}{4\pi\epsilon_0 r}\right]u(r) = 0$$

$$-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2}u(r) - \frac{e^2}{4\pi\epsilon_0 r}u(r) = E\cdot u(r)$$

$$\frac{d^2}{dr^2}u(r) = \frac{d^2}{dr^2}\left[C\cdot r e^{-r/a_0}\right] = -\frac{2Ce^{-r/a_0}}{a_0} + \frac{Cre^{-r/a_0}}{a_0^2}$$

$$= -\frac{2}{ra_0}u(r) + \frac{1}{a_0^2}u(r)$$

$$\Rightarrow -\frac{\hbar^2}{2\mu}\left[\frac{1}{a_0^2} - \frac{2}{ra_0}\right]u(r) - \frac{e^2}{4\pi\varepsilon_0 r}u(r) = E \cdot u(r)$$

$$\Rightarrow \frac{-\hbar^2}{2\mu a_0^2} + \left[\frac{\hbar^2}{\mu a_0} - \frac{e^2}{4\pi\varepsilon_0}\right]\frac{1}{r} = E$$

[ ] must equal zero if it holds for all values of r.

$$\Rightarrow \frac{\hbar^2}{\mu a_0} = \frac{e^2}{4\pi\varepsilon_0} \Rightarrow a_0 = \frac{\hbar^2 \cdot 4\pi\varepsilon_0}{\mu e^2}$$

- This is the Bohr radius found in the Bohr model!

- Let's put this expression for a_0 back into equation above:

$$\Rightarrow \quad \frac{-\hbar^2}{2\mu a_0^2} = E$$

$$\Rightarrow \quad E = \frac{-\hbar^2}{2\mu} \frac{\mu^2 e^4}{\hbar^4 (4\pi)^2 \varepsilon_0^2} = -\frac{\mu e^4}{32\pi^2 \hbar^2 \varepsilon_0^2}$$

- This is the same expression as the Bohr model energy in the ground state!

$$E = -13.6\,eV \quad \text{for } n=1$$

Normalization of the ground state

Note that $\Psi = \Psi_{100}$ and also that $\int_0^{\pi}\int_0^{2\pi} \sin\theta \, d\varphi \, d\theta = 4\pi$

$$\int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} \Psi_{100}^{*}\Psi_{100} \, r^2 \sin\theta \, d\varphi \, d\theta \, dr = 1$$

$$\int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} C^2 e^{-2r/a_0} \, r^2 \sin\theta \, d\varphi \, d\theta \, dr = 1$$

$$C^2 \int_0^{\infty} e^{-2r/a_0} \, 4\pi r^2 \, dr = 1$$

$$4\pi C^2 \int_0^{\infty} e^{-2r/a_0} \cdot r^2 \, dr = 1$$

After two integrations by parts, or just look in the appendix of your book:

$$4\pi C^2 \, \frac{a_0^3}{4} = 1 \quad \Rightarrow \quad C = \sqrt{\frac{1}{\pi a_0^3}}$$

$$\Rightarrow \quad \Psi_{100}(r,\theta,\varphi) = \sqrt{\frac{1}{\pi a_0^3}} \, e^{-r/a_0}$$

Ground state eigenfunction for Hydrogen. Same energy as Bohr model, but r is not fixed at a_0! Not a circular orbit - something like an electron cloud around nucleus.

Hydrogen Radial Wavefunctions

- Complete radial function solutions are:

$$R(r) = e^{-r/na_0} \left(\frac{r}{a_0}\right)^{\ell} L_{n\ell}\left(\frac{r}{a_0}\right)$$

n is called the principal quantum number and must be an integer with n>ℓ

$$a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{\mu e^2} \qquad L_{n\ell}\left(\frac{r}{a_0}\right)$$

These are called Associated Laguerre Polynomials

Table 7.1 Hydrogen Radial Wavefunctions $R_{n\ell}(r)$.

