ECE 162A
Mat 162A

Lecture #10:Hydrogen-like solutions
F/T: 5-5
E/R: Chapter 7
Appendix N

3 Dimensional Time Independent Schroedinger Equation

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x,y,z)+V(x,y,z)\psi(x,y,z)$$

$$=E\psi(x,y,z)$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi+V\psi=E\psi$$

$$If\ V(x,y,z)=V(r)$$

$$Switch\ coordinate\ systems$$

Solution to SE in Spherical Coordinates

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$$

$$If\ V(r,\theta,\phi) = V(r) = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$$

Then try separation of variables

$$\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)$$

Substitute and divide by $R\Theta\Phi$

$$-\frac{\hbar^2}{2mR}\left(\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)\right) + \frac{1}{\Theta r^2\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{1}{\Phi r^2\sin^2\theta}\frac{d^2\Phi}{d^2\phi} + V(r) = E$$

Solution of Φ

$$\frac{1}{\Phi}\frac{d^2\Phi}{d^2\phi} = -m_l^2$$

$$\Phi = Ae^{im_l\phi}$$

Single valued means

$$\Phi(\phi) = \Phi(\phi + 2\pi)$$

Which means m_l *is an* int*eger.*

Solution of Θ

$$\frac{m_l^2\Theta}{\sin^2\theta} - \frac{1}{\sin\theta}\frac{d}{d\theta}(\sin\theta\frac{d\Theta}{d\theta}) = l(l+1)\Theta$$

The solution is in Appendix N.
Use a power series expansion in cos θ.
The series terminates for

$$l = |m_l|, |m_l + 1|, \ldots$$

$$\Theta = \sin^{m_l}\theta\ F_{lm_l}(\cos\theta)$$

Solution of R

$$-\frac{2mr^2}{\hbar^2}(E-V(r))R+(\frac{d}{dr}(r^2\frac{dR}{dr}))=l(l+1)R$$

The solution is in Appendix N.
Use a power series expansion in r.
The series terminates for

$$E_n = -\frac{E_0}{n^2}$$

where

$$E_0 = \frac{mZ^2e^4}{(4\pi\varepsilon_0)^2 2\hbar^2} = 13.6eV$$

$$n = l+1, l+2, \ldots$$

(Z=1)

$$R_{nl}(r) = e^{-Zr/na_0}(\frac{Zr}{a_0})^l G_{nl}(Zr/a_0)$$

G(x) is a polynomial in x

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2} = .525A$$

Quantum numbers

•N,l,m_l are called quantum numbers

•The energy eigenvalue depends only on n, so N is called the principle quantum number.

•The angular momentum depends on l, so l is called the azimuthal quantum number.

•The energy in a magnetic field depends on m_l, so m_l is called the magnetic quantum number.

$$E_n = -\frac{E_0}{n^2}$$

Examination of the solution

- The solution of the spherical potential has solutions for particular quantum numbers m,l,n,E where

$$|m_l| = 0,1,2,...$$

$$l = |m_l|, |m_l| + 1,...$$

$$n = l + 1, l + 2,...$$

- This is equivalent to

$$n = 1,2,3,...$$

$$l = 0,1,2,...n - 1$$

$$m_l = -l, -l + 1,...0...l - 1, l$$

Degeneracy of the solution

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

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

$$m_l = -l,-l+1,\ldots 0\ldots l-1,l$$

- For each value of n,
  - There are n possible values of l
- For each value of l
  - There are 2l+1 values of m_l
- For each value of n,
  - There are n^2 degenerate eigenfunctions.

