# Radial solution of the H-like atoms
# (One electron system)
# Example 13.2.1, Example 15.6.1

**Hydrogenic atoms** are atoms with nucleus ($H^+$, $Fe^{26+}$, $Pb^{82+}, \cdots$) and one electron. The hydrogenic atom has an analytic solution. i.e., the solution is exact, no approximations are needed.

## Coulomb Potential $\left(\frac{Ze^2}{r}\right)$

The radial solution of the H-like atom is given by ( $Ze$ is the charge of the nucleus):

$$\left[\frac{-\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\underbrace{-\frac{Ze^2}{r}+\frac{\hbar^2 l(l+1)}{2\mu r^2}}_{\text{effective hydrogenic potential}}\right]R(r)=ER(r) \qquad \textbf{(13)}$$

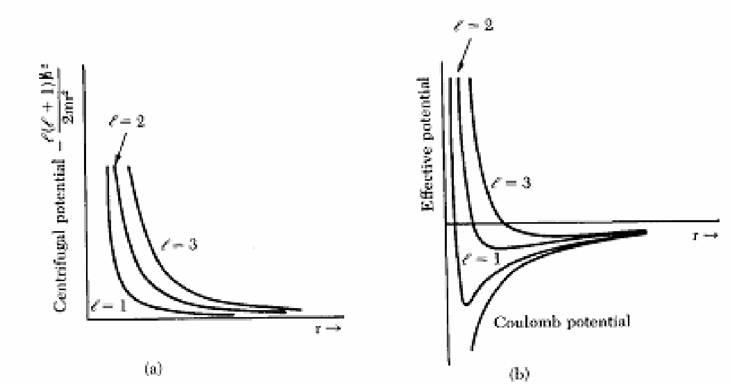


Figure (a) The centrifugal potential for several values of $\ell$ . (b) The effective hydrogenic potential due to both the Coulomb and centrifugal terms.

Use the variable $\rho = \alpha r$ , and the atomic system $(e = \mu \approx m_e = a_0 = \hbar = 1)$, equation (13) will take the form:

$$\frac{1}{\rho^2}\frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial R(\rho)}{\partial r}\right)+\left[\underbrace{\frac{2E}{\alpha^2}}_{=-1/4}+\underbrace{\frac{2Ze^2}{\alpha\,\rho}}_{=\lambda/\rho}-\frac{l(l+1)}{\rho^2}\right]R(\rho)=0$$

or

$$\frac{d^2R}{d\rho^2}+\frac{2}{\rho}\frac{dR}{d\rho}-\frac{l(l+1)}{\rho^2}R+\left(\frac{\lambda}{\rho}-\frac{1}{4}\right)R=0 \qquad \textbf{(14)}$$

Where we used the variables: $\alpha = \sqrt{-8E}$ , and $\lambda^2 = \frac{2Z}{\alpha} = Z\left(\frac{1}{-2E}\right)^{1/2}$. The value of $\frac{1}{4}$ is used for simplicity. Here we are interest in bound states only, i.e. $E = -|E|$, consequently $\alpha$ will be positive. Equation (14) cannot be solved in closed form. So, we must employ either the power series method or an analytical approach which utilizes a knowledge of the asymptotic solutions in the limits of very small and very large *r*. Choosing the latter approach, we note that for the asymptotic solution, i.e. $(\rho \to \infty)$ , of (14) reduced to:

$$\frac{d^2R_\infty}{d\rho^2}+\frac{1}{4}R_\infty=0 \quad \Rightarrow \quad R_\infty \approx e^{\pm\rho/2} \qquad \textbf{(15)}$$

The solution $e^{+\rho/2}$ will be rejected since it gives unphysical limit, $\lim_{\rho\to\infty} e^{+\rho/2} = \infty$. To solve (14) we will introduce the solution;

$$R(\rho) = e^{-\rho/2} G(\rho) \qquad \textbf{(16)}$$

Substitute from (16) to (14) one finds:

$$\frac{d^2G}{d\rho^2} - \left(1 - \frac{2}{\rho}\right)\frac{dG}{d\rho} + \left[\frac{\lambda - 1}{\rho} - \frac{l(l+1)}{\rho^2}\right] G = 0 \qquad \textbf{(17)}$$

