PH253 Lecture 18: Hydrogen atom

excited spherically-symmetric states

P. LeClair

Department of Physics & Astronomy
The University of Alabama

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Outline

So far

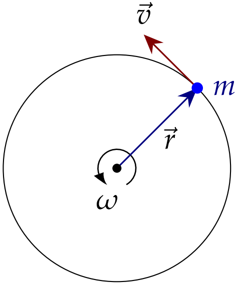
- Ground state (1s) wavefunction found
- Assumed spherical symmetry, but only aimed to find ground state
- Thereby accidentally neglected angular momentum
- Need a full solution with all radial and angular parts
- First: go back to mechanics to see what we missed!
- Specifically: look at a rotating classical system

Outline

Rotating classical system

- Point mass m rotating with angular velocity ω at r
- Energy: translational + rotational/centrifugal + potential
- Circular motion: angular momentum $L = mvr = m\omega r^2$

$$E = \frac{p^2}{2m} + \frac{L^2}{2mr^2} + V(r) = \frac{1}{2}mv^2 + \frac{1}{2}mr^2\omega^2 + V(r)$$

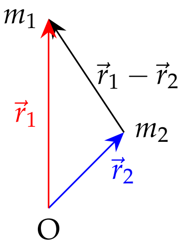


Any 2 body system

- If PE depends only on relative position, that's all you need
- Origin irrelevant: $V(\vec{r}_1, \vec{r}_2) \rightarrow V_{\text{eff}}(|\vec{r}_1 - \vec{r}_2|)$
- Can then simplify in terms of center of mass

$$E = K_{\text{CM}} + K_{\text{rel.}} + V_{\text{eff}}(\vec{r})$$

- Define relative v, position: $\vec{v} = \vec{v}_1 - \vec{v}_2$, $\vec{r} = \vec{r}_1 - \vec{r}_2$
- And reduced mass: $\mu = \frac{m_1 m_2}{m_1 + m_2}$ (note if $m_1 \gg m_2$, $\mu \approx m_2$)



Any 2 body system

$$\vec{v} = \vec{v}_1 - \vec{v}_2 \qquad \vec{r} = \vec{r}_1 - \vec{r}_2 \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

- Now the two-body problem can be written as an equivalent one-body problem, because V_{eff} depends on 1 variable.
- Need relative v, relative position, and reduced mass.
- After transforming KE terms, have relative motion as 1D problem

$$E_{\text{rel}} = \frac{p^2}{2\mu} + V_{\text{eff}}(\vec{r}) \qquad \vec{p} = \mu\vec{v}$$

- V_{eff} does contain info about rotation
- If $m_1 \gg m_2$: approximately same as fixing position of m_1, $\mu \approx m_2$
- Just need to transform to radial coordinates now
- Basically, now two 1D problems: motion of whole system and *relative motion*. First one not interesting.

Motion in radial coordinates reminder

$$E = \frac{1}{2}\mu\left[\left(\frac{dr}{dt}\right)^2 + r^2\left(\frac{d\theta}{dt}\right)^2\right] + V_{\text{eff}}(\vec{r}) = \frac{1}{2}\mu v_r^2 + \frac{1}{2}\mu r^2\omega^2 + V_{\text{eff}}(\vec{r})$$

- For mass μ: dr/dt radial velocity, $d\theta/dt = \omega$ angular velocity.
- Now: linear KE + rotational KE + potential
- No rotation: $d\theta/dt = 0$, linear motion.
- Circular/simple harmonic motion: $dr/dt = 0$
- Look at rotational term, and note $L = |\vec{r} \times \vec{p}| = m\omega r^2$
- $\frac{1}{2}\mu r^2\omega^2 = \frac{1}{2}L\omega = \frac{1}{2}|\vec{r} \times \vec{p}|\omega$ – zero if $\vec{r} \parallel \vec{p}$
- I.e., zero if radially symmetric. Angular momentum comes from angular dependence!

