

# El átomo de hidrógeno en Mecánica Cuántica

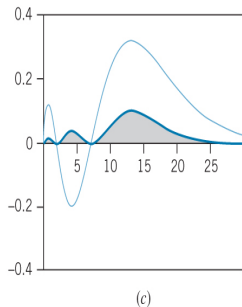
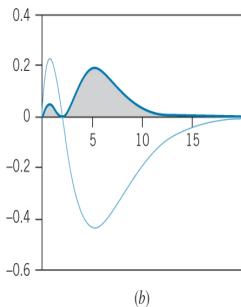
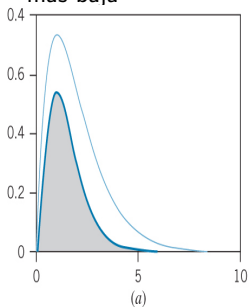
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Fundamentos Física III

# El átomo de hidrógeno en una dimensión

- Modelo de Bohr: electrón en órbita circular alrededor del núcleo
- Mecánica Cuántica : electrón  $\Leftrightarrow \Psi(x)$  con **interpretación probabilística**
- **Ejercicio de calentamiento:** potencial coulombiano en una dimensión
- $-\frac{\hbar^2}{2m} \frac{d^2\Psi(x)}{dx^2} - \frac{e^2}{4\pi\epsilon_0 x} \Psi(x) = E\Psi(x)$
- $\Psi(x) \rightarrow 0$  si  $x \rightarrow \infty$  : si  $\Psi(x) \Leftrightarrow$  estado ligado
- $\Psi(x) \rightarrow 0$  si  $x \rightarrow 0$  : cancelar polo segundo término izda. ecu. Schroe.
- Ansatz:  $\Psi(x) = Axe^{-bx} \Rightarrow b = me^2/4\pi\epsilon_0\hbar^2 = 1/a_0$  y además
- $E = -\frac{\hbar^2 b^2}{2m} = -me^4/32\pi^2\epsilon_0^2\hbar^2$  : idéntica al estado fundamental de Bohr
- Figura muestra  $\Psi(x)$  (línea) y  $|\Psi(x)|^2$  (sombreado) tres estados energía más baja

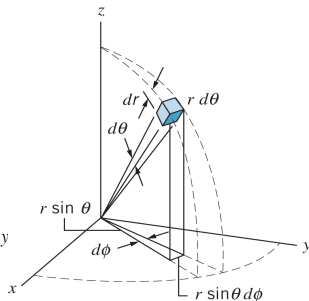
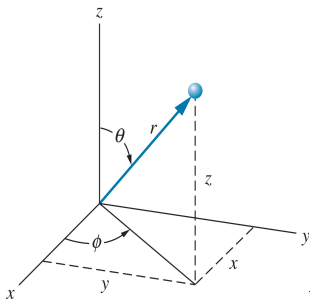


Calcular la constante de normalización en la solución anterior y la probabilidad de encontrar al electrón en su estado fundamental entre  $(0, a_0)$ . Localizar el máximo de la densidad de probabilidad.

- $\Psi(x) = Axe^{-x/a_0}$
- $\int_0^\infty |\Psi(x)|^2 dx = A^2 \int_0^\infty x^2 e^{-2x/a_0} dx = 1$
- Pero  $\int_0^\infty x^n e^{-c \cdot x} dx = \frac{n!}{c^{n+1}}$  luego si  $n = 2$  y  $c = 2/a_0$
- $A^2 \frac{2}{(2/a_0)^3} = 1 \Rightarrow A = 2a_0^{-3/2}$
- $P = \int_0^{a_0} |\Psi(x)|^2 dx = \frac{4}{a_0^3} \int_0^{a_0} x^2 e^{-2x/a_0} dx$
- $\int x^n e^{-c \cdot x} dx = -\frac{e^{-c \cdot x}}{c} \left[ x^n + \frac{nx^{n-1}}{c} + \frac{n(n-1)x^{n-2}}{c^2} + \dots + \frac{n!}{c^n} \right]$
- $P(0, a_0) = \frac{4}{a_0^3} \left[ -\frac{e^{-2x/a_0}}{2/a_0} \left( x^2 + \frac{2x}{2/a_0} + \frac{2}{(2/a_0)^2} \right) \right]_0^{a_0} = 0.323$
- $P(x) \propto x^2 e^{-2x/a_0} \Rightarrow P' \propto 2xe^{-2x/a_0} - x^2 \frac{2}{a_0} e^{-2x/a_0} = 0 \Rightarrow x = a_0!$

# Funciones de onda del átomo de hidrógeno

- $-\frac{\hbar^2}{2m} \left( \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \right) + U(x, y, z) \Psi(x, y, z) = E \Psi(x, y, z)$
- $U(x, y, z) = -e^2 / 4\pi\epsilon_0 \sqrt{x^2 + y^2 + z^2} = -e^2 / 4\pi\epsilon_0 r \Rightarrow$  **esféricas**
- $-\frac{\hbar^2}{2m} \left[ \frac{\partial^2 \Psi}{\partial r^2} + \frac{2}{r} \frac{\partial \Psi}{\partial r} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \Psi}{\partial \phi^2} \right] + U(r) \Psi(r, \theta, \phi) = E \Psi(r, \theta, \phi)$
- $\Psi(r, \theta, \phi) = R(r) Y(\theta, \phi) = R(r) \Theta(\theta) \Phi(\phi)$
- $-\frac{\hbar^2 r^2}{2m} Y(\theta, \phi) \left[ \frac{\partial^2 R(r)}{\partial r^2} + \frac{2}{r} \frac{\partial R(r)}{\partial r} \right] - \frac{\hbar^2 R(r)}{2m \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y(\theta, \phi)}{\partial \theta} \right) - \frac{\hbar^2 R(r)}{2m \sin^2 \theta} \frac{\partial^2 Y(\theta, \phi)}{\partial \phi^2} + U(r) R(r) Y(\theta, \phi) r^2 = ER(r) Y(\theta, \phi) r^2$



