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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**:

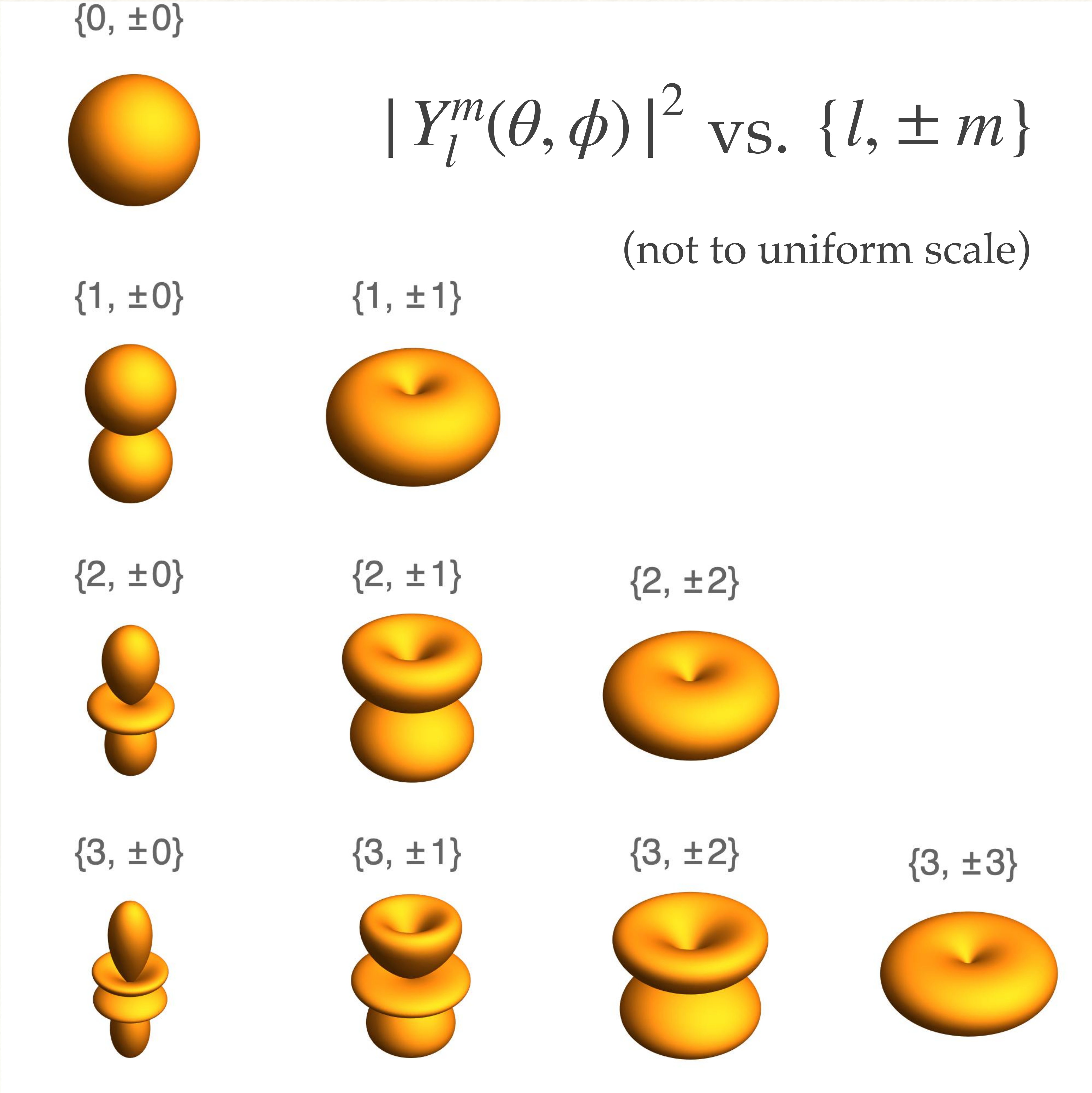
Spherical analog of
Fourier decomposition
of periodic functions.

