ECE 162A
Mat 162A

Lecture #11: Hydrogen like Solutions and Angular momentum
E/R: Chapter 7

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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 $R\Theta\Phi$

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

Separate ϕ dependence

$$\text{Re}\,arrange:$$

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

$$LHS\ \ is\ \ a\ \ function\ \ of\ \ \phi\ \ only.$$

Solution of Φ

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

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

$$\textit{Single valued means}$$

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

$$\textit{Which means m is an integer.}$$

Separation of r and θ

$$-m_l^2 = -\frac{2mr^2 \sin^2\theta}{\hbar^2}(E - V(r)) - \frac{\sin^2\theta}{R}\left(\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)\right) - \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)$$

$\mathrm{Re}\,arrange:$

$$-\frac{2mr^2}{\hbar^2}(E - V(r)) + \frac{1}{R}\left(\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)\right) = \frac{m_l^2}{\sin^2\theta} - \frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) \equiv l(l+1)$$

LHS is a function of r only and RHS is a function of θ only.

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

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

$$where$$

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

(Z=1)

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

G(x) is a polynomial in x

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

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

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.

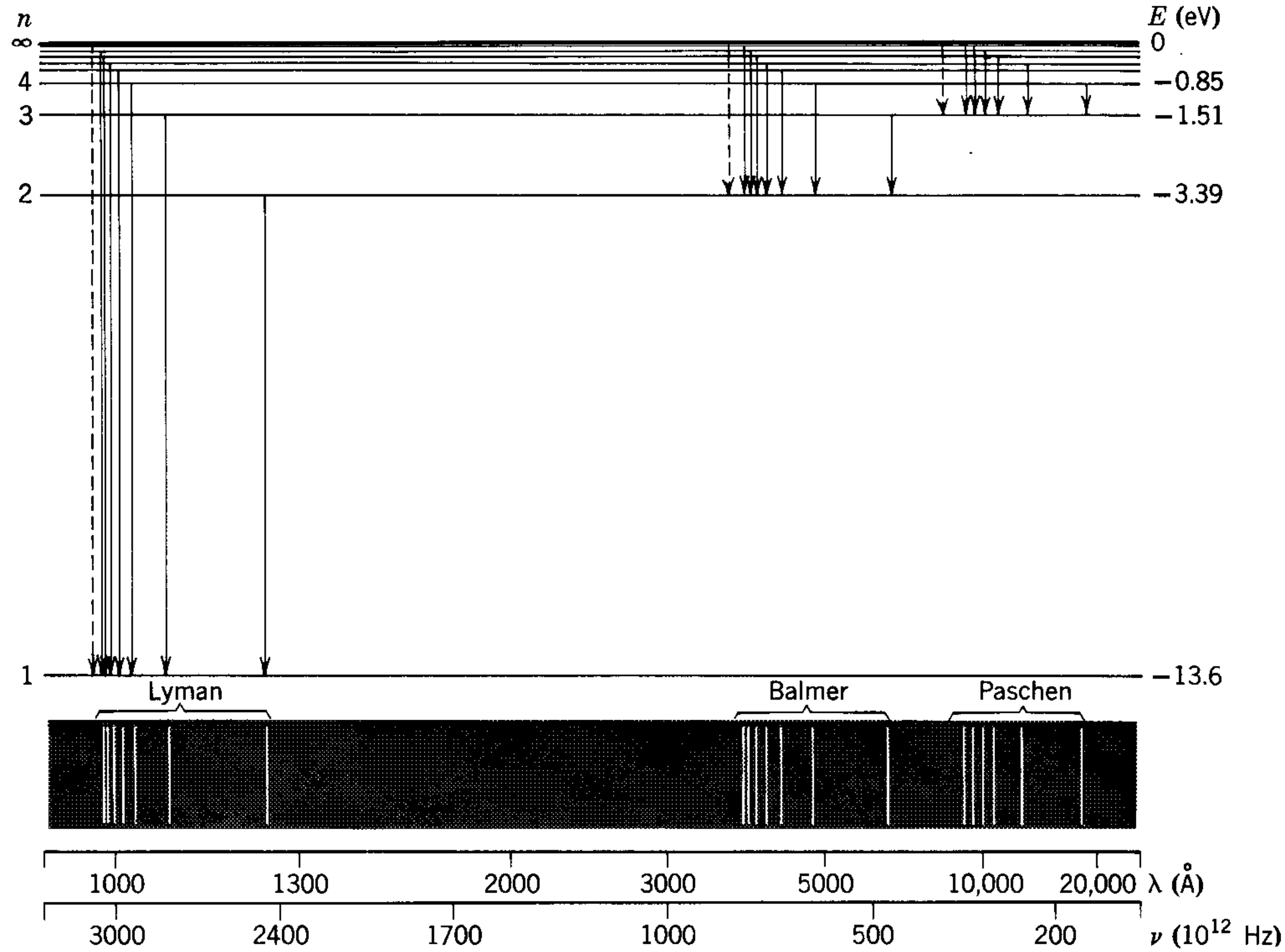
- The angular momentum depends on l, so l is called the azimuthal quantum number.

