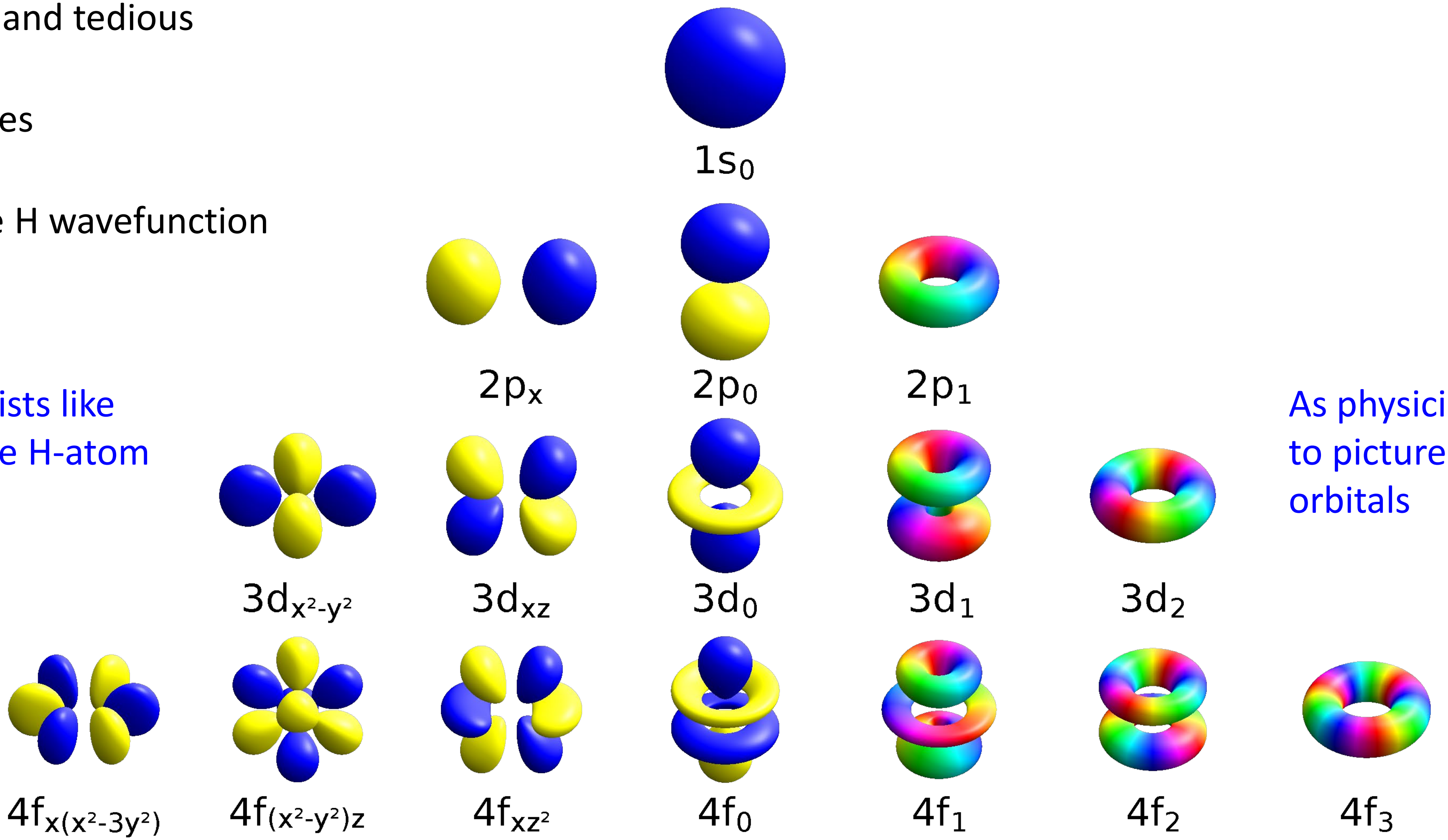
Today in Physics 237: the hydrogen atom

- The radial equation, the solution to which is long and tedious
- The Bohr series
- The complete H wavefunction



As chemists like to picture H-atom orbitals

As physicists like to picture H-atom orbitals

Geek3, [Wikimedia Commons]

Solution of the radial part of the time-independent Schrödinger equation

- Protons and neutrons are about 1836 times more massive than electrons. To excellent approximation, the H atom's center of mass is the proton's location; *r* is distance from there.

