Setting up the H atom SE

- H atom problem has Coulomb potential in 3D SE with μ = reduced mass of electron

$$i\hbar\frac{\partial\Psi}{\partial t} = E\Psi = -\frac{\hbar^2}{2m}\left(\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2}\right)+V(x,y,z)\Psi$$

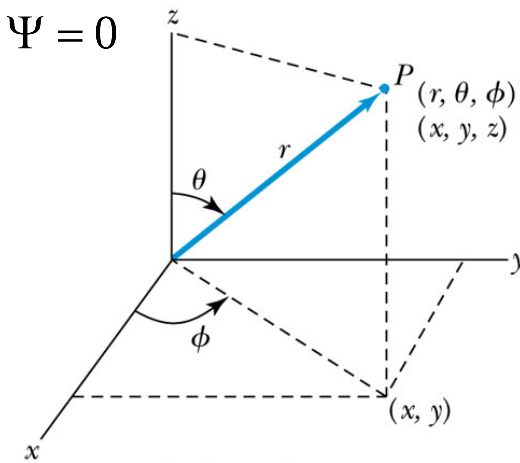
- Better to work in spherical coordinates:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\Psi}{\partial\phi^2}+\frac{2\mu}{\hbar^2}\left(E-V(r)\right)\Psi=0$$

- Try separation of variables:

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

- Work out separate equations For R, Θ, and Φ



$x = r\sin\theta\cos\phi$
$y = r\sin\theta\sin\phi$
$z = r\cos\theta$

$r = \sqrt{x^2+y^2+z^2}$

$\theta = \cos^{-1}\frac{z}{r}$ (Polar angle)

$\phi = \tan^{-1}\frac{y}{x}$ (Azimuthal angle)

Solutions

- Azimuthal eqn. is simplest: $\Phi(\phi) = e^{\pm i m_\ell \phi}$
- Radial eqn (Associated Laguerre eqn):

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \frac{2\mu}{\hbar^2}\left(E - V - \frac{\hbar^2}{2\mu}\frac{\ell(\ell+1)}{r^2}\right)R = 0$$

- One solution (to ℓ=0) is $R(r) = Ae^{-r/a_o}$

- Eqn for Θ: $\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \left[\ell(\ell+1) - \frac{m_\ell^2}{\sin^2\theta}\right]\Theta = 0$

Solutions are Legendre polynomials

Note: $\Theta(\theta)\Phi(\phi) = Y(\theta,\phi) = spherical \quad harmonics$

Quantum numbers (QN)

- These arise from separation constants:

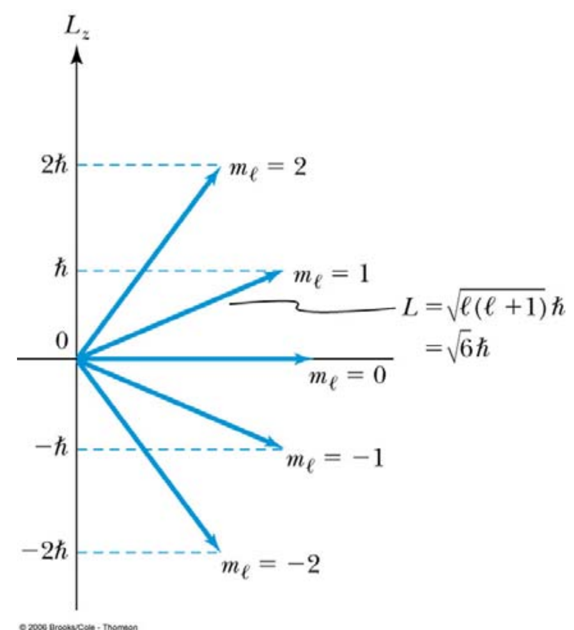
$$m_\ell, \quad \ell \quad [via \quad \ell(\ell+1)], \quad and \quad n$$