The point $\rho = 0$ is regular singular point. So, we have to use Frobenius method in the form:

$$G(\rho) = \rho^s \sum_\nu a_\nu \rho^\nu = \rho^s L(\rho), \qquad a_o \neq 0, \quad s \geq 0 \qquad \textbf{(18)}$$

Substitute (18) in (17) we have

$$\rho^2 \frac{d^2L}{d\rho^2} + \rho\left[2(s+1) - \rho\right]\frac{dL}{d\rho} + \left[\rho(\lambda - s - 1) + s(s+1) - l(l+1)\right] L = 0 \qquad \textbf{(19)}$$

Putting $\rho = 0$ in (19), we get:

$$s(s+1) - l(l+1) = 0 \quad \Rightarrow \quad (s - l)(s + l + 1) = 0$$

So, s will take the values $s = l$ and $s = -(l+1)$. The condition $\lim_{r\to 0}\left(r R(r)\right) = 0$ allows us to reject the solution. $s = -(l+1)$. See the condition in Eq. (18) for $s$.

$$\frac{d^2L}{d\rho^2} + \left[\frac{2l+2}{\rho} - 1\right]\frac{dL}{d\rho} + \left[\frac{(\lambda - l - 1)}{\rho}\right] L = 0 \qquad \textbf{(20)}$$

[* Compare equation (20) with the **associate Laguerre polynomials**:

$$\left[x\frac{d^2}{dx^2} - (r + 1 - x)\frac{d}{dx} + (q - r)\right] L_q^r(x) = 0$$

one gets $r = 2l + 1, \quad q = n + l \quad L_{n+l}^{2l+1}(\rho)$ ]

Use the substitution $L(\rho) = \sum_\nu a_\nu \rho^\nu$, Eq. (20) will reduce to

$$\sum_{\nu=0}^{\infty}[\nu(\nu-1)a_\nu\rho^{\nu-2} + \nu(\frac{2l+2}{\rho} - 1)a_\nu\rho^{\nu-1} + (\lambda - l - 1)a_\nu\rho^{\nu-1}] = 0 \qquad \textbf{(21)}$$

Putting $K = \nu - 1$ in the first term and $K = \nu$ in the other two terms, one finds

$$\sum_{K=0}^{\infty}\left\{(K+1)(K+2l+2)a_{K+1} + (\lambda - 1 - l - K)a_K\right\}\rho^{K-1} = 0 \qquad \textbf{(22)}$$

which gives the recurrence relation:

$$\frac{a_{K+1}}{a_K} = \frac{K + l + 1 - \lambda}{(K+1)(K+2l+2)} \underset{K\to\infty}{\approx} \frac{1}{K} \qquad \textbf{(23)}$$

Note that: the recurrence relation in (23) is similar to the recurrence relation in the series $e^{+\rho}$:

$$e^\rho = 1 + \rho + \frac{\rho^2}{2!} + \cdots + \frac{\rho^K}{K!} + \frac{\rho^{K+1}}{(K+1)!} \Rightarrow \frac{a_{K+1}}{a_K} = \frac{1}{(K+1)} \underset{K\to\infty}{\approx} \frac{1}{K} \qquad \textbf{(24)}$$

Thus

$$L(\rho) \approx e^\rho \quad \Rightarrow \quad R(\rho) \approx e^{\rho/2} \underset{\rho\to\infty}{\to} \infty \qquad \textbf{(25)}$$