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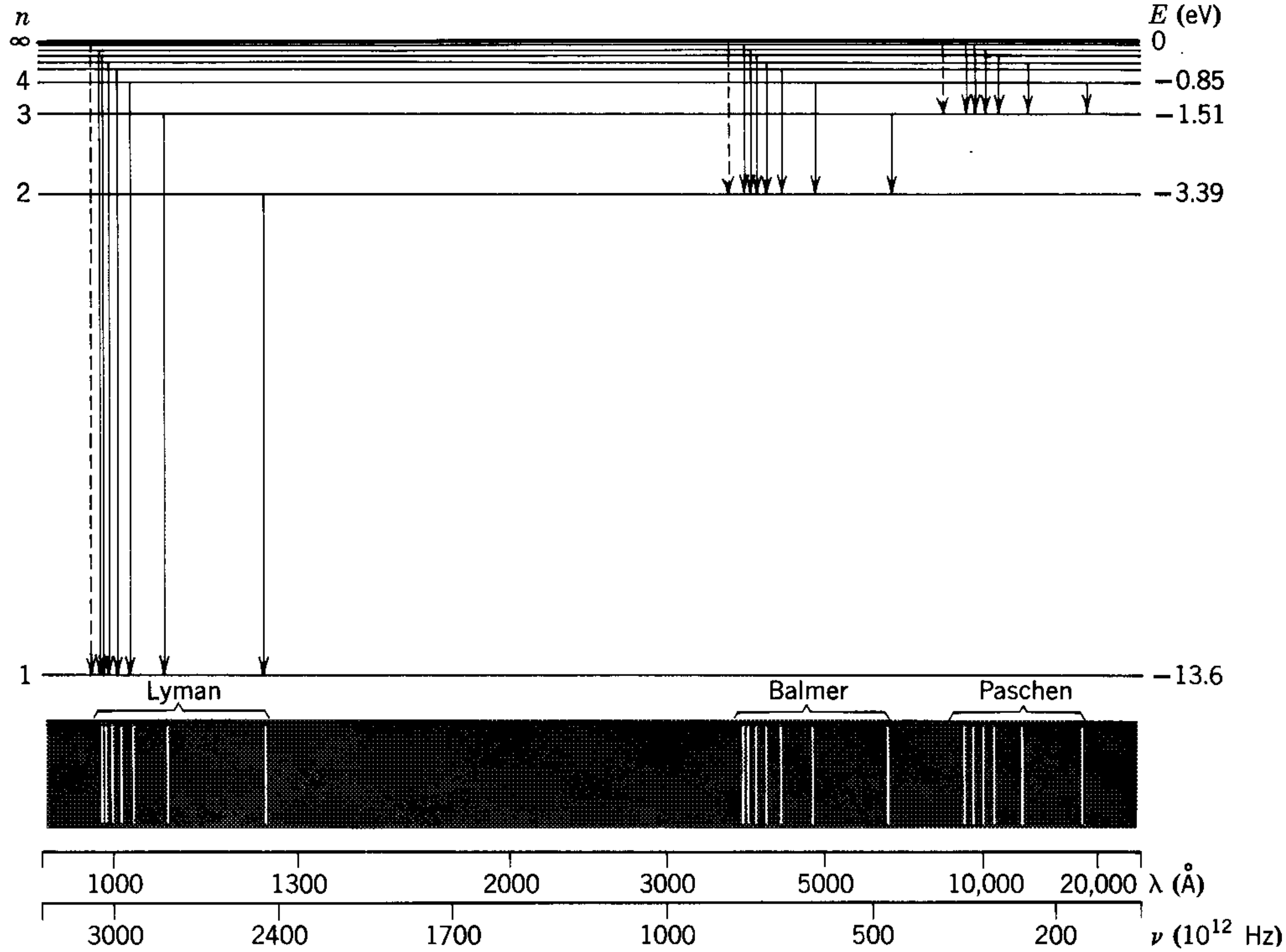
$$E_n = -\frac{E_0}{n^2}$$

The first convincing verification of Schrodinger's theory was this calculations of eigenvalues, in agreement with experiment, just as Bohr's model.

Energy Levels of Hydrogen

$$E_n = -\frac{E_0}{n^2}$$



Fine structure splitting

When the spectral lines of the hydrogen spectrum are examined at very high resolution, they are found to be closely-spaced doublets. This splitting is called fine structure (and was one of the first experimental evidences for electron spin).

How to explain with Bohr theory?
Sommerfeld's model:
Attempt to explain using elliptical orbits. . Treat relativistically.

However, dashed lines don't appear experimentally. Why? Selection rules….

How to explain with Schrodinger's theory? (Soon…)

