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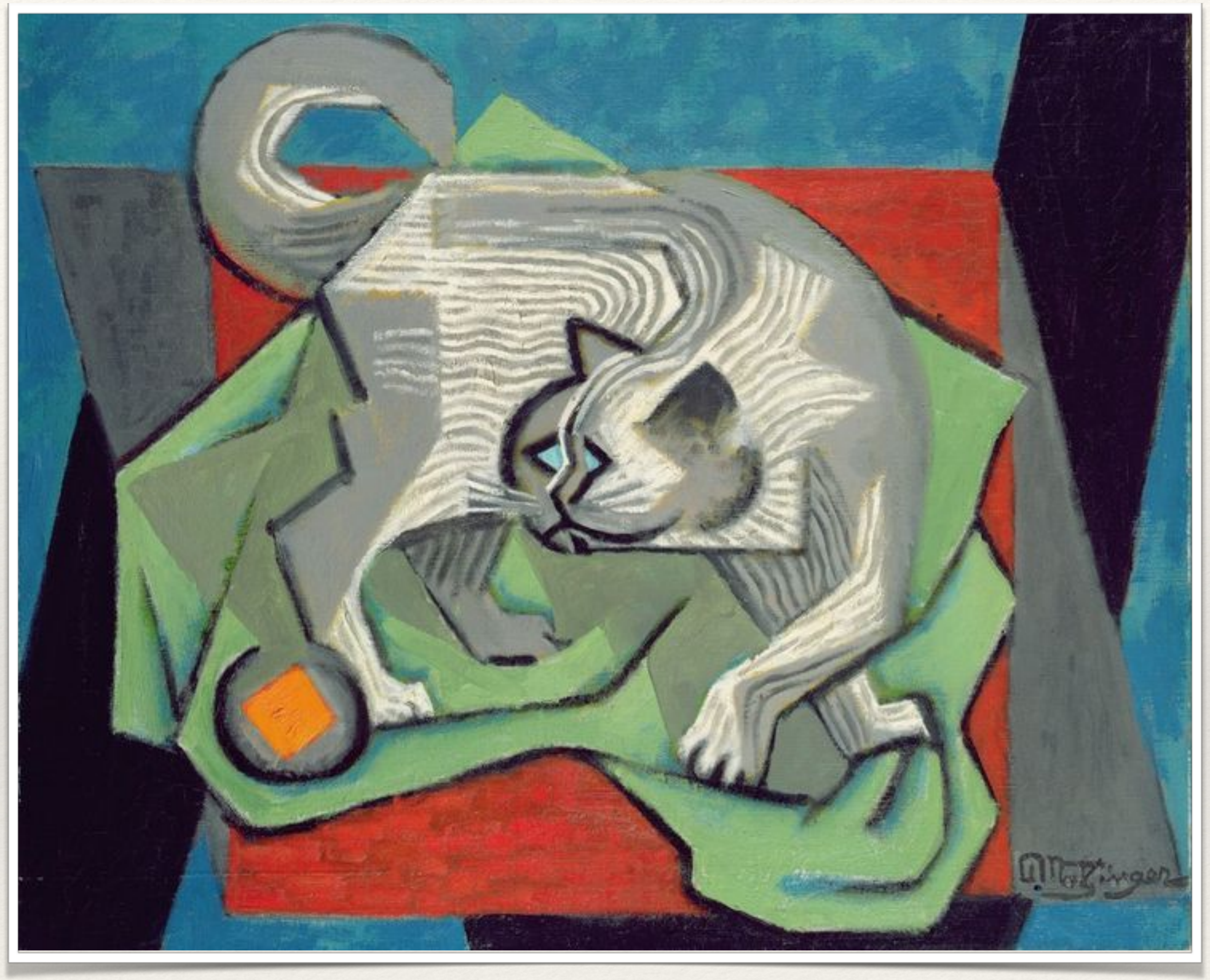
# Quantum Mechanics

Lecture 8

Spherical harmonics: what atoms look like;
Bound states of the Coulomb potential;
Quantized energy levels;
Radial wave functions;
Degeneracy.