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

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

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

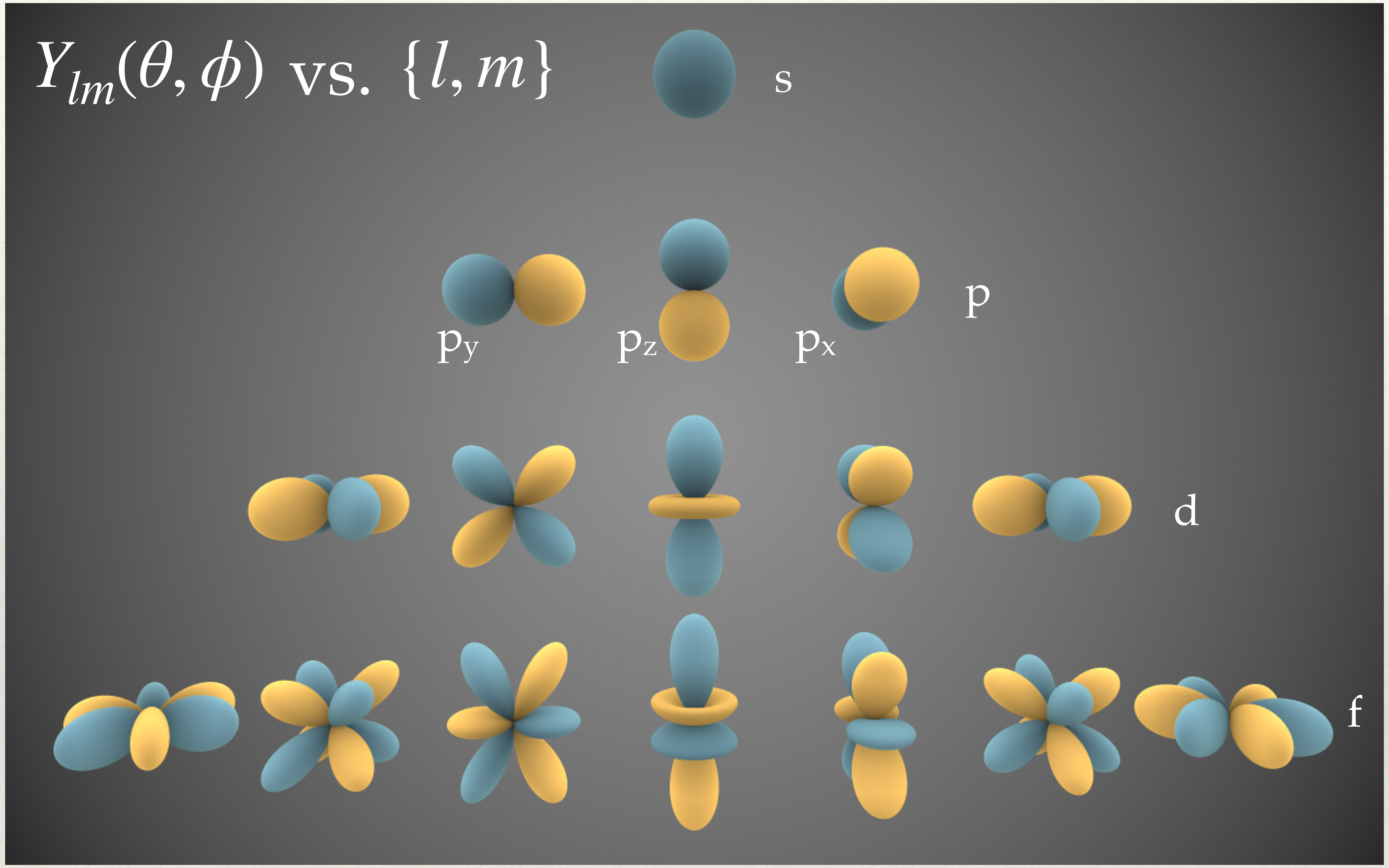
Spherical probability density



Given a wave function with an angular component in a spherical harmonic eigenstate, the probability to find the particle inside some solid angle dΩ that is situated at coordinates (θ,ϕ) is given by:

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

Phase dependence and orthogonality



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

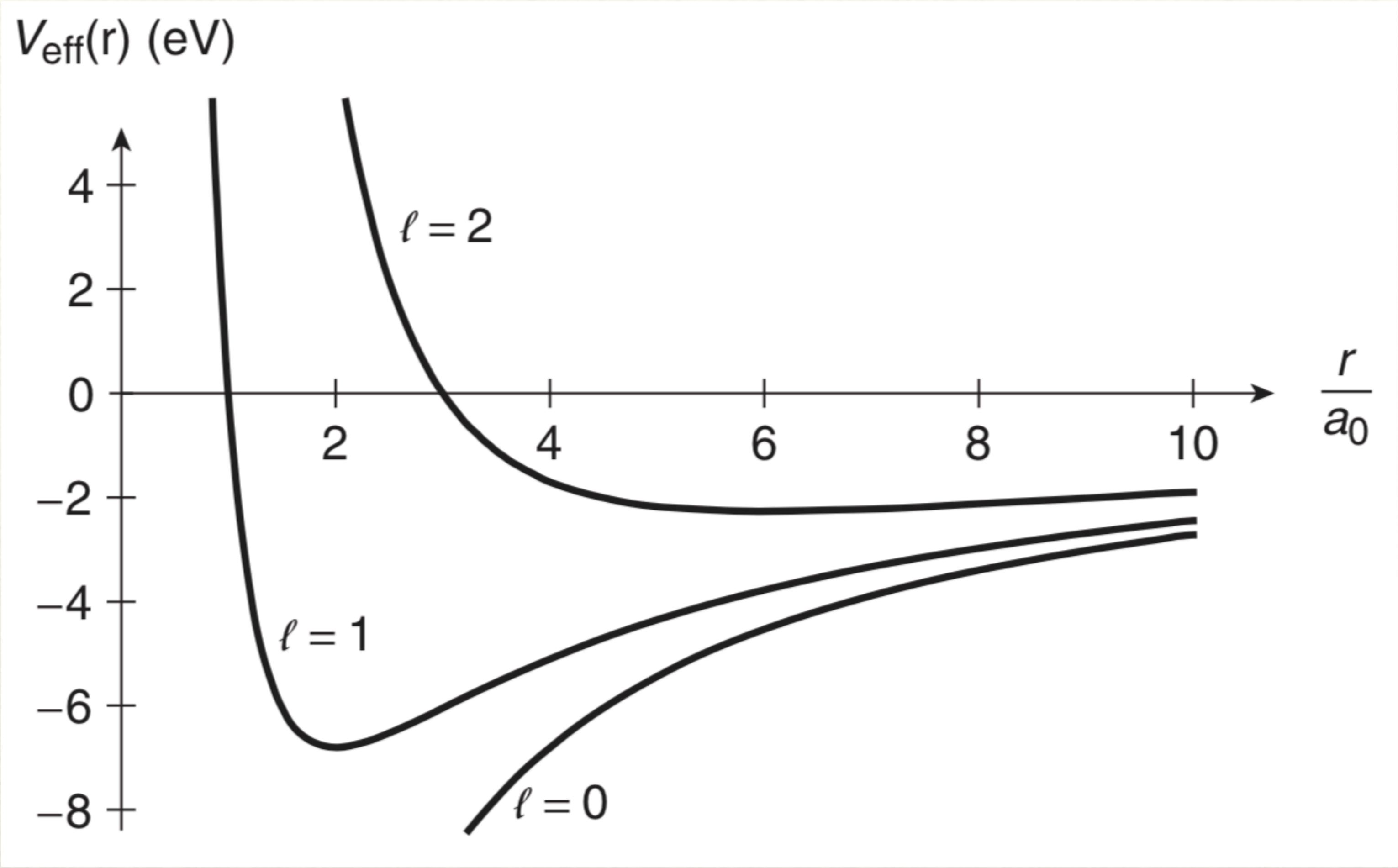
Complex linear combinations of these functions
still span the space of angular wave functions.