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

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

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

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



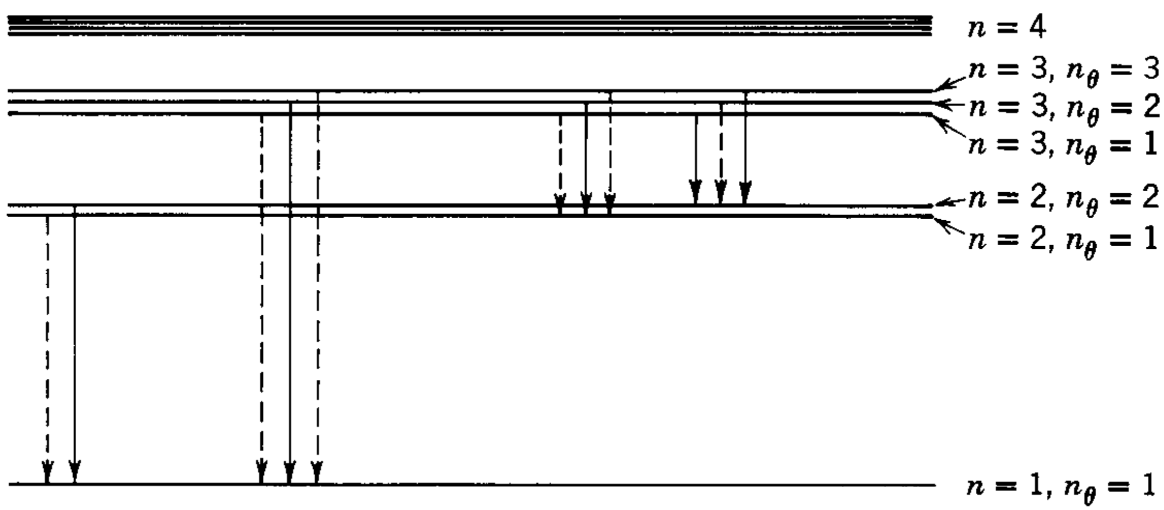
Energy Levels of Hydrogen

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

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



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

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

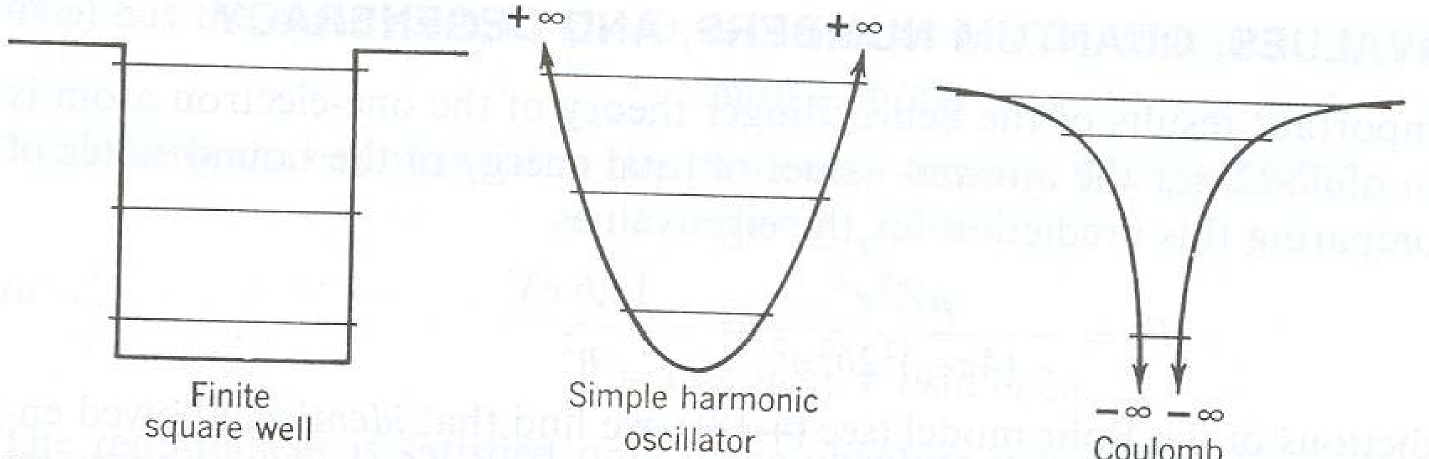
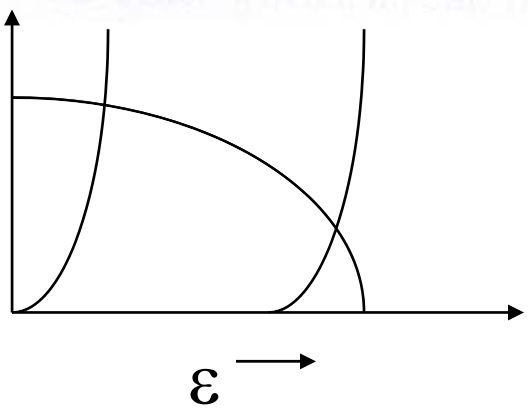


Figure 7-4 A comparison between the allowed energies of several binding potentials. The three-dimensional Coulomb potential is shown in a cross-sectional view along a diameter; the other potentials are one-dimensional.



