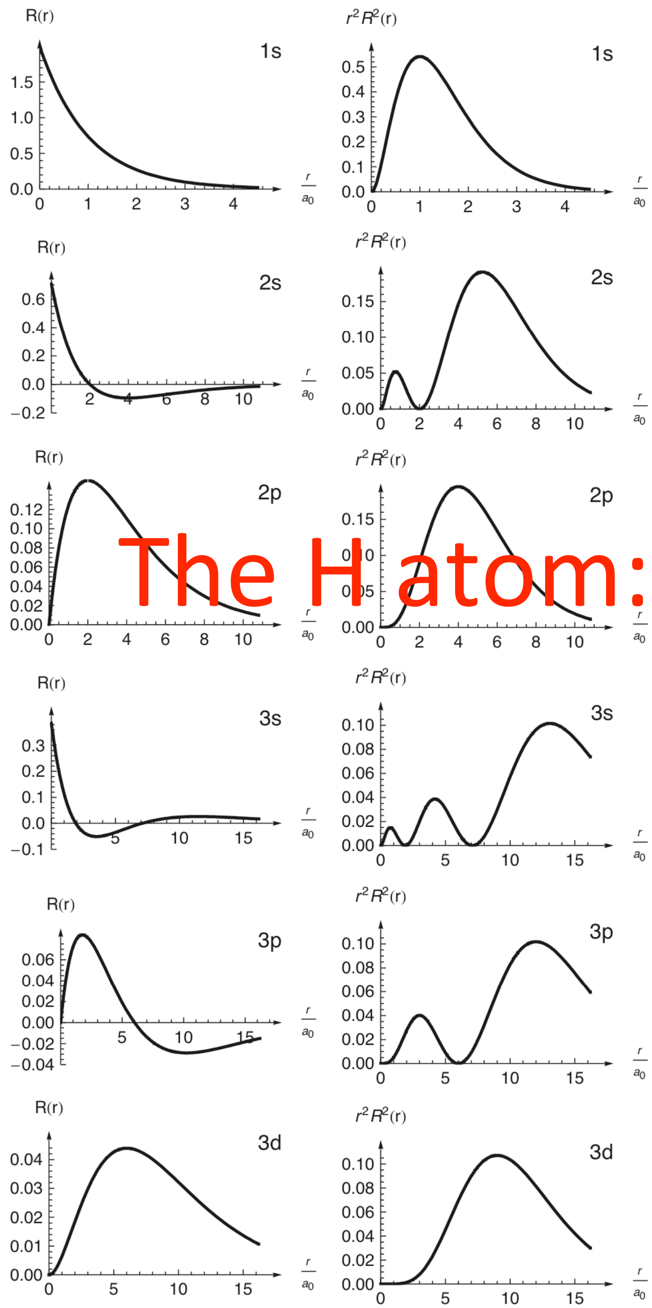
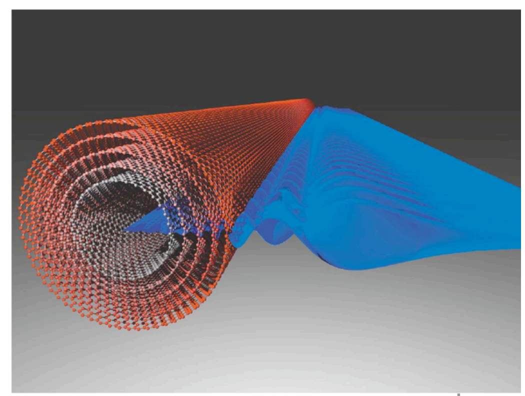
The H atom: The radial wave function

$$\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right)-\frac{2\mu}{\hbar^2}(E-V(r))r^2R(r)=\ell(\ell+1)R(r)$$

Reading: McIntyre 8.1-8.4





Summary

- So far: $$\frac{d^2\Phi(\phi)}{d\phi^2} = -m^2\Phi(\phi) \qquad \Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

$$\left[\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\right) - m^2\frac{1}{\sin^2\theta}\right]\Theta_\ell^m(\theta) = -\ell(\ell+1)\Theta_\ell^m(\theta)$$

$$\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right) - \frac{2\mu}{\hbar^2}(E - V(r))r^2 R(r) \equiv -\ell(\ell+1)R(r)$$

$$\psi_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r)\underbrace{\Theta_\ell^m(\theta)\Phi_m(\phi)}_{Y_\ell^m(\theta,\phi)}$$