Outline

Radial Schrödinger equation

$$\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial r^2}+\frac{2}{r}\frac{\partial\psi}{\partial r}\right)+\left(E+\frac{e^2}{4\pi\epsilon_o r}\right)\psi=0$$

- Expect translational + rotational/centrifugal + potential?
- What is the quantum analogue of L?
- What are $\frac{1}{r}\frac{\partial\psi}{\partial r}$ terms? Relate to L!
- Assuming spherical symmetry misses states with $L \neq 0$
- Spherically symmetric atom $\neq$ spherically symmetric solution.
- E.g., vibrating drum head - excited states have different shapes.
- Go back to the radial equation and be more careful

Schrödinger in 3D again

$$\frac{\hbar^2}{2m}\nabla^2\psi = \left(E + \frac{e^2}{4\pi\epsilon_o r^2}\right)\psi$$

- This is still right. In $x - y - z$ system, $\nabla^2 f = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2}$
- The correct way is to translate ∇^2 into spherical polar coordinates
- $(x, y, z) \rightarrow (r, \theta, \varphi)$
- It is a mess, but it has been done already.

$$\nabla^2 f = \left(\underbrace{\frac{\partial^2 f}{\partial r^2} + \frac{2}{r}\frac{\partial f}{\partial r}}_{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial f}{\partial r}\right)} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2 f}{\partial\varphi^2}\right)$$

Schrödinger in 3D again

$$\nabla^2 f = \frac{\partial^2 f}{\partial r^2} + \frac{2}{r}\frac{\partial f}{\partial r} + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial f}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 f}{\partial \varphi^2}$$

- We can plug this mess into the Schrödinger equation
- It makes a bigger mess! But! r and (φ, θ) terms separate!
- Really three separate equations: radial and two angular
- I.e., can write $\psi(r,\theta,\varphi) = R(r)Y(\theta,\varphi)$
- Tackle the radial part first and see what we missed
- More general approach - get excited states we missed (e.g., 2s)

$$\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi) + \frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial r^2}\right] = -\frac{2m}{\hbar^2}\left(E + \frac{e^2}{4\pi\epsilon_o r^2}\right)$$

Schrödinger in 3D again

$$\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi)+\frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial r^2}\right]=-\frac{2m}{\hbar^2}\left(E+\frac{e^2}{4\pi\epsilon_o r^2}\right)$$

- Sanity check: should get back previous radial equation
- Let $\partial\psi/\partial\theta=\partial\psi/\partial\varphi=0$

$$\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi)=-\frac{2m}{\hbar^2}\left(E+\frac{e^2}{4\pi\epsilon_o r^2}\right)\psi$$

-or-

$$\frac{\partial^2}{\partial r^2}(r\psi)=-\frac{2m}{\hbar^2}\left(E+\frac{e^2}{4\pi\epsilon_o r^2}\right)(r\psi)$$

-note- $\displaystyle\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi)=\frac{\partial^2\psi}{\partial r^2}+\frac{2}{r}\frac{\partial\psi}{\partial r}$ and it is the same as before

Simplifying

$$\frac{\partial^2}{\partial r^2}(r\psi) = -\frac{2m}{\hbar^2}\left(E + \frac{e^2}{4\pi\epsilon_o r^2}\right)(r\psi)$$

- Look for solutions again, but don't just guess this time.
- Prev: 1 constant for 2nd order equation, missed something!
- Clean it up a bit: make some definitions.

$$\text{let} \qquad \rho = \frac{kme^2}{\hbar^2} r = \frac{r}{a_o} \qquad \text{-and-} \qquad \epsilon = \frac{2\hbar^2}{me^4k} E = \frac{E}{E_o}$$

- Defines natural dimensionless distances, energies
- Measure in units of Bohr radius a_o, ground state energy E_o
- Best: less symbols to deal with

Simplifying

$$\frac{d^2\left(\rho\psi\right)}{d\rho^2} = -\left(\epsilon + \frac{2}{\rho}\right)\rho\psi$$

- Substituting, now simpler-looking equation
- Still second order equation. One more: let $f = \rho\psi$

$$\frac{d^2 f}{d\rho^2} = -\left(\epsilon + \frac{2}{\rho}\right)f$$

- Previous solution (ground state) is $\psi = e^{-\alpha\rho}$ or $f = \rho e^{-\alpha\rho}$, $\alpha =$constant.
- Next: factor out the known solution, see what's left.