- The potential energy of the electron-proton system is, of course,

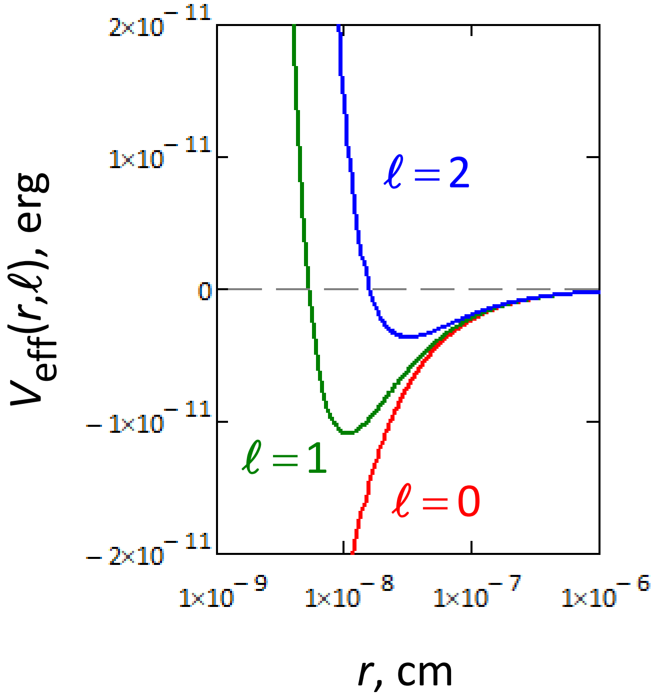
$$V(r) = -\frac{e^2}{r} \qquad \left(\text{in cgs units; replace } e^2 \text{ with } e^2/4\pi\varepsilon_0 \text{ for SI}\right) \quad .$$

- Including the centrifugal term ([Lecture 14](), page 13), the effective potential energy is

$$V_{\text{eff}}(r,\ell) = -\frac{e^2}{r} + \frac{\hbar^2}{2m_e}\frac{\ell(\ell+1)}{r^2}$$

- Using $u(r) = rR(r)$ as in [Lecture 14](), the radial equation becomes

$$-\frac{\hbar^2}{2m_e}\frac{d^2u}{dr^2} + V_{\text{eff}}(r,\ell)u = Eu \quad . \qquad \left(V_{\text{eff}}\right)_{\min} \le E \le 0 \text{ for bound states}$$



The radial part (continued)

- Now one usually makes some substitutions to render the equation dimensionless:

$$\kappa = \frac{\sqrt{-2m_e E}}{\hbar} \quad , \quad \rho = \kappa r \quad , \quad \rho_0 = \frac{2m_e e^2}{\hbar^2 \kappa} \quad :$$

so that

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2} \right] u \quad .$$

- Not a differential equation for which we know the solution. This time it will help to look at **two** solutions for **asymptotic** forms of the equation, which will give multiplicative factors of the solution. We would do so in hope that the rest of *u*(ρ) will be solved more easily than *via* the differential equation above.
  - If $\rho \to \infty$, the first term in […] is much larger than the other two, which gives a familiar differential equation:

0, to keep the wavefunction normalizable as $\rho \to \infty$

$$\rho \to \infty: \quad \frac{d^2u}{d\rho^2} \cong u \quad \Rightarrow \quad u = Ae^{-\rho} + \cancel{B}e^{\rho} = Ae^{-\rho} \quad .$$

The radial part (continued)

- In the other, $\rho \to 0$, limit, the $\ell(\ell+1)/\rho^2$ dominates:

$$\rho \to 0: \quad \frac{d^2u}{d\rho^2} \cong \frac{\ell(\ell+1)}{\rho^2}u \quad .$$

- As those who took PHYS 217 (their Lecture 10, pp. 3-4) are aware, one should try $u = C\rho^{\alpha}$ for such equations. I will suggest that $u = C\rho^{\alpha+1}$ may save a step:

$$\frac{du}{d\rho} = (\alpha+1)C\rho^{\alpha} \quad , \quad \frac{d^2u}{d\rho^2} = \alpha(\alpha+1)C\rho^{\alpha-2} = \ell(\ell+1)C\rho^{\alpha-2} \quad ;$$

$$\alpha^2 + \alpha - \ell(\ell+1) = 0 \quad \Rightarrow \quad \alpha = \frac{1}{2}\left(1 \pm \sqrt{1+4\ell(\ell+1)}\right) \quad \Rightarrow$$

$$1+4\ell(\ell+1) = 4\left(\ell^2+\ell+\frac{1}{4}\right) = 4\left(\ell+\frac{1}{2}\right)^2 \quad \Rightarrow \quad \alpha = \frac{1}{2} \pm \left(\ell+\frac{1}{2}\right) = \begin{cases} -\ell \text{ or} \\ \\ \ell+1 \end{cases} \quad .$$

The radial part (continued)

- So in this limit, the solution of the radial equation must converge on

0, to keep the wavefunction normalizable as $\rho \to 0$

$$\rho \to 0: \quad u = C\rho^{\ell+1} + \cancel{D}\rho^{-\ell} = C\rho^{\ell+1} \quad .$$

- Now we return to the full radial equation, and this time seek a solution of the form

$$u(\rho) = \rho^{\ell+1} e^{-\rho} v(\rho) \quad ,$$

which has the correct behavior as $\rho \to 0$ and $\rho \to \infty$, to seek the new function $v(\rho)$.

