The Wave Function Equations

http://panda.unm.edu/Courses/Finley/P262/Hydrogen/WaveFcns.html
http://quantummechanics.ucsd.edu/ph130a/130_notes/node233.html

The Radial Components

http://hyperphysics.phy-astr.gsu.edu/Hbase/hydwf.html#c1
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Associated Laguerre Polynomials

The Angular Components

http://oak.ucc.nau.edu/jws8/dpgraph/Yellm.html

Radial times Angular

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http://quantummechanics.ucsd.edu/ph130a/130_notes/img1944.png

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The Bohr Model
http://www.walter-fendt.de/ph11e/bohrh.htm

The Meaning of the Legendre Polynomials
the bowling pin and the discus

The Meaning of the Spherical Harmonics
the automobile

The Spherical Harmonics
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http://en.wikipedia.org/wiki/Spherical_harmonics
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Separating Radial and Angular Dependence

In this and the following three sections, we illustrate how the angular momentum and magnetic moment quantum numbers enter the symbology from a calculus based argument. In writing equation (10–2), we have used a representation, so are no longer in abstract Hilbert space. One of the consequences of the process of representation is the topological arguments of linear algebra are obscured. They are still there, simply obscured because the special functions we use are orthogonal, so can be made orthonormal, and complete, just as bras and kets in a dual space are orthonormal and complete. The primary reason to proceed in terms of a position space representation is to attain a position space description. One of the by–products of this chapter may be to convince you that working in the generality of Hilbert space in Dirac notation can be considerably more efficient. Since we used topological arguments to develop angular momentum in the last chapter, and arrive at identical results to those of chapter 11, we rely on connections between the two to establish the meanings of of l and m. They have the same meanings within these calculus based discussions.

As noted, we assume a variables separable solution to equation (10–2) of the form

$$\psi(r,\theta,\phi) = R(r)\, Y(\theta,\phi). \tag{10 – 5}$$

An often asked question is "How do you know you can assume that?" You do not know. You assume it, and if it works, you have found a solution. If it does not work, you need to attempt other methods or techniques. Here, it will work. Using equation (10–5), equation (10–2) can be written

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) R(r)\, Y(\theta,\phi) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) R(r)\, Y(\theta,\phi)$$
$$+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}R(r)\, Y(\theta,\phi) - \frac{2m}{\hbar^2}\Big[V(r)-E\Big]R(r)\, Y(\theta,\phi) = 0$$
$$\Rightarrow \quad Y(\theta,\phi)\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) R(r) + R(r)\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) Y(\theta,\phi)$$
$$+R(r)\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}Y(\theta,\phi) - \frac{2m}{\hbar^2}\Big[V(r)-E\Big]R(r)\, Y(\theta,\phi) = 0.$$

Dividing the equation by $R(r)\, Y(\theta,\phi)$, multiplying by r^2, and rearranging terms, this becomes

$$\left\{\frac{1}{R(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) R(r) - \frac{2mr^2}{\hbar^2}\Big[V(r)-E\Big]\right\}$$
$$+\left[\frac{1}{Y(\theta,\phi)\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) Y(\theta,\phi) + \frac{1}{Y(\theta,\phi)\sin^2\theta}\frac{\partial^2}{\partial\phi^2}Y(\theta,\phi)\right] = 0.$$

The two terms in the curly braces depend only on r, and the two terms in the square brackets depend only upon angles. With the exception of a trivial solution, the only way the sum of the groups can be zero is if each group is equal to the same constant. The constant chosen is known as the **separation constant**. Normally, an arbitrary separation constant, like K, is selected and then you solve for K later. In this example, we are instead going to stand on the shoulders of

The use of these generating functions was illustrated in example 11–26 as intermediate results in calculating spherical harmonics.

The first few Legendre polynomials are listed in table 10–1. Our interest in those is to generate associated Legendre functions. The first few associated Legendre polynomials are listed in table 10–2.

$$\begin{array}{ll} P_0(x) = 1 & P_3(x) = \frac{1}{2}\big(5x^3 - 3x\big) \\ P_1(x) = x & P_4(x) = \frac{1}{8}\big(35x^4 - 30x^2 + 3\big) \\ P_2(x) = \frac{1}{2}\big(3x^2 - 1\big) & P_5(x) = \frac{1}{8}\big(63x^5 - 70x^3 + 15x\big) \end{array}$$

Table 10 – 1. The First Six Legendre Polynomials.

$$\begin{array}{ll} P_{0,0}(x) = 1 & P_{2,0}(x) = \frac{1}{2}\big(3x^2 - 1\big) \\ P_{1,1}(x) = -\sqrt{1 - x^2} & P_{3,3}(x) = -15\big(\sqrt{1 - x^2}\big)^3 \\ P_{1,0}(x) = x & P_{3,2}(x) = 15x\,\big(1 - x^2\big) \\ P_{2,2}(x) = 3\big(1 - x^2\big) & P_{3,1}(x) = -\frac{3}{2}\big(5x^2 - 1\big)\sqrt{1 - x^2} \\ P_{2,1}(x) = -3x\,\sqrt{1 - x^2} & P_{3,0}(x) = \frac{1}{2}\big(5x^3 - 3x\big) \end{array}$$

Table 10 – 2. The First Few Associated Legendre Polynomials.

Two comment concerning the tables are appropriate. First, notice $P_l = P_{l,0}$. That makes sense. If the Legendre equation is the same as the associated Legendre equation with $m = 0$, the solutions to the two equations must be the same when $m = 0$. Also, many authors will use a positive sign for all associated Legendre polynomials. This is a different choice of phase. We addressed that following table 11–1 in comments on spherical harmonics. We choose to include a factor of $(-1)^m$ with the associated Legendre polynomials, and the sign of all spherical harmonics will be positive as a result.

Finally, remember the change of variables $x = \cos\theta$. That was done to put the differential equation in a more elementary form. In fact, a dominant use of associated Legendre polynomials is in applications where the argument is $\cos\theta$. One example is the generating function for spherical harmonic functions,

$$Y_{l,m}(\theta,\phi) = (-1)^m \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}}\, P_{l,m}(\cos\theta)\, e^{im\phi} \qquad m \geq 0, \qquad (10-10)$$

and

$$Y_{l,-m}(\theta,\phi) = Y^*_{l,m}(\theta,\phi), \qquad m < 0,$$

where the $P_{l,m}(\cos\theta)$ are associated Legendre polynomials. If we need a spherical harmonic with $m < 0$, we will calculate the spherical harmonic with $m = |m|$, and then calculate the adjoint.

To summarize the last three sections, we separated the angular equation into an azimuthal and a polar portion. The solutions to the azimuthal angle equation are exponentials including the magnetic moment quantum number in the argument. The solutions to the polar angle equation are the associated Legendre polynomials, which are different for each choice of orbital angular momentum and magnetic moment quantum number. Both quantum numbers are introduced into

The Reduced Mass

Equation (10–2) describes a single particle in a central potential. The hydrogen atom is a two body problem, and the potential is not central but is dependent upon the distance between the nucleus and the electron. Were we able to anchor the nucleus to a stationary location we could designate an origin, equation (10–2) would be an accurate description. This is not possible, but we can reach a similar end by picturing the center of mass being anchored to a fixed location. If we use the **reduced mass** in place of the electron mass,

$$\mu = \frac{m_p \, m_e}{m_p + m_e},$$

the radial coordinate r accurately describes the distance between the nucleus and the electron. The effect in equation (10–2) is cosmetic; where there was an m representing m_e, it is replaced by μ. Because the proton is about 1836 times more massive than the electron, the reduced mass is nearly identically the electron mass. Many authors simply retain the electron mass. Since the center of mass is not actually anchored, a second set of coordinates is required to track the center of mass using this scheme. This consideration and other details of reducing a two particle problem to a one particle problem are adequately covered in numerous texts, including Chohen–Tannoudji[5], Levine[6], and many classical mechanics texts.