The radial equation

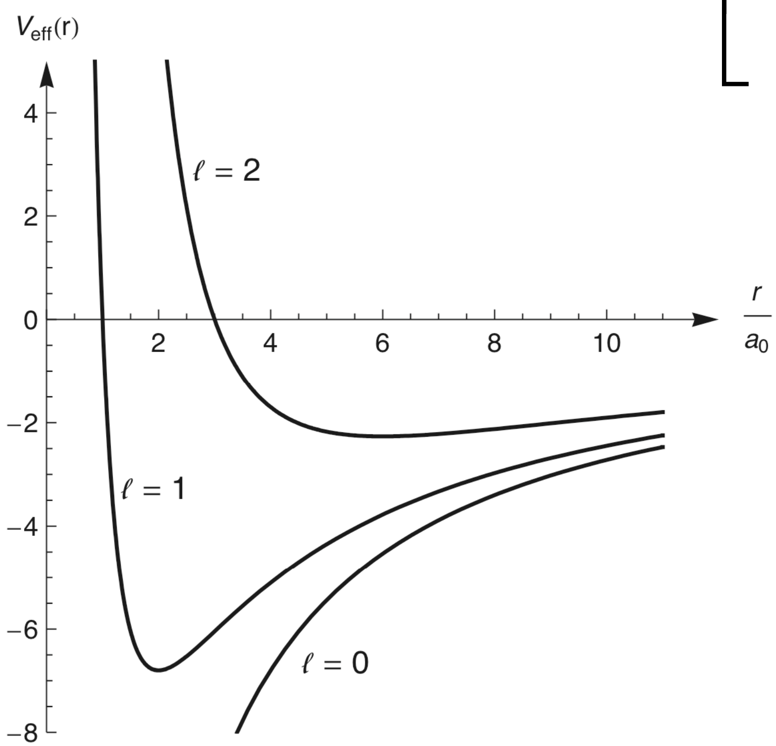
- Original problem was separated into angular and radial parts. We have solved the angular part and are now ready to tackle the radial part, which is different for every different central potential.
- Before we chose the Coulomb potential, note that the problem reduces very nicely to a 1-d eigenvalue equation with an effective potential, just like in the classical case.

$$HR(r)Y(\theta,\phi) = ER(r)Y(\theta,\phi)$$

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

The effective potential energy

$$\frac{d^2 R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \frac{2\mu}{\hbar^2}\left[E - \left\{ \underbrace{V(r) + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2}}_{V_{eff}(r)} \right\} \right] R = 0$$



- All of the terms involving *r* (not its derivatives), can be lumped into an effective potential energy.

Use dimensionless variables

$$\frac{d^2 R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \frac{2\mu}{\hbar^2}\left[E + \frac{Ze^2}{4\pi\varepsilon_0 r} - \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2}\right]R = 0$$

$$\rho = \frac{r}{a}$$

$$-\gamma^2 = \frac{E}{\left(\dfrac{\hbar^2}{2\mu a^2}\right)} \qquad a = \frac{4\pi\varepsilon_0 \hbar^2}{\mu Z e^2}$$

$$\frac{d^2 R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \left[-\gamma^2 + \frac{2}{\rho} - \frac{\ell\left(\ell+1\right)}{\rho^2}\right]R = 0$$

Asymptotic solutions: $\rho \rightarrow \infty$

$$\frac{d^2 R}{d\rho^2} + \cancel{\frac{2}{\rho}\frac{dR}{d\rho}} + \left[-\gamma^2 + \cancel{\frac{2}{\rho} - \frac{\ell(\ell+1)}{\rho^2}} \right] R = 0$$

$$R(\rho) \sim e^{-\gamma\rho}$$

- For bound states (E<0), solutions decay exponentially. What about growing term?