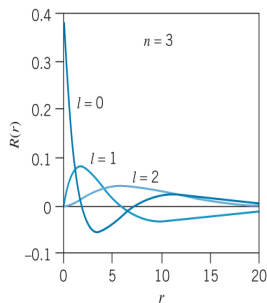
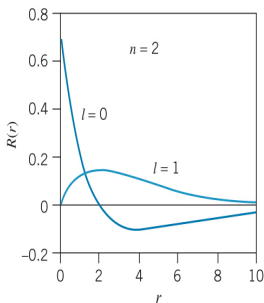
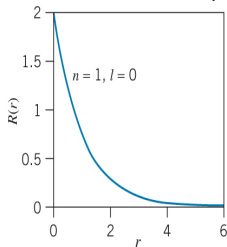
- $$-\frac{\hbar^2 r^2}{2m} Y(\theta, \phi) \left[ \frac{\partial^2 R(r)}{\partial r^2} + \frac{2}{r} \frac{\partial R(r)}{\partial r} \right] - \frac{\hbar^2 R(r)}{2m \sin\theta} \frac{\partial}{\partial \theta} \left( \sin\theta \frac{\partial Y(\theta, \phi)}{\partial \theta} \right) - \frac{\hbar^2 R(r)}{2m \sin^2\theta} \frac{\partial^2 Y(\theta, \phi)}{\partial \phi^2} + U(r)R(r)Y(\theta, \phi)r^2 = ER(r)Y(\theta, \phi)r^2 \Rightarrow \text{divido por } R(r)Y(\theta, \phi) \text{ y separo}$$
- $$-\frac{\hbar^2}{2mR(r)} \left[ \frac{\partial^2 R(r)}{\partial r^2} + \frac{2}{r} \frac{\partial R(r)}{\partial r} \right] + U(r) = E(r) + \frac{\lambda \hbar^2}{2mr^2}$$
- $$\frac{\hbar^2}{2m} \frac{1}{Y(\theta, \phi) \sin\theta} \frac{\partial}{\partial \theta} \left( \sin\theta \frac{\partial Y(\theta, \phi)}{\partial \theta} \right) + \frac{\hbar^2}{2m} \frac{1}{Y(\theta, \phi) \sin^2\theta} \frac{\partial^2 Y(\theta, \phi)}{\partial \phi^2} = \frac{\lambda \hbar^2}{2m} \Rightarrow Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$$
- $$\frac{1}{\Theta(\theta) \sin\theta} \frac{\partial}{\partial \theta} \left( \sin\theta \frac{\partial \Theta(\theta)}{\partial \theta} \right) + \frac{1}{\Phi(\phi) \sin^2\theta} \frac{\partial^2 \Phi(\phi)}{\partial \phi^2} = \lambda$$
- $$\frac{\sin\theta}{\Theta(\theta)} \frac{\partial}{\partial \theta} \left( \sin\theta \frac{\partial \Theta(\theta)}{\partial \theta} \right) + \frac{1}{\Phi(\phi)} \frac{\partial^2 \Phi(\phi)}{\partial \phi^2} = \lambda \sin^2\theta \text{ y separo una segunda vez}$$
- $$\frac{\partial^2 \Phi(\phi)}{\partial \phi^2} = -m^2 \Phi(\phi) \Rightarrow \Phi(\phi) = Ce^{im\phi}; m = 0, \pm 1, \pm 2, \dots$$
- $$\frac{\sin\theta}{\Theta(\theta)} \frac{\partial}{\partial \theta} \left( \sin\theta \frac{\partial \Theta(\theta)}{\partial \theta} \right) - m^2 = \lambda \sin^2\theta : \text{ecuación de Legendre}$$

$\Rightarrow \lambda = -l(l+1), l = 0, 1, 2, 3, \dots; m = -l, -l+1, \dots, 0, 1, \dots, l-1, l$
- Armónicos esféricos:**  $Y_{l,m}(\theta, \phi) = (-1)^m \sqrt{\frac{(2l+1)}{4\pi} \frac{(l-m)!}{(l+m)!}} P_{l,m}(\cos\theta) e^{im\phi} \Rightarrow$

$$\int_{-1}^1 \int_0^{2\pi} Y_{l,m} Y_{l',m'}^* d\cos\theta d\phi = \delta_{l,l'} \delta_{m,m'}$$
- $$P_{0,0} = 1; P_{1,0} = \cos\theta; P_{1,1} = -\sin\theta; P_{2,0} = \frac{1}{2}(3\cos^2\theta - 1); P_{2,1} = -3\cos\theta \sin\theta; P_{2,2} = 3\sin^2\theta$$
- $$P_{3,0} = \frac{1}{2}(5\cos^3\theta - 3\cos\theta); P_{3,1} = -\frac{3}{2}(5\cos^2\theta - 1)\sin\theta; P_{3,2} = 15\cos\theta \sin^2\theta; P_{3,3} = -15\sin^3\theta$$

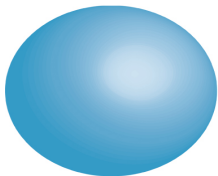
Volvamos a la parte radial

- $-\frac{\hbar^2}{2m} \left[ \frac{d^2 R(r)}{dr^2} + \frac{2}{r} \frac{dR(r)}{dr} \right] + \left[ -\frac{e^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2mr^2} \right] R(r) = ER(r) \Rightarrow R(r) = R_{n,l}(r)$
- $R_{n,l}(r) = r^l L_{n,l}(r) e^{-r/na_0}$  siendo  $L_{n,l}$  las funciones de **Laguerre**
- $E_n = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2} \frac{1}{n^2}$ ;  $n = 1, 2, 3, \dots$ ;  $l = 0, 1, 2, \dots, n-1$ ;  $m = 0, \pm 1, \pm 2, \dots, \pm l$
- $R_{1,0} = \frac{2}{a_0^{3/2}} e^{-r/a_0}$ ;  $R_{2,0} = \frac{1}{(2a_0)^{3/2}} \left( 2 - \frac{r}{a_0} \right) e^{-r/2a_0}$ ;  $R_{2,1} = \frac{1}{\sqrt{3}(2a_0)^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$
- $R_{3,0} = \frac{2}{(3a_0)^{3/2}} \left( 1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2} \right) e^{-r/3a_0}$ ;  $R_{3,1} = \frac{8}{9\sqrt{2}(3a_0)^{3/2}} \left( \frac{r}{a_0} - \frac{r^2}{6a_0^2} \right) e^{-r/3a_0}$
- $R_{3,2} = \frac{4}{27\sqrt{10}(3a_0)^{3/2}} \left( \frac{r^2}{a_0^2} \right) e^{-r/3a_0}$
- **Figura muestra  $R(r)$  para  $n=1,2,3$ . Nótese número de nodos es  $n-l-1$**