# A quick recap

A two-body system in a radially symmetric potential satisfies:

$$[\hat{\mathbf{P}}, H] = [L_z, H] = [L^2, H] = [L_z, L^2] = 0$$

Total momentum, AM, and energy conservation

$$\psi_{E,l,m}(\mathbf{r}) = \langle \mathbf{r} \,|\, E, l, m \rangle = R(r) Y_l^m(\theta, \phi)$$

common eigenstates in
position basis in spherical coordinates

The Schrödinger equation reduces to:

$$R(r) = \frac{u(r)}{r}$$

$$\left( \frac{-\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} + V_{\text{eff}}(r) \right) u(r) = E\, u(r)$$

$$V_{\text{eff}}(r) = \frac{l(l+1)\hbar^2}{2\mu r^2} + V(r)$$

Single-particle equation with an effective potential

The angular wave function is given by the **spherical harmonics**:

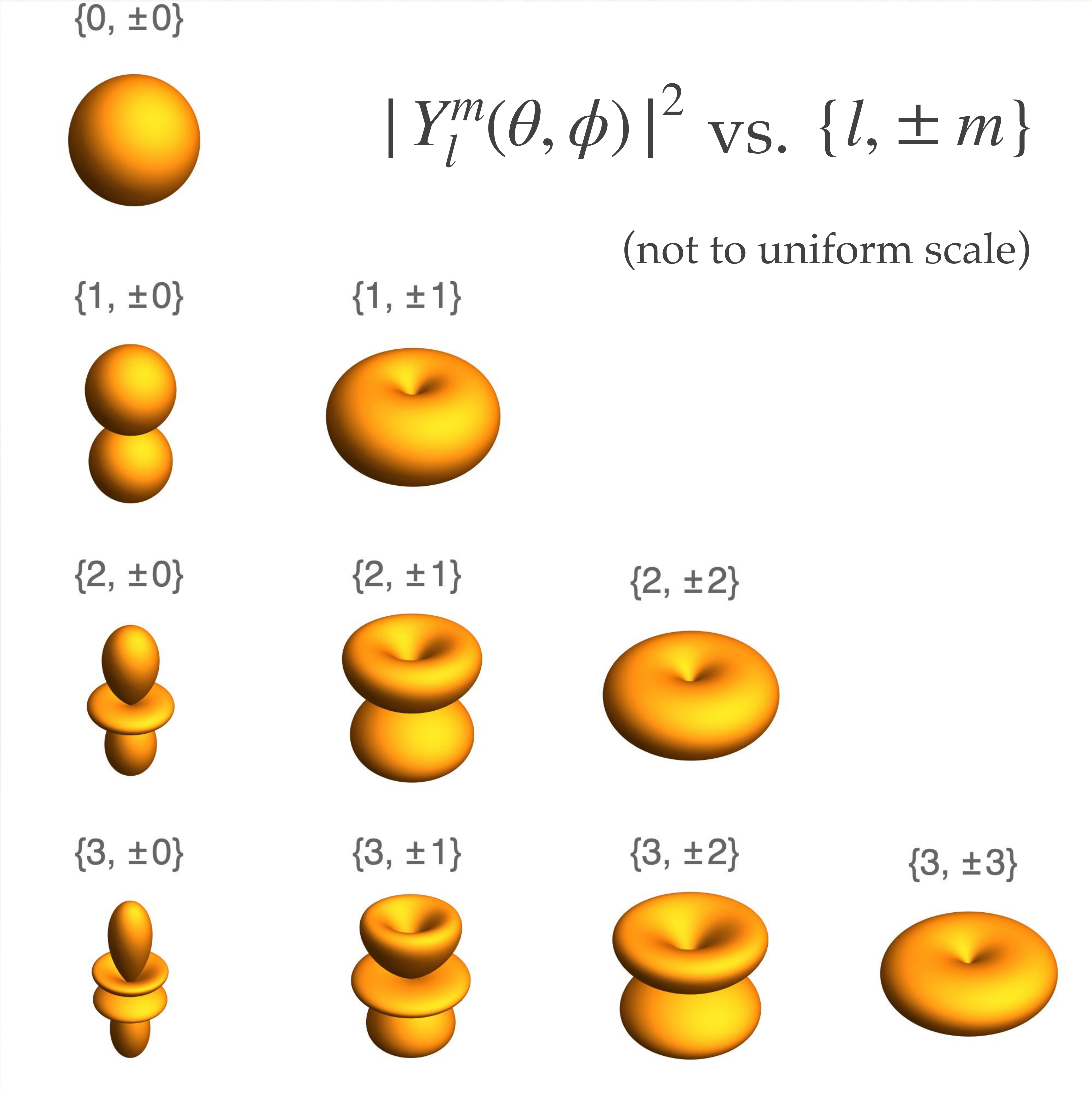
Spherical analog of
Fourier decomposition
of periodic functions.

