Particule dans un potentiel central

$$\hat{\mathcal{H}} = \frac{\hat{\vec{p}}^2}{2\mu} + \hat{V}(\vec{r})$$

représentation r, ϑ, ϕ $\rightarrow$ $-\frac{\hbar^2}{2\mu r}\frac{\partial^2}{\partial r^2} r(\cdot) + V(r) + \frac{\hat{\vec{L}}^2}{2\mu r^2}$

$\vec{L}^2$ est un opérateur qui dépend seulement de ϑ et ϕ

$$[\hat{\mathcal{H}}, \hat{\vec{L}}^2] = 0 \qquad [\hat{\mathcal{H}}, \hat{L}_z] = 0 \qquad [\hat{\vec{L}}^2, \hat{L}_z] = 0$$

$$\psi(\vec{r}) = \psi(r, \vartheta, \phi) = R_{nl}(r)\, Y_{lm}(\vartheta, \phi)$$

$$\begin{cases} \hat{\vec{L}}^2 Y_{lm}(\vartheta,\phi) = \hbar^2 l(l+1) Y_{lm}(\vartheta,\phi) \\ \hat{L}_z Y_{lm}(\vartheta,\phi) = \hbar m\, Y_{lm}(\vartheta,\phi) \end{cases}$$

$$\left[-\frac{\hbar^2}{2\mu r}\frac{\partial^2}{\partial r^2} r + V(r) + \frac{\hat{\vec{L}}^2}{2\mu r^2}\right] R_{nl}(r)\, Y_{lm}(\vartheta,\phi) = E_{nl}\, Y_{lm}(\vartheta,\phi)\, R_{nl}(r)$$

$$\left[-\frac{\hbar^2}{2\mu r}\frac{d^2}{dr^2} r + V(r) + \frac{\hbar^2 l(l+1)}{2\mu r^2}\right] R_{nl}(r) = E_{nl} R_{nl}(r)$$

$$R_{nl}(r) = \frac{u_{nl}(r)}{r}$$

$$-\frac{\hbar^2}{2\mu \cancel{r}}\frac{d^2}{dr^2} u_{nl} + V(r)\frac{u_{nl}}{\cancel{r}} + \frac{\hbar^2 l(l+1)}{2\mu r^2}\frac{u_{nl}}{\cancel{r}} = E_{nl}\frac{u_{nl}}{\cancel{r}}$$

②

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + \underbrace{V(r) + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2}}_{V_{eff}(r)}\right] u_{n\ell} = \mathcal{E}\, u_{n\ell}$$

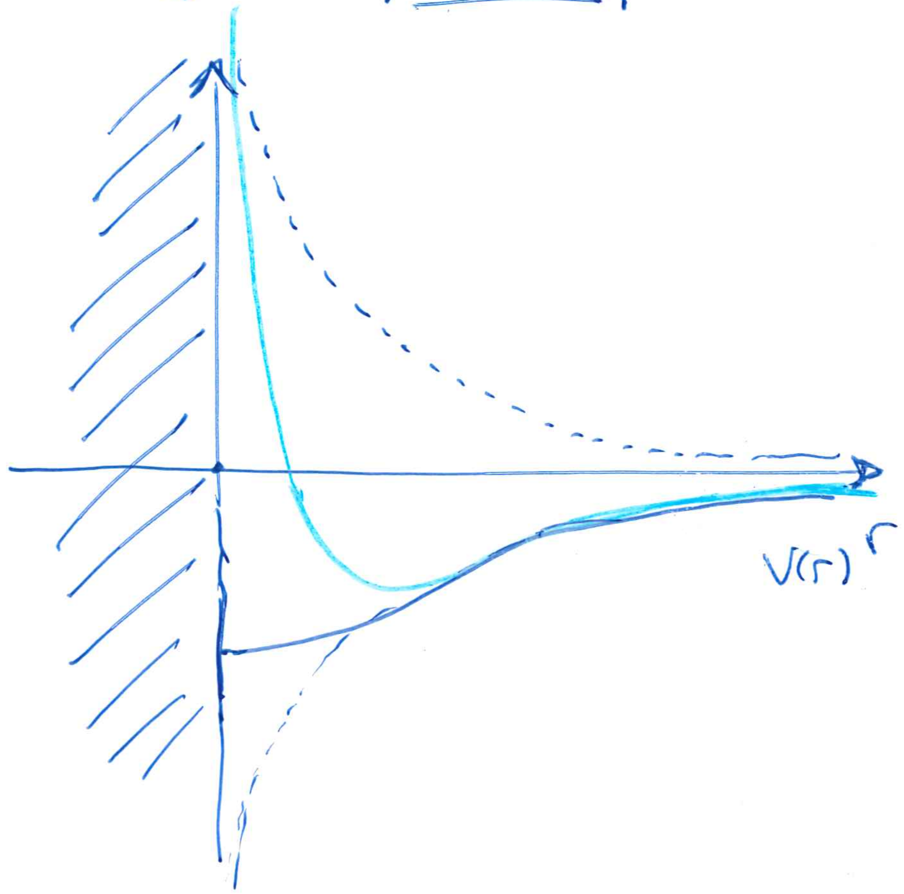
barrière centrifuge

Hypothèse sur $V(r)$: $V(r)$ ne diverge pas quand $r \to 0$ ou diverge moins vite que $\frac{1}{r^2}$