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

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

Examination of the solution

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

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

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

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

Examination of the solution

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

$$|m_l| = 0,1,2,\ldots$$

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

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

- This is equivalent to

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

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

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

Degeneracy of the solution

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

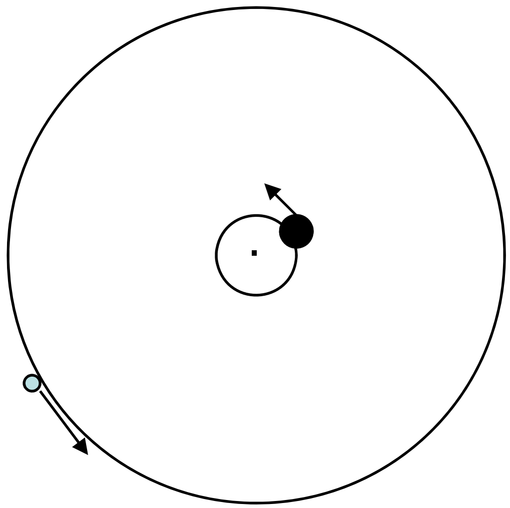
$$l = 0,1,2,\ldots n-1$$

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

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

Actual hydrogen atom

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

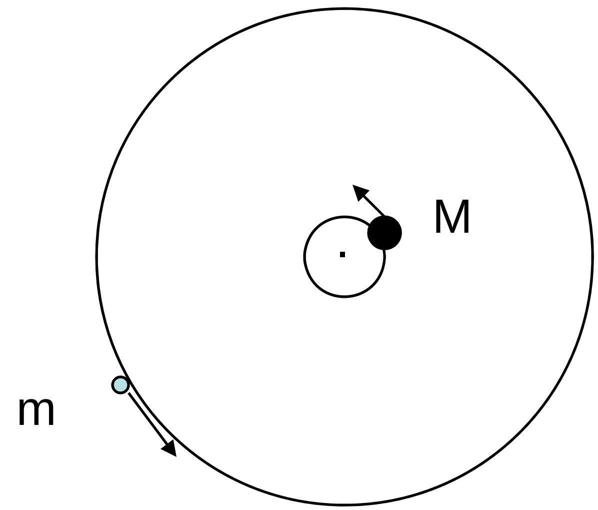


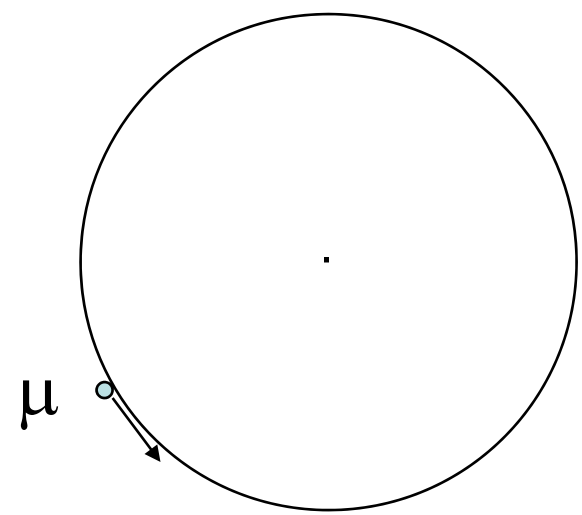
  - What to do?

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

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

$$where$$

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

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

Lowest energy solution

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

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

- The solution is spherically symmetric.

Lowest energy solution

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

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

- The solution is spherically symmetric.

What is the probability of finding the electron at a distance r?

Second lowest energy solutions

- n=2
- E=-13.6/4=-3.4 eV
- There are four degenerate solutions
- One solution is spherically symmetric.

$$\psi_{200} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$$

- One solution is cylindrically symmetric

$$\psi_{210} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)e^{-Zr/2a_0}\cos\theta$$

- Two solutions are degenerate

$$\psi_{21\pm1} = \frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)e^{-Zr/2a_0}\sin\theta\ e^{\pm i\phi}$$