$R_{10}(r) = \frac{2}{a_o^{3/2}} e^{-r/a_o}$	$R_{20}(r) = \frac{1}{(2a_o)^{3/2}}(2 - r/a_o)e^{-r/2a_o}$
$R_{21}(r) = \frac{1}{\sqrt{3}(2a_o)^{3/2}}(r/a_o)e^{-r/2a_o}$	$R_{30}(r) = \frac{2}{(3a_o)^{3/2}}\left[1 - \frac{2r}{3a_o} + \frac{2r^2}{27a_o^2}\right]e^{-r/3a_o}$
$R_{31}(r) = \frac{4\sqrt{2}}{9(3a_o)^{3/2}}(r/a_o)\left[1 - \frac{r}{6a_o}\right]e^{-r/3a_o}$	$R_{32}(r) = \frac{2\sqrt{2}}{27\sqrt{5}(3a_o)^{3/2}}(r/a_o)^2 e^{-r/3a_o}$

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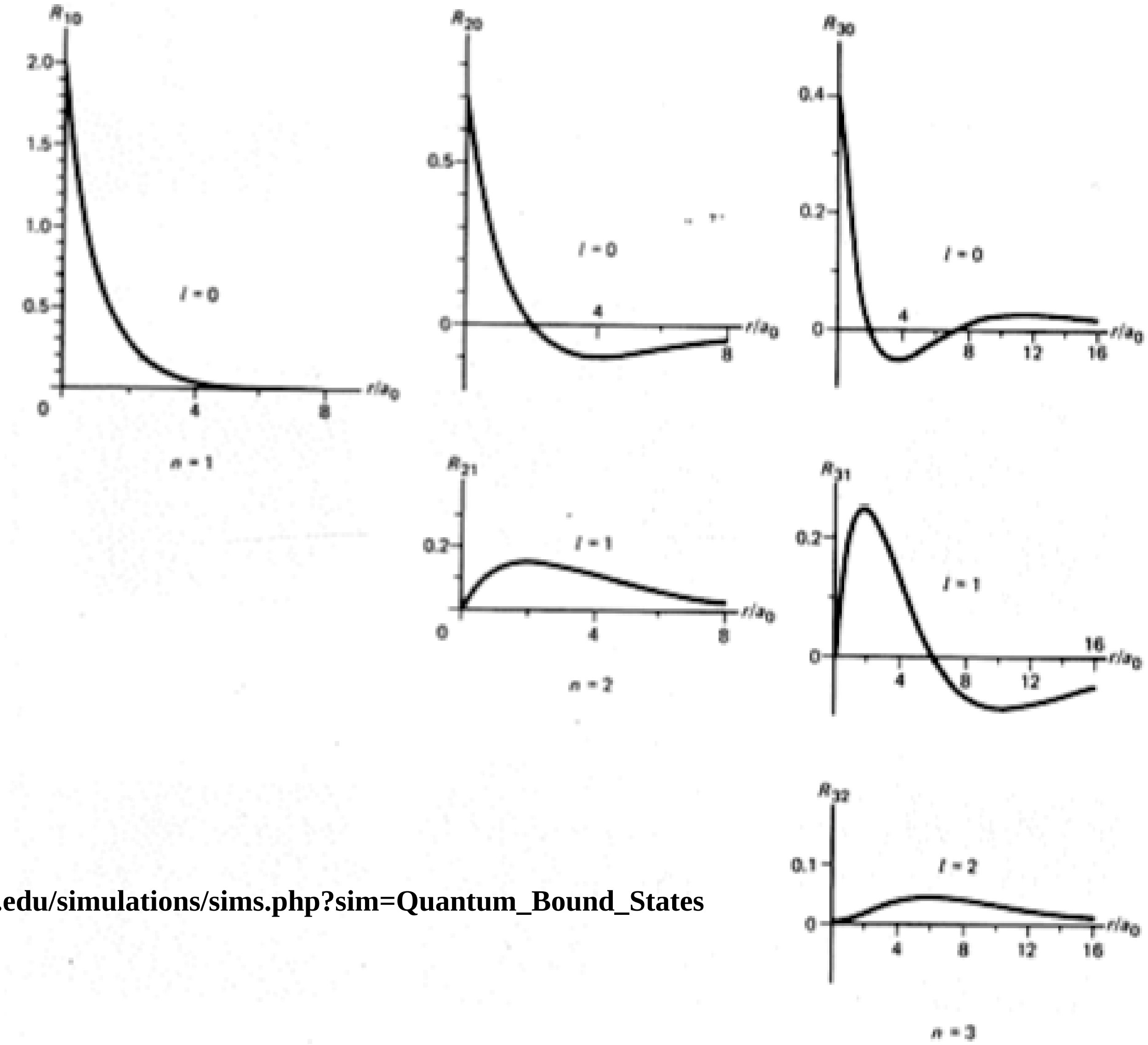
Hydrogen Radial Wavefunctions