Solution of the Radial Equation

The radial equation (10–6) using the reduced mass and the Coulomb potential, $V(r) = -e^2/r$, is

$$\begin{aligned} &\frac{1}{R(r)}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)R(r) - \frac{2\mu r^2}{\hbar^2}\Big[-\frac{e^2}{r} - E\Big] - l(l+1) = 0 \\ \Rightarrow\quad &\frac{d}{dr}\left(r^2\frac{d}{dr}\right)R(r) - \frac{2\mu r^2}{\hbar^2}\Big[-\frac{e^2}{r} - E\Big]R(r) - l(l+1)\,R(r) = 0 \\ \Rightarrow\quad &\frac{d}{dr}\left(r^2\frac{d}{dr}\right)R(r) + \Big[\frac{2\mu r^2}{\hbar^2}\frac{e^2}{r} + \frac{2\mu r^2}{\hbar^2}E - l(l+1)\Big]R(r) = 0. \qquad (10-18) \end{aligned}$$

The plan is to get (10–18) into a form comparable to equation (10–16), and we already know the solutions are equation (10–15). We will be able to glean additional information by comparing the equations term by term. The energy levels of the hydrogen atom and the meaning of the indices of the associated Laguerre polynomials, which will be quantum numbers for the hydrogen atom, will come from the comparison of individual terms.

We will make three substitutions to get the last equation into the form of equation (10–16). The first is

$$y(r) = r\,R(r) \quad \Rightarrow \quad R(r) = \frac{y(r)}{r}. \qquad (10-19)$$

[5] Cohen–Tannoudji, Diu, and Laloe, *Quantum Mechanics* (John Wiley & Sons, New York, 1977), pp. 784–788.

[6] Levine, *Quantum Chemistry* (Allyn and Bacon, Inc., Boston, Massachusetts, 1983), pp. 101–106.

per table 10–4. Then to get $L_3^1(x)$,

$$\begin{aligned}
L_3^1 &= -\frac{d}{dx}\, L_4(x) \\
&= -\frac{d}{dx}\big(x^4 - 16x^3 + 72x^2 - 96x + 24\big) \\
&= -\big(4x^3 - 48x^2 + 144x - 96\big) \\
&= -4x^3 + 48x^2 - 144x + 96,
\end{aligned}$$

per table 10–3.

Associated Laguerre polynomials are not orthogonal but **associated Laguerre functions** of the type

$$\Phi_j^k(x) = e^{-x/2} x^{k/2} L_j^k(x)$$

are orthogonal on the interval $0 \le x < \infty$, so can be made an orthonormal set. Again, the $\Phi_j^k(x)$ are not solutions to the associated Laguerre equation but are solutions to a related equation.

We are specifically interested in a slightly different associated Laguerre function than the usual first choice indicated above, *i.e.*, we are interested in

$$y_j^k(x) = e^{-x/2} x^{(k+1)/2} L_j^k(x). \qquad (10-15)$$

These are also not solutions to the associated Laguerre equation, but they are solutions to

$$y_j^{k\,''}(x) + \left(-\frac{1}{4} + \frac{2j+k+1}{2x} - \frac{k^2-1}{4x^2} \right) y_j^k(x) = 0. \qquad (10-16)$$

The reason for our interest in (10–16) and its solutions (10–15), is that equation (10–16) is a form of the radial equation, so the radial functions $R(r)$ we seek are $R_{n,l}(r) = A\, y_n^l(r)$, where A is simply a normalization constant.

Example 10–6: Show equation (10–15) satisfies equation (10–16).

Unlike some of the toy problems given as examples, this example is a critical connection...unless you take our word for it, and then you should skip this. We are going to use the result of this example as a direct link to the solution of the radial equation. We are going to simplify the notation to minimize clutter, and will explain as we go.

To attain the second derivative, we need the first derivative, and use the notation

$$y = e^{-x/2} x^{(k+1)/2} v,$$

for equation (10–15) where $v = L_j^k(x)$, because the indices do not change and only serve to add clutter, and we can remember the independent variable is x. The first derivative is

$$\begin{aligned}
y' &= -\frac{1}{2} e^{-x/2} x^{(k+1)/2} v + e^{-x/2} \left(\frac{k+1}{2}\right) x^{(k-1)/2} v + e^{-x/2} x^{(k+1)/2} v' \\
&= \left[-\frac{1}{2} v + \left(\frac{k+1}{2x}\right) v + v' \right] e^{-x/2} x^{(k+1)/2}
\end{aligned}$$

$$\Rightarrow \quad \left(e^{x/2} x^{-(k+1)/2}\right) y' = -\frac{1}{2} v + \frac{k+1}{2x}\, v + v'.$$

Making this substitution in the first term and evaluating the derivatives

$$\begin{aligned}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)R(r) &= \frac{d}{dr}\left(r^2\frac{d}{dr}\right)\left(r^{-1}\right)y(r)\\ &= \frac{d}{dr}r^2\left[\left(-r^{-2}\right)y(r)+\left(r^{-1}\right)\frac{d\,y(r)}{dr}\right]\\ &= \frac{d}{dr}\left[-y(r)+r\,\frac{d\,y(r)}{dr}\right]\\ &= -\frac{d\,y(r)}{dr}+\frac{d\,y(r)}{dr}+r\,\frac{d^2\,y(r)}{dr^2}\\ &= r\,\frac{d^2\,y(r)}{dr^2}.\end{aligned}$$

The substitution serves to eliminate the first derivative. We would have both a first and second derivative if we had evaluated the first term using $R(r)$. With this and the substitution of equation (10–19), equation (10–18) becomes

$$r\,\frac{d^2\,y(r)}{dr^2}+\left[\frac{2\mu r e^2}{\hbar^2}+\frac{2\mu r^2}{\hbar^2}E-l(l+1)\right]\frac{y(r)}{r}=0$$

$$\Rightarrow\quad \frac{d^2\,y(r)}{dr^2}+\left[\frac{2\mu e^2}{r\,\hbar^2}+\frac{2\mu E}{\hbar^2}-\frac{l(l+1)}{r^2}\right]y(r)=0.$$

The second substitution is essentially to simplify the notation, and is

$$\left(\frac{\epsilon}{2}\right)^2=-\frac{2\mu E}{\hbar^2} \qquad (10-20)$$

where the negative sign on the right indicates we are looking for bound states, states such that $E<0$, so including the negative sign here lets us have an ϵ which is real. The last equation becomes

$$\frac{d^2\,y(r)}{dr^2}+\left[\frac{2\mu e^2}{r\,\hbar^2}-\frac{\epsilon^2}{4}-\frac{l(l+1)}{r^2}\right]y(r)=0.$$