$V(r) < 0$

$\boxed{r \geq 0}$

$\boxed{\ell \neq 0}$



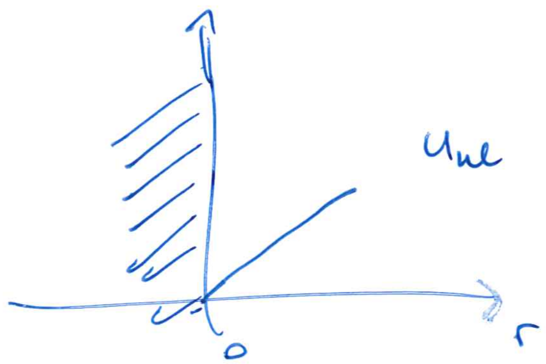
$L = I\omega$

$E = \frac{1}{2} I \omega^2$

$r \to 0$

$$\left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} - \cancel{\mathcal{E}}\right) u_{n\ell} \simeq 0$$

$u_{n\ell} \sim r^{\alpha}$



$$-\frac{\hbar^2}{2\mu}\left[\alpha(\alpha-1)\, r^{\alpha-2} - \ell(\ell+1)\, r^{\alpha-2}\right] = 0$$

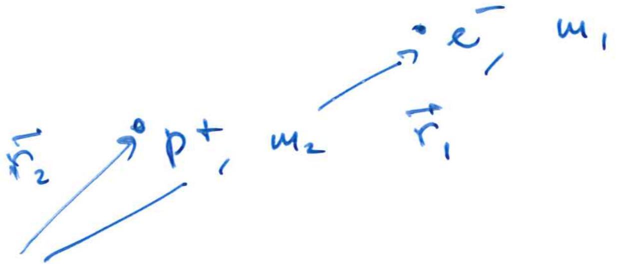
$$\alpha(\alpha-1) = \ell(\ell+1) \quad \begin{cases} \alpha = \ell+1 \\ \alpha = -\ell \end{cases}$$

$u_{n\ell} \sim r^{-\ell}$ $\quad \ell > 0$

$\boxed{u_{n\ell} \underset{r\to 0}{\sim} r^{\ell+1}}$ valable aussi pour $\underline{\ell = 0}$

$R_{n\ell} \propto r^{\ell}$

Atome d'hydrogène



$$E = \frac{1}{2} m_1 \dot{\vec r}_1^{\,2} + \frac{1}{2} m_2 \dot{\vec r}_2^{\,2} + V(\vec r_1 - \vec r_2)$$

centre de masse $\vec R = \dfrac{m_1 \vec r_1 + m_2 \vec r_2}{m_1 + m_2}$ variable relative $\vec r = \vec r_1 - \vec r_2$

$$= \frac{1}{2} \mu \dot{\vec r}^{\,2} + \underbrace{\frac{1}{2} M \dot{\vec R}^{\,2}}_{CM} + V(\vec r)$$

relative

$\mu = \dfrac{m_1 m_2}{m_1 + m_2}$ masse réduite $M = m_1 + m_2$

référentiel de repos du centre de masse $\dot{\vec R} = 0$.

$\vec p = \mu \dot{\vec r}$ impulsion relative

$$\hat H = \frac{\hat{\vec p}^{\,2}}{2\mu} + V(\vec r)$$

$V(\vec r) = V(r)$

$$\boxed{V(r) = - \frac{e^2}{4\pi \epsilon_0 r}}$$

$$\begin{cases} e = 1.6 \times 10^{-19}\ C \\ \epsilon_0 = 8.85 \times 10^{-12}\ F/m \end{cases}$$

$m_1 \simeq 10^{-30}$

$m_2 \simeq 10^{-27}$

$\vec R \simeq \vec r_2$

$\vec r = \vec r_1$

$\vec r_2 = 0$

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2}+\frac{\hbar^2 l(l+1)}{2\mu r^2}-\frac{e^2}{4\pi\epsilon_0 r}\right]u_{nl} = E_{nl}\, u_{nl}$$

$1/r a_0$

$$\left[-\frac{d^2}{dr^2}+\frac{l(l+1)}{r^2}-2\frac{\mu e^2}{4\pi\epsilon_0\hbar^2}\frac{1}{r}\right]u_{nl}=\frac{2\mu}{\hbar^2}E_{nl}\, u_{nl}$$

$$a_0^2\frac{d^2}{dr^2}=\frac{d^2}{d\rho^2}$$

$$\boxed{a_0=\frac{4\pi\epsilon_0\hbar^2}{\mu e^2} = \text{rayon de Bohr} \cong 0.5\ \text{Å} = 5\times10^{-11}\ \text{m}}$$