Outline

Simplifying

$$\frac{d^2 f}{d\rho^2} = -\left(\epsilon + \frac{2}{\rho}\right) f$$

- Know $f = e^{-\alpha\rho}$ is a solution. Look for new ones with $f = e^{-\alpha\rho} g(\rho)$
- With $g(\rho) = \rho$, original solution. Other forms for g?
- (Already know g depends only on ρ.)
- Plug in this form for f, what's left depends only on g

$$\frac{d^2 g}{d\rho^2} - 2\alpha \frac{dg}{d\rho} + \left(\frac{2}{\rho} + \epsilon + \alpha^2\right) g = 0$$

- But α is just a constant - choice of origin/units.
- Choose for convenience! Let's pick $\alpha^2 = -\epsilon$

Power series solution

$$\frac{d^2 g}{d\rho^2} - 2\alpha \frac{dg}{d\rho} + \frac{2}{\rho} g = 0$$

- Clever choice of constant α to simplify.
- Solve this, get *all* spherically-symmetric solutions (s states)
- Not just the ground state. But how?
- You can always brute force it with a power series.
- We will get lucky in the end. Trial solution:

$$g(\rho) = \sum_{k=1}^{\infty} a_k \rho^k$$

- Here a_k is just a polynomial coefficient
- Find a_k, work backwards to get ψ, done.

Power series solution

$$0 = \frac{d^2g}{d\rho^2} - 2\alpha\frac{dg}{d\rho} + \frac{2}{\rho}g \qquad g(\rho) = \sum_{k=1}^{\infty} a_k\rho^k$$

- Start by writing down the derivatives we'll need.

$$\frac{dg}{d\rho} = \sum_{k=1}^{\infty} k a_k \rho^{k-1}$$

$$\frac{d^2g}{d\rho^2} = \sum_{k=1}^{\infty} k(k-1)a_k\rho^{k-2} = \sum_{k=1}^{\infty}(k+1)k a_{k+1}\rho^{k-1}$$

- $\frac{d^2g}{d\rho^2}$: first term is zero, can shift the sum by one!
- Just keep index correct. Makes all terms have same power of ρ
- Plug into equation at top, collect terms. Cross fingers.

Power series solution

Just grind through it.

$$\sum_{k=1}^{\infty}(k+1)ka_{k+1}\rho^{k-1} - \sum_{k=1}^{\infty}2\alpha ka_k\rho^{k-1} + \sum_{k=1}^{\infty}2a_k\rho^{k-1} = 0$$

$$\sum_{k=1}^{\infty}\Big[(k+1)ka_{k+1} - 2\alpha ka_k + 2a_k\Big]\rho^{k-1} = 0$$

- Only true for all ρ if term in brackets is zero! Thus,

$$(k+1)ka_{k+1} - 2\alpha ka_k + 2a_k = 0 \qquad \text{-or-} \qquad a_{k+1} = \frac{2(\alpha k-1)}{k(k+1)}a_k$$

- Recursion relationship! Find a_1 by normalizing, have the rest.

Putting it together

$$\psi_{\text{full}} = \sum \psi_n \qquad \text{full solution = sum of all states}$$

$$\psi_k = \frac{f_k(\rho)}{\rho} = \frac{e^{-\alpha\rho}}{\rho} g_k(\rho) \qquad \text{states with particular solution factored}$$

$$g_k(\rho) = \sum_{k=1}^{\infty} a_k \rho^k \qquad \text{remaining function distinguishing states}$$

- What are the meaning of α, k? Look back at ground state.
- Recall $\epsilon = E/E_o = -\alpha^2$. To agree with prior results/expts.?
- $E/E_o = -\frac{1}{n^2} = -\alpha^2$, or $\alpha = 1/n$ with $n =$ integer
- Thus, $1/\alpha$ is just an integer indexing a state/energy level

Putting it together

$$a_{k+1}(n) = \frac{2\left(\frac{k}{n}-1\right)}{k(k+1)}a_k \quad g(\rho) = \sum_{k=1}^{\infty} a_k\rho^k \quad \psi_k = \frac{e^{-\alpha\rho}}{\rho}g_k(\rho)$$