http://phet.colorado.edu/simulations/sims.php?sim=Quantum_Bound_States

Summary of Hydrogen Atom Solutions

$$\psi_{n\ell m_\ell}(r,\theta,\varphi) = R_{n\ell}(r)\,\Theta_{\ell m}(\theta)\,\Phi_m(\varphi)\ \left(= R_{n\ell}(r)\,Y_\ell^m(\theta,\varphi)\right)$$

- Ψ is a product of
  - Φ which is just $e^{im\varphi}$
  - Θ which is a polynomial in $\cos\theta$
  - R which is a product of a decaying exponential and a polynomial in r
- Ψ depends on 3 quantum numbers
  - **Principal quantum number** n=1, 2, 3, …
  - **Orbital angular momentum quantum number** $\ell = 0, 1, 2, \ldots (n-1)$
  - **Magnetic quantum number** $m_\ell = 0, \pm 1, \ldots \pm \ell$ or $m_\ell = -\ell, -\ell+1, \ldots \ell-1, \ell$

Hydrogen Atom Wavefunctions

$$\psi_{n\ell m_\ell}(r,\theta,\varphi) = R_{n\ell}(r)\,\Theta_{\ell m}(\theta)\,\Phi_m(\varphi) \; \left(= R_{n\ell}(r)\,Y_\ell^m(\theta,\varphi)\right)$$

Table 7.2 Hydrogen Atom Wavefunctions $\psi_{n\ell m}(r,\theta,\phi)$.

$\psi_{100} = \dfrac{1}{\sqrt{\pi}\,a_0^{3/2}} e^{-r/a_0}$	$\psi_{200} = \dfrac{1}{4\sqrt{2\pi}\,a_0^{3/2}}(2 - r/a_0)e^{-r/2a_0}$
$\psi_{210} = \dfrac{1}{4\sqrt{2\pi}\,a_0^{3/2}}(r/a_0)e^{-r/2a_0}\cos\theta$	$\psi_{21\pm1} = \dfrac{1}{8\sqrt{\pi}\,a_0^{3/2}}(r/a_0)e^{-r/2a_0}\sin\theta\, e^{\pm i\phi}$
$\psi_{300} = \dfrac{1}{81\sqrt{3\pi}\,a_0^{3/2}}\left[27 - 18\dfrac{r}{a_0} + 2\dfrac{r^2}{a_0^2}\right]e^{-r/3a_0}$	$\psi_{310} = \dfrac{\sqrt{2}}{81\sqrt{\pi}\,a_0^{3/2}}(r/a_0)(6 - r/a_0)e^{-r/3a_0}\cos\theta$
$\psi_{31\pm1} = \dfrac{1}{81\sqrt{\pi}\,a_0^{3/2}}(r/a_0)(6 - r/a_0)e^{-r/3a_0}\sin\theta\, e^{\pm i\phi}$	
$\psi_{320} = \dfrac{1}{81\sqrt{6\pi}\,a_0^{3/2}}(r/a_0)^2 e^{-r/3a_0}(3\cos^2\theta - 1)$	
$\psi_{32\pm1} = \dfrac{1}{81\sqrt{\pi}\,a_0^{3/2}}(r/a_0)^2 e^{-r/3a_0}\sin\theta\cos\theta\, e^{\pm i\phi}$	$\psi_{32\pm2} = \dfrac{1}{162\sqrt{\pi}\,a_0^{3/2}}(r/a_0)^2 e^{-r/3a_0}\sin^2\theta\, e^{\pm 2i\phi}$