- n = principal QN, n = 1, 2, 3, …
  determines $E_n = -\frac{E_o}{n^2}$ as in Bohr theory
- ℓ = orbital angular momentum QN
  where ℓ = 0, 1, 2, …, (n-1)
  determines $L = \sqrt{\ell(\ell+1)}\,\hbar$
- m_ℓ = magnetic QN,
  where m_ℓ = -ℓ, -ℓ+1, …,0, …, ℓ-1, ℓ
  determines $L_z = m_\ell \hbar$

Physical Meaning of QN

- n comes from R(r) eqn – quantizes orbital r; so quantizes energy
- ℓ comes from Θ(θ) and sets magnitude of L

  s, p, d, f notation
- m_ℓ comes from Φ(Φ) and determines spatial quantization
- degeneracy

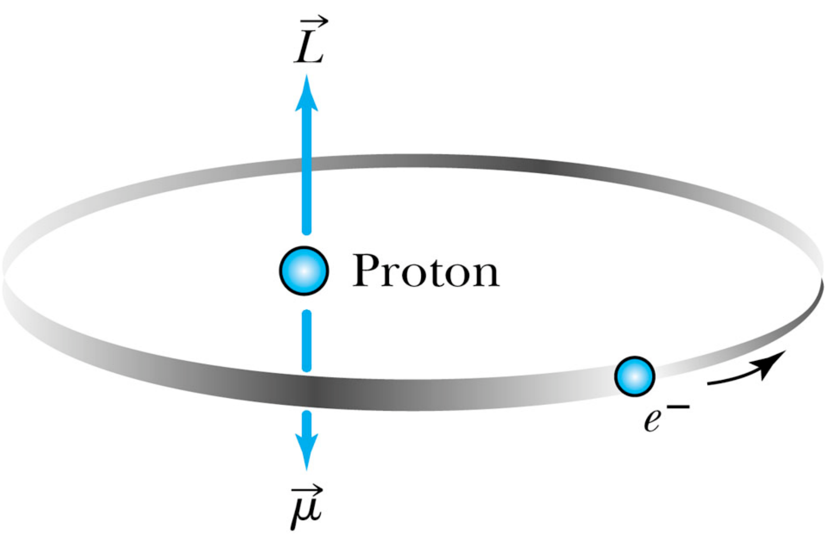


Removing Degeneracy – B fields & Zeeman Effect

- Atoms placed in a B field interact via magnetic moment to remove degeneracy – fine structure = splitting into 2 or more closely spaced energy levels
- Derive magnetic moment $\vec{\mu} = -\frac{e}{2m}\vec{L}$ and its $PE = V_B = -\vec{\mu}\bullet\vec{B}$
- Normal Zeeman effect:

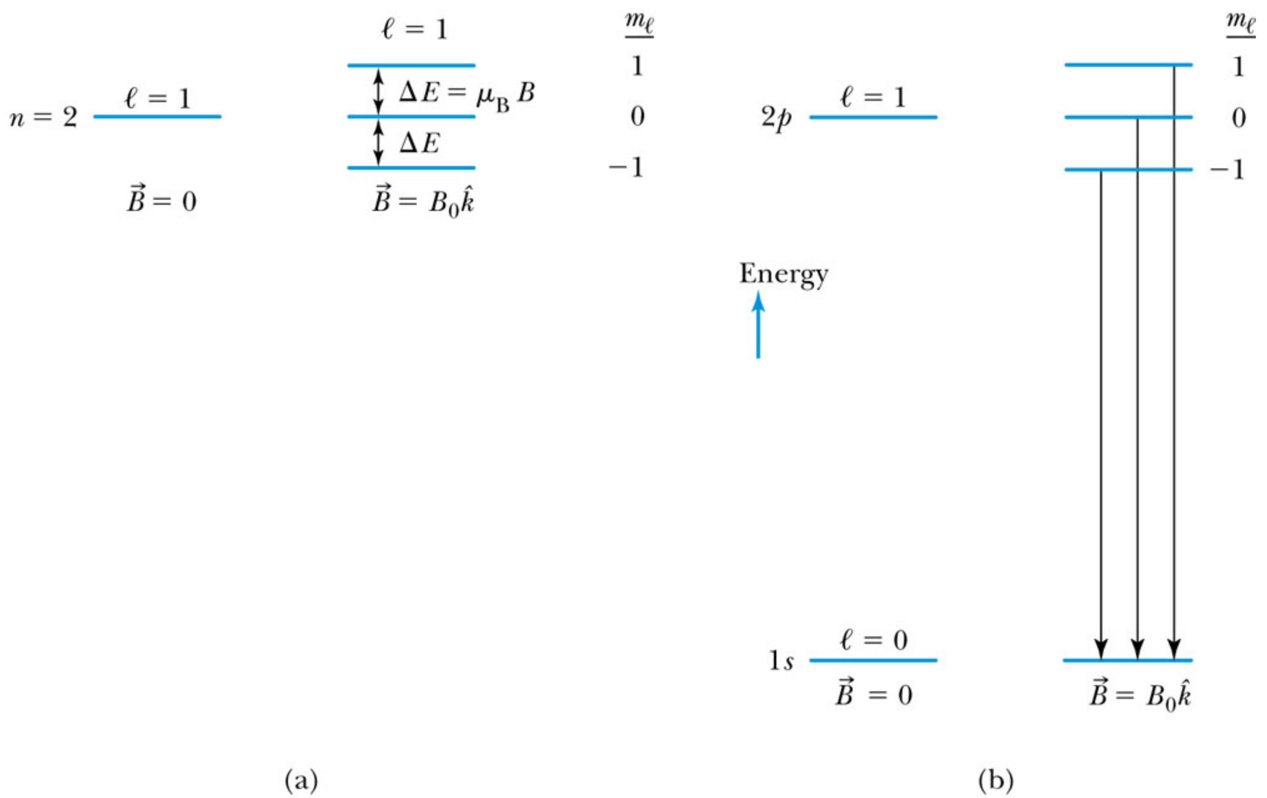
$$\mu_z = -\frac{e\hbar}{2m}m_\ell = -\mu_B m_\ell$$

$$V_B = -\mu_z B = +\mu_B m_\ell B$$



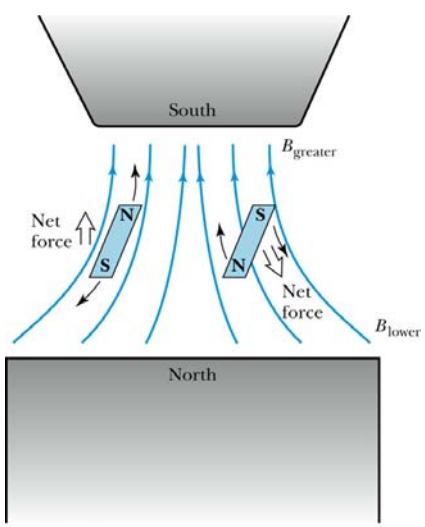
Normal Zeeman Effect

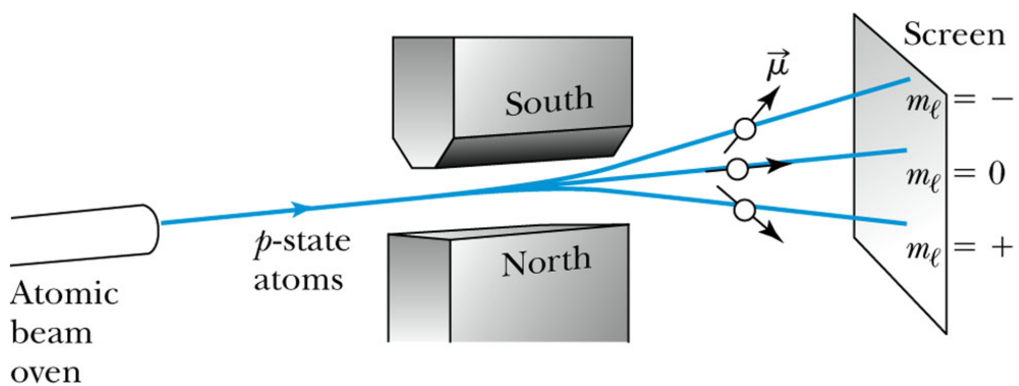
- Splitting of 2p level to give 3 different transitions – removing degeneracy