Asymptotic solutions: $\rho \rightarrow 0$

$$\frac{d^2 R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \left[-\gamma^2 + \frac{2}{\rho} - \frac{\ell(\ell+1)}{\rho^2} \right] R = 0$$

$$R(\rho) \sim \rho^q$$

$$q = \ell,\ -\ell - 1$$

- For small ρ, solutions are power law. What are powers? (sm. whiteboard)

Full solution: all ρ

$$\frac{d^2 R}{d\rho^2}+\frac{2}{\rho}\frac{dR}{d\rho}+\left[-\gamma^2+\frac{2}{\rho}-\frac{\ell\left(\ell+1\right)}{\rho^2}\right]R=0$$

$$R\left(\rho\right)\sim\rho^{\ell}e^{-\gamma\rho}H(\rho)$$

- What differential equation must $H(\rho)$ obey? (You are doing a similar problem for homework)

Full solution: all ρ

$$\rho \frac{d^2 H}{d\rho^2} + 2\left(\ell + 1 - \gamma\rho\right)\frac{dH}{d\rho} + 2\left(1 - \gamma - \gamma\ell\right)H = 0$$

$$H(\rho) = \sum_{j=0}^{\infty} c_j \rho^j$$

- Here is the differential equation. We're going to try a polynomial solution for *H.* We won't do this in class. Follow your homework example to show it.

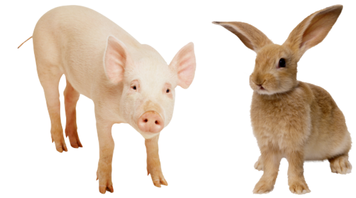
Plug and chug (fast!)

$$\frac{d}{d\rho}\sum_{j=0}^{\infty} c_j \rho^j = ?$$

$$\frac{d^2}{d\rho^2}\sum_{j=0}^{\infty} c_j \rho^j = ?$$

- Do the derivatives, carefully noting the limits.
- Which term benefits from a change of index in *j*? What should you change to?
- True for all powers of ρ.
- We'll get a (single) recurrence relation and all we need to know is c_0.

Recurrence relation

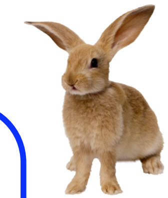


$$c_{j+1} = \frac{2\gamma\left(1+j+\ell\right)-2}{\left(j+1\right)\left(j+2\ell+2\right)}c_j$$

- Series must terminate to be normalizable. This will kill our asymptotic decay at large *r* unless we force the sum to terminate!

$$\left.\begin{aligned} &2\gamma\left(1+j_{\max}+\ell\right)-2=0 \\ &n=j_{\max}+\ell+1 \end{aligned}\right\} \Rightarrow \quad \gamma=\frac{1}{n}$$

New quantization rules!



$$-\gamma^2 = \frac{E}{\left(\frac{\hbar^2}{2\mu a^2}\right)} = \frac{1}{n^2} \quad \Rightarrow \quad E_n = -\frac{1}{n^2}\frac{Z^2 e^4 \mu}{2\left(4\pi\varepsilon_0\hbar\right)^2}$$

$$n = 1,2,3\ldots$$

- Energy is quantized! The $1/n^2$ dependence is the same as in the (incorrect) Bohr model.
- If el > n-1, j_{max} is negative, contradicting the assumption that j_{max} is non-negative.

$$\ell = 0,1,2,3\ldots n-1$$

- Energy does not depend on the el quantum number (or m), so there is degeneracy!

More important variables

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} = 0.0529 \ nm \quad \text{Bohr radius}$$

$$\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c} \cong \frac{1}{137} \quad \text{fine structure constant}$$

- You have met the Bohr radius =0.529 Å in your Modern Physics class. *Note*: it is defined with m_e, not μ, so we'll use m_e = μ from now on.
- The fine structure constant α may be new to you. It is a dimensionless constant =1/137 that appears again when we consider non-Coulomb like interactions in the H atom (that lead to fine structure in the spectrum)

Summary of quantization rules.