$\rho = r/a_0$ $\qquad v_{nl}(\rho)=u_{nl}(r)$

Rydberg

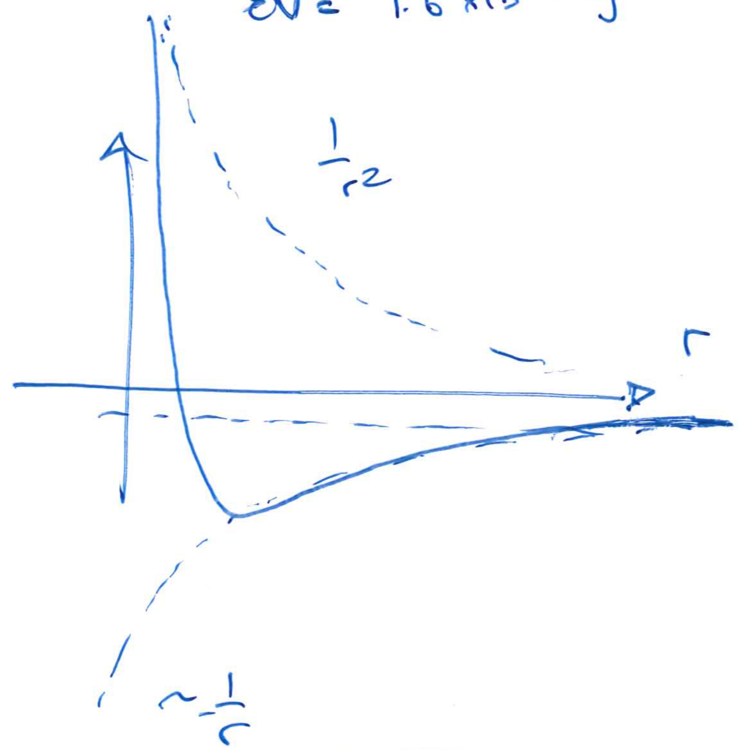
$$\left[-\frac{d^2}{d\rho^2}+\frac{l(l+1)}{\rho^2}-\frac{2}{\rho}\right]v_{nl}(\rho) = \underbrace{\frac{2\mu a_0^2}{\hbar^2}E_{nl}}_{\epsilon_{nl}}\, v_{nl}$$

$$\boxed{Ry=\frac{\hbar^2}{2\mu a_0^2} = 13.6\ \text{eV}}$$

$\text{eV} = 1.6\times10^{-19}$ J

Cherche solution pour des états liés

$\epsilon_{nl}<0$ $\qquad \epsilon_{nl}=-|\epsilon_{nl}|$ $\qquad \epsilon_{nl}=\frac{E_{nl}}{Ry}$



$$v_{nl}(\rho)\underset{\rho\to0}{\sim}\rho^{l+1}$$

$\rho\to\infty$?

$$\frac{d^2}{d\rho^2}v_{nl}=|\epsilon_{nl}|\, v_{nl}$$

$$v_{nl}\propto \exp\left(\pm\sqrt{|\epsilon_{nl}|}\,\rho\right) = \exp\left(-\sqrt{|\epsilon_{nl}|}\,\rho\right) \qquad \boxed{\sqrt{|\epsilon_{nl}|}=\lambda_{nl}}$$

$$v_{nl}(\rho) = y_{nl}(\rho)\, e^{-\lambda_{nl}\rho}$$

$$\left[-\frac{d^2}{d\rho^2} + 2\lambda_{nl}\frac{d}{d\rho} + \frac{l(l+1)}{\rho^2} - \frac{z}{\rho} \right] y_{nl}(\rho) = 0 \qquad (**)$$

$$y_{nl}(\rho) \underset{\rho \to 0}{\sim} \rho^{l+1}$$

$$\boxed{y_{nl}(\rho) = \rho^{l+1} \sum_{q=0}^{\infty} c_q\, \rho^q} \qquad (*)$$

$$\boxed{c_0 \neq 0}$$

en injectant $(*)$ en $(**)$ $\rightarrow$ $\sum_{q=0}^{\infty} A_q(\{c_q\})\, \rho^q = 0$ $\qquad \underline{A_q = 0} \quad \forall q$

$$\underline{c_q = \frac{2\left[(q+l)\lambda_{nl} - 1\right]}{q(q+2l+1)}\, c_{q-1}}$$

$q \to \infty$ $\qquad c_q \simeq \dfrac{2\lambda_{nl}}{q}\, c_{q-1}$

$$\frac{c_q}{c_{q-1}} \underset{q \to \infty}{\simeq} \frac{2\lambda_{nl}}{q}$$

$$\boxed{\rho \to \infty}$$

$$\exp(2\lambda_{nl}\rho) = \sum_{q=0}^{\infty} \overbrace{\frac{(2\lambda_{nl})^q}{q!}}^{\tilde{c}_q}\, \rho^q \qquad \frac{\tilde{c}_q}{\tilde{c}_{q-1}} = \frac{\frac{(2\lambda_{nl})^q}{q!}}{\frac{(2\lambda_{nl})^{q-1}}{(q-1)!}} = \frac{2\lambda_{nl}}{q}$$

$$y_{nl}(\rho) \xrightarrow{\rho \to \infty} \exp(2\lambda_{nl}\rho)$$

$$v_{nl}(\rho) \underset{\rho\to\infty}{\sim} e^{-\lambda_{nl}\rho} \quad e^{2\lambda_{nl}\rho} = e^{\lambda_{nl}\rho}$$