Radial Dependence

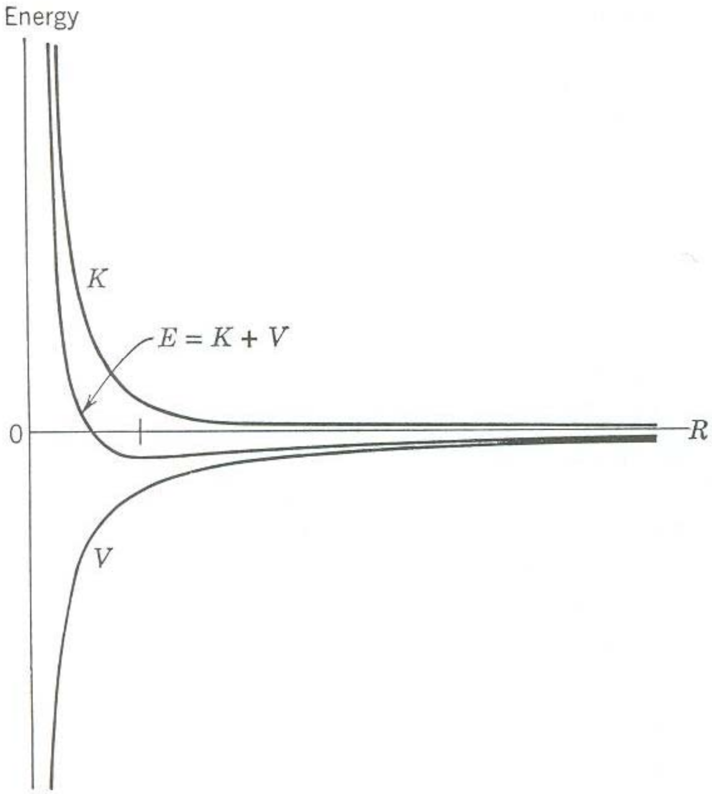


Figure 7-6 The qualitative behavior of the kinetic e
energy E of a hydrogen atom, as functions of the size
more rapidly than V decreases because $K \propto 1/R$
becomes negligible compared to V. As a result, E h
(indicated by the mark on the R axis), and at this si

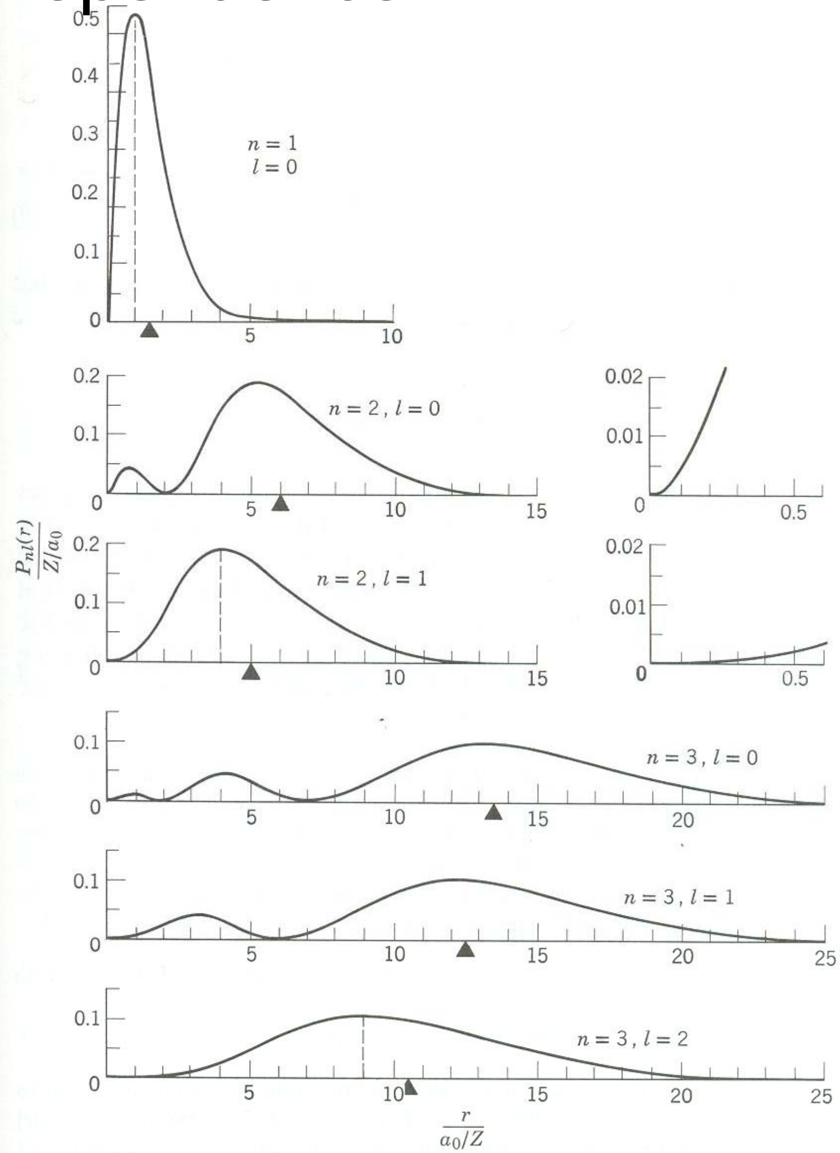


Figure 7-5 The radial probability density for the electron in a one-electron atom for $n =$ 1, 2, 3 and the values of l shown. The triangle on each abscissa indicates the value of $\overline{r_{nl}}$ as given by (7-29). For $n = 2$ the plots are redrawn with abscissa and ordinate scales expanded by a factor of 10 to show the behavior of $P_{nl}(r)$ near the origin. Note that in the three cases for which $l = l_{max} = n - 1$ the maximum of $P_{nl}(r)$ occurs at $r_{Bohr} = n^2 a_0/Z$, which is indicated by the location of the dashed line.

