THE HYDROGEN ATOM

(1) Central Force Problem
(2) Rigid Rotor
(3) H Atom

CENTRAL FORCE PROBLEM: The potential energy function has no angular (θ, ϕ) dependence

$$V = V(r)$$

The force is a vector & is defined as the gradient of the potential

$$\mathbf{F} = - \nabla V(x,y,z)$$

∇ is a vector quantity, the gradient operator:

$$\nabla = \mathbf{i}\,\partial/\partial x + \mathbf{j}\,\partial/\partial y + \mathbf{k}\,\partial/\partial z$$

$$\mathbf{F} = - (\mathbf{i}\,\partial V/\partial x + \mathbf{j}\,\partial V/\partial y + \mathbf{k}\,\partial V/\partial z)$$

Or, by transforming coordinates from Cartesian (x,y,z) to Spherical Polar (r, θ, ϕ), one can give the gradient operator in spherical polar coordinates. Since V depends only on r, not θ& φ, the resulting force depends only on r:

$$\mathbf{F} = - (dV(r)/dr) (\mathbf{r}/r) \quad \text{for } V = V(r).$$

To express the Hamiltonian for a Central Force problem, use spherical polar coordinates where

$$\nabla^2 = \partial^2/\partial r^2 + (2/r)\,\partial/\partial r + (1/ r^2)\,\partial^2/\partial\theta^2 +$$

$$+ (1/r^2) \cot \theta\, \partial/\partial\theta + 1/(r^2 \sin^2 \theta)\, \partial^2/\partial\phi^2$$

$$= \partial^2/\partial r^2 + (2/r)\, \partial/\partial r - 1/(r^2\underline{h}^2)\, L^2$$

where

$$L^2 = - \underline{h}^2 (\partial^2/\partial\theta^2 + \cot \theta\, \partial/\partial\theta + (1/ \sin^2 \theta) (\partial^2/\partial\phi^2).$$

Then $H = T + V = - (\underline{h}^2/2m)\, \nabla^2 + V(r)$

$$= - (\underline{h}^2/2m) (\partial^2/\partial r^2 + (2/r)\, \partial/\partial r) + L^2/(2m\, r^2) + V(r)$$

Will the angular momentum be conserved (constant)? Can we specify both angular momentum & energy (i.e. does H commute with L^2 and L_z? Let's see:

$$[H, L^2] = [T + V, L^2] = [T , L^2] + [V, L^2]$$

$$= [- (\underline{h}^2/2m) (\partial^2/\partial r^2 + (2/r)\, \partial/\partial r) + L^2/(2m\, r^2) , L^2]$$

$$+ [V, L^2]$$

$$= [- (\underline{h}^2/2m) (\partial^2/\partial r^2 + (2/r)\, \partial/\partial r) , L^2] + [L^2/(2m\, r^2) , L^2]$$

$$+ [V, L^2]$$

In the first & third commutators above, the left-hand side depends only on r; the right, only on θ & ϕ. So these commutators equal 0. In the second commutator, an operator always commutes with itself, so this is 0, too. Therefore,

$[H, L^2] = 0$ if V is independent of θ & ϕ.
Since L_z doesn't depend on r & $[L^2,L_z] = 0$, then $[L_z,H] = 0$.

So, H, L^2, & L_z have a common set of eigenfunctions ψ:

$$H \psi = E \psi$$

$$L^2 \psi = l\,(l+1)\,\underline{h}^2 \psi \qquad l = 0,1,2,3...$$

$$L_z \psi = m\,\underline{h}\,\psi \qquad m = -l, -l+1, ..., l-1, l$$

$(H - E)\,\psi = 0 \Rightarrow$

$$[-(\underline{h}^2/2m)\,(\partial^2/\partial r^2 + (2/r)\,\partial/\partial r) + l(l+1)\,\underline{h}^2/(2m\,r^2)$$

$$+ V(r) - E]\,\psi = 0$$

Separation of Variables: Let $\psi(r,\theta,\phi) = R(r)\,Y^m{}_l(\theta,\phi)$

Then one can divide through by $Y^m{}_l(\theta,\phi)$ to get an eqn. for R, which defines the **Central Force Problem**:

$$[-(\underline{h}^2/2m)\,(\partial^2/\partial r^2 + (2/r)\,\partial/\partial r) + l(l+1)\,\underline{h}^2/(2m\,r^2)$$

$$+ V(r) - E]\,R(r) = 0.$$

This is the eqn. for the radial part of the wavefunction. One can solve for R(r) when the functional form of V(r) is known. We want to use this approach for the H atom, but in that case there are **two** particles (electron, proton). Need to reduce the two-particle problem to a one-particle problem. If we transaform coordinates from Cartesian to relative center of mass coordinates, this will allow us to separate off the translational from the internal motion & results in a simplified Hamiltonian.
See Fig. 6.1

Here, $\mathbf{r}$ = vector from particle 1 to particle 2

$\mathbf{R}$ = vector from the origin to C, the center of mass

$\mathbf{r_1}$ = vector from the origin to particle 1

$\mathbf{r} = \mathbf{r_2} - \mathbf{r_1}$

$\mathbf{R} = (m_1 r_1 + m_2 r_2)/(m_1 + m_2) = (m_1/M)\,\mathbf{r_1} + (m_2/M)\,\mathbf{r_2}$

where M = total mass of system = $m_1 + m_2$.

Let μ = reduced mass = $m_1 m_2/(m_1 + m_2)$

Kinetic Energy = T

$= (1/2)\, m_1 |\mathbf{v_1}|^2 + (1/2)\, m_2\, |\mathbf{v_2}|^2$

where $\mathbf{v_1} = d\,\mathbf{r_1}/dt$, etc.

One can show that

$$T = (1/2)\, M\, |d\mathbf{R}/dt|^2 + (1/2)\, \mu\, |d\mathbf{r}/dt|^2$$

$$= 1/(2M)\, |\mathbf{p_M}|^2 + 1/(2\mu)\, |\, \mathbf{p}_\mu\, |^2$$

The first term on the right is the kinetic energy due to the translational motion of the system & is not of interest. The 2nd term is the kinetic energy due to the internal motion of the system (i.e. vibration, rotation) & is what we want to work with.

$$H = T + V = 1/(2M)\, p_M^2 + 1/(2\mu)\, p_\mu^2 + V(x,y,z)$$

RIGID ROTOR

Consider the two-particle rigid rotor as a model of the rotational motion of a diatomic molecule. It is rigid because it is not allowed to vibrate. The two particles are connected by a massless rod & are at a fixed distance (see Fig 6.2):

$V = 0$ --no potential energy

$H = H_{trans} + H_{rot}$

$$= 1/(2M)\, p_M^2 + 1/(2\mu)\, p_\mu^2$$

Since we are not interested in translational energy, just solve the rotational part for the rotational energy. Set up the problem in relative spherical polar coordinates, rather than Cartesians. Essentially, this means we have a particle of mass μ constrained to move on the surface of a sphere of radius d.