The solution in (25) is not acceptable since it does not satisfy the condition of quantum mechanics. So, we have to terminate our series by putting the coefficients $a_{K+1} = 0$. To satisfy this condition we have to use numerator $K + l + 1 - \lambda = 0$ in (23) to find:

$$n = \lambda = n_r + l + 1, \qquad n_r \geq 0 \tag{26}$$

where $(n = 1, 2, \cdots)$ is the principle quantum number, and $(l = 0, 1, 2, \cdots, n-1)$ is the orbital quantum number, in which $(n \geq l + 1, \quad n_r \geq 0)$. Finally, we have

$$E_n = -\frac{Z^2}{2n^2} \text{ a.u.} \tag{27}$$

Using the following values:

$e = 1.602 \times 10^{-19}$ C, $1\text{J} = 6.242 \times 10^{18}$ eV, $\hbar = 1.054 \times 10^{-34}$Js, $\mu = \dfrac{m_e m_p}{m_e + m_p} \approx m_e = 9.109 \times 10^{-31}$ kg,

we have

$$1\,a.u. = 2\,\text{Ry} = \frac{2\mu e^4}{2\hbar^2} = 27.2 \text{ eV}. \tag{27a}$$

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| $n$ | Level | $l$ | orbit | $m$ | Degeneracy $d_l$ | Degeneracy $d_n$ | $E_n$(Ry) |
|---|---|---|---|---|---|---|---|
| 1 | K | 0 | s | 0 | 1 | 1 | -1 |
| 2 | L | 0 | s | 0 | 1 | 4 | -1/4 |
| | | 1 | p | -1,0,1 | 3 | | |
| 3 | M | 0 | s | 0 | 1 | 9 | -1/9 |
| | | 1 | p | -1,0,1 | 3 | | |
| | | 2 | d | -2,-1,0,1,2 | 5 | | |
| 4 | N | 0 | s | 0 | 1 | 16 | -1/16 |
| | | 1 | p | -1,0,1 | 3 | | |
| | | 2 | d | -2,-1,0,1,2 | 5 | | |
| | | 3 | f | -3,-2,-1,0,1,2,3 | 7 | | |

# Radial wave equation of the H-like atoms

Finally the radial solution of (13) will be:

$$R_{nl}(\rho) = -N_{nl}\, e^{-\rho/2} \rho^l L_{n+l}^{2l+1}(\rho) \tag{28}$$

With the normalization condition:

$$N_{nl}^2 \int_0^\infty \rho^2 d\rho e^{-\rho} \rho^{2l} \left[L_{n+l}^{2l+1}(\rho)\right]^2 = N_{nl}^2 \frac{2n\left[(n+l)!\right]^3}{(n-l-1)!} = 1 \tag{29}$$

One gets:

$$\begin{aligned} R_{nl}(r) &= -\left(\frac{2Z}{na_o}\right)^{3/2} \sqrt{\frac{(n-l-1)!}{2n\left[(n+1)!\right]^3}}\, \rho^l e^{-Zr/na_o} L_{n+l}^{2l+1}(\rho), \\ &= \left(\frac{2Z}{n}\right)^{3/2} \frac{1}{(2l+1)!} \sqrt{\frac{(n+l)!}{2n\,(n-l-1)!}}\, \rho^l e^{-\rho/2} F\left(-(n-l-1), 2l+2, \rho\right) \end{aligned} \tag{30}$$

Where the negative sign is chosen to make $R_{10}(r)$ (which contains $L_1^1 = -1$ ) positive. Here we used $\rho = \dfrac{2Zr}{na_o}$ and $a_o = \hbar^2/\mu e^2$ for Bohr radius. The $L_{n+\ell}^{2\ell+1}(\rho)$ is the **associate Laguerre polynomials.** $F$ is the (confluent) hypergeometric function:

$$F(\alpha,\beta,x)=1+\frac{\alpha}{\beta\cdot 1!}x+\frac{\alpha(\alpha+1)}{\beta(\beta+1)\,2!}x^2+\cdots .$$

Another useful function:

$$F(\alpha,\beta,\gamma,x)=\sum_{\nu}\frac{\alpha(\alpha+1)\cdots(\alpha+\nu-1)\beta(\beta+1)\cdots(\beta+\nu-1)}{\gamma\cdots(\gamma+\nu-1)\,\nu!}x^{\nu}$$

is the hypergeometric function.