Radial Dependence

Table 7-2 Some Eigenfunctions for the One-Electron Atom

Quantum Numbers n	l	m_l	Eigenfunctions
1	0	0	$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
2	0	0	$\psi_{200} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$
2	1	0	$\psi_{210} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \cos\theta$
2	1	± 1	$\psi_{21\pm1} = \frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \sin\theta\, e^{\pm i\varphi}$
3	0	0	$\psi_{300} = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(27 - 18\frac{Zr}{a_0} + 2\frac{Z^2r^2}{a_0^2}\right) e^{-Zr/3a_0}$
3	1	0	$\psi_{310} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6 - \frac{Zr}{a_0}\right)\frac{Zr}{a_0} e^{-Zr/3a_0} \cos\theta$
3	1	± 1	$\psi_{31\pm1} = \frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6 - \frac{Zr}{a_0}\right)\frac{Zr}{a_0} e^{-Zr/3a_0} \sin\theta\, e^{\pm i\varphi}$
3	2	0	$\psi_{320} = \frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0}(3\cos^2\theta - 1)$
3	2	± 1	$\psi_{32\pm1} = \frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0} \sin\theta\cos\theta\, e^{\pm i\varphi}$
3	2	± 2	$\psi_{32\pm2} = \frac{1}{162\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0} \sin^2\theta\, e^{\pm 2i\varphi}$

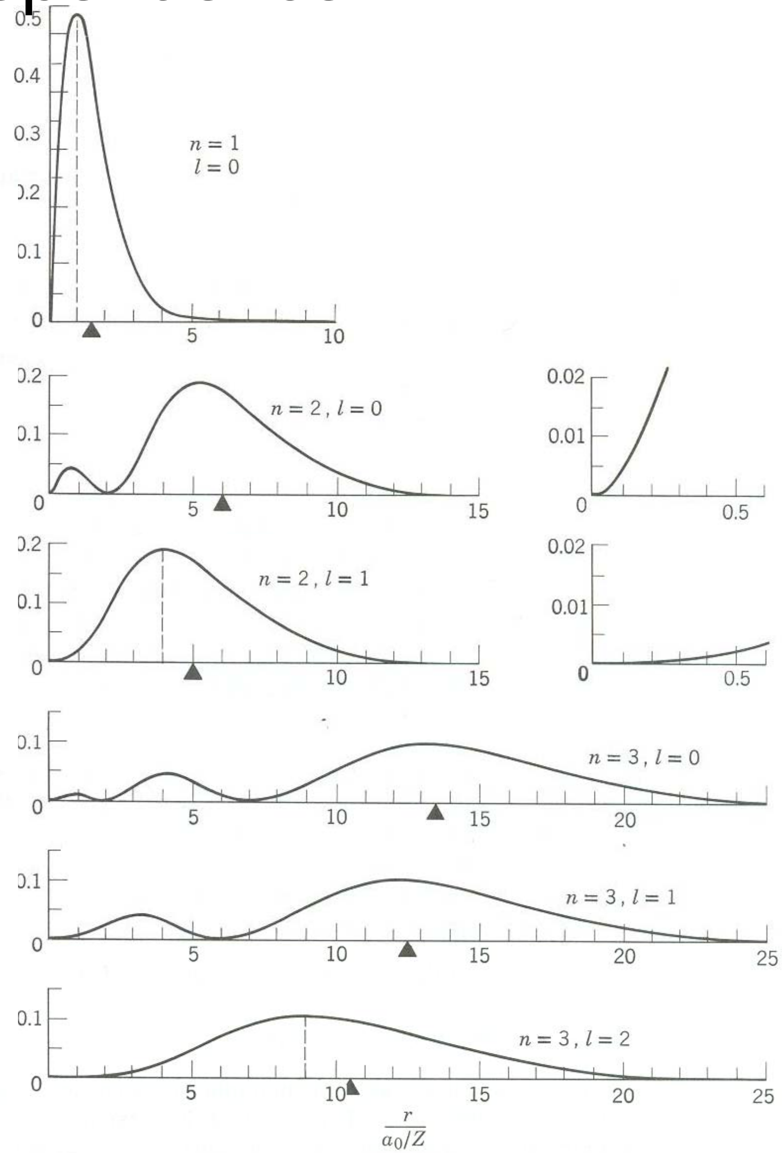
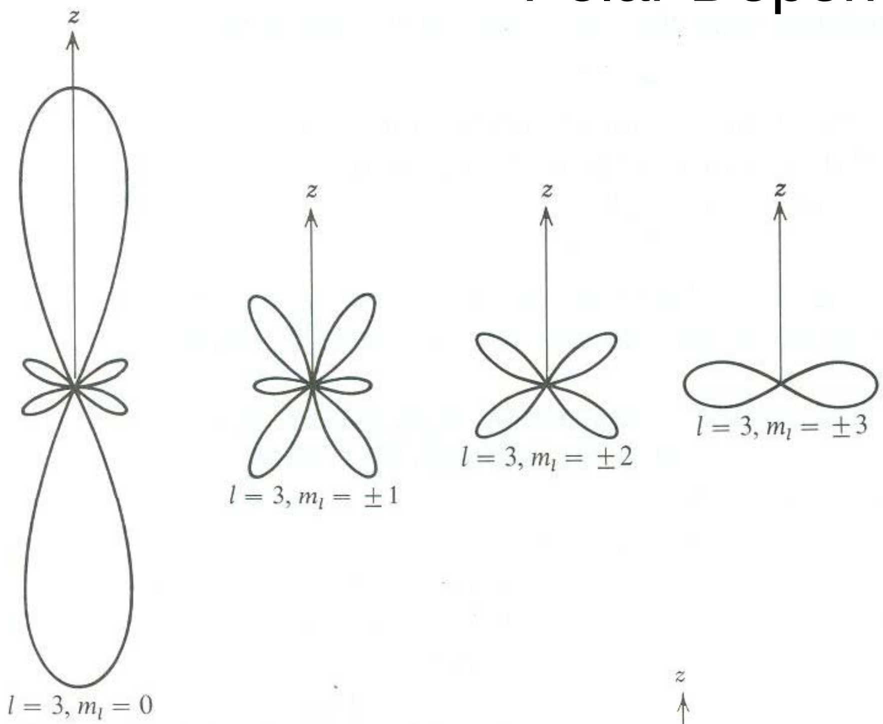