Remember: when H is a sum of non-interacting terms, E is a sum of corresponding terms, & ψ is a product of the separate wavefunctions. For the **Rigid Rotor**

$$H_{rot} = 1/(2\mu)\, p_{\mu}^{2} = - \underline{h}^{2}/(2\mu)\, \nabla^{2}$$

We could use relative Cartesian coordinates, but the mathematics is much simpler if we use relative spherical polar coordinates. Since the particles are constrained to be distance d apart, r = d = constant and ψ depends only on θ & ϕ. Since

$$\nabla^{2} = \partial^{2}/\partial r^{2} + (2/r)\, \partial/\partial r - L^{2}/(r^{2}\, \underline{h}^{2}),$$

then $\nabla^{2}\, \psi\, (\theta,\phi) = 0 - L^{2}/(r^{2}\, \underline{h}^{2})\, \psi\, (\theta,\phi).$

$H_{rot}\, \psi = E\, \psi \Rightarrow \qquad 1/(2\mu)\, L^{2}/d^{2}\, \psi = E\, \psi$

But we already know the eigenfunctions of L^{2}--the spherical harmonics, $Y^{m}_{l}(\theta, \phi)$. So

$$\psi = Y^{m}_{l}(\theta, \phi).$$

Use a different symbol, J, to indicate rotational states:

J = rotational quantum number= quantum number for the total rotational angular momentum

M = quantum number for the z-component of the total rotational angular momentum

$$L^{2}\, Y^{M}_{J}(\theta, \phi) = J\, (J+1)\, \underline{h}^{2}\, Y^{M}_{J}(\theta, \phi)$$

Therefore

$$J(J+1)\,\underline{h}^2/(2\mu\, d^2)\,\psi = E\,\psi \;\Rightarrow$$

$$J(J+1)\,\underline{h}^2/(2\mu\, d^2) = E \qquad J = 0,1,2,\ldots$$

We can give the energy levels of the rigid rotor in terms of the moment of inertia of the two-particle system. The moment of inertia of a system of N particles about a particular axis is

$$I = \sum_{I=1}^{N} m_i\, \rho_i^2$$

where m_i = mass of i-th particle

ρ_i = distance from i-th particle to the axis perpendicular to the line connecting the particles

For the rigid rotoor, choose the axis to pass through the center of mass. Then for the chosen axis

$$I = m_1\rho_1^2 + m_2\rho_2^2 = m_1 m_2/(m_1 + m_2)\,(\rho_1^2 + \rho_2^2) = \mu d^2$$

So $E = J(J+1)\,\underline{h}^2/(2I) \qquad J = 0,1,2\ldots$

Note: The Energy depends only on the total angular momentum quantum number J & not on the z-component

Essentially, E_J of the rigid rotor is the part of the rotational kinetic energy obtained by fixing the interatomic distance R at the equilibrium distance, R_e. As with the Harmonic Oscillator, one can obtain corrections to E_J

Selection Rules

The molecule must have a permanent electric dipole moment, μ:

$<\mu>$ is not equal to zero for the Rigid Rotor if Δ **J = $\underline{+}$ 1**

Absorption from state J: $\Delta E = h\,\nu = E_{J+1} - E_J$

$= \underline{h}^2/\,(2I)\ \{\ (J+1)\,(J+2) - J\,(J+1)\ \}$

$= \underline{h}^2/\,(2I)\ \{\ (J+1)\,(J+2) - J\ \}$

$= \underline{h}^2/\,(2I)\ \{\ 2(J+1)\ \}$

$\nu = \Delta E\,/\,h = \underline{h}^2/\,(2I)\ \{\ 2(J+1)\ \}/h = B_e\ \ 2(J+1)$,

where B_e is the rotational constant $\underline{h}^2/\,(h2I_e)$

The rotational absorption spectrum of a diatomic molecule consists of a series of equally spaced lines:

$J' \rightarrow J''$	ν	$\Delta\nu$
$0 \rightarrow 1$	$2\ B_e\ (0+1) = 2\ B_e$	
		$2\ B_e$
$1 \rightarrow 2$	$2\ B_e\ (1+1) = 4\ B_e$	
		$2\ B_e$
$2 \rightarrow 3$	$2\ B_e\ (2+1) = 6\ B_e$	

etc.

Emission from state J: $\Delta E = h\nu = E_J - E_{J-1}$

$$= \underline{h}^2/(2I)\ \{ J(J+1) - (J-1)(J-1+1) \}$$

$$= \underline{h}^2/(2I)\ \{ J(J+1 - J + 1)\}$$

$$= \underline{h}^2/(2I)\ \{ 2J \}$$

$$\nu = \Delta E / h = \underline{h}^2/(2I)\ \{ 2J \}/h = B_e\ 2J$$

The rotational emission spectrum of a diatomic molecule consists of a series of equally spaced lines:

$J' \rightarrow J''$	ν	$\Delta\nu$
$1 \rightarrow 0$	$2\ B_e$	
		$2\ B_e$
$2 \rightarrow 1$	$4\ B_e$	
		$2\ B_e$
$3 \rightarrow 2$	$6\ B_e$	

The rotational spectra occur in the microwave region.