Tronquer la série : $\exists\ k = q_{max}$: $\quad c_{k-1} \neq 0$

$$c_k = \frac{2\left[(k+l)\lambda_{nl} - 1\right]}{k(k+2l+1)} \quad c_{k-1} = 0$$

$$\boxed{\lambda_{nl} = \frac{1}{k+l} = \frac{1}{n}}$$

$k \geq 1$

$n = l + k \quad \in \mathbb{N}^*$

$l = 0, 1, 2, \ldots \qquad \boxed{n = 1, 2, \ldots}$

si vous fixez n : $\quad l = 0, 1, \ldots, n-1$

$$E_{nl} = -R_y(\epsilon_{nl}) = -R_y\,\lambda_{nl}^2 = -\frac{R_y}{n^2} = E_n$$

$\boxed{n = \text{nombre quantique principale}}$

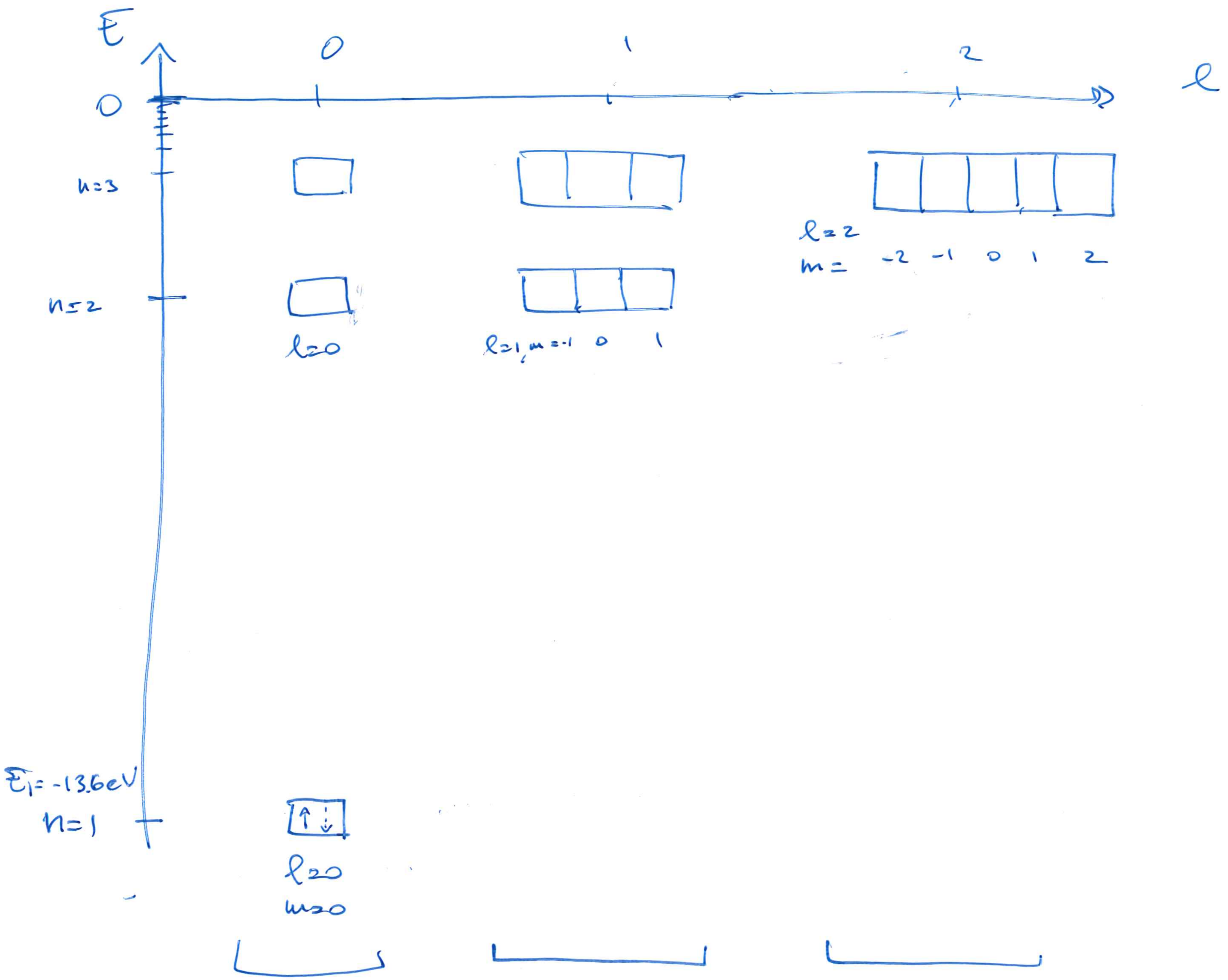
$$\psi = R_{nl}(r)\, Y_{lm}(\theta, \phi) = \psi_{nlm}$$