Figure 7-5 The radial probability density for the electron in a one-electron atom for $n =$ 1, 2, 3 and the values of l shown. The triangle on each abscissa indicates the value of $\overline{r_{nl}}$ as given by (7-29). For $n = 2$ the plots are redrawn with abscissa and ordinate scales expanded by a factor of 10 to show the behavior of $P_{nl}(r)$ near the origin. Note that in the three cases for which $l = l_{\max} = n - 1$ the maximum of $P_{nl}(r)$ occurs at $r_{\text{Bohr}} = n^2 a_0/Z$, which is indicated by the location of the dashed line.

Polar Dependence



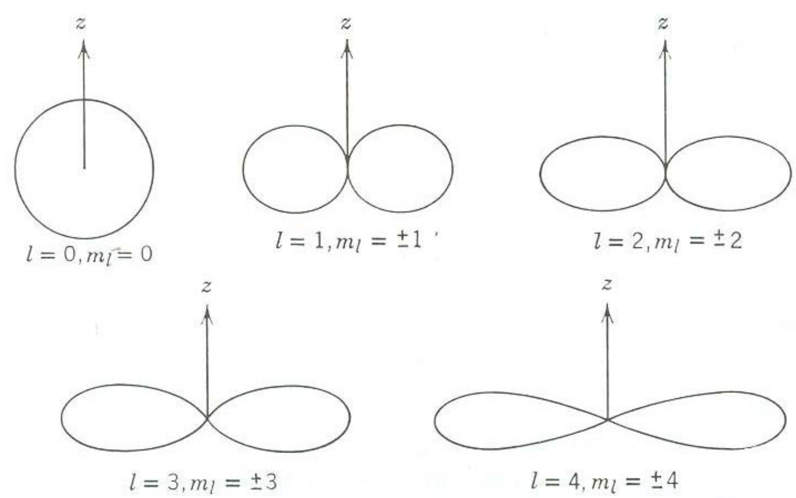


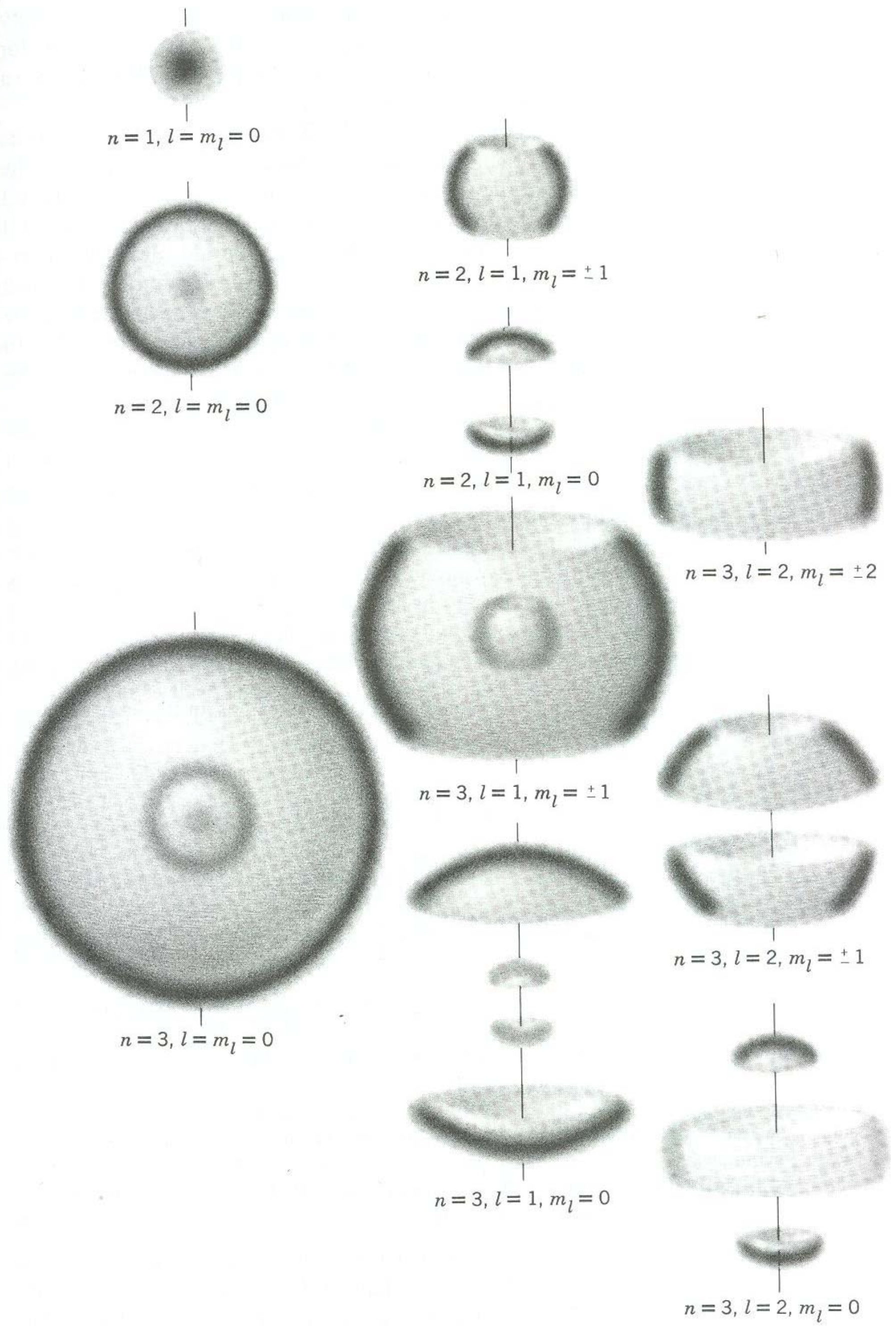
Figure 7-9 Polar diagrams of the directional dependence of the one-electron probability densities for $l = 0, 1, 2, 3, 4$; $m_l = \pm l$.

L=0 L=1 L=2

N=1

N=2

N=3



Classical Angular Momentum

$$\vec{L} = \vec{r} \times \vec{p}$$

$$L_x = yp_z - zp_y$$

$$L_y = zp_x - xp_z$$

$$L_z = zp_x - xp_z$$

Angular momentum (Cartesian coordinates)

Classical

$$\vec{L} = \vec{r} \times \vec{p}$$

$$L_x = yp_z - zp_y$$

$$L_y = zp_x - xp_z$$

$$L_z = xp_y - yp_x$$

Quantum Mechanical

$$\hat{L} = \vec{r} \times \hat{p}$$

$$\hat{L}_x = -i\hbar(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y})$$