It is helpful for dealing with these functions to have some idea of their form which are shown in the figure below.

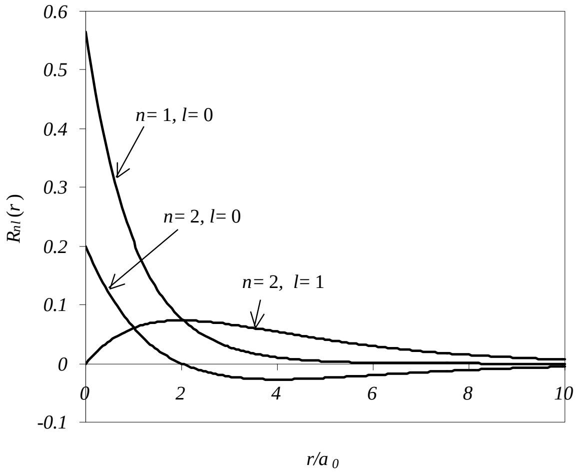



**Figure:** Radial part of the wavefunction $R_{n,l}(r)$ for $n$ = 1, $l$ = 0; $n$ = 2, $l$ = 0, 1.

***A Table of Radial Wavefunctions,*** $R_{nl}$

| $n$ | $l$ | orbit | $R_{nl}$ |
|---|---|---|---|
| 1 | 0 | **1**s | $2(Z)^{3/2}e^{-Zr}$ |
| 2 | 0 | **2**s | $\frac{1}{\sqrt{2}}(Z)^{3/2}(1-\frac{Zr}{2})e^{-Zr/2}$ |
| | 1 | **2**p | $\frac{1}{2\sqrt{6}}(Z)^{5/2}re^{-Zr/2}$ |
| 3 | 0 | **3**s | $\frac{2}{3\sqrt{3}}(Z)^{3/2}\left(1-\frac{2}{3}Zr+\frac{2}{27}(Zr)^2\right)e^{-Zr/3}$ |
| | 1 | **3**p | $\frac{8}{27\sqrt{6}}(Z)^{3/2}\left(Zr-\frac{1}{6}(Zr)^2\right)e^{-Zr/3}$ |
| | 2 | **3**d | $\frac{4}{81\sqrt{30}}(Z)^{7/2}r^2e^{-Zr/3}$ |
| 4 | 0 | 4s | $6(\mathrm{Z})^{\frac{3}{2}}\left(192-144\mathrm{Zr}+24(\mathrm{Zr})^2+(\mathrm{Zr})^3\right)\mathrm{e}^{-\mathrm{Zr}/4}$ |
| | 1 | 4p | $\frac{1}{256\sqrt{15}}(\mathrm{Z})^{\frac{5}{2}}\left(80\,\mathrm{r}-20\mathrm{Zr}^2+\mathrm{Z}^2\mathrm{r}^3\right)\mathrm{e}^{-\mathrm{Zr}/4}$ |
| | 2 | 4d | $\frac{1}{768\sqrt{15}}(\mathrm{Z})^{\frac{7}{2}}\left(12\,\mathrm{r}^2-\mathrm{Zr}^3\right)\mathrm{e}^{-\mathrm{Zr}/4}$ |
| | 3 | 4f | $\frac{4}{768\sqrt{35}}(\mathrm{Z})^{\frac{9}{2}}\,\mathrm{r}^4\,\mathrm{e}^{-\mathrm{Zr}/4}$ |

In general the hydrogenic wavefunction is a product of the radial wavefunction and the spherical harmonic:

$$\left|n\ell m\right\rangle = \Psi_{n\ell m}\left(r,\theta,\phi\right) = R_{nl}(r) Y_{\ell}^{m}\left(\theta,\phi\right) = \frac{1}{r} P_{n\ell}(r) Y_{\ell}^{m}\left(\theta,\phi\right)$$

$\Psi_{nlm}$ are orthonormal wave function, due to the fact:

$$\underbrace{\int_0^\infty R^*_{n',l'}(r) R_{n,l}(r) r^2 dr}_{\delta_{n,n'}\delta_{l,l'}} \underbrace{\int_0^{2\pi}\int_0^{\pi} Y^*_{l',m'}(\theta,\varphi) Y_{l,m}(\theta,\varphi) \sin\theta d\theta d\varphi}_{\delta_{l,l'}\delta_{m,m'}} = 1$$

H.W. Do exercises 13.2.9.