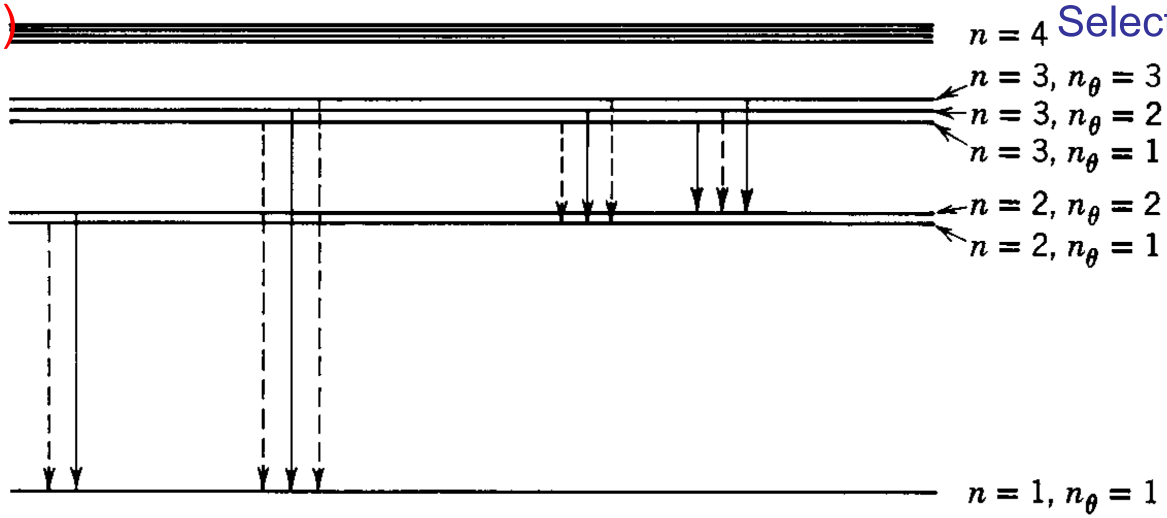


Figure 4-19 The fine-structure splitting of some energy levels of the hydrogen atom. The splitting is greatly exaggerated. Transitions which produce observed lines of the hydrogen spectrum are indicated by solid arrows.

Comparison of Solutions

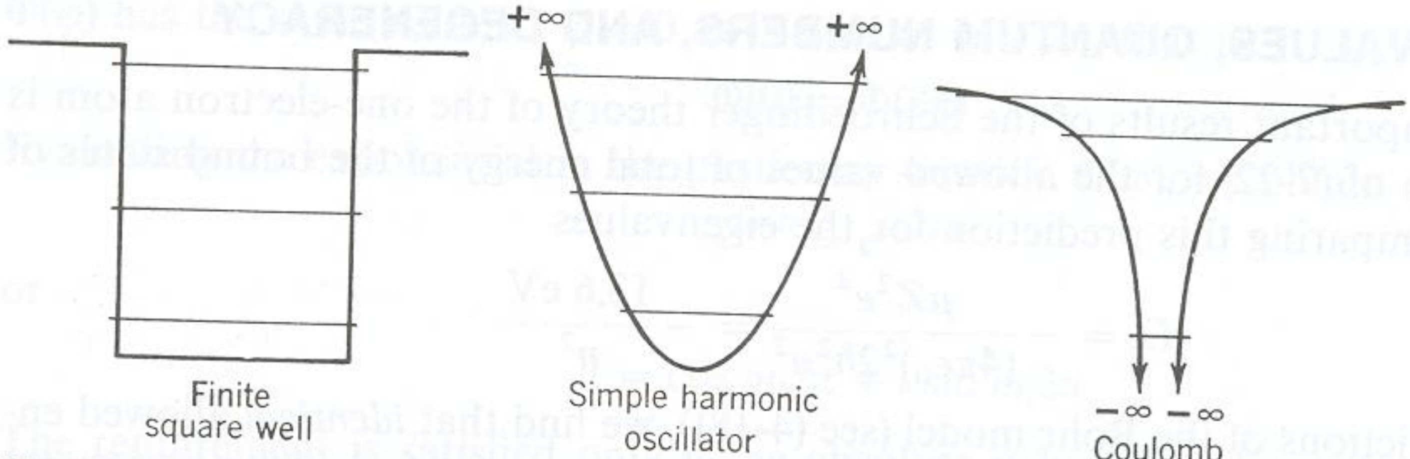
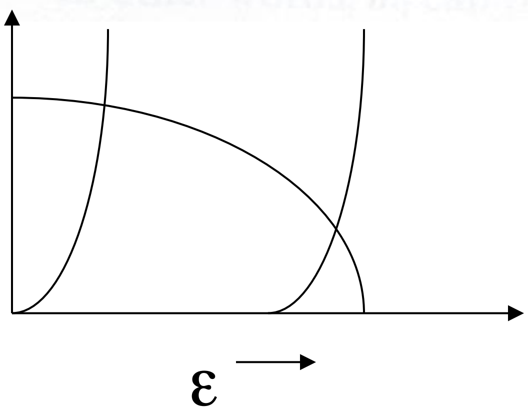


Figure 7-4 A comparison between the allowed energies of several binding potentials. The three-dimensional Coulomb potential is shown in a cross-sectional view along a diameter; the other potentials are one-dimensional.