$l = 0, 1, \ldots, n-1 \quad$ nombre quantique de $\vec{L}^2$

$m = -l, \ldots, l \quad$ " " de L_z

dégénérescence :
$$\boxed{g_n = \sum_{l=0}^{n-1} (2l+1) = 2\,\frac{n(n-1)}{2} + n = n^2}$$

Spectre de l'atome d'hydrogène $\quad E_n = -\frac{R_y}{n^2} \quad n = 1, 2, \ldots$



orbitales s $\qquad$ orbitales p $\qquad$ orbitales d $\qquad$ f $\qquad$ g

$\uparrow e^+$ $\qquad$ $|\uparrow\rangle$ $\quad$ $|\downarrow\rangle$

p^+

dégénérescence $= 2g_n = 2n^2$

$|n\,l\,m\,;\,s\,m_s\rangle$ $\quad m_s \to \pm \hbar/2$

$\hat{H}, \hat{L}^2, \hat{L}^z, \hat{S}^2, \hat{S}^z$ forment un ECOC

Structure des fonctions propres

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)\, Y_{lm}(\theta, \phi)$$

$$R_{nl}(r) = \frac{1}{r}\, v_{nl}\left(\frac{r}{a_0}\right) = \underbrace{\frac{1}{r}\, Y_{nl}\left(\frac{r}{a_0}\right)}_{\text{polynomes d'ordre } (n-1)} e^{-r/na_0}$$

$$\lambda_{nl}\, \rho = \frac{r}{na_0}$$

$q_{max} = k$

$k + l = n$

$k = n - l$

$$Y_{nl}(\rho) = \underbrace{\rho^{l+1} \sum_{q=0}^{n-l-1} c_q\, \rho^q}_{\text{polynomes d'ordre } n}$$

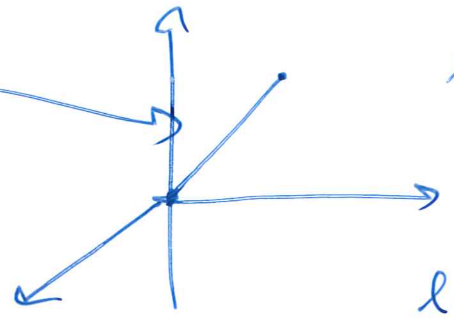
$$\begin{cases} R_{10} = \dfrac{1}{2a_0^{3/2}}\, e^{-r/a_0} \\[2ex] R_{20} = \dfrac{2}{(2a_0)^{3/2}} \left(1 - \dfrac{r}{2a_0}\right) e^{-r/2a_0} \\[2ex] R_{21} = \dfrac{1}{(2a_0)^{3/2}}\, \dfrac{r}{\sqrt{3}\, a_0}\, e^{-r/2a_0} \end{cases}$$