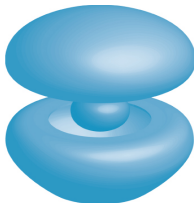


La figura muestra superficies 'equiprobables' obtenidas así:

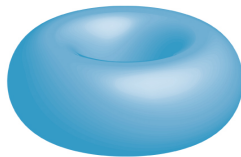
$$|\Psi_{n,l,m_l}|^2 dV = |R_{n,l}(r)|^2 r^2 dr |Y_{l,m_l}(\theta, \phi)|^2 d\cos\theta d\phi \quad (1)$$



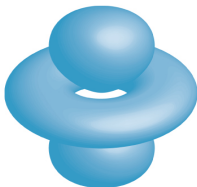
$l = 0, m_l = 0$



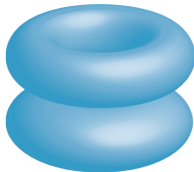
$l = 1, m_l = 0$



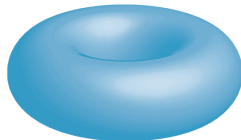
$l = 1, m_l = 1$



$l = 2, m_l = 0$



$l = 2, m_l = 1$

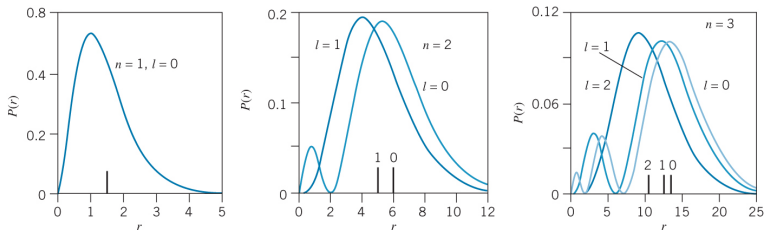


$l = 2, m_l = 2$

La probabilidad de encontrar al electrón entre dos esferas de radios  $r$  y  $r+dr$  es

$$P(r)dr = |R_{n,l}(r)|^2 r^2 dr \quad (2)$$

La figura adjunta muestra densidades radiales para los tres primeros estados, los valores  $\langle r \rangle$  vienen indicados por las barras en el eje de abscisas.



Demostrar que la distancia más probable de un electrón en el estado  $n = 2, l = 1$  es  $4a_0$

- $P(r) = r^2 |R_{2,1}|^2 = r^2 \frac{1}{24a_0^3} \frac{r^2}{a_0^2} e^{-r/a_0}$
- $\frac{dP(r)}{dr} = \frac{1}{24a_0^5} \frac{d}{dr} (r^4 e^{-r/a_0}) = \frac{1}{24a_0^5} [4r^3 - \frac{r^4}{a_0}] e^{-r/a_0} = 0 \Rightarrow r = 4a_0$



Determinar  $\langle r \rangle$  para un electrón en el átomo de hidrógeno en los estados 1s, 2p y 2s

Sol:

- $$\bullet \text{ 1s: } \langle r \rangle = \int_0^\infty rP(r)dr = \int_0^\infty r^3 |R_{1,0}|^2 dr = \frac{4}{a_0^3} \int_0^\infty r^3 e^{-2r/a_0} dr = \frac{4}{a_0^3} \frac{3!}{(2/a_0)^4} = \frac{3}{2} a_0$$
- $$\bullet \text{ 2s: } \langle r \rangle = \int_0^\infty rP(r)dr = \int_0^\infty r^3 |R_{2,0}|^2 dr = \frac{1}{8a_0^3} \int_0^\infty r^3 (2 - \frac{r}{a_0})^2 e^{-r/a_0} dr = \frac{1}{8a_0^3} \int_0^\infty (4r^3 - 4\frac{r^4}{a_0} + \frac{r^5}{a_0^2}) e^{-r/a_0} dr = \frac{1}{8a_0^3} [4\frac{3!}{(1/a_0)^4} - \frac{4}{a_0} \frac{4!}{(1/a_0)^5} + \frac{1}{a_0^2} \frac{5!}{(1/a_0)^6}] = 6a_0$$
- $$\bullet \text{ 2p: } \langle r \rangle = \int_0^\infty rP(r)dr = \int_0^\infty r^3 |R_{2,1}|^2 dr = \frac{1}{24a_0^5} \int_0^\infty r^5 e^{-r/a_0} dr = \frac{1}{24a_0^5} \frac{5!}{(1/a_0)^6} = 5a_0$$
- $$\bullet \text{ Conclusión : } \langle r \rangle_{2s} > \langle r \rangle_{2p}$$

Determinar  $\langle 1/r \rangle$  para un electrón en el estado fundamental del átomo de hidrógeno. Usar este resultado para calcular la energía cinética media.

Sol:

- $E_1 = -\frac{m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2} = -\frac{m_e c^2 e^4}{32\pi^2 \epsilon_0^2 \hbar^2 c^2} = -\frac{\alpha^2 m_e c^2}{2}$  ;  $\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c}$
- $\langle 1/r \rangle = \int_0^\infty R_{1,0}(r) \frac{1}{r} R_{1,0}(r) r^2 dr = \frac{4}{a_0^3} \int_0^\infty e^{(-2r/a_0)} r dr = \frac{1}{a_0} = \frac{m_e c^2}{4\pi\epsilon_0 \hbar^2}$
- $\langle V(r) \rangle = \langle \frac{-e^2}{4\pi\epsilon_0 r} \rangle = \frac{-e^2}{4\pi\epsilon_0 a_0} = -\alpha^2 m_e c^2$
- $\langle \frac{p^2}{2m} \rangle = \langle K \rangle = E - \langle V(r) \rangle = -\frac{\alpha^2 m_e c^2}{2} - (-\alpha^2 m_e c^2) = \frac{\alpha^2 m_e c^2}{2}$
- $\langle K \rangle = -\frac{1}{2} \langle V(r) \rangle$  : versión mecano cuántica del teorema del virial clásico

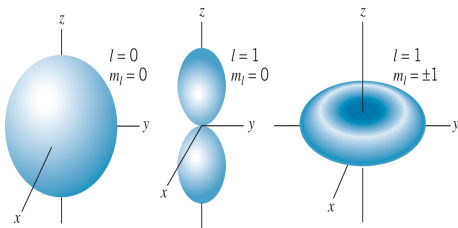
Comparar las probabilidades de encontrar el electrón del átomo de hidrógeno dentro del radio de Bohr en los estados (2,0) y (2,1)