Example: By measuring the spacing of the rotational lines, get B_e, then calculate I_e & R_e. For NO, $\Delta\nu$, the separation of rotational lines is 102.1690 kMHz or 102.1690×10^9Hz

$$\Delta\nu = 2\ B_e$$

$$B_e = \Delta\nu / 2 = 51.0854 \text{ kMHz} = \underline{h}^2 / (h2I_e)$$

So, $I_e = \underline{h}^2 / (h2B_e)$

$= (1.05459 \text{ x } 10^{-34}\text{ Js})^2/2\ (6.626\text{x}10^{-34}\text{ Js})\ (51.0845\text{x}10^9\text{ s}^{-1})$

$= (1.05459)^2\text{x}10^{-68}\text{ Js}^2/2\ (6.626)\ (51.0845)$; $\quad \text{J s}^2 = \text{kg m}^2$

$= 1.6436\text{x}10^{-80}\text{ kg m}^2\ (10^3\text{g/kg})\ (10^{10}\text{A/m})^2\ (6.023\text{x}10^{23}\text{amu/g})$;

A = Angstrom

$= 1.6436\text{x}6.023\text{x}10^{-34}\text{ amu A}^2$

$I_e = \mu\ d^2 = \mu\ R_e^2$

$R_e = (I_e / \mu)^{1/2}$

μ = reduced mass
$= (14.00307)(15.99491)/(14.00307 + 15.99491)$ amu

$R_e = 1.15108$ A

Diatomic Rotation-Vibration Spectra

At high resolution, a peak corresponding to a vibrational transition is made up of many individual lines (rotational fine structure) because J changes simultaneously with v. If one neglects the interaction between vibrational & rotational motions, such as the distortion caused by centrifugal force & the dependence of the moment of inertia on the vibrational state, then one can approximate the system by a

Rigid Rotor Harmonic Oscillator:

$$E_{nucl} = E_{vib} + E_{rot}$$

$$= (v + 1/2)\, h\nu + J\,(J + 1)\, \underline{h}^2/(2I)$$

The same selection rules apply: $\Delta v = \underline{+}1$, $\Delta J = \underline{+}1$

But, there are 4 possible combinations:

$\Delta v = 1$ $\Delta J = 1$ or -1
$\Delta v = -1$ $\Delta J = 1$ or -1

So each set of absorption or emission lines associated with a *single* vibrational transition contains two groups, or “branches”, of lines for rotational transitions:

P branch for $\Delta J = -1$, decreasing rotational energy
R branch for $\Delta J = 1$, increasing rotational energy

The intensity of the absorption line is proportional to the population of that state, i.e. the # of molecules with that particular energy:

$$N_i = g_i\, e^{-Ei/kT}$$

THE HYDROGEN ATOM - a familiar problem

Bohr Model: Postulates that an electron moves in orbits around the nucleus like planets around the sun. However, this is physically incorrect because it violates the Uncertainty Principle because both the position and momentum of the electron would be specified. The Bohr Model could only predict the line spectrum of H. It failed for atoms with more than one electron.

We will treat the H atom with all the techniques of quantum mechanics to come up with an approach that is applicable to many electron atoms & molecules. And yet, the H atom is still a ***Model Problem.*** It is the only atom whose energy levels can be found without making approximations to the wavefunction. Since it is a one-electron problem, the wavefunction can be solved exactly, yielding atomic orbitals. These types of wavefunctions are used as a first approximation for many electron systems. In many electron systems there are complicated electron-electron repulsions which disallow using an exact functional form for the wavefunction.

The Hydrogenlike Atom (H, He^+, Li^{+2})

The nucleus has a charge of +Ze, Z = atomic #
The electron has a charge of -e

For a two particle system with positive & negative particles interacting according to Coulomb's Law:

$$\mathbf{F} = - Z (e')^2/r^2 (\mathbf{r}/r),$$

where e' = proton charge in statcoulombs = $e/\sqrt{(4\pi\varepsilon_o)}$
e= proton charge in coulombs
ε_o = permitivity of a vacuum = 8.85419 x 10^{-12} C^2/Nm^2

Also $\mathbf{F} = -[dV(r)/dr]\ (\mathbf{r}/r)$

So, combining both expressions gives

$$dV(r)/dr = -\ Z\ (e')^2/r^2$$

Solving for V(r):

$$V(r) = -Z\ (e')^2 \int dr/r^2 = -\ Z\ (e')^2/r$$

(Choose an integration constant = 0 to have V(∞) = 0)

In general, for two charges Q_1 & Q_2 separated by distance r_{12},

$$V = Q_1\ Q_2/\ r_{12} \qquad \text{Coulomb's Law}$$

Since the potential energy depends only on the relative coordinate, r_{12}, the problem can be reduced from a two-particle problem to two one-particle problems, as before.

One particle has the total mass M & contributes a term to the Hamiltonian which just gives the translational kinetic energy:

$$p_M{}^2/(2M)$$

Since we are interested in the internal (electronic))states of the atom, we can ignore this term. It will only add a constant.

Focus on the Hamiltonian for Internal Motion:

This Hamiltonian depends on the kinetic energy of the particle with the reduced mass of the system, as well as the potential energy:

$$H = p_\mu{}^2/(2\mu) + V(r)$$

$$= - \underline{h}^2/(2\mu)\ \nabla^2 - Z\ (e')^2/r$$

Since V depends only on r, this is a one-particle central force problem. Apply the Separation of Variables Technique:

$$\psi\ (r,\theta,\phi) = R(r)\ Y_l^m\ (\theta,\phi) \qquad l = 0, 1, 2, ...;\ |m| < l$$

$$\nabla^2 = \partial^2/\partial r^2 + (2/r)\ \partial/\partial r\ - 1/(r^2\underline{h}^2)\ L^2$$

$$L^2\ Y_{\mathrm{l}}^m\ (\theta,\phi) = l\ (l{+}1)\ \underline{h}^2\ Y_l^m\ (\theta,\phi)$$

So $\nabla^2\ \psi\ (r,\theta,\phi) = Y_l^m\ (\theta,\phi)\ (\partial^2 R/\partial r^2 + (2/r)\ \partial R/\partial r)$

$$- R/(r^2\underline{h}^2)\ L^2\ Y_l^m\ (\theta,\phi)$$

$$= Y_l^m\ (\theta,\phi)\ (\partial^2 R/\partial r^2 + (2/r)\ \partial R/\partial r)$$

$$- R/(r^2\underline{h}^2)\ [l(l{+}1)\ \underline{h}^2]\ Y_l^m\ (\theta,\phi)$$

$$= Y_l^m\ (\theta,\phi)(\partial^2/\partial r^2 + (2/r)\ \partial/\partial r) - [l(l{+}1)]/r^2)R$$