$$\int_0^\infty dr\, P_{nl}(r) = 1 = \int_0^\infty dr\, r^2 |R_{nl}|^2$$

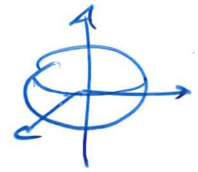
$$P_{nl}(r) = r^2 |R_{nl}(r)|^2$$

Harmoniques sphériques

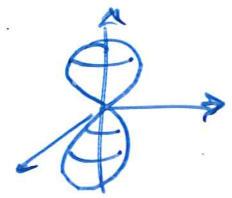
$|Y(\theta, \phi)|^2$



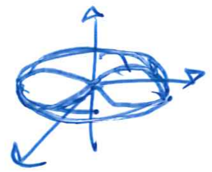
$l=0 \quad |Y_{00}|^2 = \frac{1}{4\pi}$



$l=1 \quad |Y_{10}|^2 = \frac{3}{4\pi} \cos^2\theta$

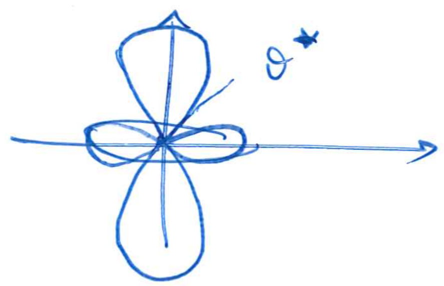


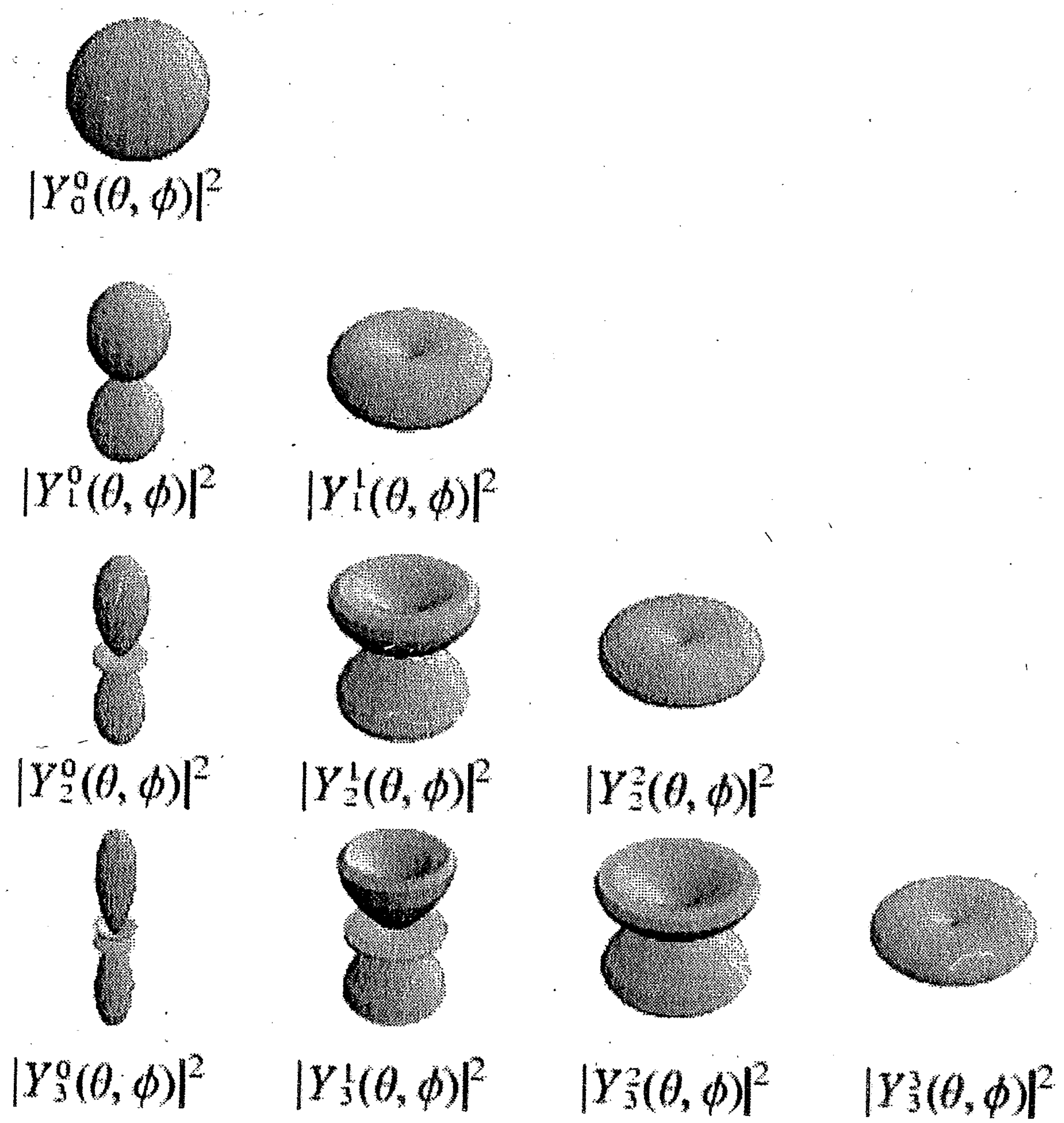
$|Y_{11}|^2 = \frac{3}{8\pi} \sin^2\theta$