Sol:

- $\int x^n e^{-cx} dx = -\frac{e^{-cx}}{c} [x^n + \frac{nx^{n-1}}{c} + \frac{n(n-1)x^{n-2}}{c^2} + \dots + \frac{n!}{c^n}]$
- $P_{2,0} = \int_0^{a_0} \frac{r^2}{8a_0^3} (2 - \frac{r}{a_0})^2 e^{-r/a_0} dr = \frac{1}{8a_0^3} \int_0^{a_0} (4r^2 - \frac{4r^3}{a_0} + \frac{r^4}{a_0^2}) e^{-r/a_0} dr = 0.034$
- $P_{2,1} = \frac{1}{24a_0^3} \int_0^{a_0} \frac{r^4}{a_0^2} e^{-r/a_0} dr = 0.037$

$$P(\theta, \phi) = |Y_{l,m_l}(\theta, \phi)|^2 \quad (3)$$

- Densidades angulares tienen **simetría cilíndrica** i.e. no dependen de  $\phi$
- Figura adjunta : densidades angulares para  $(l, m_l) = (0, 0); (1, 0); (1, \pm 1)$
- Recordar que clásicamente  $\vec{L} \perp \text{órbita}$



Ejemplo: Para el estado  $(n, l) = (2, 1)$  del átomo de hidrógeno determinar la dirección espacial que maximiza la probabilidad de localización, considerando los casos  $m_l = 0, \pm 1$

- $l = 1, m_l = 0 \Rightarrow P(\theta, \phi) = \frac{3}{4\pi} \cos^2 \theta \Rightarrow \frac{dP}{d\theta} = -\frac{3}{2\pi} \sin \theta \cos \theta = 0 \Rightarrow \theta = 0, \pi$   
con mínimo en  $\theta = \frac{\pi}{2}$
- $l = 1, m_l = \pm 1 \Rightarrow P(\theta, \phi) = \frac{3}{8\pi} \sin^2 \theta \Rightarrow \frac{dP}{d\theta} = \frac{3}{4\pi} \sin \theta \cos \theta = 0 \Rightarrow \theta = \frac{\pi}{2}$   
con mínimo en  $\theta = 0, \pi$
- Resumiendo para  $(l, m) = (1, 0)$  máximo ocurre según eje Z, para  $(l, m_l) = (1, \pm 1)$  máximo ocurre en el plano XY

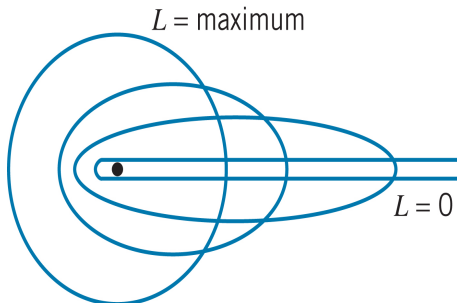
Volvamos de nuevo a la parte radial

- $-\frac{\hbar^2}{2m} \left[ \frac{d^2 R(r)}{dr^2} + \frac{2}{r} \frac{dR(r)}{dr} \right] + [V(r) + \frac{l(l+1)\hbar^2}{2mr^2}] R(r) = ER(r)$
- Nótese que  $\frac{d^2 R(r)}{dr^2} + \frac{2}{r} \frac{dR(r)}{dr} = \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR(r)}{dr} \right)$
- Luego  $\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR(r)}{dr} \right) + \frac{2m}{\hbar^2} ([E - V(r)] - \frac{l(l+1)}{r^2}) R(r) = 0$
- Definamos  $R(r) = \frac{\chi(r)}{r} \Rightarrow \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR(r)}{dr} \right) = \frac{1}{r} \frac{d^2 \chi(r)}{dr^2}$
- Este cambio de variables permite escribir la parte radial de la ecuación de Schrödinger así:
- $\frac{d^2 \chi(r)}{dr^2} + \frac{2m}{\hbar^2} ([E - V(r)] - \frac{l(l+1)}{r^2}) \chi(r) = 0$
- **Estado fundamental i.e.**  $l = 0 \Rightarrow \frac{d^2 \chi(r)}{dr^2} + \frac{2m}{\hbar^2} ([E - V(r)]) \chi(r) = 0$

Ejemplo : Determinar la función de onda del estado fundamental de un electrón confinado en una cavidad hueca impenetrable de radio  $a$

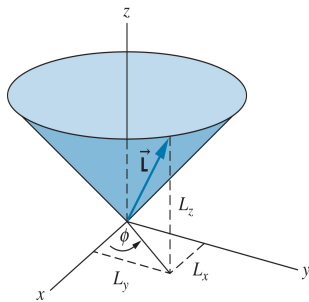
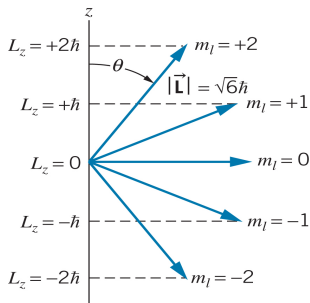
- $\frac{d^2 \chi(r)}{dr^2} + \frac{2mE}{\hbar^2} \chi(r) = 0 \Rightarrow \chi(r) = \sqrt{\frac{2}{a}} \sin \frac{\pi r}{a}$
- La energía vendrá dada por  $E = \frac{\pi^2 \hbar^2}{2ma^2}$
- $R(r) = \sqrt{\frac{2}{a}} \frac{1}{r} \sin \frac{\pi r}{a}$

- $\vec{L} = \vec{r} \times \vec{p} \Rightarrow$
- Movimiento planetario :  $\vec{L} \perp \text{plano órbita}$
- Energia total movimiento orbital  $\Leftrightarrow$  distancia media Sol y planeta
- $L \Leftrightarrow$  excentricidad de la órbita
- $\vec{L} \Leftrightarrow (L_x, L_y, L_z)$