- k = degree of polynomial in each solution
- n = energy level, as in Bohr model/Balmer equation = $1/\alpha$
- Notice: if $k=n$, $a_{k+1}=0$, as are all higher terms $k>n$
- Thus, state n has $\left(\frac{e^{-\alpha\rho}}{\rho}\right)$(polynomial in ρ of order n)
- Simplify: (polynomial of order $n-1$) $\times$ (overall $e^{-\rho/n}$ decay)
- Fixing n determines range of k, $0<k\leq n$

$$\psi_1 = \frac{e^{-\rho/n}}{\rho}(a_1\rho) = e^{-\rho/n}a_1 \quad \psi_2 = \frac{e^{-\alpha\rho}}{\rho}\left(a_1\rho + a_2\rho^2\right) = e^{-\rho/n}\left(a_1+a_2\rho\right)$$

Putting it together

- Since we have to normalize anyway, can just pick $a_1 = 1$
- Generate the rest by recursion

$n=1$	$n=2$	...	n
$a_1 = 1$	$a_1 = 1$		$a_1 = 1$
$a_2 = 0$	$a_2 = -\frac{1}{2}$		$a_2 = \frac{1}{n} - 1$
$a_3 = 0$	$a_3 = 0$		$a_3 = \frac{1}{3}\left(\frac{2}{n^2} - \frac{3}{n} + 1\right)$
$\vdots$	$\vdots$		$a_{n+1} = 0$

- For a given n, only first n coefficients are non-zero
- Can now also generate $g_n(\rho)$ and ψ_n functions

Outline

s states of hydrogen

$$\psi_n = \frac{f(\rho)}{\rho} = \frac{e^{-\rho/n}}{\rho} g_n(\rho) \qquad g_n(\rho) = \sum_{k=1}^{\infty} a_k(n)\rho^k$$

- Using previous table:
- $g_1(\rho) = \rho$
- $g_2(\rho) = \rho^2(\frac{1}{n} - 1)$
- $g_3(\rho) = \frac{1}{3}\rho^2(\frac{2}{n^2} - \frac{3}{n} + 1)$
- For $n = 1$,

$$\psi_1 = \frac{e^{-\rho/1}}{\rho}\rho = e^{-\rho} = e^{-r/a_o} \quad \checkmark$$

- Correctly recover ground state ($1s$) solution
- ψ_2 is the $2s$ excited state …

s states of hydrogen

- With $g_1 = \rho$, $g_2(\rho) = \rho^2(\frac{1}{n} - 1) = -\frac{1}{2}\rho^2$, $n = 2$:

$$\psi_2 = \frac{e^{-\rho/2}}{\rho}\left(\rho - \frac{1}{2}\rho^2\right) = e^{-\rho/2}\left(1 - \frac{\rho}{2}\right) = e^{-r/2a_o}\left(1 - \frac{r}{2a_o}\right)$$

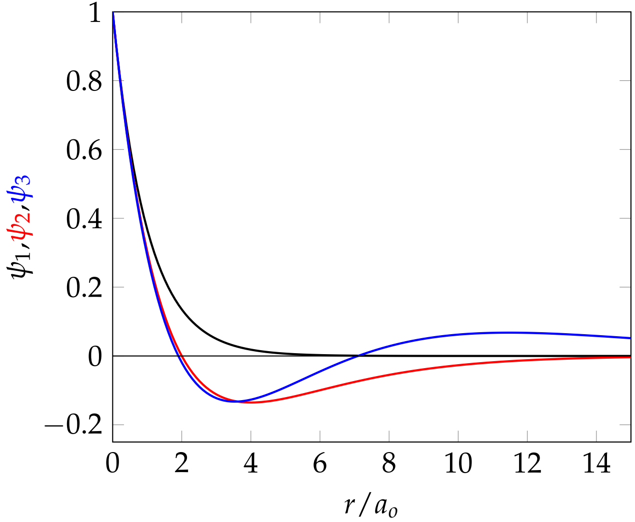
- Can keep generating higher order s states now, e.g.

$$\psi_3 = e^{-r/3a_o}\left(1 - \frac{2r}{3a_o} + \frac{2r^2}{27a_o^2}\right)$$

- Decay gets faster, as $e^{-r/n}$. Length scale is a_o in general.
- Polynomial of order $n-1$? $n-1$ zero crossings/oscillations for ψ
- Now have all s states. What do they look like?

s states of hydrogen: wave functions

Not normalized, ψ_2, ψ_3 will have lower amplitude - spread out more.