The third substitution is a change of variables, and notice it relates radial distance and energy through equation (10-20),

$$x=r\epsilon\quad\Rightarrow\quad r=\frac{x}{\epsilon}, \qquad (10-21)$$

$$\Rightarrow\quad dr=\frac{dx}{\epsilon}\quad\Rightarrow\quad \frac{d^2\,y(r)}{dr^2}=\frac{d}{dr}\frac{d\,y(r)}{dr}=\epsilon\frac{d}{dx}\,\epsilon\frac{d\,y(x)}{dx}=\epsilon^2\frac{d^2\,y(x)}{dx^2},$$

so our radial equation becomes

$$\epsilon^2\frac{d^2\,y(x)}{dx^2}+\left[\frac{2\mu e^2\epsilon}{x\,\hbar^2}-\frac{\epsilon^2}{4}-\epsilon^2\frac{l(l+1)}{x^2}\right]y(x)=0$$

$$\Rightarrow\quad \frac{d^2\,y(x)}{dx^2}+\left[-\frac{1}{4}+\frac{2\mu e^2}{\hbar^2\epsilon x}-\frac{l(l+1)}{x^2}\right]y(x)=0, \qquad (10-22)$$

and equation (10–22) is equation (10–16) where

$$l(l+1)=\frac{k^2-1}{4}, \qquad (10-23)$$

the respective differential equations as separation constants. Since we assumed a product of the two functions to get solutions to the azimuthal and polar parts, the solutions to the original angular equation (10–7) are the products of the two solutions $P_{l,m}(\cos\theta)\, e^{im\phi}$. These factors are included in equation (10–10). All other factors in equation (10–12) are simply normalization constants. The products $P_{l,m}(\cos\theta)\, e^{im\phi}$ are the spherical harmonic functions, the alternating sign and radical just make the orthogonal set orthonormal.

Associated Laguerre Polynomials and Functions

The azimuthal equation was easy, the polar angle equation a little more substantial, but you will likely percieve the solution to the radial equation as plain, old heavy! There is no easy way to do this. Our approach will be to relate the radial equation to the associated Laguerre equation, for which the associated Laguerre functions are solutions. A popular option to solve the radial equation is a power series solution, for which we will refer you to Griffiths[3], or Cohen–Tannoudji[4].

Laguerre polynomials are solutions to the Laguerre equation

$$x\, L_j^{''}(x) + \big(1 - x\big)\, L_j^{'}(x) + j\ L_j(x) = 0.$$

The first few Laguerre polynomials are listed in table 10–3.

$$\begin{aligned}
L_0(x) &= 1 \\
L_1(x) &= -x + 1 \\
L_2(x) &= x^2 - 4x + 2 \\
L_3(x) &= -x^3 + 9x^2 - 18x + 6 \\
L_4(x) &= x^4 - 16x^3 + 72x^2 - 96x + 24 \\
L_5(x) &= -x^5 + 25x^4 - 200x^3 + 600x^2 - 600x + 120 \\
L_6(x) &= x^6 - 36x^5 + 450x^4 - 2400x^3 + 5400x^2 - 4320x + 720
\end{aligned}$$

Table 10 – 3. The First Seven Laguerre Polynomials.

Laguerre polynomials of any order can be calculated using the generating function

$$L_j(x) = e^x\, \frac{d^j}{dx^j}\, e^{-x}\, x^j.$$

The Laguerre polynomials do not form an orthogonal set. The related set of **Laguerre functions**,

$$\phi_j(x) = e^{-x/2} L_j(x) \qquad (10-13)$$

is orthonormal on the interval $0 \le x < \infty$. The Laguerre functions are not solutions to the Laguerre equation, but are solutions to an equation which is related.

Just as the Legendre equation becomes the associated Legendre equation by adding an appropriate term containing a second index, the associated Laguerre equation is

$$x\, L_j^{k''}(x) + \big(1 - x + k\big)\, L_j^{k'}(x) + j\ L_j^k(x) = 0, \qquad (10-14)$$

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[3] Griffiths, *Introduction to Quantum Mechanics* (Prentice Hall, Englewood Cliffs, New Jersey, 1995), pp. 134–141.

[4] Cohen–Tannoudji, Diu, and Laloe, *Quantum Mechanics* (John Wiley & Sons, New York, 1977), pp. 794–797.

which reduces to the Laguerre equation when $k = 0$. The first few associated Laguerre polynomials are

$L_0^0(x) = L_0(x)$	$L_0^2(x) = 2$
$L_1^0(x) = L_1(x)$	$L_3^0(x) = L_3(x)$
$L_1^1(x) = -2x + 4$	$L_3^1(x) = -4x^3 + 48x^2 - 144x + 96$
$L_0^1(x) = 1$	$L_2^3(x) = 60x^2 - 600x + 1200$
$L_2^0(x) = L_2(x)$	$L_3^3(x) = -120x^3 + 2160x^2 - 10800x + 14400$
$L_2^1(x) = 3x^2 - 18x + 18$	$L_3^2(x) = -20x^3 + 300x^2 - 1200x + 1200$
$L_2^2(x) = 12x^2 - 96x + 144$	$L_1^3(x) = -24x + 96$
$L_1^2(x) = -6x + 18$	$L_0^3(x) = 6$

Table 10 – 4. Some Associated Laguerre Polynomials.

Notice $L_j^0 = L_j$. Also notice the indices are all non–negative, and either index may assume any integral value. We will be interested only in those associated Laguerre polynomials where $k < j$ for hydrogen atom wave functions.

Associated Laguerre polynomials can be calculated from Laguerre polynomials using the generating function

$$L_j^k(x) = \big(-1\big)^k \frac{d^k}{dx^k} L_{j+k}(x).$$

Example 10–5: Calculate $L_3^1(x)$ starting with the generating function.

We first need to calculate $L_4(x)$, because

$$L_j^k(x) = \big(-1\big)^k \frac{d^k}{dx^k} L_{j+k}(x) \quad \Rightarrow \quad L_3^1(x) = \big(-1\big)^1 \frac{d^1}{dx^1} L_{3+1}(x) = -\frac{d}{dx} L_4(x).$$

Similarly, if you want to calculate L_3^2, you need to start with L_5, and to calculate L_4^3, you need to start with L_7. So using the generating function,

$$\begin{aligned}
L_4(x) &= e^x \frac{d^4}{dx^4} e^{-x} x^4 \\
&= e^x \frac{d^3}{dx^3} \Big(-e^{-x} x^4 + e^{-x}\, 4x^3\Big) \\
&= e^x \frac{d^2}{dx^2} \Big(e^{-x} x^4 - e^{-x}\, 4x^3 - e^{-x}\, 4x^3 + e^{-x}\, 12x^2\Big) = e^x \frac{d^2}{dx^2} \Big(e^{-x} x^4 - e^{-x}\, 8x^3 + e^{-x}\, 12x^2\Big) \\
&= e^x \frac{d}{dx} \Big(-e^{-x} x^4 + e^{-x}\, 4x^3 + e^{-x}\, 8x^3 - e^{-x}\, 24x^2 - e^{-x}\, 12x^2 + e^{-x}\, 24x\Big) \\
&\qquad\qquad = e^x \frac{d}{dx} \Big(-e^{-x} x^4 + e^{-x}\, 12x^3 - e^{-x}\, 36x^2 + e^{-x}\, 24x\Big) \\
&= e^x \Big(e^{-x} x^4 - e^{-x}\, 4x^3 - e^{-x}\, 12x^3 + e^{-x}\, 36x^2 + e^{-x}\, 36x^2 - e^{-x}\, 72x - e^{-x}\, 24x + e^{-x}\, 24\Big) \\
&= e^x e^{-x} \Big(x^4 - 16x^3 + 72x^2 - 96x + 24\Big) \\
&= x^4 - 16x^3 + 72x^2 - 96x + 24,
\end{aligned}$$

per table 10–4. Then to get $L_3^1(x)$,

$$
\begin{aligned}
L_3^1 &= -\frac{d}{dx}\, L_4(x) \\
&= -\frac{d}{dx}\big(x^4 - 16x^3 + 72x^2 - 96x + 24\big) \\
&= -\big(4x^3 - 48x^2 + 144x - 96\big) \\
&= -4x^3 + 48x^2 - 144x + 96,
\end{aligned}
$$

per table 10–3.