# Momento angular en Mecánica Cuántica

- $\vec{L} = \vec{r} \times \vec{p} \Rightarrow L_x = yp_z - zp_y ; L_y = zp_x - xp_z ; L_z = xp_y - yp_x$
- $p_x = -i\hbar \frac{\partial}{\partial x} ; p_y = -i\hbar \frac{\partial}{\partial y} ; p_z = -i\hbar \frac{\partial}{\partial z}$
- $L_x = -i\hbar(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y}) ; L_y = -i\hbar(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z}) ; L_z = -i\hbar(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x})$
- $L^2 = L_x^2 + L_y^2 + L_z^2 = -\hbar^2(\frac{1}{\sin\theta} \frac{\partial}{\partial \theta}(\sin\theta \frac{\partial}{\partial \theta}) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2}) ; L_z = -i\hbar \frac{\partial}{\partial \phi}$
- $L^2 Y_{l,m}(\theta, \phi) = \hbar^2 l(l+1) Y_{l,m}(\theta, \phi) ; L_z Y_{l,m}(\theta, \phi) = \hbar m Y_{l,m}(\theta, \phi)$
- En QM momento angular viene dado por **dos** cantidades, no por tres
  - $L = |\vec{L}| = \hbar\sqrt{l(l+1)}$ ,  $l = 0, 1, 2, 3, \dots \Rightarrow$  puede ser 0, no así en Bohr
  - $L_z = m\hbar$ ,  $m = 0, \pm 1, \dots, \pm l \Rightarrow \cos\theta = m/\sqrt{l(l+1)} < 1$  incluso si  $m = l$ !
  - Si  $L_z = L$  entonces  $L_x = L_y = 0$  violando la
  - Relación incertidumbre para momento angular :  $\Delta L_z \Delta \phi \geq \hbar$



Demostremos que  $L_z = -i\hbar \frac{\partial}{\partial \phi}$  en esféricas sabiendo  $L_z = -i\hbar(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x})$  en cartesianas

- $x = r \sin \theta \cos \phi$  ;  $y = r \sin \theta \sin \phi$  ;  $z = r \cos \theta \Rightarrow$
- $\frac{\partial x}{\partial \phi} = -r \sin \theta \sin \phi = -y$
- $\frac{\partial y}{\partial \phi} = r \sin \theta \cos \phi = x$
- $\frac{\partial z}{\partial \phi} = 0$
- $\frac{\partial \Psi}{\partial \phi} = \frac{\partial \Psi}{\partial x} \frac{\partial x}{\partial \phi} + \frac{\partial \Psi}{\partial y} \frac{\partial y}{\partial \phi} + \frac{\partial \Psi}{\partial z} \frac{\partial z}{\partial \phi} = -y \frac{\partial \Psi}{\partial x} + x \frac{\partial \Psi}{\partial y} = (x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x}) \Psi \Rightarrow$
- $L_z = -i\hbar \frac{\partial}{\partial \phi} = -i\hbar(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x})$  Q.E.D.

Análogamente  $L_x = i\hbar(\sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi})$

- $\frac{\partial x}{\partial \theta} = r \cos \theta \cos \phi = z \cos \phi$
- $\frac{\partial y}{\partial \theta} = r \cos \theta \sin \phi = z \sin \phi$
- $\frac{\partial z}{\partial \theta} = -r \sin \theta$
- $\frac{\partial \Psi}{\partial \theta} = \frac{\partial \Psi}{\partial x} \frac{\partial x}{\partial \theta} + \frac{\partial \Psi}{\partial y} \frac{\partial y}{\partial \theta} + \frac{\partial \Psi}{\partial z} \frac{\partial z}{\partial \theta} = \frac{\partial \Psi}{\partial x} z \cos \phi + \frac{\partial \Psi}{\partial y} z \sin \phi - \frac{\partial \Psi}{\partial z} r \sin \theta \Rightarrow$
- $\sin \phi \frac{\partial \Psi}{\partial \theta} + \cot \theta \cos \phi \frac{\partial \Psi}{\partial \phi} =$   
 $\sin \phi [z \cos \phi \frac{\partial \Psi}{\partial x} + z \sin \phi \frac{\partial \Psi}{\partial y} - r \sin \theta \frac{\partial \Psi}{\partial z}] + \cot \theta \cos \phi [-y \frac{\partial \Psi}{\partial x} + x \frac{\partial \Psi}{\partial y}] =$   
 $[z \sin \phi \cos \phi - y \cot \theta \cos \phi] \frac{\partial \Psi}{\partial x} + [z \sin^2 \phi + x \cot \theta \cos \phi] \frac{\partial \Psi}{\partial y} - r \sin \theta \sin \phi \frac{\partial \Psi}{\partial z} =$   
 $0 \frac{\partial \Psi}{\partial x} + [z \sin^2 \phi + z \cos^2 \phi] \frac{\partial \Psi}{\partial y} - y \frac{\partial \Psi}{\partial z} = -y \frac{\partial \Psi}{\partial z} + z \frac{\partial \Psi}{\partial y} \Rightarrow$
- $L_x = i\hbar(\sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi}) = -i\hbar(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y})$  Q.E.D.

Demostremos que  $\vec{L}^2 = -\hbar^2 \left[ \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$

- $L_x = i\hbar \left( \sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right)$
- $L_y = i\hbar \left( -\cos \phi \frac{\partial}{\partial \theta} + \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right)$
- $L_z = -i\hbar \frac{\partial}{\partial \phi}$
- $L_x^2 = -\hbar^2 \left[ \sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right] \left[ \sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right] =$   
 $-\hbar^2 \left[ \sin^2 \phi \frac{\partial^2}{\partial \theta^2} - \frac{1}{\sin^2 \theta} \sin \phi \cos \phi \frac{\partial}{\partial \phi} + \cot \theta \sin \phi \cos \phi \frac{\partial^2}{\partial \theta \partial \phi} + \cot \theta \cos^2 \phi \frac{\partial}{\partial \theta} - \cot^2 \theta \sin \phi \cos \phi \frac{\partial}{\partial \phi} + \cot^2 \theta \cos^2 \phi \frac{\partial^2}{\partial \phi^2} \right]$
- $L_y^2 = -\hbar^2 \left[ -\cos \phi \frac{\partial}{\partial \theta} + \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right] \left[ -\cos \phi \frac{\partial}{\partial \theta} + \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right] =$   
 $-\hbar^2 \left[ \cos^2 \phi \frac{\partial^2}{\partial \theta^2} + \frac{1}{\sin^2 \theta} \sin \phi \cos \phi \frac{\partial}{\partial \phi} - \cot \theta \sin \phi \cos \phi \frac{\partial^2}{\partial \theta \partial \phi} + \cot \theta \sin^2 \phi \frac{\partial}{\partial \theta} + \cot^2 \theta \sin \phi \cos \phi \frac{\partial}{\partial \phi} + \cot^2 \theta \sin^2 \phi \frac{\partial^2}{\partial \phi^2} \right]$
- $L_z^2 = -\hbar^2 \frac{\partial^2}{\partial \phi^2}$
- $L_x^2 + L_y^2 + L_z^2 = -\hbar^2 \left[ \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \cot^2 \theta \frac{\partial^2}{\partial \phi^2} + \frac{\partial^2}{\partial \phi^2} \right] =$   
 $-\hbar^2 \left[ \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] = -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$  Q.E.D.
- $\frac{\sin \theta}{\theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta(\theta)}{\partial \theta} \right) - m^2 = \lambda \sin^2 \theta$  : ecuación de Legendre  $\lambda = l(l+1)$
- Comparando dos últimas ec.  $\Rightarrow L^2 Y_{l,m}(\theta, \phi) = \hbar^2 l(l+1) Y_{l,m}(\theta, \phi)$