$$Y_l^m(\theta, \phi) \propto \mathrm{e}^{im\phi} P_l^m(\cos\theta)$$

$$l = 0, 1, 2, \ \dots$$

$$m = -l, \ \dots \ , l$$

# Spherical probability density



$|Y_l^m(\theta,\phi)|^2$ vs. $\{l, \pm m\}$

(not to uniform scale)

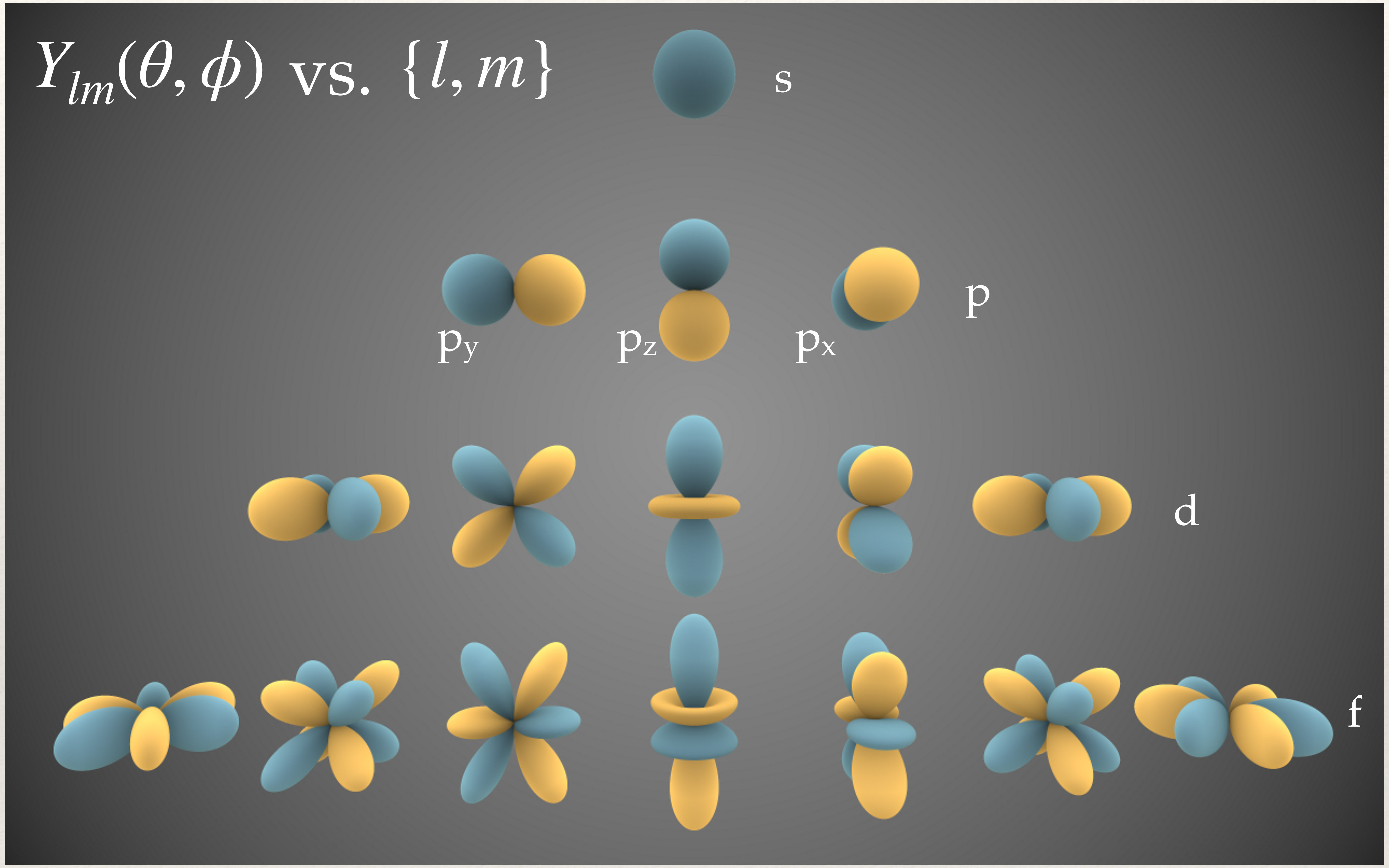
Given a wave function with an angular component in a spherical harmonic eigenstate, the probability to find the particle inside some solid angle d$\Omega$ that is situated at coordinates ($\theta$,$\phi$) is given by:

$$|Y_l^m(\theta,\phi)|^2 \mathrm{d}\Omega$$

This interpretation is consistent with the **normalization** condition:

$$\int |Y_l^m(\theta,\phi)|^2 \mathrm{d}\Omega = 1$$

# Phase dependence and orthogonality



The real-form spherical harmonics;
**blue** = positive, **yellow** = negative.