Associated Laguerre polynomials are not orthogonal but **associated Laguerre functions** of the type

$$\Phi_j^k(x) = e^{-x/2} x^{k/2} L_j^k(x)$$

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These are also not solutions to the associated Laguerre equation, but they are solutions to

$$y_j^{k\,''}(x) + \left(-\frac{1}{4} + \frac{2j+k+1}{2x} - \frac{k^2-1}{4x^2} \right) y_j^k(x) = 0. \qquad (10-16)$$

The reason for our interest in (10–16) and its solutions (10–15), is that equation (10–16) is a form of the radial equation, so the radial functions $R(r)$ we seek are $R_{n,l}(r) = A\, y_n^l(r)$, where A is simply a normalization constant.

Example 10–6: Show equation (10–15) satisfies equation (10–16).

Unlike some of the toy problems given as examples, this example is a critical connection...unless you take our word for it, and then you should skip this. We are going to use the result of this example as a direct link to the solution of the radial equation. We are going to simplify the notation to minimize clutter, and will explain as we go.

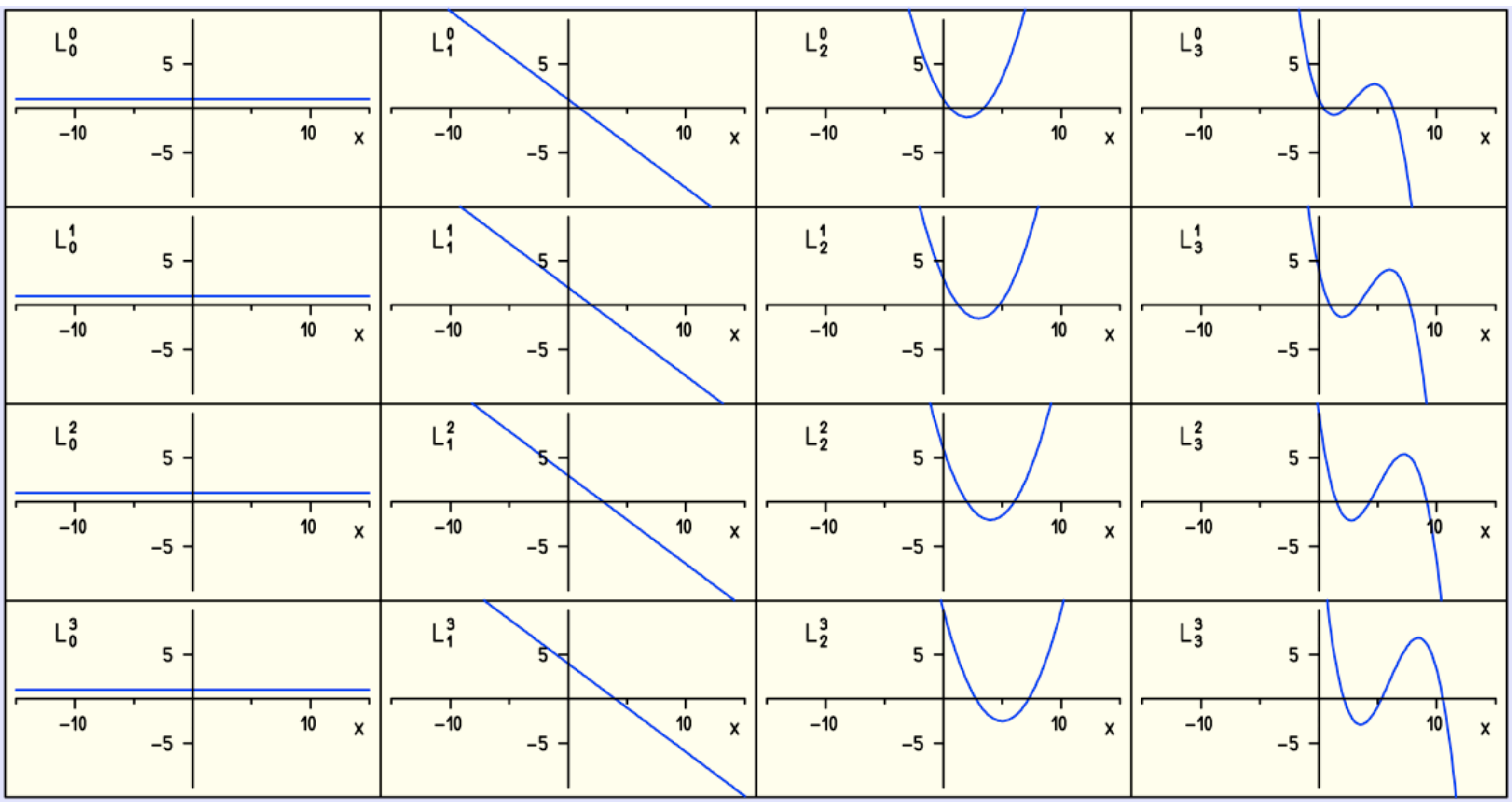
To attain the second derivative, we need the first derivative, and use the notation

$$y = e^{-x/2} x^{(k+1)/2} v,$$

for equation (10–15) where $v = L_j^k(x)$, because the indices do not change and only serve to add clutter, and we can remember the independent variable is x. The first derivative is

$$
\begin{aligned}
y' &= -\frac{1}{2} e^{-x/2} x^{(k+1)/2} v + e^{-x/2} \left(\frac{k+1}{2} \right) x^{(k-1)/2} v + e^{-x/2} x^{(k+1)/2} v' \\
&= \left[-\frac{1}{2} v + \left(\frac{k+1}{2x} \right) v + v' \right] e^{-x/2} x^{(k+1)/2}
\end{aligned}
$$

$$\Rightarrow \quad \left(e^{x/2} x^{-(k+1)/2} \right) y' = -\frac{1}{2} v + \frac{k+1}{2x}\, v + v'.$$