$l=2 \quad |Y_{20}|^2 = \frac{5}{16\pi} (3\cos^2\theta - 1)^2$

$\theta^* \simeq 54°$





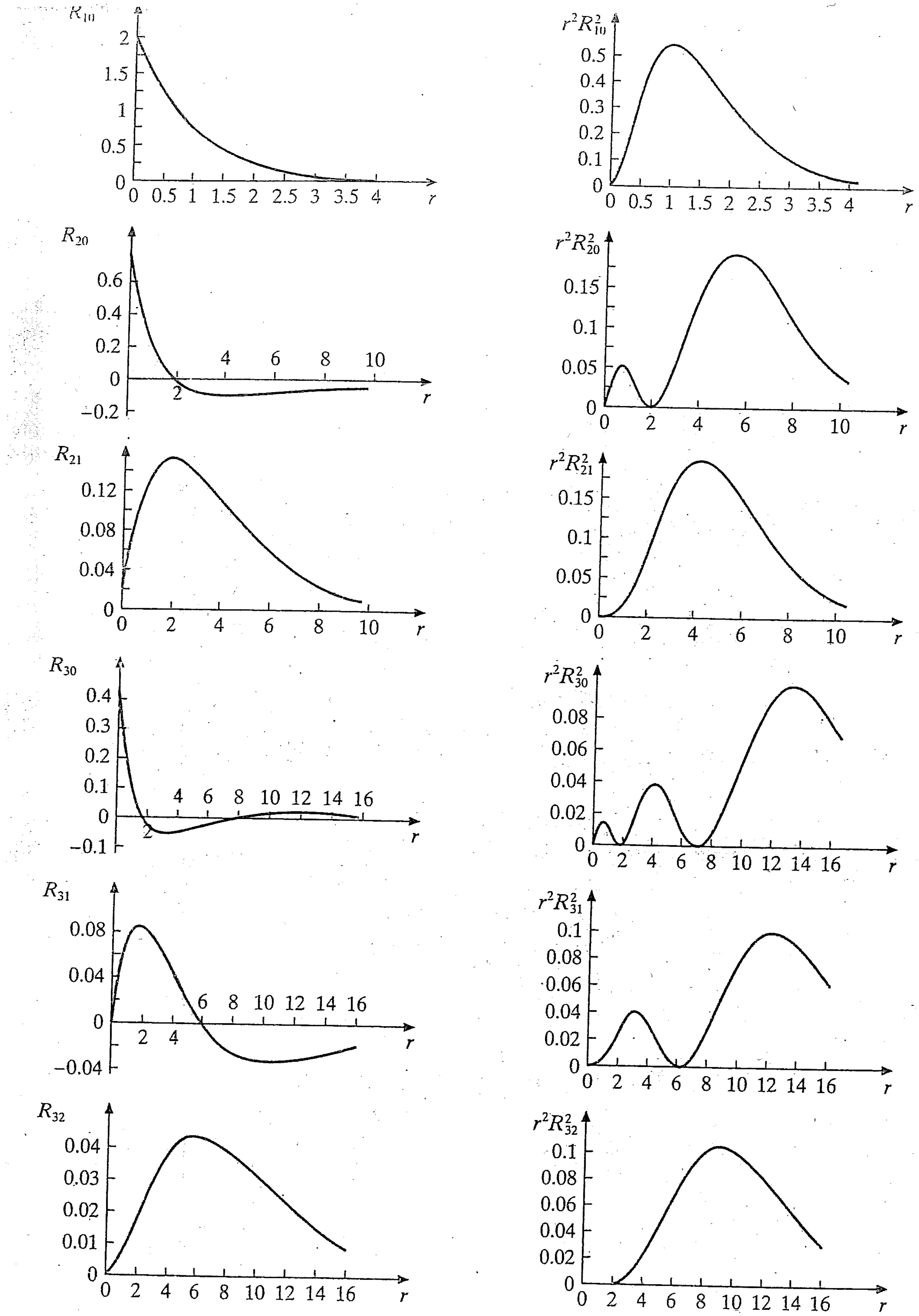
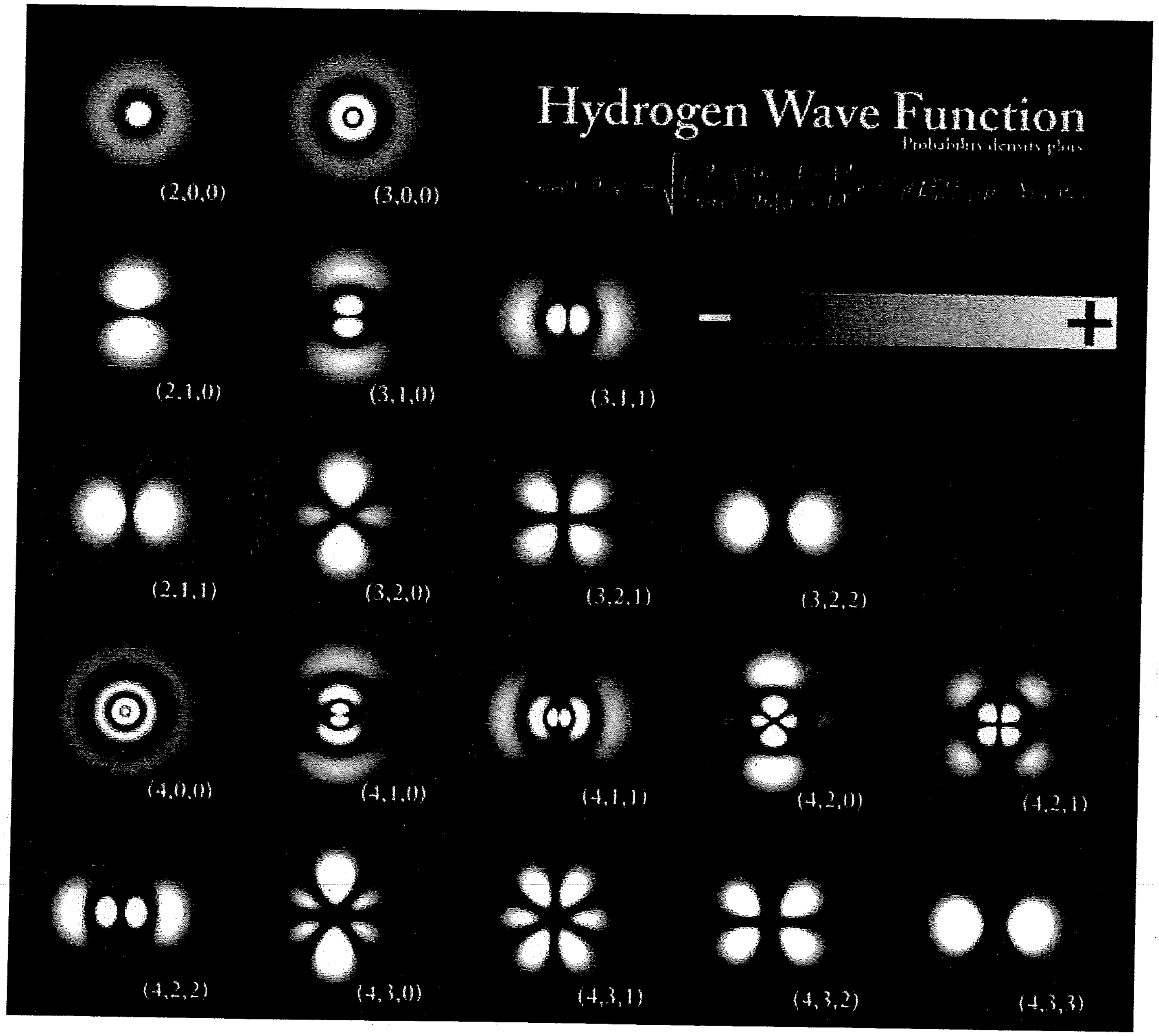
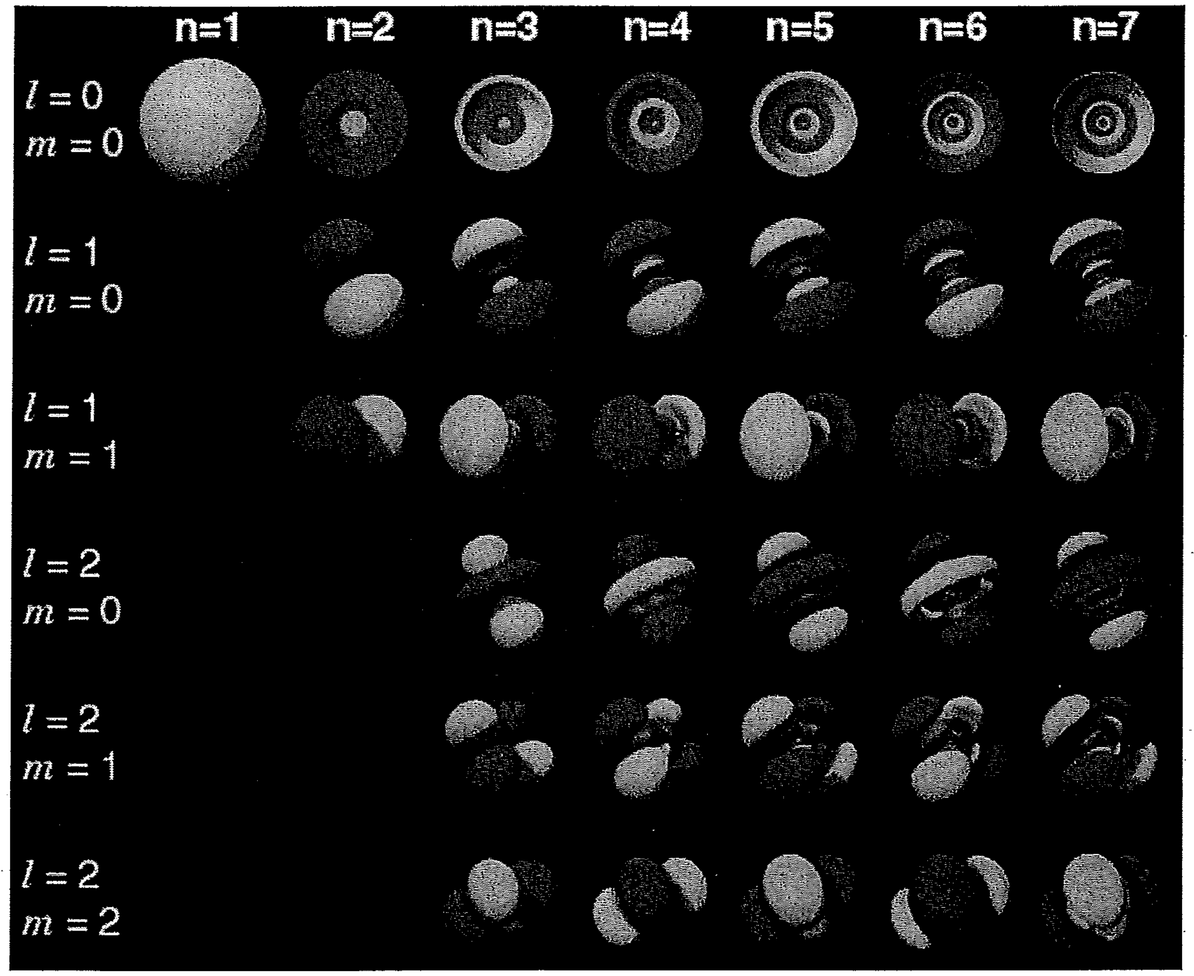


Figure 3.3 Radial functions $R_{nl}(r)$ and radial distribution functions $r^2R_{nl}^2(r)$ for atomic hydrogen.



http://sevencolors.org/images/photo/hydrogen_density_plots.jpg



http://chemistry.beloit.edu/Stars/images/orbitals.jpg