

# Intermediate Quantum Mechanics

## Lecture 19 Notes (4/6/15)

### The Hydrogen Atom II

#### Eigenstates for $l = 0$

- The energy eigenstates with  $l = 0$  corresponding to energy eigenvalues  $E_n$  are given by:

$$\psi_{n00}(r, \theta, \phi) = R_{n0}(r)Y_0^0(\theta, \phi)$$

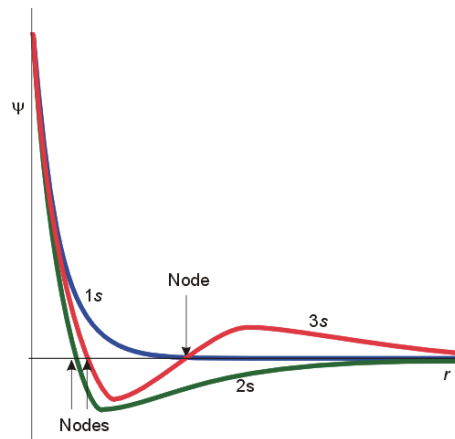
- Since  $Y_0^0(\theta, \phi) = 1/\sqrt{4\pi}$  is spherically symmetric, these states do not depend on the angles  $\theta$  and  $\phi$ .
- The expressions of the first few radial wave functions are given below where I have suppressed the uninteresting normalization factors:

$$R_{10}(r) \propto e^{-r/a_0}$$

$$R_{20}(r) \propto \left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0}$$

$$R_{30}(r) \propto \left(1 - \frac{2r}{3a_0} + \frac{2}{27} \left(\frac{r}{a_0}\right)^2\right) e^{-r/3a_0}$$

Plots of these are shown below. Notice that the number of nodes (zero crossings) increases with  $n$ . This makes sense because the energy and therefore the momentum increases as  $n$  increases. That means the wave function wiggles more.



#### Radial probability density

- Prob =  $\langle \psi_{nlm} | \psi_{nlm} \rangle = \int_0^\infty \int_0^\pi \int_0^{2\pi} \psi_{nlm}^*(r, \theta, \phi) \psi_{nlm}(r, \theta, \phi) r^2 d\phi d\cos\theta dr$

- The volume probability density is:

$$\frac{d\text{Prob}}{dV} = \frac{d\text{Prob}}{d\phi d\cos\theta r^2 dr} = \psi_{nlm}^*(r, \theta, \phi) \psi_{nlm}(r, \theta, \phi)$$

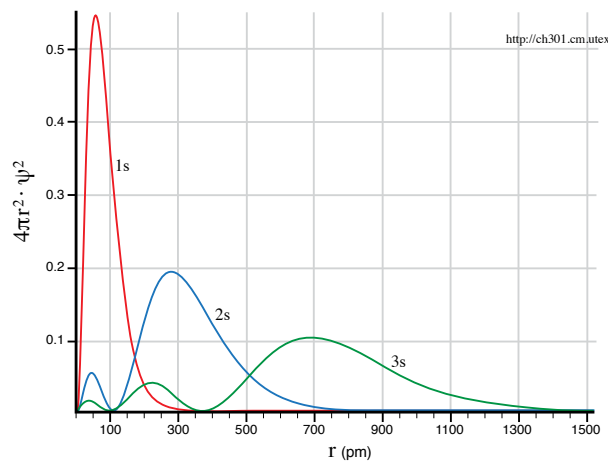
- The radial probability density is:

$$\begin{aligned} \frac{d\text{Prob}}{dr} &= \int r^2 \psi_{nlm}^*(r, \theta, \phi) \psi_{nlm}(r, \theta, \phi) d\Omega \\ &= \int r^2 R_{nl}^*(r) R_{nl}(r) Y_l^{*m}(\theta, \phi) Y_l^m(\theta, \phi) d\Omega = r^2 R_{nl}^*(r) R_{nl}(r) \end{aligned}$$

- For  $l = 0$  we have:

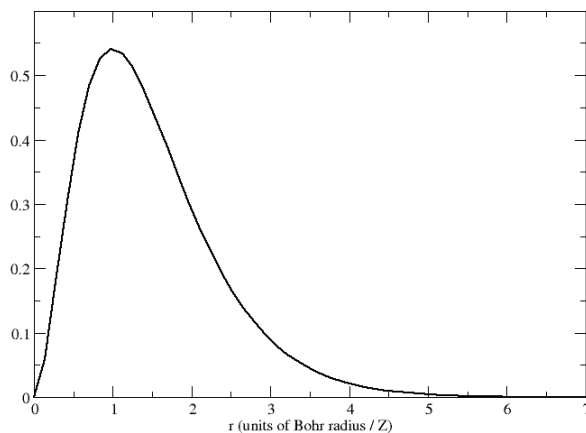
$$\frac{d\text{Prob}}{dr} = r^2 R_{n0}^*(r) R_{n0}(r)$$

The figure below shows plots of the first few of these.



- For the ground state ( $n = 1, l = 0$ ) the radial probability density is:

$$\frac{d\text{Prob}}{dr} = r^2 R_{10}^*(r) R_{10}(r) \propto r^2 e^{-2r/a_0}$$



- We can find the most probable value of the radial position,  $r_{10}^{\text{mp}}$ , by setting the derivative of  $r^2 e^{-2r/a_0}$  equal to zero.

$$\frac{d}{dr} (r^2 e^{-2r/a_0}) = 0 \quad \Rightarrow \quad r_{10}^{\text{mp}} = a_0$$

- The average value of the radial position,  $\bar{r}_{10}$ , is given by:

$$\begin{aligned}\bar{r}_{10} &= \int_0^\infty r (r^2 R_{10}^*(r) R_{10}(r)) dr = \int_0^\infty r^3 R_{10}^*(r) R_{10}(r) dr \\ &= \frac{\int_0^\infty r^3 e^{-2r/a_0} dr}{\int_0^\infty r^2 e^{-2r/a_0} dr} = \frac{3}{2} a_0\end{aligned}$$

- The general expression for the average radius is:

$$\bar{r}_{nl} = \frac{a_0}{2} [3n^2 - l(l+1)]$$

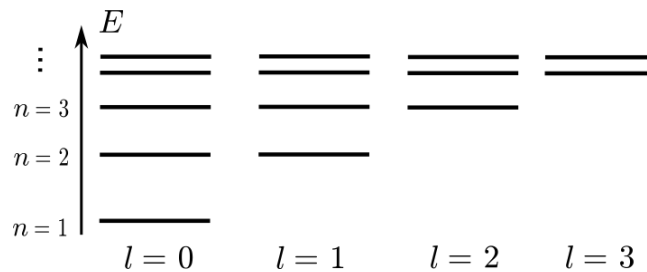
Note that for a given  $n$ , the average radius is smaller for larger values of  $l$ . This makes sense since the potential energy decreases (become more negative) as the radius decreases but the angular momentum barrier term,  $l(l+1)\hbar^2/2mr^2$ , increases with decreasing  $r$ . These changes in energy can balance so that for larger  $l$  the energy is the same as for smaller  $l$  if the average radius is less.

### Degeneracy of Energy Levels

- As we have seen, for  $l = 0$  there is an infinite set of energy levels varying as  $1/n^2$  from  $E_1 = -13.6$  eV for  $n = 1$  to  $E \rightarrow 0$  for  $n \rightarrow \infty$ :

$$E_n = \frac{E_1}{n^2} = -\frac{13.6 \text{ eV}}{n^2}$$

- For higher values of  $l$  we expect similar sets of energy levels varying from some minimum value to zero for each  $l$ . What is totally unexpected is that the energy levels for different  $l$  are degenerate as shown here:



- For a given  $n$  and  $l$ , we know that the states with different  $m_l$  will be degenerate because, for spherical symmetry, the Hamiltonian commutes with the angular momentum raising and lower operators:  $[\hat{H}, \hat{L}_\pm] = 0$ . The fact that the energy levels for different  $l$  are degenerate means that there is another symmetry (another operator that commutes with the Hamiltonian) that we haven't identified yet. That operator is the Laplace-Runge-Lenz operator.