Complex linear combinations of these functions still span the space of angular wave functions.

More generally, we have the orthogonality condition

$$\int Y_l^m(\theta, \phi)^*\, Y_{l'}^{m'}(\theta, \phi)\mathrm{d}\Omega = \delta_{l,l'}\delta_{m,m'}$$

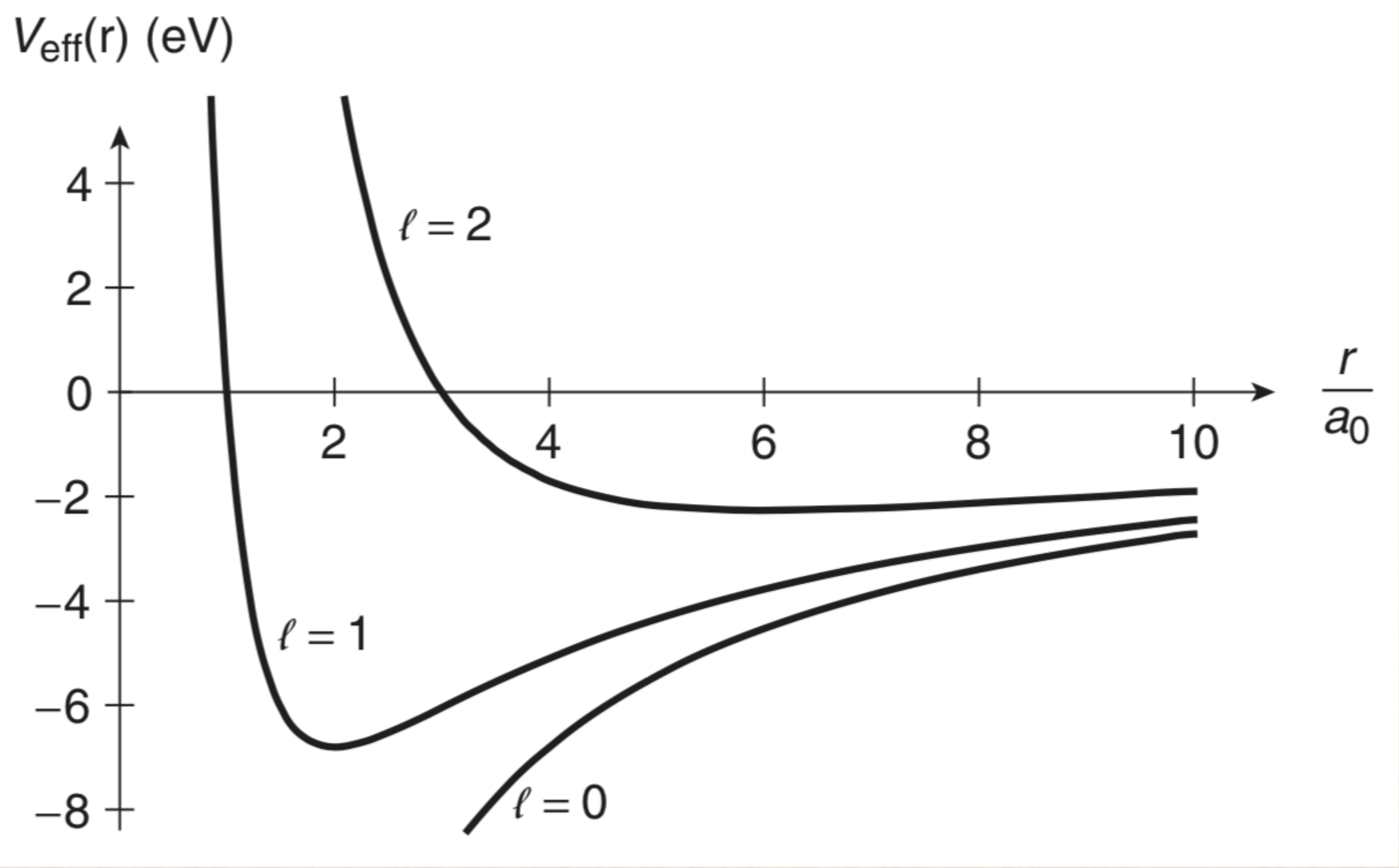
Alternative real form:

$$Y_{lm} = \begin{cases} \frac{i}{\sqrt{2}}\left(Y_l^m - (-1)^m\, Y_l^{-m}\right) & \text{if } m < 0 \\ Y_l^0 & \text{if } m = 0 \\ \frac{1}{\sqrt{2}}\left(Y_l^{-m} + (-1)^m\, Y_l^m\right) & \text{if } m > 0. \end{cases}$$

$$= \begin{cases} \sqrt{2}\,(-1)^m\, \mathrm{Im}[Y_l^{|m|}] & \text{if } m < 0 \\ Y_l^0 & \text{if } m = 0 \\ \sqrt{2}\,(-1)^m\, \mathrm{Re}[Y_l^m] & \text{if } m > 0. \end{cases}$$

# Bound states of Coulomb potentials

A **hydronic atom** has nuclear charge $Ze$ and one electron.



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

Coulomb potential
(For hydrogen, $Z = 1$.)

$$V_{\text{eff}}(r) = -\frac{Ze^2}{r} + \frac{l(l+1)\hbar^2}{2\mu r^2}$$

Bound states will have negative energy $E < 0$ ,
so introduce dimensionless variables to obtain:

$$\rho = \sqrt{\frac{8\mu|E|}{\hbar^2}}r \qquad \lambda = \frac{Ze^2}{\hbar}\sqrt{\frac{\mu}{2|E|}} \qquad \Rightarrow \frac{d^2u}{d\rho^2} - \frac{l(l+1)}{\rho^2}u + \left(\frac{\lambda}{\rho} - \frac{1}{4}\right)u = 0$$

The limiting behavior of this equation is given by:

$$\rho \to \infty \;\Rightarrow\; \frac{d^2u}{d\rho^2} = \frac{u}{4}$$

$$\Rightarrow\; u = \cancel{Ae}^{\rho/2} + Be^{-\rho/2}$$

(blows up)

$$\rho \to 0 \;\Rightarrow\; \frac{d^2u}{d\rho^2} = \frac{l(l+1)}{\rho^2}u$$

$$\Rightarrow\; u = A\rho^{l+1} + \cancel{B\rho}^{-l}$$

(blows up)

These two limits suggest a change of variables that matches and interpolates.

# Bound states of Coulomb potentials

To match the limiting behavior, try: $u = \rho^{l+1} \mathrm{e}^{-\rho/2} F(\rho)$

match $\rho \to 0$

match $\rho \to \infty$

interpolating function

$$\frac{d^2u}{d\rho^2} - \frac{l(l+1)}{\rho^2}u + \left(\frac{\lambda}{\rho} - \frac{1}{4}\right)u = 0$$

Now we have a new ODE for F:

$$\rho\frac{d^2F}{d\rho^2} + (2l + 2 - \rho)\frac{dF}{d\rho} + \big(\lambda - (l+1)\big)F = 0$$

Solvable by a power series, but we can look up the solution!
This equation was solved by Laguerre (1879) and by Sonin (1880).

Solutions are known as **associated Laguerre polynomials**.

Solutions are singular unless: $\lambda = (l+1) + k \ , \quad k = 0,1,\ldots$

To avoid singularities, $\lambda$ must be **quantized** into positive integers!

Define the **principle quantum number**: $\lambda \to n \ , \quad n = 1, 2, \ \ldots$

Also:

$\Rightarrow \ l \leq n - 1$

# Quantized energy levels

Recall our substitutions:

$$\lambda \rightarrow n = \frac{Ze^2}{\hbar}\sqrt{\frac{\mu}{2|E|}}$$

Solve for the $n$th energy level:

$$E_n = -\frac{\mu Z^2 e^4}{2\hbar^2 n^2} = -\frac{\mu c^2 Z^2 \alpha^2}{2n^2}$$

$$\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}$$

The **fine structure constant**:
a dimensionless fundamental constant

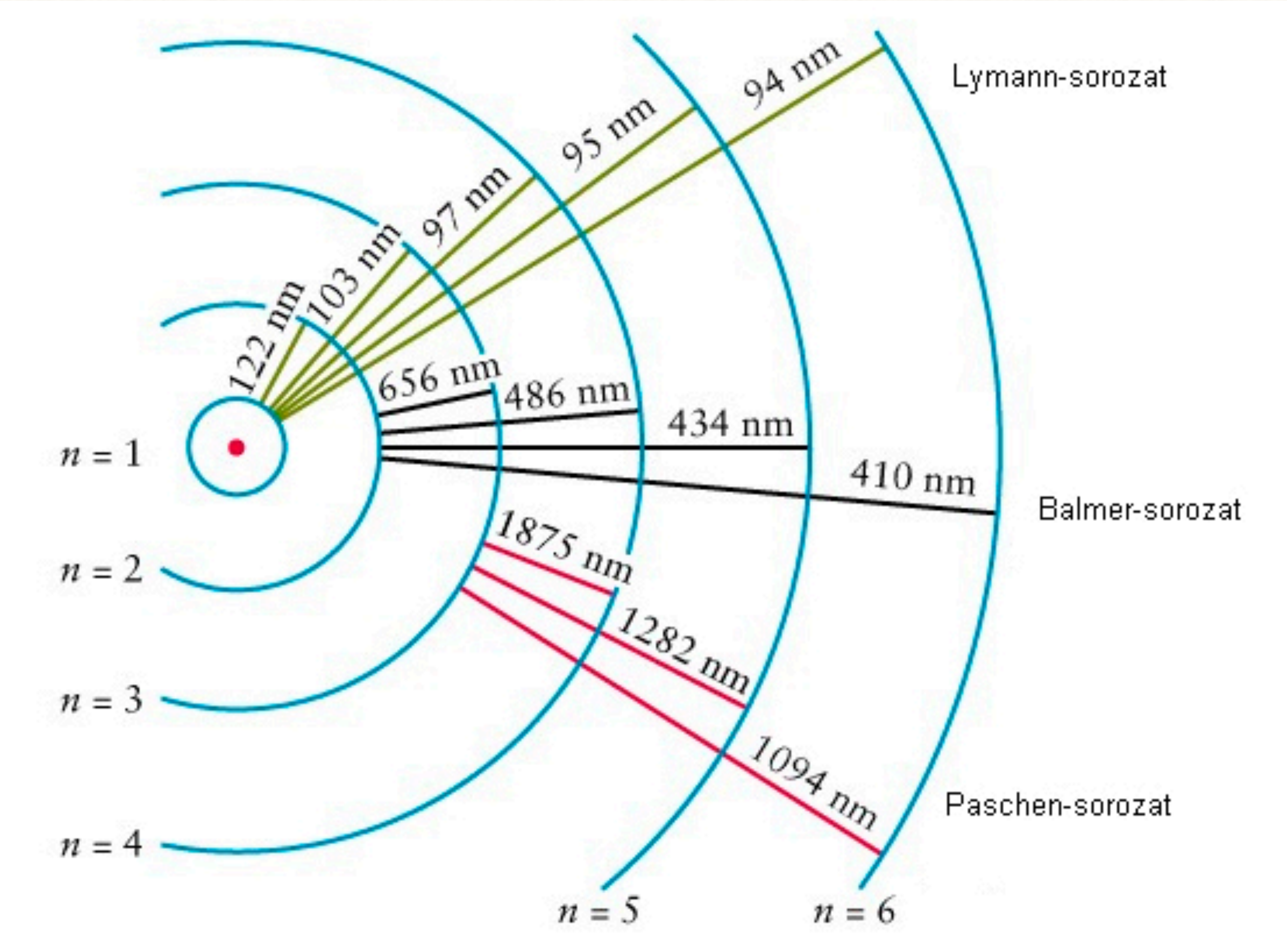
For hydrogen ($Z = 1$) in the ground state $n = 1$:

$\mu c^2$ has units of energy, and is about 0.511 MeV for hydrogen.