- Convert the derivatives of *u* to those of *v*, doing the algebra slowly. First derivative:

$$\frac{du}{d\rho} = (\ell+1)\rho^{\ell} e^{-\rho} v - \rho^{\ell+1} e^{-\rho} v + \rho^{\ell+1} e^{-\rho} \frac{dv}{d\rho} = \rho^{\ell} e^{-\rho} \left[(\ell + 1 - \rho) v + \rho \frac{dv}{d\rho} \right] \quad .$$

The radial part (continued)

- Second derivative:

$$\frac{d^2u}{d\rho^2} = \left(\ell\rho^{\ell-1}e^{-\rho} - \rho^{\ell}e^{-\rho}\right)\left[(\ell+1-\rho)v + \rho\frac{dv}{d\rho}\right] + \rho^{\ell}e^{-\rho}\left[-v + (\ell+1-\rho)\frac{dv}{d\rho} + \frac{dv}{d\rho} + \rho\frac{d^2v}{d\rho^2}\right]$$

$$= \rho^{\ell}e^{-\rho}\left\{\left(\frac{\ell}{\rho}-1\right)\left[(\ell+1-\rho)v + \rho\frac{dv}{d\rho}\right] - v + (\ell+2-\rho)\frac{dv}{d\rho} + \rho\frac{d^2v}{d\rho^2}\right\}$$

$$= \rho^{\ell}e^{-\rho}\left\{\left[\frac{\ell(\ell+1)}{\rho} - \ell - (\ell+1) + \rho - 1\right]v + 2(\ell+1-\rho)\frac{dv}{d\rho} + \rho\frac{d^2v}{d\rho^2}\right\}$$

$$= \rho^{\ell}e^{-\rho}\left\{\left[\frac{\ell(\ell+1)}{\rho} - 2(\ell+1) + \rho\right]v + 2(\ell+1-\rho)\frac{dv}{d\rho} + \rho\frac{d^2v}{d\rho^2}\right\} \quad .$$

The radial part (continued)

- Combine in the radial equation to produce a differential equation for $v(\rho)$:

$$\frac{d^2u}{d\rho^2}=\left[1-\frac{\rho_0}{\rho}+\frac{\ell(\ell+1)}{\rho^2}\right]u \quad \Rightarrow$$

$$\rho^{\ell}e^{-\rho}\left\{\left[\frac{\ell(\ell+1)}{\rho}-2(\ell+1)+\rho\right]v+2(\ell+1-\rho)\frac{dv}{d\rho}+\rho\frac{d^2v}{d\rho^2}\right\}=\rho^{\ell+1}e^{-\rho}\left[1-\frac{\rho_0}{\rho}+\frac{\ell(\ell+1)}{\rho^2}\right]v$$

$$\rho\frac{d^2v}{d\rho^2}+2(\ell+1-\rho)\frac{dv}{d\rho}+\left[\cancel{\frac{\ell(\ell+1)}{\rho}}-2(\ell+1)+\cancel{\rho}\right]v=\rho\left[\cancel{1}-\frac{\rho_0}{\rho}+\cancel{\frac{\ell(\ell+1)}{\rho^2}}\right]v$$

$$\rho\frac{d^2v}{d\rho^2}+2(\ell+1-\rho)\frac{dv}{d\rho}+\left[\rho_0-2(\ell+1)\right]v=0 \quad .$$

That helped more than it probably looks; all the terms in $1/\rho$ are gone.

The radial part (continued)

- And since all the terms in 1/*ρ* are gone, it works better to propose a power-series solution, $v(\rho)=\sum_{n=0}^{\infty} c_n\rho^n$.
  - … at the risk of re-admitting the solution we rejected by setting *D* = 0 on page 3; **see below, page 11**.

- Again calculate the derivatives:

$$\frac{dv}{d\rho}=\sum_{n=0}^{\infty} nc_n\rho^{n-1}=\sum_{j=-1}^{\infty}(j+1)c_{j+1}\rho^j=\cancel{(-1+1)\frac{c_0}{\rho}}+\sum_{j=0}^{\infty}(j+1)c_{j+1}\rho^j \quad , \quad \frac{d^2v}{d\rho^2}=\sum_{j=0}^{\infty} j(j+1)c_{j+1}\rho^{j-1} \quad .$$