More generally, we have the orthogonality condition

Alternative real form:

Bound states of Coulomb potentials

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



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

The limiting behavior of this equation is given by:

Bound states of Coulomb potentials

To match the limiting behavior, try:

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

Now we have a new ODE for F:

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

Solutions are singular unless:

Quantized energy levels

Recall our substitutions:

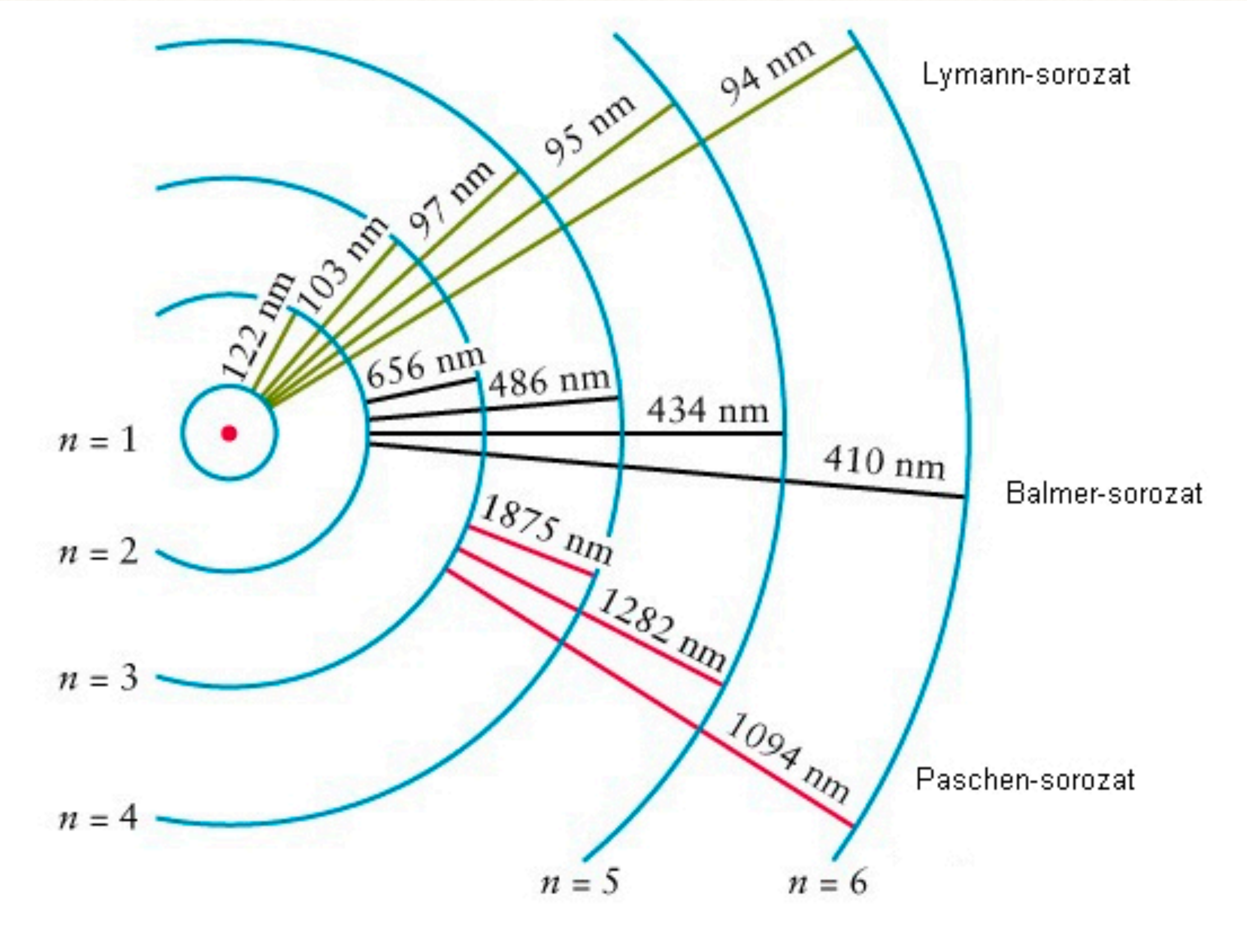
$$\lambda \to n = \frac{Ze^2}{\hbar}\sqrt{\frac{\mu}{2|E|}}$$