$H\psi = E\psi \;\Rightarrow$

$$Y_l^m(\theta,\phi)\,\{-\,\underline{h}^2/(2\mu)\,[\partial^2/\partial r^2 + (2/r)\,\partial/\partial r)$$

$$-\,[l(l+1)]/r^2] - Z\,(e')^2/r\}R(r) = Y_l^m(\theta,\phi)\,E\,R(r)$$

or, dividing through by $Y_l^m(\theta,\phi)$,

$$\{-\,\underline{h}^2/(2\mu)\,[\partial^2/\partial r^2 + (2/r)\,\partial/\partial r) - [l(l+1)]/r^2] - Z\,(e')^2/r\}\;R(r)$$

$$= E\,R(r)$$

or, dividing through by $1/\{-\,\underline{h}^2/(2\mu)\}$,

$$\{\partial^2/\partial r^2 + (2/r)\,\partial/\partial r) - [l(l+1)]/r^2 - Z\,(e')^2/r\}\;R(r)$$

$$= E\,R(r)$$

$$\{\partial^2/\partial r^2 + (2/r)\,\partial/\partial r) - [l(l+1)]/r^2 + (2\mu/\,\underline{h}^2)\,Z\,(e')^2/r\}\;R(r)$$

$$= -\,(2\mu/\underline{h}^2)\,E\,R(r)$$

To simplify the expression, define $a = \underline{h}^2/[\mu(e')^2]$

so that $\mu/\underline{h}^2 = 1/[a(e')^2]$

Then

$$\{\partial^2/\partial r^2 + (2/r)\,\partial/\partial r) - [l(l+1)]/r^2 + (2/a)\,Z/r\}\;R(r)$$

$$= -\,2/[a(e')^2]\,E\,R(r)$$

$$R'' + (2/r)\,R' + \{2/[a(e')^2]\,E - (2/a)\,Z/r - [l(l+1)]/r^2\}R = 0$$

Solve by a Power Series Solution:

Choose a form that will give a two-term (rather than a three-term or greater) recursion relationship. We can find the form from the behavior of R as $r \Rightarrow \infty$:

$$R'' + \{2E /[a(e')^2]\}\ R = 0$$

This is a linear homogeneous eq. with constant coefficients of the form:

$$Y'' + P\ Y' + Q\ Y = 0, \quad P = 0, \quad Q = 2E /[a(e')^2]$$

Solving the auxiliary eq.:

$$s^2 + Ps + Q = 0$$

$$s^2 + Q = 0 \qquad \Rightarrow \quad s = \pm\sqrt{(-Q)} = \pm\sqrt{-\{2E /[a(e')^2]\}}$$

So $R = c_1 \exp [\sqrt{-\{2E /[a(e')^2]\}}r]$

$$+ c_2 \exp [-\sqrt{-\{2E /[a(e')^2]\}}r]; \qquad \exp\ [f(r)] = e^{f(r)}$$

Continuum States: E > 0

If $E > 0$, $\pm\sqrt{-\{2E /[a(e')^2]\}} < 0$ and

$$R \approx c_1 \exp [i\sqrt{\{2E /[a(e')^2]\}}r]$$

$$+ c_2 \exp [-i\sqrt{\{2E /[a(e')^2]\}}r]$$

behaves as a free particle, i.e. it oscillates. There are no conditions on E since R is finite for all E's. So all the values of E are allowed, i.e. continuous values of E

R is the radial part of a continuum eigenfunction, Y_l^m is the angular part. The wavefunction is not normalized in the usual sense, as with a free particle.

Bound States: $E < 0$

$$R \approx c_1 \exp [\surd\{-2E /[a(e')^2]\}r]$$

$$+ c_2 \exp [-\surd\{-2E /[a(e')^2]\}r]$$

For R to be finite as $r \Rightarrow \infty$, $c_1 = 0$. Then

$$R \approx c_2 \exp [-\surd\{-2E /[a(e')^2]\}r]$$

$$= c_2 \exp [-c\ r], \qquad c = \surd\{-2E /[a(e')^2]$$

Choose a form for R for all regions (not just large r) to be:

$$R(r) = e^{-cr} K(r)$$

where K(r) is a power series in r. Note that K(r) will have to be truncated in order to have the appropriate asymptotic form of R.

So $R' = -c\ e^{-cr} K(r) + e^{-cr} K'(r) = (-cK + K')\ e^{-cr}$

and $R'' = -c\ e^{-cr} (-cK + K') + (-cK' + K'')\ e^{-cr}$

$$= e^{-cr} (c^2K - 2cK' + K'')$$

Substitute these expressions into
$R'' + (2/r)\ R' + \{2/[a(e')^2]\ E + (2/a)\ Z/r - [l(l+1)]/r^2\}R = 0$

or $R'' + (2/r)\ R' + \{-c^2 + (2/a)\ Z/r - [l(l+1)]/r^2\}R = 0$

or $e^{-cr} (c^2K - 2cK' + K'') + (2/r)\ (-cK + K')\ e^{-cr}$

$$+ \{-c^2 + (2/a)\, Z/r - [l(l+1)]/r^2\}\, e^{-cr}\, K(r) = 0$$

Divide through by e^{-cr} to get an eq. in K:

$$K'' + K' (-2c + 2/r) + K (c^2 - 2c/r - c^2 + 2Z/(ar)$$

$$- [l(l+1)]/r^2) = 0$$

Multiply by r^2

$$K''r^2 + K' (-2c\, r^2 + 2r) + K\{(- 2cr + 2Z/a)r - l(l+1)\} = 0$$

Let $K(r) = r^s M(r)$, where $M(r) = \sum_{j=0}^{\infty} b_j r^j$

Then $K' = sr^{s-1} M + r^s M'$,

$$K'' = s(s-1)\, r^{s-2} M + s\, r^{s-1} M' + s\, r^{s-1} M' + r^s M''$$

$$= s(s-1)\, r^{s-2} M + 2\, s\, r^{s-1} M' + r^s M''$$

Substitute into the Eq. for K:

$$r^2[s(s-1)\, r^{s-2} M + 2\, s\, r^{s-1} M' + r^s M'']$$

$$+ (2r - 2cr^2)\, [sr^{s-1} M + r^s M']$$

$$+ \{(- 2cr + 2Z/a)r - l(l+1)\}\, r^s M = 0$$

Rearrange:

$$M''\, r^{s+2} + M' [2sr^{s+1} + (2r - 2cr^2)r^s]$$

$$+ M[s(s-1)r^s + (2r - 2cr^2)sr^{s-1} + \{(- 2c + 2Z/a)r - l(l+1)\}\, r^s\,] = 0$$

$= r^s \{M''r^2 + M' [2sr + 2r - 2cr^2]$

$+ M[s^2 - s + 2s - 2csr + (-2c + 2Z/a)r - l(l+1)]\}$

Or $M''r^2 + M' [(2s+1)r - 2cr^2]$

$+ M[s(s+1) + 2(Z/a - c - cs)r - l(l+1)] = 0$

To find s, consider the behavior at r = 0:

$$M(r) = \sum_{j=0}^{\infty} b_j r^j = b_0 + b_1 r + b_2 r^2 + b_3 r^3 + \ldots$$