- Energy is quantized

$$E_n = -\frac{1}{n^2}\frac{Z^2\alpha^2 m_e c^2}{2}; \quad n = 1,2,3\ldots$$

$$E_n = -\frac{13.6}{n^2}eV \quad \text{for Z=1}$$

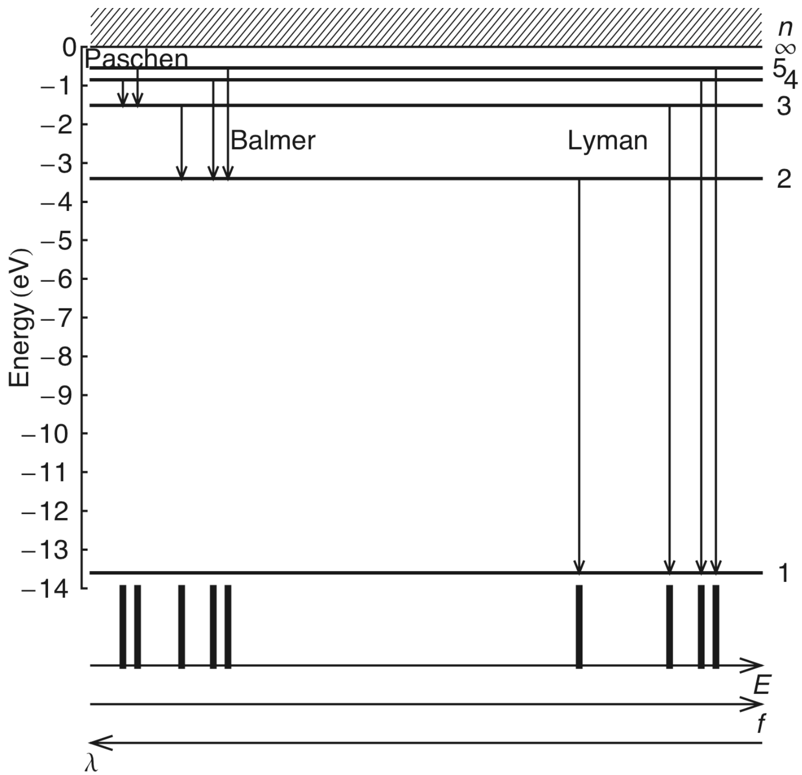
- Angular momentum magnitude (L^2) is quantized

$$\ell\left(\ell+1\right)\hbar^2; \quad \ell = 0,1,2,3\ldots n-1$$

- The *z*-component of the angular momentum is quantized.