$$\hat{L}_y = -i\hbar(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z})$$

$$\hat{L}_z = -i\hbar(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x})$$

Angular Momentum in Spherical Coordinates

$$\hat{L} = \vec{r} \times \hat{p}$$

$$\hat{L} = -i\hbar \vec{r} \times \hat{\nabla}$$

$$\hat{L}_x = -i\hbar(\sin\theta \frac{\partial}{\partial\theta} + \cot\theta\cos\phi \frac{\partial}{\partial\phi})$$

$$\hat{L}_y = -i\hbar(-\cos\theta \frac{\partial}{\partial\theta} + \cot\theta\sin\phi \frac{\partial}{\partial\phi})$$

$$\hat{L}_z = -i\hbar(\frac{\partial}{\partial\phi})$$

What is the z component of angular momentum?

- Calculate the expectation value

$$\overline{L}_z = \int_0^\infty r^2 dr \int_0^\pi d\theta \int_0^{2\pi} d\phi \, \psi^* \hat{L}_z \psi$$

$$\psi = R_{nl}(r)\Theta_{lm_l} e^{im_l\phi}$$

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial\phi}$$

$$\hat{L}_z \psi = -i\hbar \frac{\partial}{\partial\phi} e^{im_l\phi} = \hbar m_l e^{im_l\phi}$$

$$\overline{L}_z = \int_0^\infty R_{nl}*(r) R_{nl}(r) r^2 dr \int_0^\pi \Theta_{lm_l} * \Theta_{lm_l} d\theta \int_0^{2\pi} d\phi \, \hbar m_l$$

$$\overline{L}_z = \hbar m_l$$

So, the z component of angular momentum has the average value given above.

What is the total (squared) angular momentum?