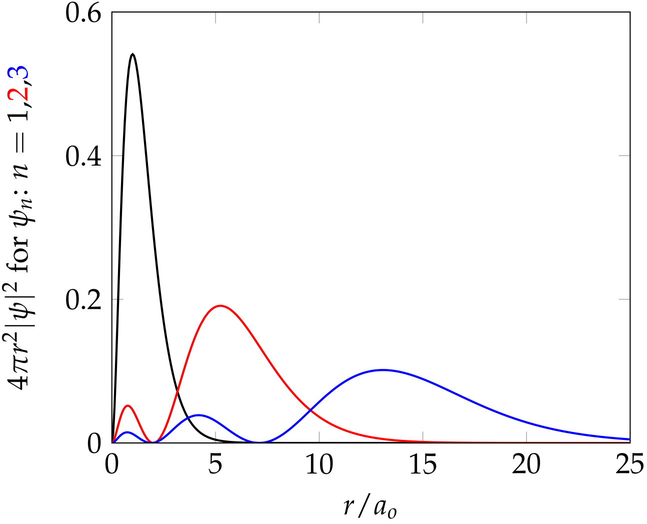
s states of hydrogen

- Now we can do all the things (after normalizing).
- Find $\langle r \rangle$, $P(r) = 4\pi r^2 |\psi|^2$, etc.
- Energies as before (can plug ψ_n into Schrödinger).

$$E = \epsilon E_o = -\alpha^2 E_o = -\frac{E_o}{n^2} \approx -\frac{13.6\,\mathrm{eV}}{n^2}$$

s states of hydrogen: Probability densities

Normalized. Note $\langle r \rangle \uparrow$ as $n \uparrow$



s states of hydrogen

- $1s$: $\langle r \rangle = \frac{3a_o}{2}$ as before
- $2s$: $\langle r \rangle = 6a_o$
- $3s$: $\langle r \rangle = \frac{27a_o}{2}$

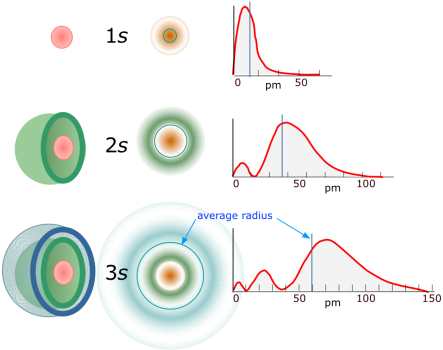
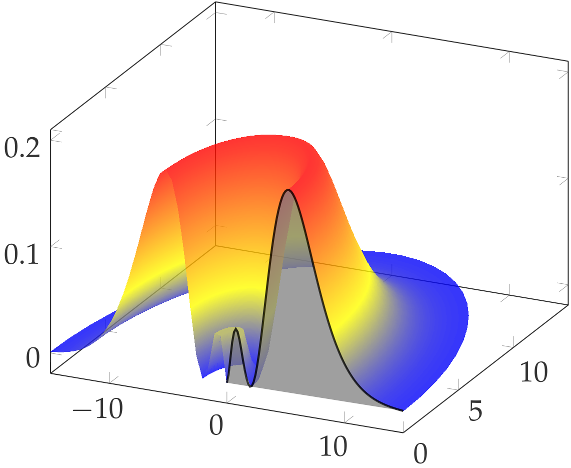


Figure: https://chem.libretexts.org/Bookshelves/General_Chemistry/Book%3A_Chem1_(Lower)/05%3A_Atoms_and_the_Periodic_Table/5.05%3A_The_Quantum_Atom

2s state 3-d cross section

Solutions so far still have spherical (radial) symmetry



Outline

What's left?

- Still only states with $L = 0$ - no p, d, f orbitals
- Have to solve angular part for full solution
- Will skip most of the math on that and get to the main results
- With other orbitals: keys to understanding bonding
- Enough knowledge to figure out periodic table
- Energy levels in molecules and solids
- Next time: angular dependence and angular momentum
- Then: multi-electron atoms