Comprobar que el esférico armónico  $Y_{1,1}(\theta, \phi) = \sqrt{\frac{3}{8\pi}} \sin\theta e^{i\phi}$  es función propia de  $L^2$  y de  $L_z$  y encontrar los autovalores correspondientes.

Sol.:

$$\bullet L^2 Y_{1,1} = -\hbar^2 \left( \frac{\partial^2}{\partial \theta^2} + \cot\theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right) \sqrt{\frac{3}{8\pi}} \sin\theta e^{i\phi} = -\hbar^2 \sqrt{\frac{3}{8\pi}} \left[ -\sin\theta + \cot\theta \cdot \cos\theta + \frac{1}{\sin^2\theta} \cdot \sin\theta \cdot i^2 \right] e^{i\phi}$$

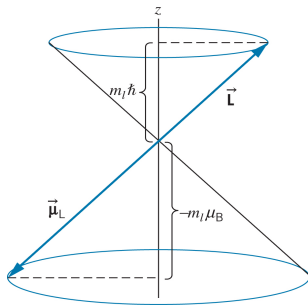
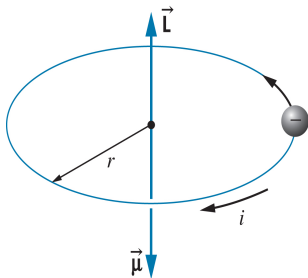
$$\bullet -\sin\theta + \frac{\cos^2\theta}{\sin\theta} - \frac{1}{\sin\theta} = -\sin\theta + \frac{\cos^2\theta - 1}{\sin\theta} = -2\sin\theta$$

$$\bullet L^2 Y_{1,1} = 2\hbar^2 \sqrt{\frac{3}{8\pi}} \sin\theta e^{i\phi} = 2\hbar^2 Y_{1,1} = \hbar^2 l(l+1) Y_{1,1} \Rightarrow l = 1$$

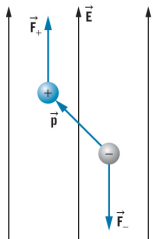
$$\bullet L_z Y_{1,1} = -i\hbar \frac{\partial}{\partial \phi} \sqrt{\frac{3}{8\pi}} \sin\theta e^{i\phi} = -i\hbar(i) \sqrt{\frac{3}{8\pi}} \sin\theta e^{i\phi} = \hbar \sqrt{\frac{3}{8\pi}} \sin\theta e^{i\phi} = \hbar Y_{1,1} = \hbar m Y_{1,1} \Rightarrow m = 1 \text{ Q.E.D.}$$

# Momento angular intrínseco: spin

- Manera de observar la cuantificación espacial es colocar átomo en presencia  $\vec{B}_{ext}$
- Expectativas:  $(2l+1)$  componentes de la interacción  $\vec{\mu}$  con  $\vec{B}_{ext}$
- Experimento Stern-Gerlach : se ven  $2(2l+1)$  estados
- Bohr :  $T = \frac{2\pi r}{v} = \frac{2\pi m r}{p} \Rightarrow \mu = iA = \frac{q}{2\pi r m/p} \pi r^2 = \frac{q}{2m} r p = \frac{q}{2m} L$
- $\vec{\mu}_{\vec{L}} = -\frac{e}{2m} \vec{L} \Rightarrow \mu_{L,z} = -\frac{e}{2m} L_z = -\frac{e}{2m} m_l \hbar = -\frac{e\hbar}{2m} m_l = -m_l \mu_B$
- $\mu_B = \frac{e\hbar}{2m} = 9.274 \times 10^{-24} \text{ J/T} = 4.5 \times 10^{-5} \text{ eV/T} \equiv \text{magnetón de Bohr}$

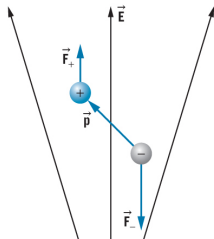


# Momento angular intrínseco: spin (Continuación)



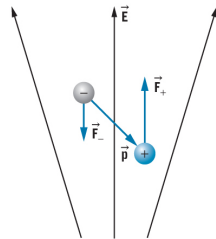
$$\vec{F}_{\text{net}} = 0$$

(a)



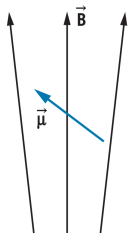
$$\vec{F}_{\text{net}} \downarrow$$

(b)

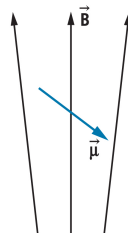


$$\vec{F}_{\text{net}} \uparrow$$

(c)