- Calculate the expectation value

$$\overline{L}^2 = \int_0^\infty r^2 dr \int_0^\pi d\theta \int_0^{2\pi} d\phi \, \psi^* \hat{L}^2 \psi$$

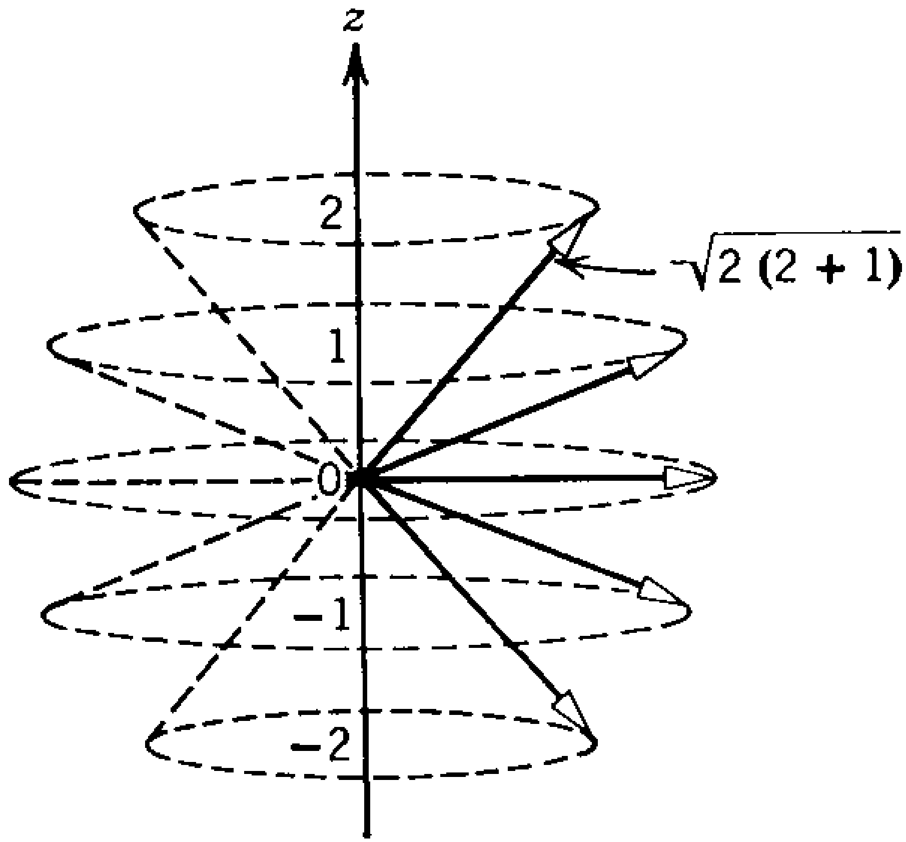
$$\psi = R_{nl}(r)\Theta_{lm_l} e^{im_l\phi}$$

$$\hat{L}^2 = -\hbar^2 \left(\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial^2\phi} \right)$$

$$\hat{L}^2 \psi = l(l+1)\hbar^2 \psi$$

$$\overline{L}^2 = l(l+1)\hbar^2$$

Vector picture of angular momentum



The arrow has length $\sqrt{2(2+1)}$

While the vertical component has length 2,1,0,-1,-2

The average value of LxLy is zero.

The energy of the atom does not depend on m_l (i.e. orientation of ang. Momentum).

Quantization

- We showed that the average value of L_z is $m\hbar$. That doesn't mean that L_z is quantized.
- However, since

$$\hat{L}_z \psi = -i\hbar \frac{\partial}{\partial \phi} e^{im_l \phi} = \hbar m_l e^{im_l \phi}$$

$$\overline{L_z} = \hbar m_l$$

$$\hat{L}_z^2 \psi = -\hbar^2 \frac{\partial^2}{\partial^2 \phi} e^{im_l \phi} = \hbar^2 m_l^2 e^{im_l \phi}$$

$$\overline{L_z^2} = \hbar^2 m_l^2$$

- The average of a set can only equal the average of the square of the set if all values are equal. Hence, L_z is quantized.

- In general, if the quantity f has the value F in the quantum state described by ψ, then

$$\hat{f}\psi = F\psi$$

- Where $\hat{f}$ is the operator corresponding to f.

- Note:

$$\hat{L}_x \psi \neq l_x \psi$$

$$\hat{L} y \psi \neq l_y \psi$$

- So L_x and L_y are not quantized.

$$[L_x, L_y] = i\hbar L_z$$

$$[L_y, L_z] = i\hbar L_x$$

$$[L_z, L_x] = i\hbar L_y$$

- Under what conditions can two or more observable properties of a quantum system have unique eigenvalues for a given quantum state?

- If two operators commute, then the eigenvalues associated with those operators are simultaneous eigenvalues.

- If two operators do not commute, then the eigenvalues associated with those two operators typically exhibit an uncertainty relation.

- If two operators do not commute, then the eigenvalues associated with those two operators typically exhibit an uncertainty relation.

- Exception:
- Sometimes the values are zero. For example for zero total angular momentum, $L_x=L_y=L_z=0$