$$m\hbar; \quad m = -\ell, -\ell+1, \ldots -1, 0, 1, \ldots \ell-1, \ell$$

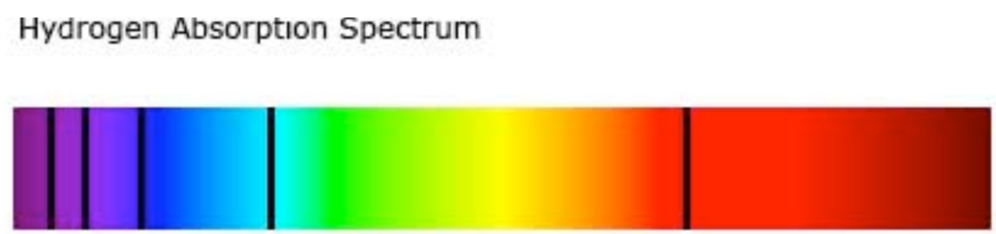
H atom spectroscopy

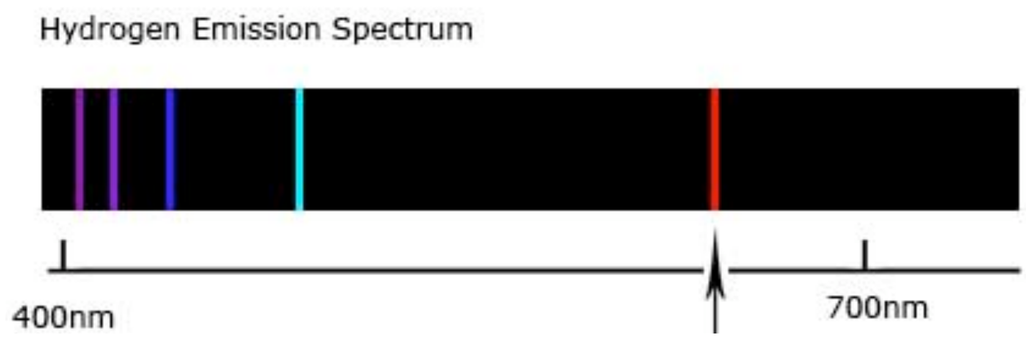


- Energy is quantized

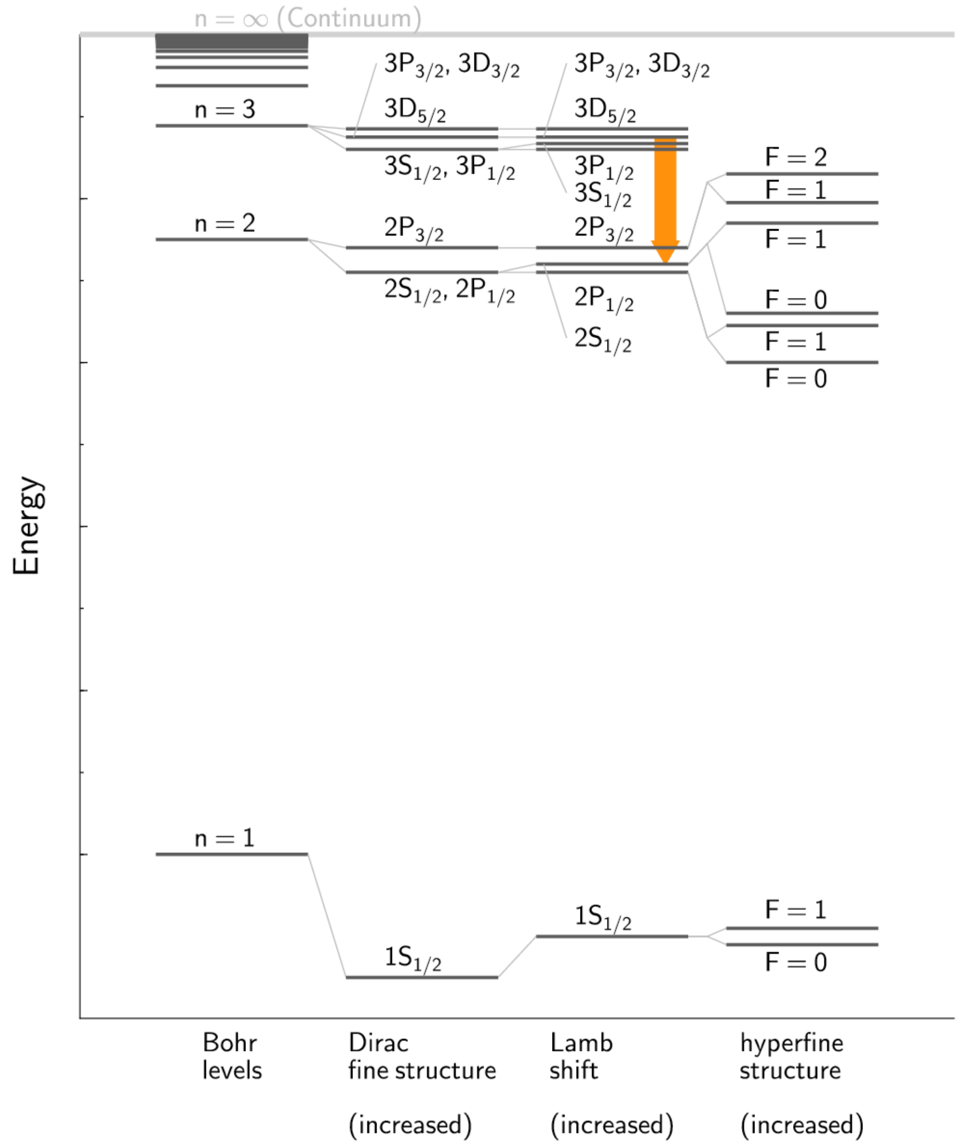
$$E_n = -\frac{13.6}{n^2} eV \quad \text{for } Z=1$$

- This is the Balmer series

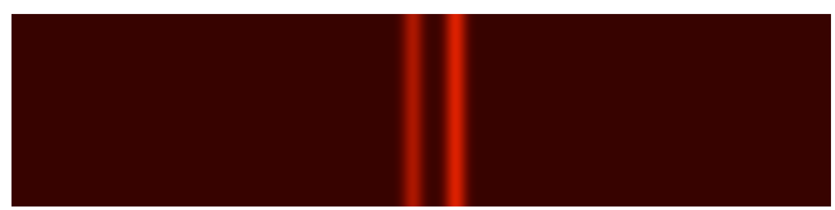




H atom spectroscopy



- Fine structure from non-Coulomb terms (spin-orbit coupling, which is a magnetic effect)
- Hyperfine structure from coupling to nuclear angular momentum



Summary

- The fact that the series must be a finite polynomial is what (mathematically) leads to a maximum (and integer) value of *n*!
- We pull out the asymptotic dependencies of the wave function (power law at small *r* and exp decay at large *r*); what remains is an associated Laguerre polynomial.
- The radial wave functions depend on *n* and *el*, but the energy depends only on *n*.
- Refer to the summary slide of the quantization rules.