L_0^0
L_1^0
L_2^0
L_3^0
L_0^1
L_1^1
L_2^1
L_3^1
L_0^2
L_1^2
L_2^2
L_3^2
L_0^3
L_1^3
L_2^3
L_3^3
−10
10
x
5
−5

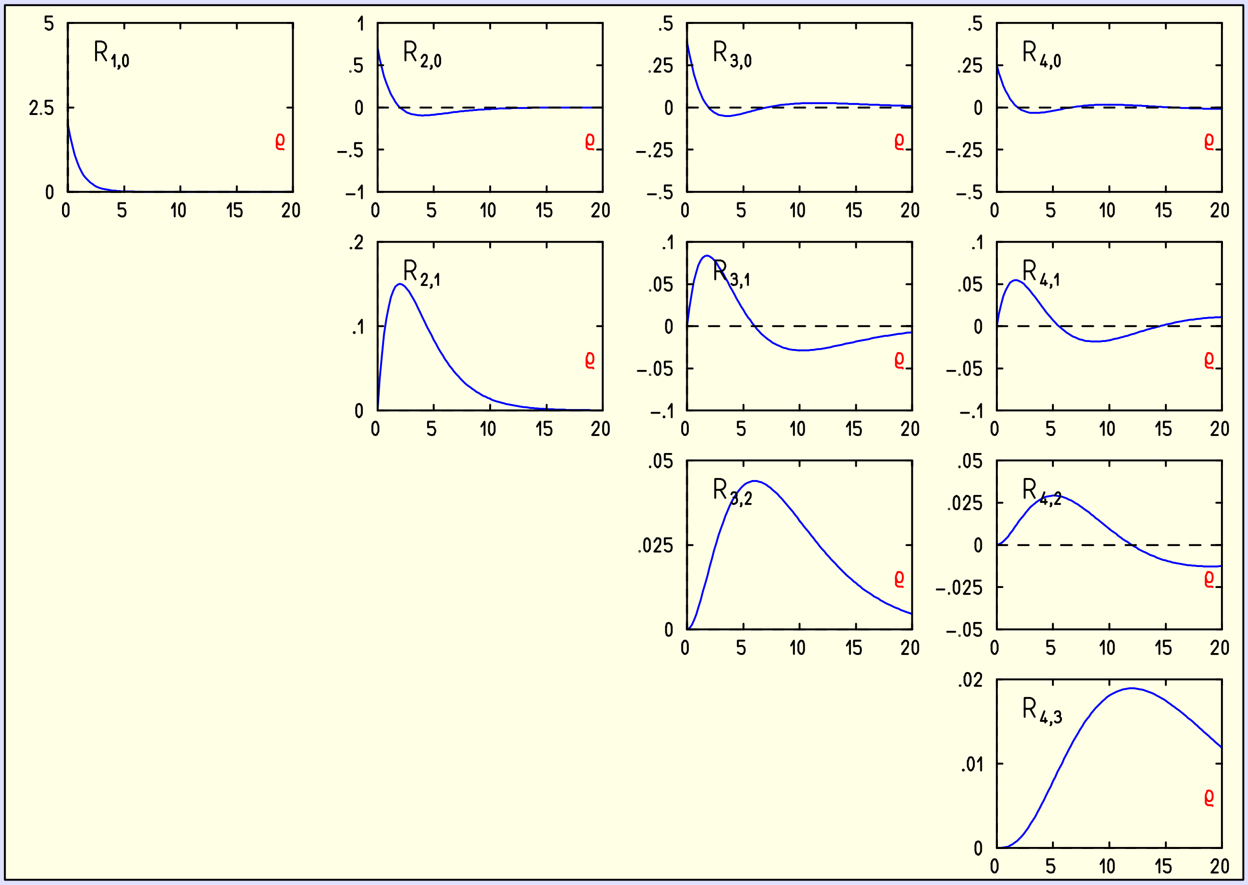
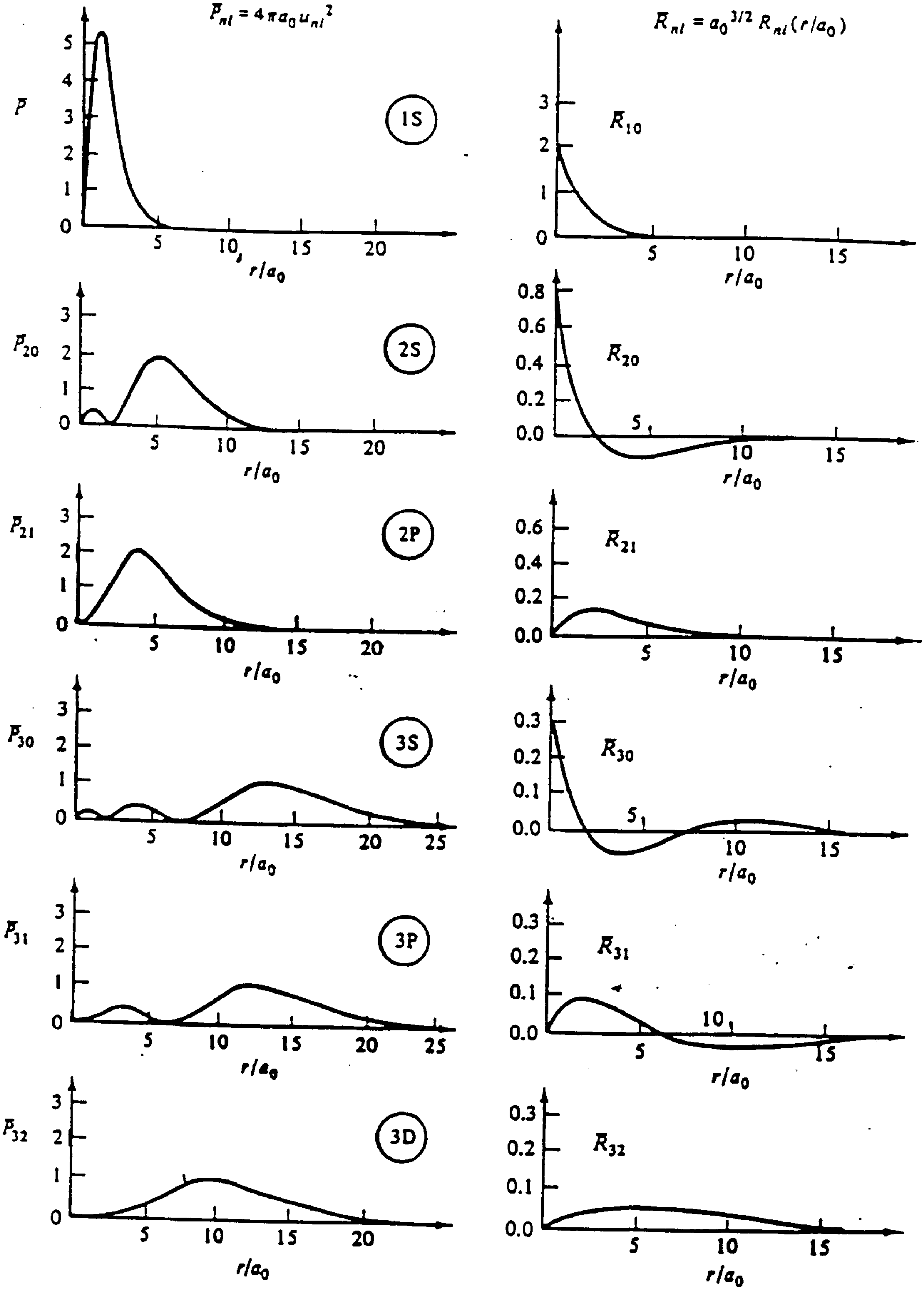
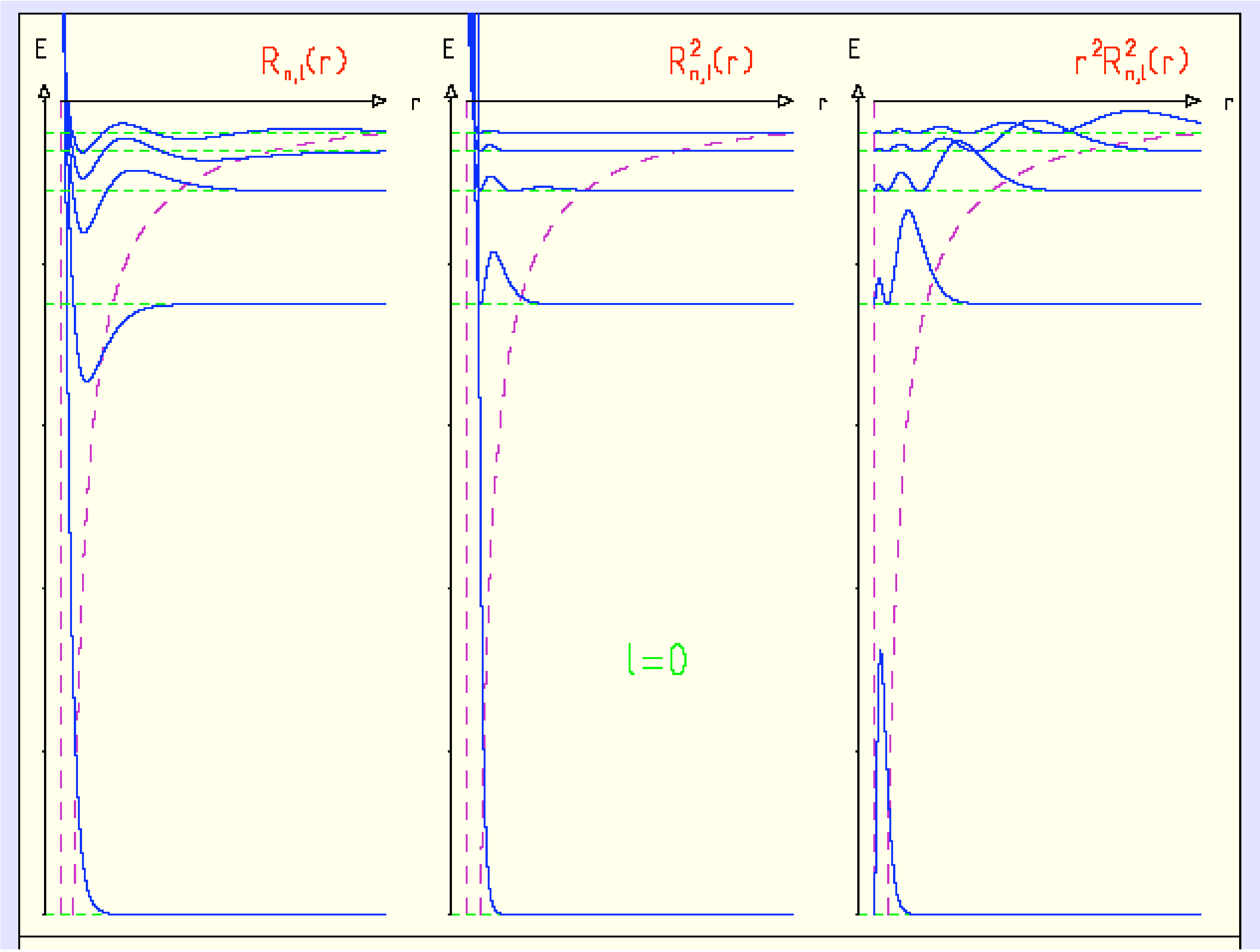