$M(r=0) = b_0$

$M'(r) = b_1 + 2b_2 r + 3b_3 r^2 + \ldots$

$M'(r=0) = b_1$

$M''(r) = 2b_2 + 6b_3 r + \ldots$

$M''(r=0) = 2b_2$

So, the only term not multiplied by r in the eq. for M is:

$[s(s+1) - l(l+1)]M = [s(s+1) - l(l+1)]\, b_0$, at r=0

Since b_0 is not equal to 0, then must have $s(s+1) - l(l+1) = 0$

or $s = l$ or $-(l+1)$

These roots correspond to two linearly independent solutions. Which ones can we use?

$$R(r) = e^{-cr} K(r) = e^{-cr} r^s \sum_{j=0}^{\infty} b_j r^j$$

Since s was determined from the condition r = 0, consider R for small r:

$$e^{-cr} = 1 - cr + c^2r^2/2 - .... \Rightarrow 1 \text{ as } r \Rightarrow 0$$

So $R(r) \Rightarrow r^s\, b_0$ as $r \Rightarrow 0$ for $s = l, -l-1$

$$= r^l\, b_0 = 0 \text{ at } r = 0$$

$$= b_0\, /r^{l+1} \Rightarrow \infty \text{ at } r = 0$$

So let s = *l* and determine R by solving for a ***Recursion Relation*** for the b_j's

$$R(r) = e^{-cr}\, r^l\, M(r)$$

Substitute s = *l* into

$$M''r^2 + M'\ [(2s+1)r\ - 2cr^2]$$

$$+ M[s(s+1) + 2(Z/a - c - cs)r - l(l+1)] = 0$$

$$M''r^2 + M'\ [(2l+1)r\ - 2cr^2]$$

$$+ M[l(l+1) + 2(Z/a - c - cl)r - l(l+1)] = 0$$

$$M''r^2 + M'\ [(2l+1)r\ - 2cr^2] + M2[Z/a - c(l + 1)]r = 0$$

$$M''r + M'\ [(2l+1)\ - 2cr] + M2[Z/a - c(l + 1)] = 0$$

Rewrite the eq. as a factor {...} times r^j in order to get the recursion relation:

$$M(r) = \sum_{j=0}^{\infty} b_j r^j = b_0 + b_1 r + b_2 r^2 + b_3 r^3 + ...$$

$$M'(r) = b_1 + 2b_2 r + 3b_3 r^2 + \ldots$$

$$= \sum_{j=1}^{\infty} j b_j r^{j-1} \qquad \text{(use as coefficient of the } r^1 \text{ term)}$$

$$= \sum_{j=0}^{\infty} j\, b_j\, r^{j-1}$$

Let j = k+1 & rewrite the summation

$$= \sum_{k=0}^{\infty} (k+1)\, b_{k+1}\, r^k$$

But j & k are dummy indices, so

$$M'(r) = \sum_{j=0}^{\infty} (j+1)\, b_{j+1}\, r^j \text{ (use as coefficient of the } r^0 \text{ term)}$$

$$M''(r) = 2b_2 + 6b_3 r + \ldots$$

$$= \sum_{j=2}^{\infty} j(j-1)\, b_j\, r^{j-2}$$

$$= \sum_{j=1}^{\infty} j(j-1)\, b_j\, r^{j-2}$$

$$= \sum_{j=0}^{\infty} j(j-1)\, b_j\, r^{j-2}$$

Let j = k+1 & rewrite the summation

$$M''(r) = \sum_{k=0}^{\infty} (k+1)k\, b_{k+1}\, r^{k-1} \qquad \text{(use as coefficient of the } r^1 \text{ term)}$$

But j & k are just dummy indices, so could write the summation as

∞

$$M''(r) = \sum_{j=0} (j+1)j\, b_{j+1}\, r^{j-1}$$

Substitute these power series into

$$r M'' + 2(l + 1 - cr) M' + 2 (Z/a - c - cl) M = 0$$

$$r \sum_{j=0}^{\infty} (j+1)j\, b_{j+1}\, r^{j-1} + 2(l + 1) \sum_{j=0}^{\infty} (j+1)\, b_{j+1}\, r^{j} - 2cr \sum_{j=0}^{\infty} j\, b_j\, r^{j-1}$$

$$+ 2[Z/a - c(l+1)] \sum_{j=0}^{\infty} b_j r^j = 0$$

$$= \sum_{j=0}^{\infty} [(j+1)j\, b_{j+1} r^j + 2(l + 1)(j+1)\, b_{j+1}\, r^j - 2c\, j\, b_j r^j + 2[Z/a -$$

$$c(l+1)]b_j r^j]$$

Get a Recursion Relationship for b_{j+1} in terms of b_j by setting the coefficient of $r^j = 0$:

$$0 = [j(j+1) + 2(l+1)(j+1)]\, b_{j+1} + [-2cj + 2(Z/a-c(l+1)]\, b_j$$

$$b_{j+1} /b_j = 2\, [cj - Z/a + c(l+1)]/[j(j+1) + 2(l+1)(j+1)]$$

How does R(r) behave as $r \Rightarrow \infty$?

(1) Consider the behavior of the series for large r (i.e. terms in large j will dominate)

$$b_{j+1} /b_j = 2\, [- Z/a + c(j+l+1)]/[j(j+1) + 2(l+1)(j+1)]$$

$$\Rightarrow \quad 2cj/j^2 = 2c/j \qquad \text{for large } j$$

(2) Consider the behavior of the power series e^{2cr} for large r. Look at the successive terms:

$$e^{2cr} = 1 + 2cr + ... + (2c)^j r^j/j! + (2c)^{j+1} r^{j+1}/(j+1)! + ...$$

(j+1)st-coefficient/j-th coefficient $=[(2c)^{j+1}/(j+1)!]/[(2c)^{j}/j!]$

$= 2c\ j!/(j+1)! = 2c/(j+1) \Rightarrow 2c/j$ for large j

So the power series M(r) behaves as e^{2cr} for large r

$M(r) \Rightarrow e^{2cr}$ for large r

So $R(r) \approx e^{-cr} r^{l} e^{2cr} = r^{l} e^{cr} \Rightarrow \infty$ as $r \Rightarrow \infty$

So the power series must be truncated after a finite # of terms (choose k). As with the Harmonic Oscillator, truncation of the power series results in energy quantization.