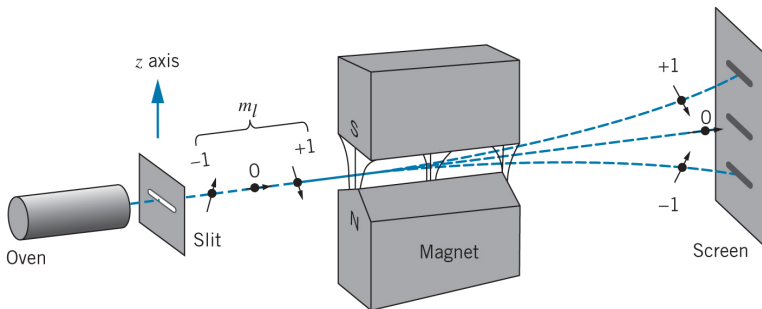
$$\vec{F}_{\text{net}} \downarrow$$



$$\vec{F}_{\text{net}} \uparrow$$

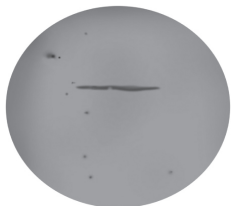
# El experimento de Stern-Gerlach

- W. Gerlach y O. Stern, 1922 : supongamos estudio interacción estados átomo hidrógeno con  $l = 1$  con  $\vec{B}_{ext}$
- Deberia ver  $2l + 1 = 3$  imágenes equidistantes en pantalla, la central asociada a  $m_l = 0$ .
- Difícil preparar  $H$  en estado específico  $(n,l)$ . Experimento real con átomos de  $Ag$  con electrón capa más externa con  $l = 0$ .
- Si veo DOS  $\Rightarrow l = 1/2$ : imposible según Schroedinger que exige  $l = \text{entero}$

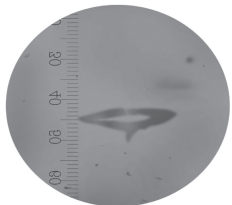


# El experimento de Stern-Gerlach: resultados e interpretación

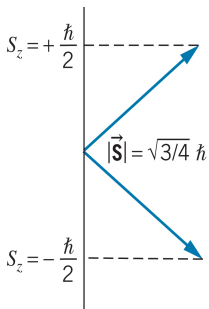
- Figura izquierda muestra resultados exp. S-G con B off (a) y on (b)
- S.A. Goudsmidt, G.E. Uhlenbeck, 1925: electrón tiene momento angular intrínseco  $s = 1/2 \Rightarrow m_s = \pm 1/2$
- $s = 1/2 \Rightarrow |\vec{S}| = \sqrt{s(s+1)}\hbar = \sqrt{\frac{3}{4}}\hbar \Rightarrow S_z = m_s\hbar \Rightarrow m_s = \pm 1/2 \Rightarrow \vec{\mu}_S = -e/m \cdot \vec{S}$



(a)



(b)



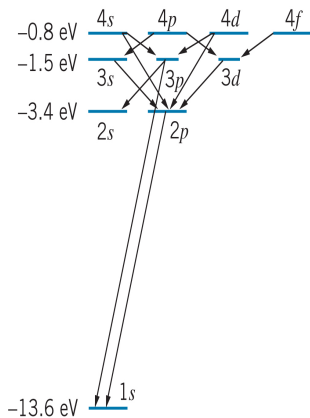
En un experimento del tipo de Stern-Gerlach, el campo magnético externo varía como  $dB_z/dz = 1.4 \text{ T/mm}$ . La distancia recorrida en él es de  $3.5 \text{ cm}$ . A la salida del horno los átomos de  $Ag$ ,  $m_{Ag} = 1.8 \times 10^{-25} \text{ kg}$  y  $\mu_{Ag} = 1\mu_B$ , tienen  $v = 750 \text{ m/s}$  como velocidad más probable. Encontrar la separación de los haces en pantalla.

Sol:

- $U = -\vec{\mu}_{Ag} \cdot \vec{B} = -\mu_z \cdot B_z \Rightarrow F_z = -dU/dz = \mu_z dB_z/dz$
- $a_z = \frac{F_z}{m} = \frac{\mu_z dB_z/dz}{m}$
- $\Delta z = \frac{1}{2} a_z t^2 = \frac{1}{2} a_z \left(\frac{x}{v}\right)^2 \Rightarrow d = 2\Delta_z$
- $d = \frac{\mu_z (dB_z/dz) x^2}{mv^2} = \frac{(9.27 \times 10^{-24} \text{ J/T})(1.4 \times 10^3 \text{ T/m})(3.5 \times 10^{-2} \text{ m})}{(1.8 \times 10^{-25} \text{ kg})(750 \text{ m/s})^2} = 1.6 \times 10^{-4} \text{ m} = 0.16 \text{ mm}$

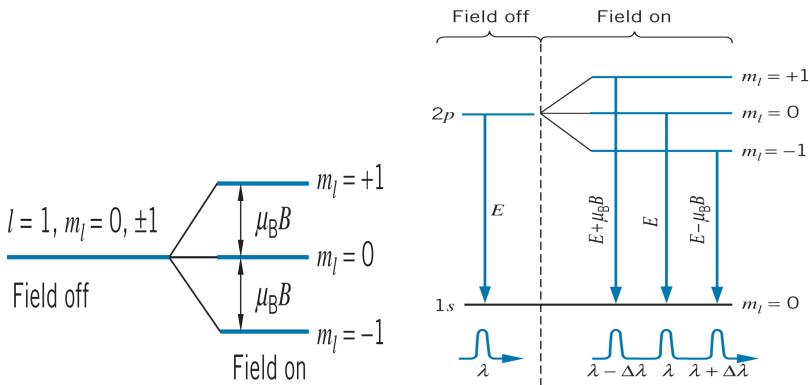
## Niveles de energía y notación espectroscópica: reglas de selección

- Caracterizar electrón en átomo de Hidrógeno:  $(n, l, m_l, m_s)$
- A veces en lugar de  $l = 0, 1, 2, 3, 4, 5, 6$  se usa la notación  $s, p, d, f, g, h, i$  de sharp, principal, diffuse and fundamental,...
- Figura adjunta indica un diagrama de los niveles de energía del Hidrógeno
- Flechas indican algunas transiciones de un estado de energía a otro más bajo con emisión de fotones
- Como el spin del fotón es uno: regla de selección  $\Delta l = \pm 1$