This is the one we derived.
Ground state wavefunction

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Energy Degeneracy

- Energy only depends on n
- For each n, there are n values of ℓ (from zero to n-1)
- For each ℓ, there are $(2\ell+1)$ values of m_ℓ (from $-\ell$ to ℓ)
- So, for each n, the degeneracy is:

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

$$= 2\frac{(n-1)(n)}{2} + n$$

$$= n^2 - n + n = \underline{\underline{n^2}}$$

Quantum numbers and Degeneracy

n	ℓ	m_ℓ	$(2\ell+1)$	DEGENERACY
1	0	0	1	1
2	0	0	1	4
	1	$0, \pm 1$	3	
3	0	0	1	9
	1	$0, \pm 1$	3	
	2	$0, \pm 1, \pm 2$	5	

- Question: So if energy is the same, what's different about the various degenerate states?
- Answer: The probability distribution of the electron around the nucleus, i.e. the shape of the electron cloud.

Spectroscopic Notation

For historical reasons, all states with same quantum number n are said to form a shell.

And states having the same value of both n and ℓ are said to form a subshell (s, p, d, f, …)

The probability distributions for these different states have important features, which we will cover next time.

- In Schrodinger theory, different ℓ states with same n have same energy
  - Called ℓ-degeneracy
- Energy level diagram omits different m_ℓ states - independent of m_ℓ due to spherical symmetry of the atom.
  - This is for no external magnetic field!

Probability Distribution

- What is the probability of finding the electron in a volume of space dV?

Probability $= \psi^* \psi \, dV = \psi^* \psi r^2 \sin\theta \, dr \, d\theta \, d\phi$: $dV = r^2 \sin\theta \, dr \, d\theta \, d\phi$

Probability density $= \psi^* \psi$

Example

- What is the probability of finding the electron at a distance r < r_0 for the ground state ($\psi_{1,0}$) ?

$$P(r<r_0) = \int_0^{r_0}\int_0^{\pi}\int_0^{2\pi} \psi^*\psi\, r^2 \sin\theta\, dr\, d\theta\, d\varphi$$

$$= \int_0^{r_0} \frac{1}{\pi a_0^3} e^{-2r/a_0}\, 4\pi r^2 dr$$

$$= 1 - \int_{r_0}^{\infty} \frac{1}{\pi a_0^3} e^{-2r/a_0}\, 4\pi r^2 dr$$

$$= 1 - \frac{4}{a_0^3}\int_{r_0}^{\infty} e^{-2r/a_0}\, r^2 dr$$

$$= 1 - e^{-2r_0/a_0}\left(2\frac{r_0^2}{a_0^2} + 2\frac{r_0}{a_0} + 1\right)$$

(Hint: change variables from r to $z = 2r/a_0$)

- Use this to determine the probability of finding the electron inside the first Bohr radius ($r<a_0$)? Or $r<2a_0$ or $r<3a_0$?

$$P(r<a_0) = 1 - 5e^{-2} = 0.323$$
$$P(r<2a_0) = 1 - 13e^{-4} = 0.762$$
$$P(r<3a_0) = 1 - 25e^{-6} = 0.938$$

Summary/Announcements

- Next time:

  More on the probability distributions of the Hydrogen atom

- Next homework due on Monday Nov 14.
- QUIZ next class, covering topics since Midterm!