H.W. Do exercises 15.6.1 to 15.6.12.

## Degeneracy of atomic orbitals

**Degeneracy of p orbitals:** The wavefunctions for p orbitals are in terms of the spherical harmonics $Y_\ell^{m_\ell}(\theta,\phi)$ are:

$$Y_1^0(\theta,\phi)=\left(\frac{3}{4\pi}\right)^{\frac{1}{2}}\cos\theta, \qquad Y_1^1(\theta,\phi)=\left(\frac{3}{8\pi}\right)^{\frac{1}{2}}\sin\theta\, e^{i\phi} \quad , \quad Y_1^{-1}(\theta,\phi)=\left(\frac{3}{8\pi}\right)^{\frac{1}{2}}\sin\theta\, e^{-i\phi}$$

Note that: $Y_1^1(\theta,\phi)$ and $Y_1^{-1}(\theta,\phi)$ are complex functions and we are not able to visualize a complex orbital. However, since $Y_1^1(\theta,\phi)$ and $Y_1^{-1}(\theta,\phi)$ are degenerate, any linear combination of them is also a solution to the Schrödinger equation. We can make real wavefunction by taking the following linear combinations

$$p_x=\frac{1}{\sqrt{2}}\left(Y_1^1+Y_1^{-1}\right)=\left(\frac{3}{16\pi}\right)^{\frac{1}{2}}\sin\theta\left(e^{i\phi}+e^{-i\phi}\right)=\left(\frac{3}{4\pi}\right)^{\frac{1}{2}}\sin\theta\cos\phi$$

$$p_y=\frac{-i}{\sqrt{2}}\left(Y_1^1-Y_1^{-1}\right)=-i\left(\frac{3}{16\pi}\right)^{\frac{1}{2}}\sin\theta\left(e^{i\phi}-e^{-i\phi}\right)=\left(\frac{3}{4\pi}\right)^{\frac{1}{2}}\sin\theta\sin\phi$$

There is no substantial difference between the $Y_1^1(\theta,\phi)$ and $Y_1^{-1}(\theta,\phi)$ and the $p_x(\theta,\phi)$ and $p_y(\theta,\phi)$ orbitals. Choosing one set over another is matter of convenience.

| State | Spherical Harmonics |
|---|---|
| s | $Y_0^0=\left(\frac{1}{4\pi}\right)^{1/2}$ |
| p | $Y_1^0(\theta,\phi)=\left(\frac{3}{4\pi}\right)^{\frac{1}{2}}\cos\theta$, $\quad Y_1^{\pm1}(\theta,\phi)=\left(\frac{3}{8\pi}\right)^{\frac{1}{2}}\sin\theta\, e^{\pm i\phi}$ |
| d | $Y_2^0(\theta,\phi)=\left(\frac{5}{16\pi}\right)^{\frac{1}{2}}\left(3\cos^2\theta-1\right)$, $\quad Y_2^{\pm1}(\theta,\phi)=\left(\frac{15}{8\pi}\right)^{\frac{1}{2}}\sin\theta\cos\theta e^{\pm i\phi}$ <br> $Y_2^{\pm2}(\theta,\phi)=\left(\frac{15}{32\pi}\right)^{\frac{1}{2}}\sin^2\theta e^{\pm 2i\phi}$ |