### The Laplace-Runge-Lenz operator

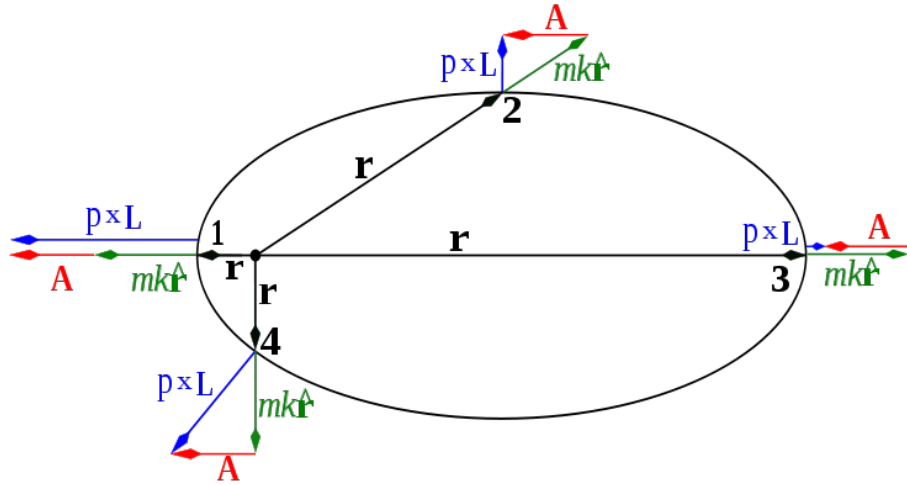
- A symmetry, as we've seen, necessarily results in a conserved quantity. In order to identify the symmetry causing the degeneracy of the different  $l$  states, we need to identify another conserved quantity.

- Consider first a classical system of a planet orbiting a star. We know that in addition to energy the angular momentum vector,  $\vec{L} = \vec{r} \times \vec{p}$ , is conserved since the gravitation force is a central force. That means that the orbit of the planet is contained in a plane.
- In addition to  $E$  and  $\vec{L}$ , there is another conserved quantity called the Laplace-Runge-Lenz vector:

$$\vec{A} = \frac{\vec{p} \times \vec{L}}{m} - GmM \frac{\vec{r}}{r}$$

where  $m$  is the mass of the planet and  $M$  is the mass of the star.

This vector is indicated in red in the following figure



- Since the Coulomb potential between the electron and the proton is also a  $1/r$  potential like the gravitational potential in the planetary system, there is a Laplace-Runge-Lenz-operator,  $\hat{A}$ , whose observable is a conserved quantity.
- A general rule in going from classical physics to quantum mechanics is to replace classical kinematic quantities (momentum, position, angular momentum, etc.) with operators. We have to be careful, though, about the order of operators since in general they don't commute. In that case, you need to split the difference. In the present case of the Laplace-Runge-Lenz-operator, since momentum and angular momentum don't commute,  $[\hat{p}, \hat{L}] \neq 0$ , the  $\hat{A}$  operator must be written as:

$$\hat{A} = \frac{1}{2m} (\hat{p} \times \hat{L} - \hat{L} \times \hat{p}) - \frac{e^2}{4\pi\epsilon_0} \frac{\vec{r}}{r}$$

- From the Runge-Lenz operator, we can construct raising and lowering operators:

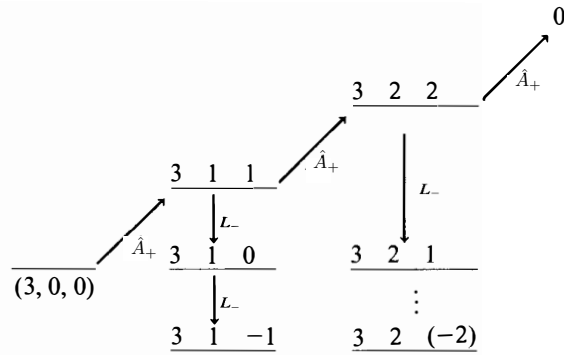
$$\hat{A}_+ = \hat{A}_x + i\hat{A}_y \quad \hat{A}_- = \hat{A}_x - i\hat{A}_y$$

The raising operator increase the  $l$  and  $m_l$  quantum numbers of a state by one.

$$\hat{A}_+ |n, l, l\rangle = c |n, l + 1, l + 1\rangle$$

while for a given  $n$ , the maximum value of  $l$  is  $n - 1$ :

$$\hat{A}_+ |n, n - 1, n - 1\rangle = |0\rangle$$



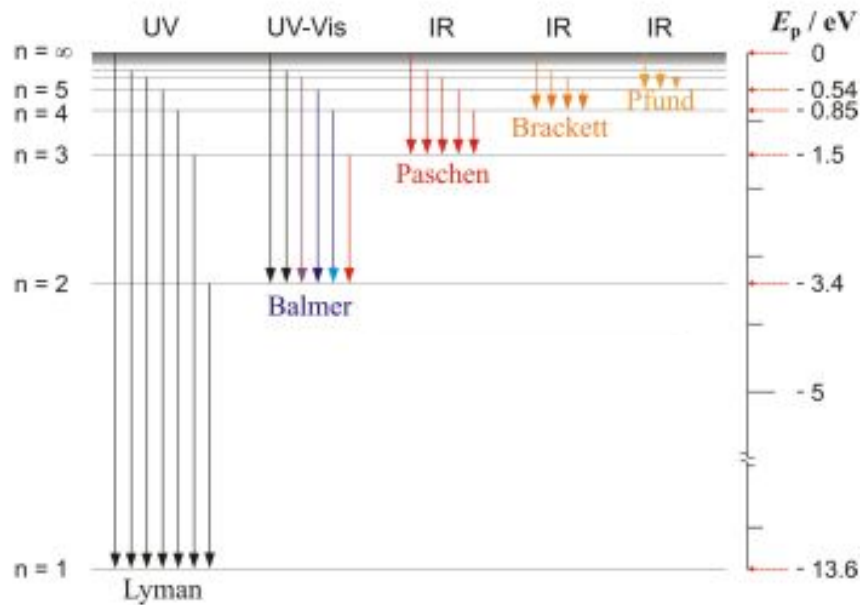
- Since the Hamiltonian commutes with the Runge-Lenz raising and lowering operators,  $[\hat{H}, \hat{A}_\pm]$

### Hydrogen spectral lines

- As mentioned before, in the early 20th century the hydrogen atom provided an excellent system for testing the new theory of quantum mechanics. Atomic spectroscopy, measuring the wavelengths of light emitted by excited hydrogen atoms determined the values of the hydrogen energy levels that could then be compared with theoretical calculations.
- In a transition from a higher energy state to a lower one, conservation of energy gives that the energy of the emitted photon is equal to the difference in the energies of the initial and final atomic states:

$$E_\gamma = E_i - E_f = -E_1 \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = \frac{mc^2 \alpha^2}{2} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = 13.6 \text{ eV} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

- There are various series of spectral lines, one for each final level, as shown in the figure below.



- Since the photon energy is related to its wavelength by:  $E_\gamma = pc = hc/\lambda$ . We have:

$$\frac{1}{\lambda} = \frac{mc^2\alpha}{2h} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = \frac{mca^2}{4\pi\hbar} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = (1.10 \times 10^7 \text{ m}^{-1}) \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

- The Lyman series lines are all in the UV. The first few of the Balmer lines are in the visible while the higher energy ones are in the UV. The Paschen lines are all in the IR.