Stern-Gerlach Expt

- In a non-uniform B field, there will be a force on a magnetic dipole (in addition to a torque)
- The force is given by $F_z = -\frac{dV_B}{dz} = \mu_z \frac{dB}{dz} = -\mu_B m_\ell \frac{dB}{dz}$
- With silver atoms in s state saw 2 lines, not 0 or 3



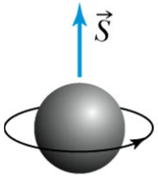


Electron Spin

- Pauli first proposed a fourth QN to explain Stern-Gerlach results but its significance was not clear
- Goudsmit & Uhlenbeck proposed electron spin s = ½ and m_s= ±½
- Gyromagnetic ratios:

$$\vec{\mu}_\ell = -\frac{g_e \mu_B \vec{L}}{\hbar} = -\frac{\mu_B \vec{L}}{\hbar} \rightarrow V_B = \mu_B m_\ell B$$

$$\vec{\mu}_s = -\frac{g_s \mu_B \vec{S}}{\hbar} = -2\frac{\mu_B \vec{S}}{\hbar} \rightarrow V_B = 2\mu_B m_s B$$



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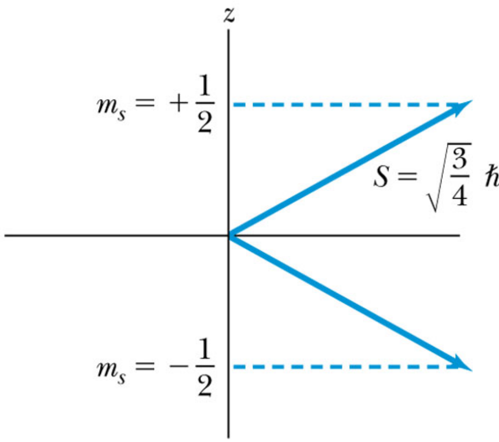


(b)

H atom energy levels, transitions & selection rules

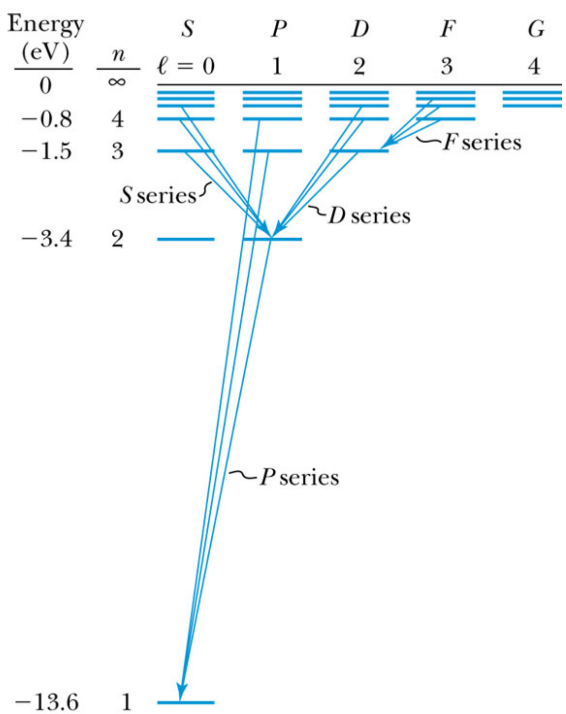
- 4 QN : n, ℓ, m_ℓ, m_s – in H n determines energies; in many electron atoms, degeneracy is removed from internal B fields
- Selection rules: allowed

$$\Delta\ell = \pm 1$$

$$\Delta m_\ell = 0, \pm 1$$

vs forbidden

- Due to photon carrying one unit of L or (ħ)



Probability Distribution Functions

- Wave picture of H atom:

$$dP = \psi^*(r,\theta,\phi)\psi(r,\theta,\phi)\,d\tau \quad where \quad d\tau = r^2 \sin\theta\, dr\, d\theta\, d\phi$$

- If we want to look at the radial dependence then

$$P(r)dr = r^2 R^*(r)R(r)dr$$

- Example of most probable radius in 1s and 2p vs. average r vs. probability r>a_o