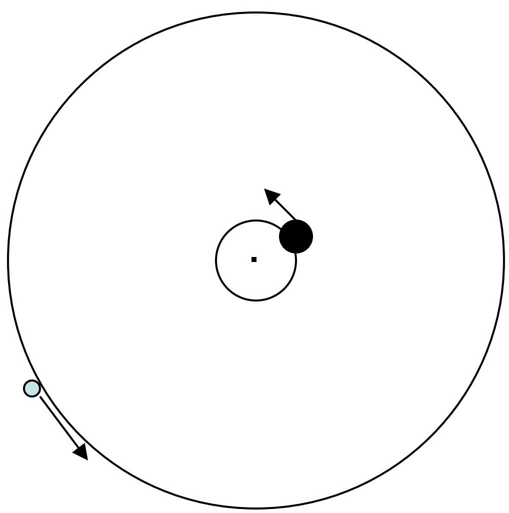


$E_n=(n+1/2)h\nu$

$$E_n = -\frac{E_0}{n^2}$$

Actual hydrogen atom

- 6 spatial coordinates:
  - x_e, y_e, z_e
  - x_p, y_p, z_p

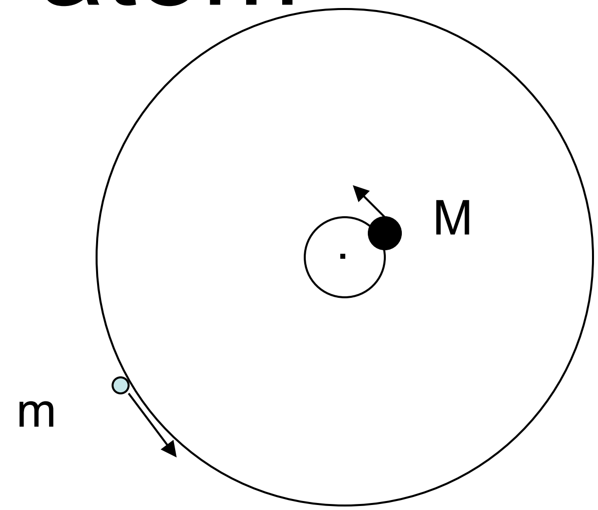


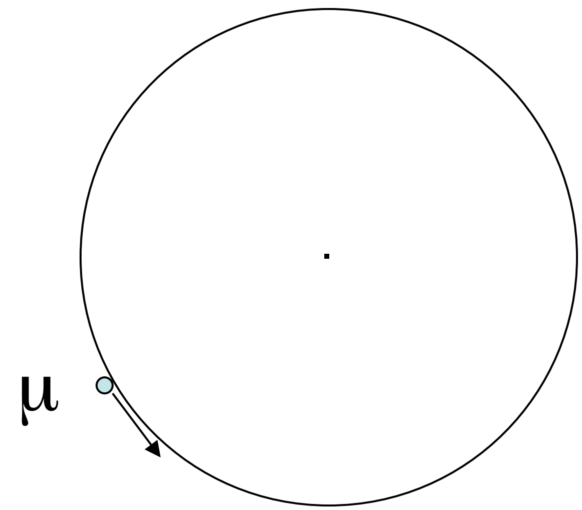
  - What to do?

Actual hydrogen atom

- 6 spatial coordinates:
  - x_e, y_e, z_e
  - x_p, y_p, z_p
- Switch to center of mass coordinates
- The electron moves about a stationary, infinite mass nucleus. The problem reduces to 3 spatial coordinates
  - x_{re}, y_{re}, z_{re}
  - With reduced mass μ

$$\mu = \frac{M}{M+m} m$$





3 spatial variables, 3 quantum numbers

$$m = 9.1\ 10^{-31} kg$$

$$M = 1672\ 10^{-31} kg$$

$$\mu = 9.05\ 10^{-31} kg$$

A small, but measurable correction

$$E_n = -\frac{E_0}{n^2}$$

where

$$E_0 = \frac{\mu Z^2 e^4}{(4\pi\varepsilon_0)^2 2\hbar^2} = 13.6 eV$$

$$a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{\mu e^2} = .525 A$$

Lowest energy solution

- n=1
- l=0
- m_l=0
- E=-13.6 eV
- There is only one solution (no degeneracy)

$$\psi_{100} = \frac{1}{\sqrt{\pi}}(\frac{Z}{a_0})^{3/2} e^{-Zr/a_0}$$

- The solution is spherically symmetric.