Fig. 13.14. Radial eigenfunctions $R_{n\ell}(\rho)$ for the electron in the hydrogen atom. Their zeros are the $n-\ell-1$ zeros of the Laguerre polynomials $L_{n-\ell-1}^{2\ell+1}(2\rho/n)$. Here the argument of the Laguerre polynomial is $2\rho/n$ with n being the principal quantum number and $\rho = r/a$ the distance between electron and nucleus divided by the Bohr radius a.

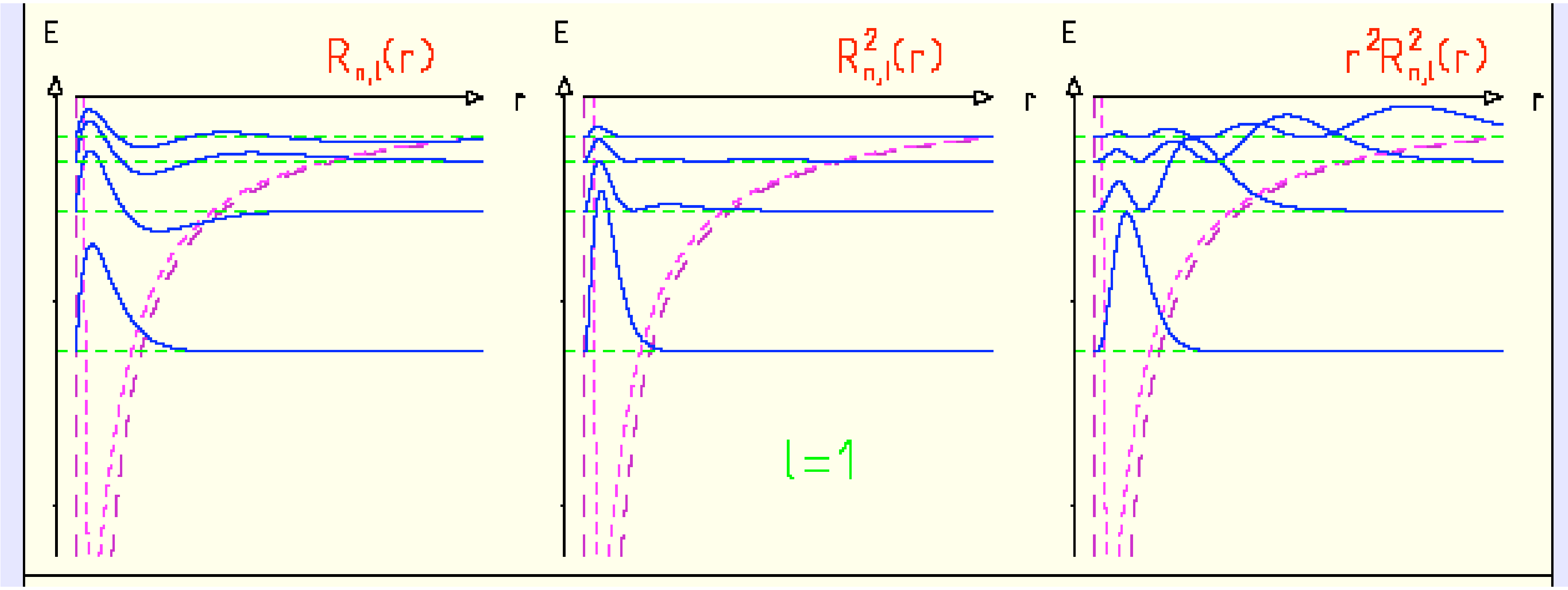


$\bar{P}_{nl} = 4\pi a_0 u_{nl}^2$
$\bar{R}_{nl} = a_0^{3/2} R_{nl}(r/a_0)$
$\bar{P}$
1S
$\bar{R}_{10}$
r/a_0
$\bar{P}_{20}$
2S
$\bar{R}_{20}$
$\bar{P}_{21}$
2P
$\bar{R}_{21}$
$\bar{P}_{30}$
3S
$\bar{R}_{30}$
$\bar{P}_{31}$
3P
$\bar{R}_{31}$
$\bar{P}_{32}$
3D
$\bar{R}_{32}$