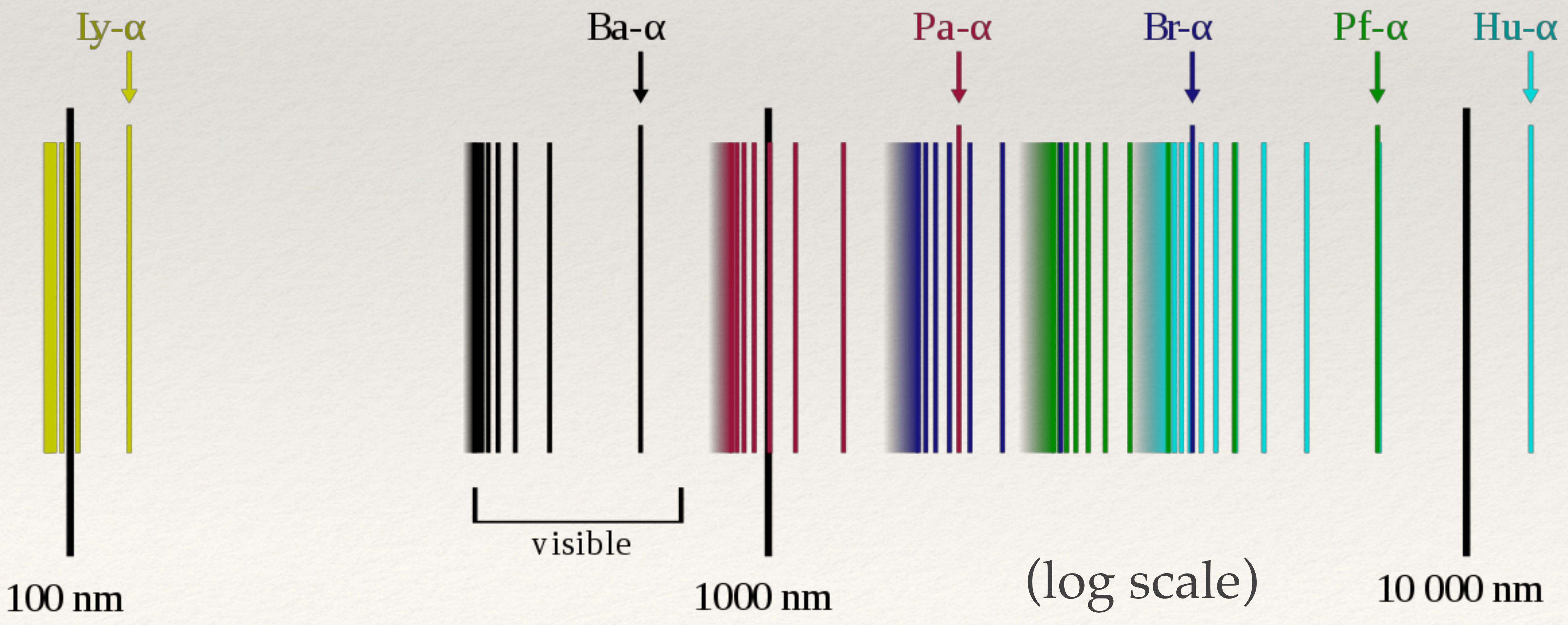
Solve for the nth energy level:

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

Hydrogen emission spectrum

We can predict the spectral lines of hydrogen.