# El efecto Zeeman : 1897

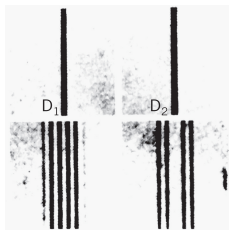
- Supongamos despreciamos efectos de spin
- $U = -\vec{\mu}_L \cdot \vec{B}_{ext} = m_l \cdot \mu_B \cdot B_{ext}$
- Sea estado átomo de hidrógeno en  $(n, l) = (2, 1)$
- Sea una transición  $(2, 1) \Rightarrow (1, 0) \Rightarrow E_\gamma = 10.2 \text{ eV} \Leftrightarrow \lambda = 122 \text{ nm}$
- En presencia campo magnético:  
 $E_{\gamma_1} = 10.2\text{eV} + \mu_B \cdot B_{ext}$ ,  $E_{\gamma_2} = 10.2\text{eV}$ ,  $E_{\gamma_3} = 10.2\text{eV} - \mu_B \cdot B_{ext}$
- $E = hc/\lambda \Rightarrow dE = -\frac{hc}{\lambda^2} d\lambda \Rightarrow \Delta\lambda = \frac{\lambda^2}{hc} \Delta E = \frac{\lambda^2}{hc} \cdot \mu_B \cdot B_{ext}$



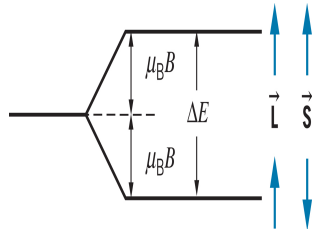
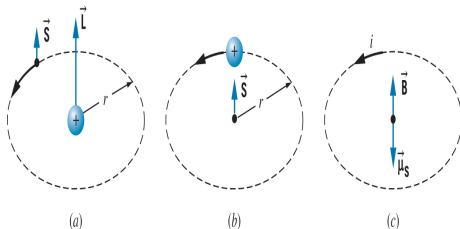


Calcular el cambio en la longitud de onda del fotón del caso anterior cuando  $B = 2 \text{ T}$ .

- $E = -13.6 \text{ eV} \left[ \frac{1}{2^2} - \frac{1}{1^2} \right] = 10.2 \text{ eV} \Rightarrow \lambda = hc/E = (1240 \text{ eV}\cdot\text{nm})/10.2 \text{ eV} = 122 \text{ nm}$
- $\Delta E = \mu_B \cdot B = (9.27 \times 10^{-24} \text{ J/T})(2.0 \text{ T}) = 18.5 \times 10^{-24} \text{ J} = 11.6 \times 10^{-5} \text{ eV}$
- $\Delta\lambda = \frac{\lambda^2}{hc} \Delta E = \frac{(122 \text{ nm})^2}{1240 \text{ eV}\cdot\text{nm}} 11.6 \times 10^{-5} \text{ eV} = 0.00139 \text{ nm!}$
- En la realidad hay que tener también en cuenta el splitting debido al spin por lo que el desdoblamiento líneas espectrales puede ser más complicado que simplemente en  $m_l$  líneas, como se ve en la figura adjunta.



- Hecho experimental : Mayoría de líneas espectrales  $H$  están desdobladas aún en ausencia campo magnético externo.
- Origen observación : interacción  $\vec{\mu}_S$  electrón con **campo magnético creado por el protón**  $\Rightarrow U = -\vec{\mu}_S \cdot \vec{B} = (e/m)S_z \cdot B = \pm \frac{e\hbar}{2m} B = \pm \mu_B \cdot B$
- Punto vista electrón: protón gira a su alrededor  $\Rightarrow$  corriente circular crea en su centro campo  $B$
- $B = \frac{\mu_0 i}{2r} = \frac{\mu_0}{2r} \frac{e}{T} = \frac{\mu_0}{2r} \frac{ev}{2\pi r} \Rightarrow \Delta E = 2\mu_B \cdot B = \frac{\mu_0 ev}{2\pi r^2} \mu_B = \frac{\mu_0 e^2 \hbar^2 n}{4\pi m^2 r^3}$  pues  $v = n\hbar/mr$  ;  $\mu_B = e\hbar/2m$
- $\Delta E = \frac{\mu_0 e^2 \hbar^2 n}{4\pi m^2} \left(\frac{me^2}{4\pi\epsilon_0 \hbar^2} \frac{1}{n^2}\right)^3 = \frac{\mu_0 m e^8}{256\pi^4 \epsilon_0^3 \hbar^4} \frac{1}{n^5} = mc^2 \alpha^4 \frac{1}{n^5}$  ;  $\alpha = e^2/4\pi\epsilon_0 \hbar c = 1/137$
- Hemos utilizado la relación:  $c^2 = \frac{1}{\epsilon_0 \mu_0}$
- Para el nivel  $n=2$  :  
 $\Delta E = (0.511 \text{ MeV})(1/137)^4 \frac{1}{2^5} = 4.53 \times 10^{-5} \text{ eV} \Rightarrow \Delta E/E \sim 10^{-5}!$



- Momento angular orbital:  $|\vec{L}| = \sqrt{l(l+1)}\hbar$  ;  $l = 0, 1, 2, 3, \dots$
- Número cuántico magnético orbital :  $L_z = m_l \hbar$  ;  $m_l = 0, \pm 1, \pm 2, \dots \pm l$
- Cuantificación espacial:  $\cos\theta = \frac{L_z}{|\vec{L}|} = \frac{m_l}{\sqrt{l(l+1)}}$
- Relaciones incertidumbre  $\Delta L_z \Delta \phi \geq \hbar$
- Números cuánticos hidrógeno:  
 $n = 1, 2, 3, \dots$ ;  $l = 0, 1, 2, \dots, n-1$ ,  $m_l = 0, \pm 1, \pm 2, \dots \pm l$
- Niveles energía hidrógeno:  $E_n = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2} \frac{1}{n^2}$
- Momento dipolar orbital:  $\vec{\mu}_L = -(e/2m)\vec{L}$
- Momento magnético :  $\vec{\mu}_S = -(e/m)\vec{S}$
- Spin :  $|\vec{S}| = \sqrt{s(s+1)}\hbar = \sqrt{3/4}\hbar$  para el electrón pues  $s = 1/2$
- Tercera componente del spin:  $S_z = m_s \hbar$  ;  $m_s = \pm 1/2$
- Reglas de selección para emisión fotones :  $\Delta l = \pm 1$  ;  $\Delta m_l = 0, \pm 1$
- Efecto Zeeman :  $\Delta\lambda = \frac{\lambda^2}{hc} \Delta E = \frac{\lambda^2}{hc} \mu_B \cdot B$
- Estructura fina:  $\Delta E = mc^2 \alpha^4 / n^5$  ;  $\alpha = e^2 / 4\pi\epsilon_0 \hbar c \sim 1/137$