After linear combination of d-state, we have:

$$d_{z^2}(\theta,\phi)=Y_2^0(\theta,\phi)=\left(\frac{5}{16\pi}\right)^{\frac{1}{2}}\left(3\cos^2\theta-1\right), \quad d_{xz}=\frac{1}{\sqrt{2}}\left(Y_2^1+Y_2^{-1}\right)=\left(\frac{15}{4\pi}\right)^{\frac{1}{2}}\sin\theta\cos\theta\cos\phi$$

$$d_{yz}=\frac{-i}{\sqrt{2}}\left(Y_2^1-Y_2^{-1}\right)=\left(\frac{15}{4\pi}\right)^{\frac{1}{2}}\sin\theta\cos\theta\sin\phi, \quad d_{x^2-y^2}=\frac{1}{\sqrt{2}}\left(Y_2^2+Y_2^{-2}\right)=\left(\frac{15}{16\pi}\right)^{\frac{1}{2}}\sin^2\theta\cos 2\phi$$

$$d_{xy}=\frac{-i}{\sqrt{2}}\left(Y_2^2-Y_2^{-2}\right)=\left(\frac{15}{16\pi}\right)^{\frac{1}{2}}\sin^2\theta\sin 2\phi$$

# Laguerre Polynomials $L_n(x)$

Differential equation

$$\left[x\frac{d^2}{dx^2}-(1-x)\frac{d}{dx}+n\right]L_n(x)=0$$

Definition

$$L_n(x)=e^x\frac{d^n}{dx^n}\left(e^{-x}x^n\right), \qquad n=0,1,2,3,\cdots$$

Generating function

$$\frac{e^{-xt/(1-t)}}{(1-t)}=\sum_{n=0}^{\infty}\frac{t^n}{\Gamma(n+1)}L_n(x); \qquad |t|<1$$

Recurrence relations

$$L_{n+1}(x)=(2n+1-x)L_n(x)-n^2L_{n-1}(x);$$

$$x\frac{d}{dx}L_n(x)=nL_n(x)-n^2L_{n-1}(x)$$

Orthogonality relation

$$\int_0^{\infty}e^{-x}L_n(x)L_m(x)dx=\left(\Gamma(n+1)\right)^2\delta_{mn}$$

**H.W.** Check the following table

| $n$ | $L_n(x)$ | $n$ | $L_n(x)$ |
|---|---|---|---|
| 0 | $1$ | **2** | $x^2-4x+2$ |
| 1 | $-x+1$ | **3** | $-x^3+9x^2-18x+6$ |

# Associated Laguerre Polynomials $L_n^m(x)$

Differential equation

$$\left[x\frac{d^2}{dx^2}-(m+1-x)\frac{d}{dx}+(n-m)\right]L_n^m(x)=0$$

Definition

$$L_n^m(x)=\frac{d^m}{dx^m}\left[L_n(x)\right] \qquad m,n=0,1,2,3,\cdots$$

$$L_n^0(x)=L_n(x); \qquad L_n^m(x)=0 \quad \text{if } m>n$$

Generating function

$$\frac{(-1)^m t^m}{(1-t)^{m+1}}e^{-xt/(1-t)}=\sum_{n=m}^{\infty}\frac{t^n}{\Gamma(n+1)}L_n^m(x); \qquad |t|<1$$

Recurrence relations

$$\frac{(n-m+1)}{n+1}L_{n+1}^{m}(x)=(2n-m+1-x)L_{n}^{m}(x)-n^{2}L_{n-1}^{k}(x);$$

$$x\frac{d}{dx}L_{n}^{m}(x)=(x-m)L_{n}^{m}(x)-\left(m-n-1\right)L_{n}^{m-1}(x)$$

$$\frac{d}{dx}L_{n}^{m}(x)=L_{n}^{m+1}(x)$$

Orthogonality relation

$$\int_{0}^{\infty}e^{-x}x^{k}L_{n}^{k}(x)L_{m}^{k}(x)dx=\frac{\left[\Gamma(n+1)\right]^{3}}{\Gamma(n-m+1)}\delta_{mn}$$