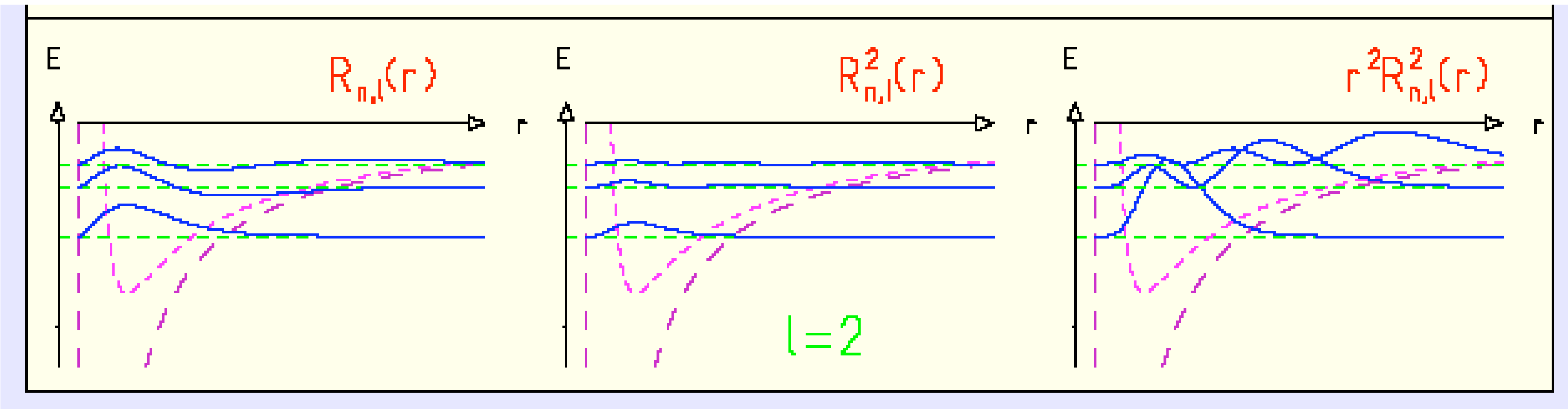
1s, 2s, 3s, 4s, 5s



2p, 3p, 4p, 5p



3d, 4d, 5d



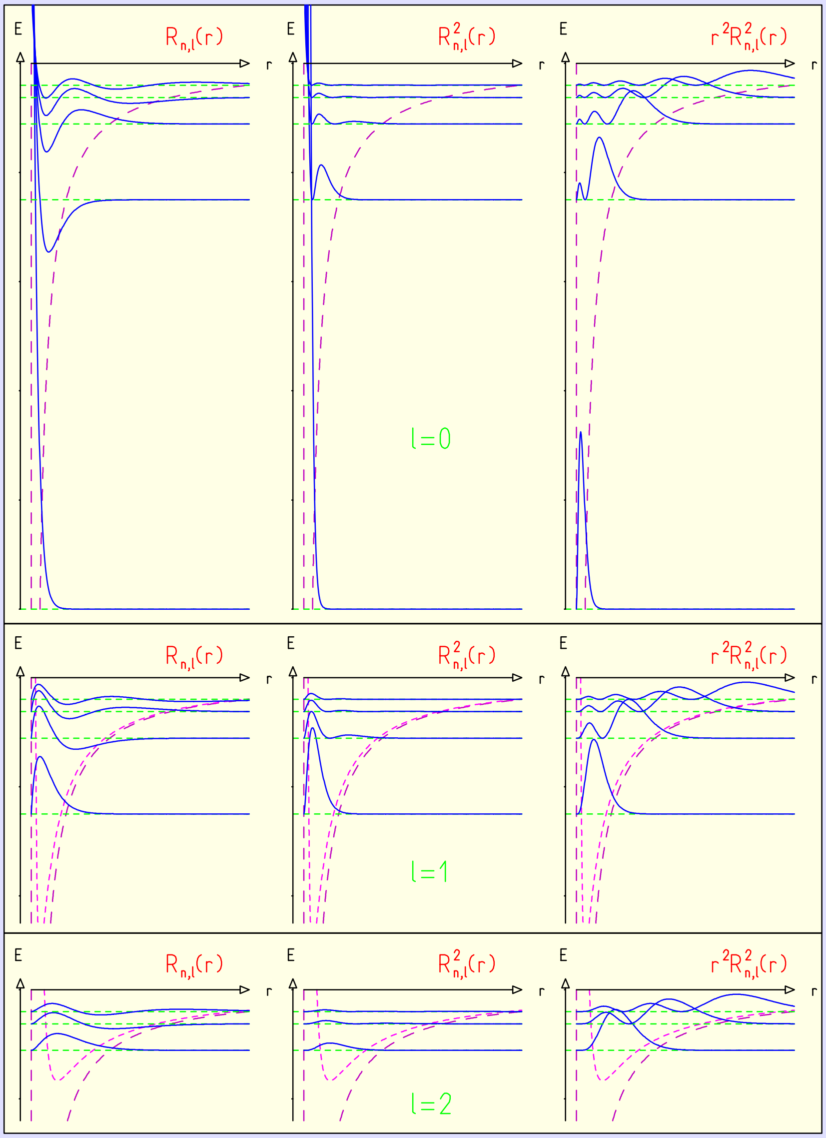
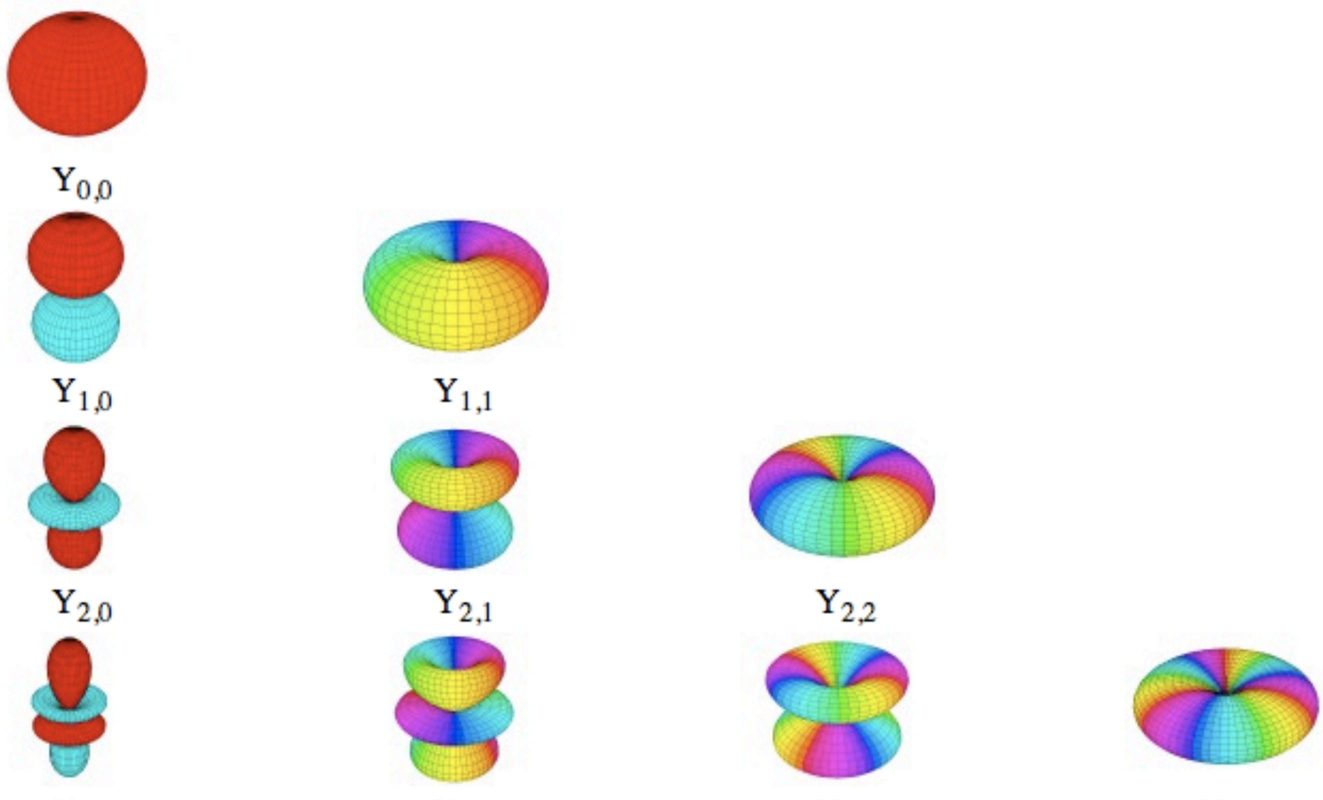


Fig. 13.15. Radial eigenfunctions $R_{n\ell}(r)$, their squares $R^2_{n\ell}(r)$, and the functions $r^2R^2_{n\ell}(r)$ for the lowest eigenstates of the electron in the hydrogen atom and the lowest angular-momentum quantum numbers $\ell = 0, 1, 2$. Also shown are the energy eigenvalues as horizontal dashed lines, the form of the Coulomb potential $V(r)$, and, for $\ell \neq 0$, the forms of the effective potential $V_\ell^{\mathrm{eff}}(r)$. The eigenvalue spectra are degenerate for all ℓ values, except that the minimum value of the principal quantum number is $n = \ell + 1$.