$$E_1 = -\frac{\mu c^2 \alpha^2}{2} \approx -13.6\text{eV}$$

# Hydrogen emission spectrum

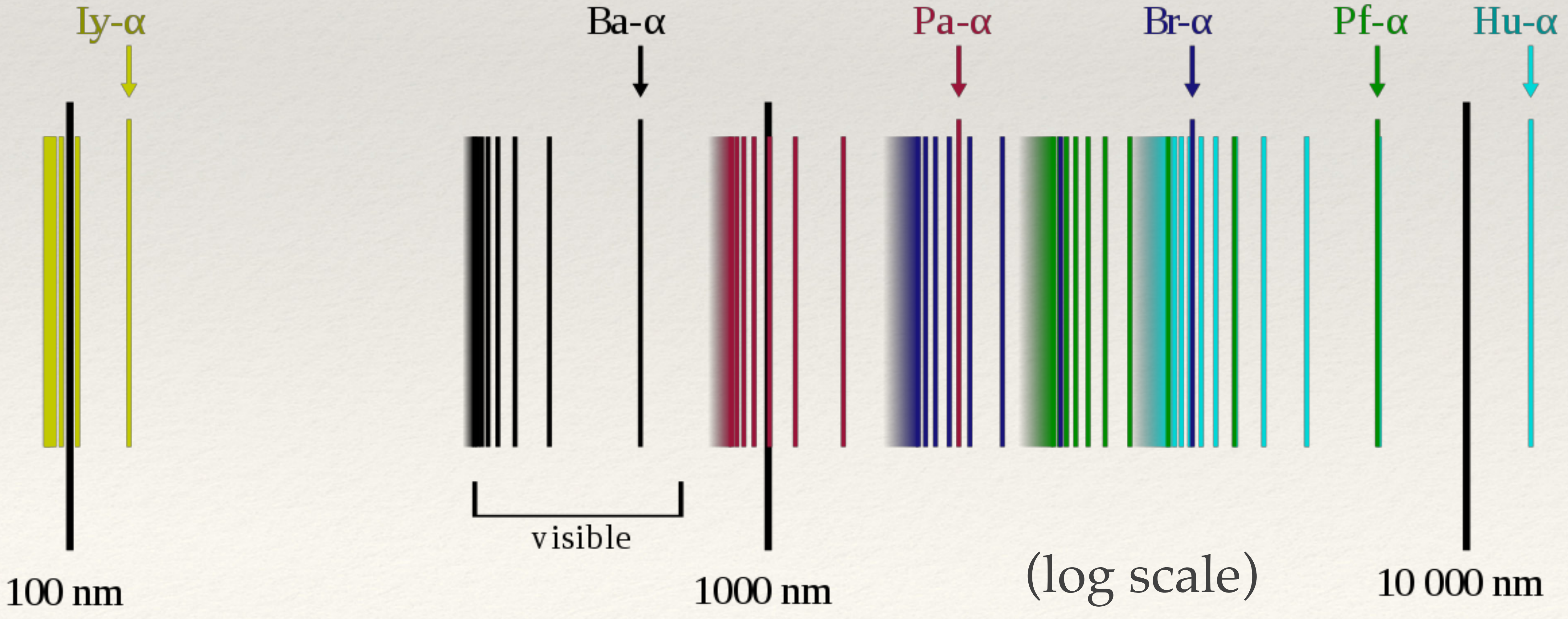
We can predict the spectral lines of hydrogen.



$$\nu = \frac{1}{\lambda} = \frac{1}{h}(E_i - E_f) = R_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

$$R_H = \frac{\mu c^2 Z^2 \alpha^2}{2h}$$

Rydberg constant



# Radial wave functions

Recall these are given in terms of the associated Laguerre polynomials $L_s^t$.

$$u = R/r = \rho^{l+1}\mathrm{e}^{-\rho/2}F(\rho) \qquad \rho = \sqrt{\frac{8\mu|E|}{\hbar^2}}r = \frac{2\mu cZ\alpha}{n\hbar}r = \frac{2Zr}{na_0^*}$$

Bohr radius:

$$a_0 := \frac{\hbar}{m_e c\alpha} \approx \frac{\hbar}{\mu c\alpha} =: a_0^*$$

Characteristic length for $Z = 1$, $n = 1$.

$$\rho\frac{d^2F}{d\rho^2} + (2l + 2 - \rho)\frac{dF}{d\rho} + \big(\lambda - (l+1)\big)F = 0$$

Solutions, after normalization, look like the following:

$$R_{nl}(r) = \left(\frac{2}{na_0^*}\right)^{3/2}\sqrt{\frac{(n-l-1)!}{2n(n+l)!}}\mathrm{e}^{-r/2}r^l L_{n-l-1}^{2l+1}(r)$$

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

$$l = 0,\ldots,n-1$$

$$m = -l,\ldots,l$$

In total: $\psi_{nlm}(r,\theta,\phi) = R_{nl}\Big(\frac{2Zr}{na_0^*}\Big)Y_l^m(\theta,\phi)$