$$L_{0}^{k}(x)=1;\quad L_{1}^{k}(x)=-x+k+1;\quad L_{2}^{k}(x)=\frac{x^{2}}{2}-(k+2)x+\frac{\left(k+1\right)\left(k+2\right)}{2}$$

$$L_{n}^{k}(0)=\frac{\left(n+k\right)!}{n!k!}$$

**H.W.** Check the following table

| $n$ | $m$ | $L_n^m(x)$ | $n$ | $m$ | $L_n^m(x)$ |
|---|---|---|---|---|---|
| **1** | **1** | **-1** | **3** | **1** | $-3x^{2}+18x-18$ |
| **2** | 1 | $2x-4$ | **3** | **2** | $-6x+18$ |
| **2** | **2** | 2 | **3** | **3** | $-6$ |

In[1]:= `(* Hydrogen atom *)`

In[2]:= $R[Z\_, n\_, L\_, r\_] := \frac{1}{(1+2L)!}\sqrt{\frac{(n+L)!}{(2n)\,(n-L-1)!}}\left(\frac{2Z^3}{n}\right)^{3/2} e^{-\frac{Zr}{n}}\left(\frac{2Zr}{n}\right)^{L}$ Hypergeometric1F1$\left[-(n-L-1),\ 2L+2,\ \frac{2Zr}{n}\right]$;

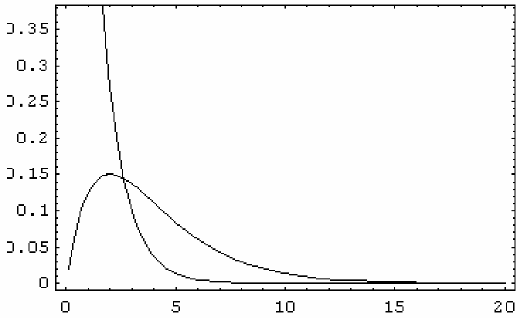
In[3]:= $\Psi 1s = R[1, 1, 0, r]$

Out[3]= $2\,e^{-r}$

In[4]:= $\Psi 2p = R[1, 2, 1, r]$

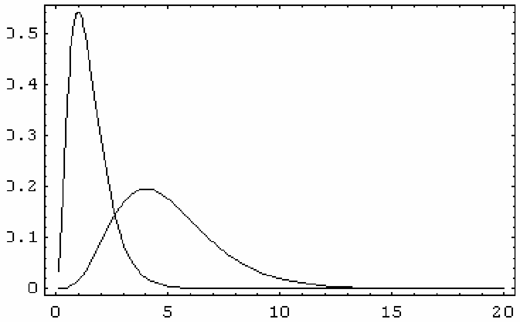
Out[4]= $\frac{e^{-r/2}\,r}{2\sqrt{6}}$

In[13]:= `Plot[{Ψ1s, Ψ2p}, {r, 0.1, 20}, Frame → True]`




Out[13]= - Graphics -

In[12]:= `Plot[{`$r^2\,\Psi 1s^2$`, `$r^2\,\Psi 2p^2$`}, {r, 0.1, 20}, Frame → True]`



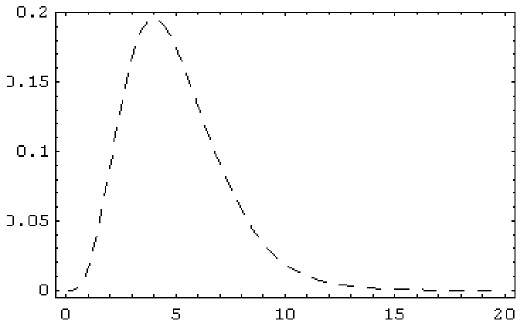

Out[12]= - Graphics -

In[6]:= `(* orthogolality *)`

In[7]:= $\int_0^{\infty} (\Psi 2p)^2\, r^2\, dr$

Out[7]= 1

In[8]:= `ph1 = Plot[ (r Ψ2p)`$^2$`, {r, 0.1, 20}, Frame → True, PlotStyle → Dashing[{0.03}]]`




Out[8]= - Graphics -