$Y_{0,0}$
$Y_{1,0}$
$Y_{1,1}$
$Y_{2,0}$
$Y_{2,1}$
$Y_{2,2}$
$Y_{3,0}$
$Y_{3,1}$
$Y_{3,2}$
$Y_{3,3}$

Associated Laguerre Polynomials

Some wag once said the nice thing about standards is that there are so many to choose from. I have been trying to come to grips with the difference between what I presented in class and the formulae in Sakurai. It is easy to explain the differences on the basis of different conventions about the associated Laguerre polynomials.

If you want to skip details, a main result is that Sakurai and *Mathematica* use different conventions. If we call $\mathcal{L}_n^q(\rho)$ the convention of Sakurai and $L_p^{(q)}(\rho)$ the convention of *Mathematica*, we have

$$\mathcal{L}_{p+q}^q(\rho) = (p+q)!(-1)^q L_p^{(q)}(\rho) \ .$$

Below are the details. They are presented somewhat in the order of my investigation and not according to the shorted derivation of the above result.

Differential equation

I have consulted two well known books on mathematical functions that adhere to the same index convention, but have different normalization conventions. The first book that I consulted by Abramowitz & Stegun states on pg 778, Eqs. (22.5.16) and (22.5.17):

$$L_n^{(0)}(x) = L_n(x)$$

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

Also, on pg 781, in Eq. (22.6.15), the differential equation is given.

$$x\frac{d^2}{dx^2}L_n^{(\alpha)}(x) + (\alpha+1-x)\frac{d}{dx}L_n^{(\alpha)}(x) + nL_n^{(\alpha)}(x) = 0 \ .$$

The differential equation is very valuable, but being linear, does not tell us anything about the normalization.

Another well known book by Morse & Feshbach on pg 784, in an unnumbered equation three lines from the bottom of the page gives their convention for the associated Laguerre polynomials.

$$L_n^m(z) = (-1)^m \frac{d^m}{dx^m}[L_{n+m}^0(z)] \ .$$

The differential equation is also given a few lines above:

$$z\frac{d^2}{dz^2}L_n^a(z) + (a+1-z)\frac{d}{dz}L_n^a(z) + nL_n^a(z) = 0 \ .$$

Morse & Feshbach do not put the upper index in parentheses, otherwise, it looks like these conventions might agree. We can be pretty certain that in these two books the $L_n^{(a)}$ is a polynomial of degree n. However, we will soon see that the normalizations don't agree in the two books.

Sakurai convention

Now, let's turn to Sakurai. On pg 454 in Eq. (A.6.4), we find

$$L_p^q(\rho) = \frac{d^q}{d\rho^q} L_p(\rho) \ .$$

This leads us to conclude that L_p^q is of degree $p - q$, and makes the result above plausible. In fact, if the normalizations were the same, we would expect:

$$\mathcal{L}_{p+q}^q(\rho) = \frac{d^q}{d\rho^q} L_{p+q}(\rho) = (-1)^q L_p^{(q)}(\rho) \qquad \textbf{Not quite correct!} \ .$$

Class Derivation

In class, I presented the differential equation for the associated Laguerre polynomials as stated by *Mathematica*,

$$xy'' + (a + 1 - x)y' + ny = 0 \ .$$

This is the same convention as Abramowitz & Stegun and Morse & Feshbach.

In class, we found we needed to solve this differential equation:

$$\rho L'' + (2(l + 1) - \rho)L' + (\lambda - l - 1)L = 0 \ ,$$

but $\lambda = n$, the total quantum number, and $n - l - 1 = n'$ the radial quantum number. So, we have

$$\rho L'' + (2l + 1 + 1 - \rho)L' = n'L = 0 \ .$$

In the notation of Abramowitz & Stegun, *Mathematica* or the Morse & Feshbach index convention, the solution to the differential equation is

$$L_{n'}^{(2l+1)}(\rho) = L_{n-l-1}^{(2l+1)}(\rho) \ .$$

In Sakurai notation, $L_{n-l-1}^{(2l+1)}(\rho) = (-1)^{2l+1}\mathcal{L}_{n+l}^{2l+1} = -\mathcal{L}_{n+l}^{2l+1}$. This explains the indices for R_{nl} in Sakurai in the equation above (A.6.3).

Pinning Down the Normalizations

We still need to consider normalization conventions, and that can be done from the generating function or from what is know as Rodrigues' formula. In fact, in retrospect, it seems that just looking at the Rodrigues' formulae in the three books might have been the easiest way to proceed.

In Abramowitz & Stegun, we find on pg 785, Eq. (22.11.6)

$$L_n^{(\alpha)}(x) = \frac{1}{n!} e^x x^{-\alpha} \frac{d^n}{dx^n}[x^{n+\alpha} e^{-x}] \ .$$

On pg 784 of Morse & Feshbach, we find

$$L_n^a(z) = \frac{\Gamma(a+n+1)}{\Gamma(n+1)} \frac{e^z}{z^\alpha} \frac{d^n}{dz^n} [z^{a+n} e^{-z}] \ .$$

If we set α and a to zero, we can compare with Sakurai, which states in Eq. (A.6.5)

$$L_p(\rho) = e^\rho \frac{d^p}{d\rho^p} (\rho^p e^{-\rho}) \ .$$

We immediately see that Sakurai agrees in normalization with Morse & Feshbach, at least for the Laguerre polynomials, if not for the associated Laguerre polynomials. However, the two books on mathematical methods differ by a factor of $(n+a)!$ in their normalizations with Abramowitz & Stegun convention being smaller by division by that factor. Morse & Feshbach include a small table of associated Laguerre polynomials at the bottom of page 784. They have $L_0^n = n!$, whereas Abramowitz & Stegun according to Eq. (22.4.7) have $L_0^{(\alpha)} = 1$. The only remaining mystery is which normalization convention *Mathematica* obeys. With this command

$$\mathrm{Table}[\{\mathrm{n}, \mathrm{LaguerreL}[0, \mathrm{n}, \mathrm{x}]\}, \{\mathrm{n}, 0, 6\}]$$

you will easily find that all results are 1 and *Mathematica* follows the Abramowitz & Stegun normalization.

Further, I coded up the Rodrigues' formula with the Sakurai convention and compared with $(p+q)!(-1)^q L_p^{(q)}$ where the I used the *Mathematica* function `LaguerreL[p,q,x]`. They were in agreement.

Mystery solved! Quantum mechanics and children can now sleep soundly at night.