Radial wave functions

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

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

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

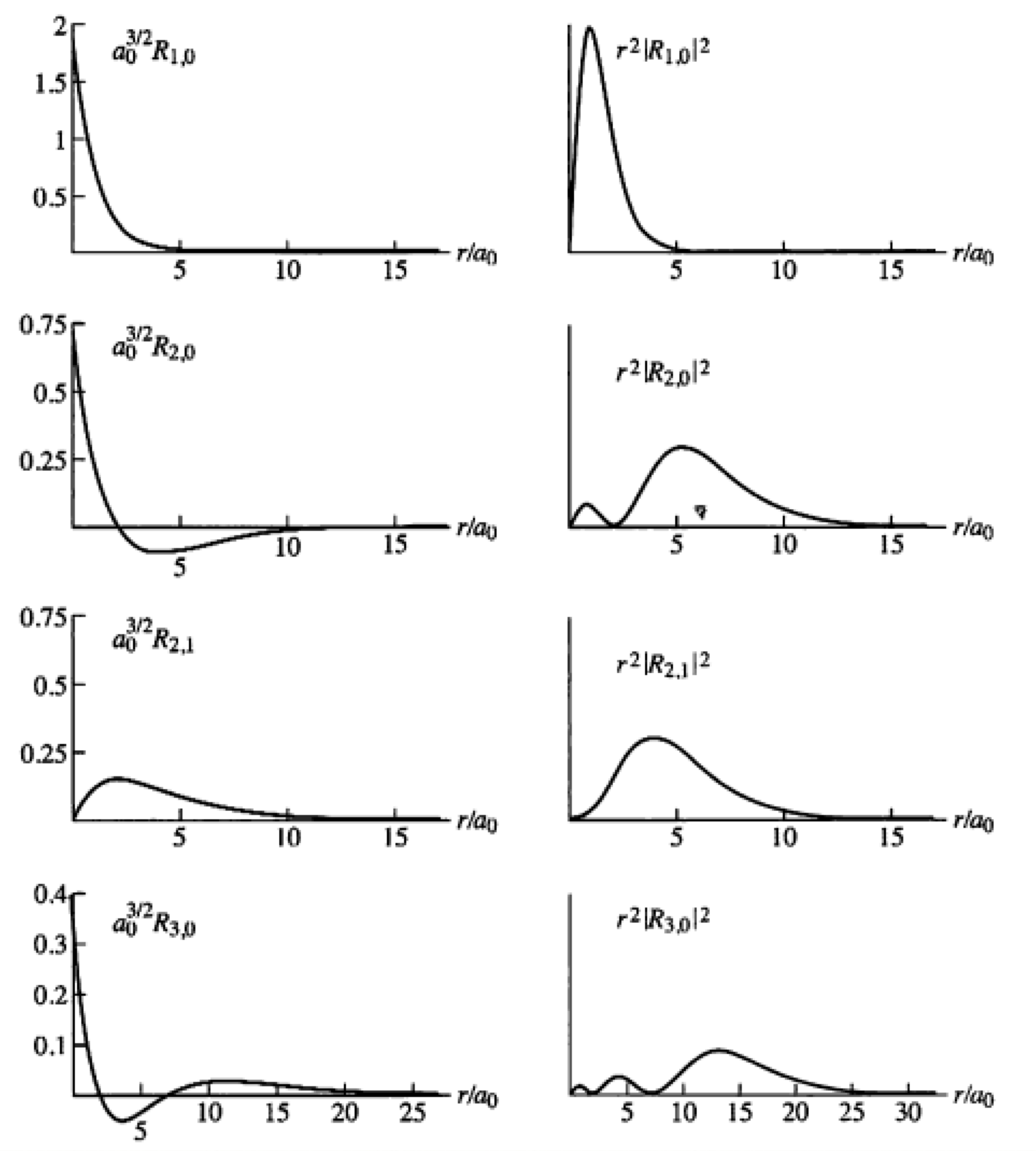
Solutions, after normalization, look like the following:

Radial wave functions

Visualizing the radial wave functions.

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

$$R_{nl}\left(\frac{2Zr}{na_0^*}\right) \qquad n = 1,2,3,\ldots \quad l = 0,\ldots,n-1$$



Degeneracy

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

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

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