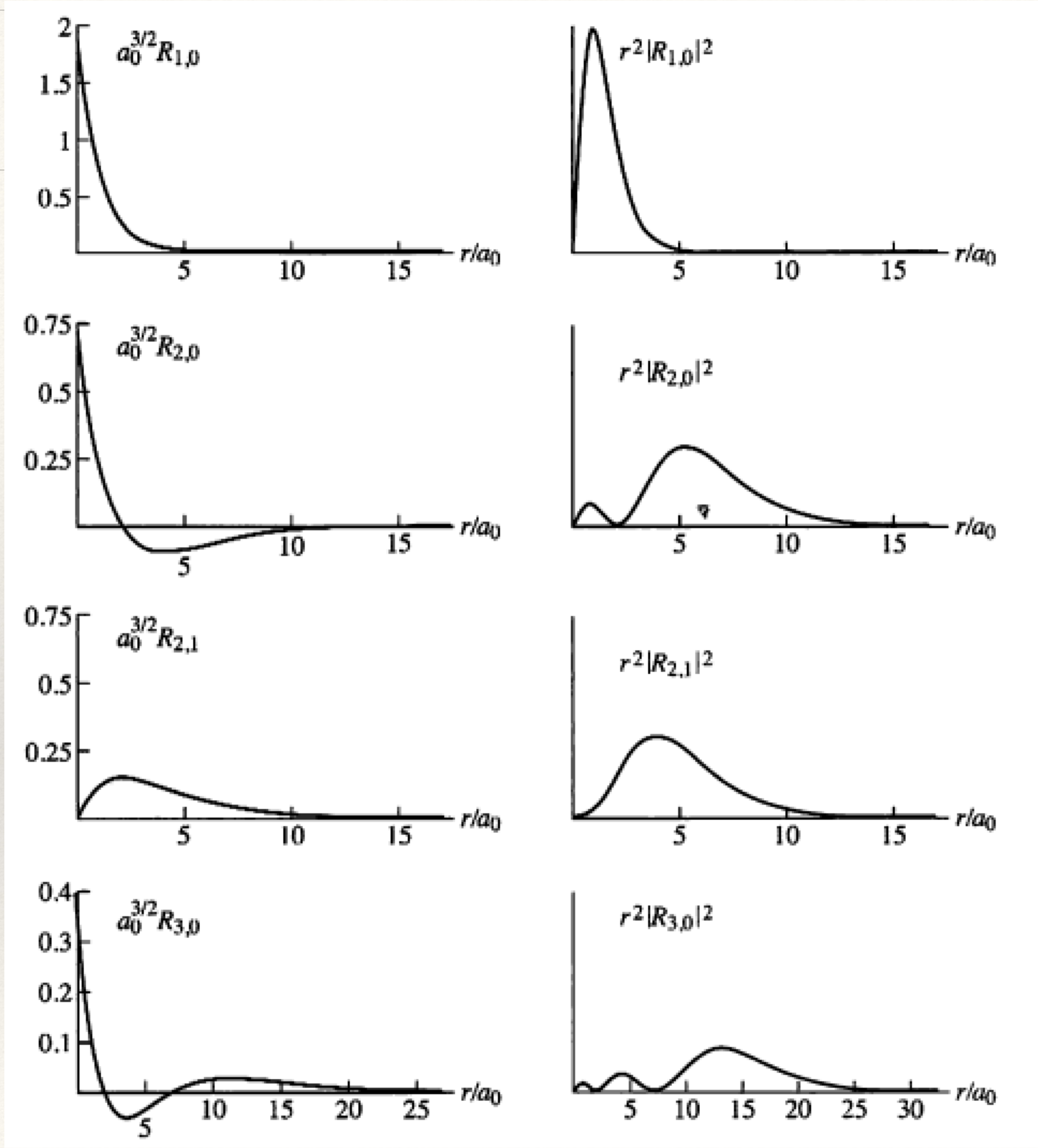
# Radial wave functions

Visualizing the radial wave functions.

$$R_{nl}(r) = \left(\frac{2}{na_0^*}\right)^{3/2}\sqrt{\frac{(n-l-1)!}{2n(n+l)!}}e^{-r/2}r^l L_{n-l-1}^{2l+1}(r)$$

$$R_{nl}\left(\frac{2Zr}{na_0^*}\right) \qquad n = 1,2,3,\dots$$

$$l = 0,\dots,n-1$$



# Degeneracy

These solutions have a large number of degenerate states at the same energy.

$$l = 0, \ldots, n - 1$$

$$m = -l, \ldots, l$$

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

For hydrogen, we have also ignored spin states of the electron and proton.

$$2 \times 2 \times n^2 = 4n^2$$

Next lecture, we will see that these degeneracies can be broken when we take into account various complications like spin.