If the series is truncated at k,

$b_{k+1} = 0 = b_{k+2} = b_{k+3}, \ldots.$

Since b_k is not equal to zero, the coefficient of b_k in the power series must be set equal to zero in order to make that term zero (& all higher b_k's zero):

$2[ck - Z/a + c(l+1)] = 0$

$c(k + l + 1) = Z/a \qquad k = 0,1,2,3,\ldots$

Define a new quantum number:

$n = k + l + 1 \qquad n = 1,2,3,\ldots$

$n-1 = k+l \qquad k = 0,1,2,3,\ldots$

So $n-1 \geq l$ (equal to l when $k = 0$)

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

So $cn = Z/a$ $\quad c^2n^2 = (Z/a)^2$ $\quad c = \sqrt{\{-2E /[a(e')^2]\}}$

$-2E\, n^2 /[a(e')^2] = (Z/a)^2$

Solve for E: $\quad E = -[Z^2/n^2]\,[(e')^2/(2a)]$ $\quad a = \underline{h}^2/[\mu(e')^2]$

$E = -[Z^2/n^2]\,[(e')^4\mu/(2\underline{h}^2)$

As $n \Rightarrow \infty$, $E \Rightarrow 0$. See Fig. 6.6
$E \leq 0$ Discrete States, $E > 0$, Continuum States.

ν = frequency of absorption or emission = c/λ

$1/\lambda$ = wavenumber = $\nu/c = \Delta E/hc$, $\Delta E = E_2 - E_1$

$= -Z^2(e')^2/(hc2a)[1/n_2^2 - 1/n_1^2]$

$= Z^2(e')^2/(hc2a)[1/n_1^2 - 1/n_2^2]$

For $Z = 1$, $R = (e')^2/(hc2a) = 109{,}677\ \text{cm}^{-1}$

= Rydberg constant for H (Balmer obtained by fitting)

Are the Hydrogen Atom levels degenerate?

The energy depends only on n, but each state ψ depends on n, l, m

$n = 1,2,3,...$
$l = 0,1,...(n-1)$ n values of l
$m = -l, -l+1,...(l-1),l$ $2l+1$ values of m

So each bound state has degeneracy = $\sum_{l=0}^{n-1} (2l+1)$

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

Each continuum state is infinitely degenerate because there are no restrictions on l.

Hydrogen Atom Bound State Wavefunctions and Probability Densities

We found that $R(r) = e^{-cr} r^l M(r)$ with $M(r) = \sum_{j=0}^{\infty} b_j r^j$

But we had to truncate M after term j = k, where $k = n - l - 1$

So $M(r) = \sum_{j=0}^{n-l-1} b_j r^j$

We also found that $c = Z/(na)$ & $a = \underline{h}^2/[\mu\,(e')^2]$

So

$$R_{nl}(r) = r^l e^{-[Zr/(na)]} \sum_{j=0}^{n-l-1} b_j r^j$$

and $$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)\, Y_l^m(\theta, \phi)$$

$$= R_{nl}(r)\, S_{lm}(\theta)\, e^{im\phi} \sqrt{(2\pi)}$$

Nodes of R_{nl}:

$R_{nl} = 0 \qquad r = \infty$
$\quad = 0 \qquad r = 0, \quad l$ not equal to 0
$\quad = 0 \qquad M(r) = 0$

M(r) is a polynomial of degree (highest power of r) n-*l*-1

So there are (n-*l*-1) roots or nodes of this polynomial

Typical energy units:

1 eV (electron volt) = 1.6022×10^{-19} J = 1.6022×10^{-12} erg

Find the Bohr radius (radius of electron in first Bohr orbit, a_o) **:**

For the ground state of the H atom, $E_1 = - 13.60$ eV
(This is the ionization energy)

Reduced mass = $\mu_H = m_p\, m_e/(m_p + m_e)$,

where m_p = mass of proton, m_e = mass of electron;

$m_p + m_e \approx m_p$ so $\mu_H = m_e$

Then $a = \underline{h}^2/[\mu\,(e')^2] \Rightarrow a_o = \underline{h}^2/[\,m_e\,(e')^2] = 0.529$ Angstroms

(But Bohr considered the electron to be confined to a circle. This is impossible, according to the Uncertainty Principle.)

Hydrogen-Like Atom Wavefunctions:

$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\, Y_l^m(\theta,\phi) = R_{nl}(r)\, S_{l,m}(\theta)\, e^{im\phi}/\sqrt{(2\pi)}$

See Table 5.1 for the values of $S_{l,m}(\theta)$, Table 6.1 for $R_{nl}(r)$

Ground State Wavefunction: n=1, *l*=0, m=0

$Y_0^0(\theta,\phi) = S_{0,0}(\theta)\, e^0/\sqrt{(2\pi)} = (\sqrt{2}/2)\cdot 1\cdot /\sqrt{(2\pi)} = 1/\sqrt{(4\pi)}$

$R_{10}(r) = b_0\, e^{-Zr/a}$

Find b_0 by normalization:

$$\int_0^\infty |R_{10}(r)|^2\, r^2\, dr = 1 = |b_0|^2 \int_0^\infty e^{-2Zr/a}\, r^2\, dr$$

$$= |b_0|^2\, 2!/(2Z/a)^3 \Rightarrow b_0 = (2Z/a)^{3/2}/\sqrt{2} = 2\,(Z/a)^{3/2}$$

Therefore,

$$R_{10}(r) = 2\,(Z/a)^{3/2}\, e^{-Zr/a}$$

And

$$\psi_{100}(r,\theta,\phi) = 2\,(Z/a)^{3/2}\, e^{-Zr/a}\sqrt{(4\pi)} = (Z/a)^{3/2}\, e^{-Zr/a}\sqrt{\pi}$$

Old spectroscopic notation relates the values of *l* to letters:

l = 0(s), 1(p), 2(d), 3(f), 4(g), 5(h), 6(i), 7(k).... (no j)

For n=2, $l = 0,1$. For $l = 0$, m = 0 (ψ_{2s});

For $l = 1$, m= -1 (ψ_{2p-1} or ψ_{21-1}), 0 (ψ_{2p0} or ψ_{210}), 1 (ψ_{2p+1} or ψ_{211})

Using Tables 5.1 & 6.1,

$$\psi_{21-1}(r,\theta,\phi) = R_{2p}(r)Y_1^{-1}(\theta,\phi)$$

$$= 1/(2\sqrt{6})\,(Z/a)^{5/2}\, r\, e^{-Zr/2a}\, 1/\sqrt{(2\pi)}\,\sqrt{3/2}\,\sin\theta\, e^{-i\phi}$$

$$= 1/(8\sqrt{\pi})\,(Z/a)^{5/2}\, r\, e^{-Zr/2a}\,\sin\theta\, e^{-i\phi}$$

Probability Density

The probability of finding the electron between r+dr, θ+dθ, and ϕ+dϕ is

$$|\psi|^2\, d\tau = |R_{nl}(r)|^2\, r^2\, dr\, |Y_l^m(\theta,\phi)|^2 \sin\theta\, d\theta\, d\phi,$$

where $d\tau = r^2\, dr \sin\theta\, d\theta\, d\phi$. If we just consider the probability of finding the electron in the shell r+dr with no restrictions on θ & ϕ, then we can integrate over θ & ϕ to get the ***Radial Distribution Function*** (i.e. the probability density for the radial part of the wavefunction):

$$\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta\, |Y_l^m(\theta,\phi)|^2\, |R_{nl}(r)|^2\, r^2\, dr = |R_{nl}(r)|^2\, r^2\, dr$$

since the Spherical Harmonics are normalized. The Radial Distribution Functions for n = 1, 2, 3 are plotted in Fig. 6.8

The function a $[R_{nl}(r)]^2 r^2 dr$ is plotted in Fig. 6.9. Note that the maximum in the 1s radial distribution function, $a[R_{10}(r)]^2r^2$, occurs at $r = a$. How could you prove this mathematically? (Find the value of r for which $\partial/\partial r[a[R_{10}(r)]^2 r^2] = 0$.)

Construct Real Wavefunctions

Since ψ_{nlm} goes as $e^{im\phi}$, the hydrogenlike ψ's are imaginary. For convenience, it is easier to use real wavefunctions. We can construct the real wavefunctions by taking certain linear combinations of the imaginary wavefunctions. They will still be an eigenfunction of the Hamiltonian operator with the same eigenvalue. We already proved that

If $H\,\psi_N = E\,\psi_N$, $N = 1,\ldots,m$

then $H\,(\psi_1 + \ldots + \psi_m) = E\,(\psi_1 + \ldots + \psi_m)$.

In other words, a linear combination of eigenfunctions of an operator will also be an eigenfunction of the operator with the same eigenvalue.

From Tables 5.1 & 6.1

$\psi_{2p1} = 1/(8\sqrt{\pi})\ (Z/a)^{5/2}\ r\ e^{-Zr/(2a)} \sin\theta\ e^{i\phi}$

$\psi_{2p-1} = 1/(8\sqrt{\pi})\ (Z/a)^{5/2}\ r\ e^{-Zr/(2a)} \sin\theta\ e^{-i\phi}$

$2\cos\phi = e^{i\phi} + e^{-i\phi}$

So $\psi_{2p1} + \psi_{2p-1} = 1/(8\sqrt{\pi})\ (Z/a)^{5/2}\ r\ e^{-Zr/(2a)} \sin\theta\ (e^{i\phi} + e^{-i\phi})$

$= 1/(8\sqrt{\pi})\ (Z/a)^{5/2}\ r\ e^{-Zr/(2a)} \sin\theta\ 2\cos\phi$

$= 1/(4\sqrt{\pi})\ (Z/a)^{5/2}\ r\ e^{-Zr/(2a)} \sin\theta\ \cos\phi$

Remember $x = r \sin\theta \cos\phi$. So $\psi_{2p1} + \psi_{2p-1}$

$= 1/(4\sqrt{\pi})\ (Z/a)^{5/2}\ e^{-Zr/(2a)}\ x$

Define $\psi_{2px} = 1/\sqrt{2}\ (\psi_{2p1} + \psi_{2p-1})$

$= 1/[4\sqrt{(2\pi)}]\ (Z/a)^{5/2}\ e^{-Zr/(2a)}\ x$,

where $1/\sqrt{2}$ is a normalization factor. Prove that ψ_{2px} is normalized. In the next chapter, we will see that the Spherical Harmonics are orthonormal or orthogonal functions. That is

$\int Y_l^m\ Y_{l'}^{m'}\ d\tau = \delta_{ll'}\delta_{mm'}$, where $\delta_{ll'}=0$ unless $l=l'$

So if $l=1$ & $l'=-1$, the integral is zero.

$\int |\psi_{2px}|^2\ d\tau = \int \psi_{2px}^*\ \psi_{2px}\ d\tau$

$$= \int 1/\sqrt{2}\,(\psi_{2p1} + \psi_{2p-1})^{*}\, 1/\sqrt{2}\,(\psi_{2p1} + \psi_{2p-1})\, d\tau$$

$$= 1/2\,(\int \psi_{2p1}^{*}\,\psi_{2p1}\, d\tau + \int \psi_{2p1}^{*}\,\psi_{2p-1}\, d\tau + \int \psi_{2p-1}^{*}\,\psi_{2p1}\, d\tau$$

$$+ \int \psi_{2p-1}^{*}\,\psi_{2p-1}\, d\tau)$$

The first & fourth terms, $\int \psi_{2p1}^{*}\,\psi_{2p1}\, d\tau$ & $\int \psi_{2p-1}^{*}\,\psi_{2p-1}\, d\tau$, are equal to 1 because the hydrogenlike wavefunctions are normalized. The second & third terms are equal to 0 because they contain spherical harmonics with different m values (+1 & -1) & $\delta_{mm'}=0$ unless m=m'. One can show this by looking at the integral over ϕ for m= +1 & -1:

$$\int_0^{2\pi} (e^{-i\phi})^{*}(e^{i\phi})d\phi = \int_0^{2\pi} e^{2i\phi}\, d\phi$$

$$= 1/2\ \int_0^{4\pi} e^{iy}\, dy = 1/2\ e^{iy} \Big|_0^{4\pi} = 1/2\,(\cos y + i \sin y)\ \Big|_0^{4\pi}$$

$$= 1/2\,(\cos 4\pi + i\cdot 0 - \cos 0 - i\cdot 0) = 1/2\,(1-1) = 0$$

So

$$\int\ |\psi_{2px}|^2\, d\tau = 1/2\,(\ 1 + 0 + 0 + 1) = 1$$

Other real wavefunctions for n=2:

$$\psi_{2py} = 1/(i\sqrt{2})\,(\psi_{2p1} - \psi_{2p-1})$$

$$= 1/(4\sqrt{(2\pi)})\,(Z/a)^{5/2}\, r \sin\theta \sin\phi\ e^{-Zr/(2a)}$$

$$= 1/(4\sqrt{(2\pi)})\,(Z/a)^{5/2}\, y\ e^{-Zr/(2a)}$$

$$\psi_{2pz} = \psi_{2p0} = 1/\sqrt{\pi}\,(Z/a)^{5/2}\, z\ e^{-Zr/(2a)}$$

Table 6.2 gives the real wavefunctions for n=1,2,3

Are the real wavefunctions eigenfunctions of L^2 & L_z?

$$L^2\,\psi_{2p-1} = l(l+1)\hbar^2\psi_{2p-1} = 2\,\hbar^2\psi_{2p-1}$$

$$L^2\,\psi_{2p1} = l(l+1)\hbar^2\psi_{2p1} = 2\,\hbar^2\psi_{2p1}$$

$$L^2\,(\psi_{2p1} + \psi_{2p-1}) = 2\,\hbar^2(\psi_{2p1} + \psi_{2p-1}) \qquad \text{yes}$$

But $L_z\psi_{2p-1} = m\hbar\psi_{2p-1} = -\,\hbar\psi_{2p-1}$

$$L_z\psi_{2p1} = m\hbar\psi_{2p1} = \hbar\psi_{2p1}$$

$$L_z(\psi_{2p1} + \psi_{2p-1}) = \hbar\psi_{2p1} - \hbar\psi_{2p-1} = \hbar\,(\psi_{2p1} - \psi_{2p-1}) \qquad \text{no}$$

Hydrogenlike Orbitals

Fig. 6.14 shows the probability densities for some hydrogen atom states

Fig. 6.13 shows the shapes of some hydrogen atom orbitals. The 2s orbital has one spherical node (not visible); the 3s orbital has two spherical nodes (not visible). The $3p_z$ orbital has a spherical node (dashed line) & a nodal plane (xy plane). The $3d_{z**2}$ has two nodal cones. The $3d_{x**2-y**2}$ orbital has two nodal planes.

The Zeeman Effect

When the hydrogen atom is put into an external magnetic field, a triplet of lines is observed for the 1s → 2p transition, rather than the single line seen in the absence of a magnetic field. This means that, in the presence of the external magnetic field, the 2p state is no longer degenerate.

Magenetic Dipole: The motion of an electron around a closed loop results in a magnetic dipole vector μ of magnitude

$$|\mu| = \mu = iA$$

where i is the current (1 amp = 1 Coul/sec) & A is the area of the loop in square meters. If the loop is circular,

$$A = \pi r^2$$

where r is the radius. The current, i, is equal to

$$i = Qv/(2\pi r)$$

where Q is the charge & v is the velocity. So

$$\mu = iA = [Qv/(2\pi r)]\, \pi r^2 = Qvr/2.$$

For a noncircular loop, the magnetic moment due to orbital motion is

$$\mu_L = Q/2(\mathbf{r} \text{ x } \mathbf{v}).$$

Since L = $\mathbf{r}$ x $\mathbf{p}$ & $\mathbf{p} = m\mathbf{v}$, then

$$\mu_L = Q/(2m)\, \mathbf{L}$$

where the direction of μ & **L** is perpendicular to the plane of motion.

For an electon, $\mu_L = -e/(2m_e)\, \mathbf{L}$,

where -e is the charge on the electron & m_e is the mass of the electron.

Since $|\mathbf{L}| = \underline{h}\sqrt{[l(l+1)]}$, then $|\mu_L| = |-e/(2m_e)\,\mathbf{L}| = |-e|/(2m_e)\;|\mathbf{L}|$

$$= e/(2m_e)\,\hbar\sqrt{[l(l+1)]}.$$

The Bohr magneton is defined by

$$\beta_e = e\hbar/(2m_e) = 9.274\times10^{-24}\ \text{J/T}$$

T=Tesla; 1 Tesla = 1 $NC^{-1}\,m^{-1}\,s$ = 1 N/(amp·m)

So $|\mu_L| = \beta_e\sqrt{[l(l+1)]}$.

The energy of interaction between a magnetic dipole, μ, & an external magnetic field is

$$E_B = -\mu\cdot\mathbf{B} = e/(2m)\,\mathbf{L}\cdot\mathbf{B}.$$

Assume the magnetic field is applied in the z-direction:

$$\mathbf{B} = B\,\mathbf{k}$$

and $E_B = e/(2m)\,(L_x\mathbf{i} + L_y\mathbf{j} + L_z\mathbf{k})\cdot(B\mathbf{k}) = e/(2m)\,L_zB$

$$E_B = (\beta_e/\hbar)\,L_zB$$

So the corresponding Hamiltonian operator for the interaction of the electron with the magnetic field is

$$H_B = (\beta_e/\hbar)\,L_zB.$$

So the Hamiltonian that describes the behavior of the hydrogen atom in the magnetic field is the sum of the Hamiltonian in the absence of the field & H_B:

$$(H + H_B)\,\psi = E\,\psi.$$

Since we know the eigenfunctions of L_z, we know ψ:

$$\psi = R(r)\, Y_l^m(\theta, \phi).$$

$(H + H_B)\, \psi = (H + H_B)\, R(r)\, Y_l^m(\theta, \phi)$

$= H\, R(r)\, Y_l^m(\theta, \phi) + H_B\, R(r)\, Y_l^m(\theta, \phi)$

$H\, R(r)\, Y_l^m(\theta, \phi) = (-Z^2/n^2)\, [(e')^2/(2a)]\, R(r)\, Y_l^m(\theta, \phi)$

$H_B\, R(r)\, Y_l^m(\theta, \phi) = (\beta_e/\underline{h})\, L_z B\, R(r)\, Y_l^m(\theta, \phi)$

$= (\beta_e/\underline{h})\, B\, R(r)\, L_z\, Y_l^m(\theta, \phi)$

$= (\beta_e/\underline{h})\, B\, R(r)\;\; m\underline{h} Y_l^m(\theta, \phi)$

$= \beta_e m\, B\, R(r) Y_l^m(\theta, \phi)$

$(H + H_B)\, \psi = \{(-Z^2/n^2)\, [(e')^2/(2a)] + \beta_e m\, B\}\, R(r) Y_l^m(\theta, \phi)$

So $E = \{(-Z^2/n^2)\, [(e')^2/(2a)] + \beta_e m\, B\}$

For each n, there is a different energy depending on m. This removes the m-fold degeneracy.

In the presence of the magnetic field, the n=2 level (1 line)

$E_{2s} = E_{2p} = E_2 = (-Z^2/4)\, [(e')^2/(2a)]$

is split into 3 levels (3 lines) with

$E_{2p+1} = E_2 + \beta_e B \qquad (m = +1)$

$E_{2p0} = E_{2s} = E_2 \qquad (m = 0)$

$$E_{2p-1} = E_2 - \beta_e B \qquad (m = -1)$$