- Into the differential equation they go:

$$\rho\frac{d^2v}{d\rho^2}+2(\ell+1-\rho)\frac{dv}{d\rho}+\left[\rho_0-2(\ell+1)\right]v=0$$

$$\sum_{j=0}^{\infty} j(j+1)c_{j+1}\rho^j+2(\ell+1)\sum_{j=0}^{\infty}(j+1)c_{j+1}\rho^j-2\sum_{j=0}^{\infty}(j+1)c_{j+1}\rho^{j+1}+\left[\rho_0-2(\ell+1)\right]\sum_{j=0}^{\infty}c_j\rho^j=0$$

The radial part (continued)

- The third term can be re-indexed for ease of comparing coefficients of ρ^j:

$$2\sum_{j=0}^{\infty}(j+1)c_{j+1}\rho^{j+1} = 2\sum_{n=1}^{\infty} nc_n\rho^n = 2\sum_{j=0}^{\infty} jc_j\rho^j \quad .$$

Can start sum at zero instead of 1, since the first term is zero regardless.

- This leaves

$$\sum_{j=0}^{\infty} j(j+1)c_{j+1}\rho^j + 2(\ell+1)\sum_{j=0}^{\infty}(j+1)c_{j+1}\rho^j - 2\sum_{j=0}^{\infty} jc_j\rho^j + [\rho_0 - 2(\ell+1)]\sum_{j=0}^{\infty} c_j\rho^j = 0 \quad ,$$

or

$$\sum_{j=0}^{\infty}\left\{[j(j+1)+2(\ell+1)(j+1)]c_{j+1} + [\rho_0 - 2(\ell+1) - 2j]c_j\right\}\rho^j = 0 \quad .$$

- For this to be valid at all values of ρ, the coefficient of each ρ^j must be zero:

The radial part (continued)

$$c_{j+1} = \frac{2(\ell+1)+2j-\rho_0}{j(j+1)+2(\ell+1)(j+1)}c_j = \boxed{\frac{2(\ell+j+1)-\rho_0}{(j+1)(j+2\ell+2)}c_j} \quad .$$

- If we know any of the c_j, this formula gives us all the rest.
  - We can always count on knowing one – say, c_0 – from normalization. Thus we **almost** have the solution.
- However, one nuance remains, as suspected on page 8. Consider the coefficients at large j, for which

$$j \gg 1: \quad c_{j+1} \cong \frac{2j}{j(j+1)}c_j = \frac{2}{j+1}c_j \quad .$$

- In this limit,

$$c_1 \cong \frac{2}{1}c_0, \quad c_2 \cong \frac{2}{2}c_1 = \frac{2\cdot 2}{2\cdot 1}c_0, \quad c_3 \cong \frac{2}{3}c_2 = \frac{2\cdot 2\cdot 2}{3\cdot 2\cdot 1}c_0, \quad \ldots \quad c_j \cong \frac{2^j}{j!}c_0 \quad .$$

Ionization and normalization

- If this were an exact result instead of an approximation, then the radial solution would be

$$v(\rho)=\sum_{j=0}^{\infty}c_j\rho^j=c_0\sum_{j=0}^{\infty}\frac{1}{j!}(2\rho)^j=c_0e^{2\rho}\quad\Rightarrow\quad u(\rho)=\rho^{\ell+1}e^{-\rho}v(\rho)=c_0\rho^{\ell+1}e^{+\rho}\xrightarrow[\rho\to\infty]{}\infty\quad .$$

  That is, it would not be normalizable: with the power-series form for $v(\rho)$, **we have inadvertently re-admitted the *D* ≠ 0 solutions we ruled out on page 3.**

- So, out they go again. The easiest way to exclude them is to **terminate the sum**, rather than taking it to infinity. That is, there is some index N such that

$$c_{N-1}\neq 0\quad ,\quad c_N=0\quad ,\quad c_{N+1}=\frac{2}{(N+1)!}c_N=0\quad ,\quad \ldots\quad ,\quad c_{M\geq N}=0\quad .$$

- Good news: there is a natural point at which to terminate the sum, as follows.

Ionization and normalization (continued)

- From page 10, for *j* = *N*, we have $c_N = \frac{2(\ell+N)-\rho_0}{N(N+2\ell+1)} c_{N-1} = 0 \quad \Rightarrow \quad \ell + N = \frac{\rho_0}{2}$.

- Define $\boxed{n = N + \ell \quad , \quad n = 1, 2, 3, \ldots}$ **Principal quantum number**

- Then, from page 3,

$$\rho_0 = \frac{2m_e e^2}{\hbar^2 \kappa} = \frac{2m_e e^2}{\hbar\sqrt{-2m_e E}} = 2n \quad \Rightarrow \quad \boxed{E_n = -\frac{m_e e^4}{2\hbar^2}\frac{1}{n^2}} \quad \left[-\frac{m_e e^4}{(4\pi\varepsilon_0)^2 2\hbar^2}\frac{1}{n^2} \text{ in SI units} \right]$$

Bohr series

- The Bohr series limit, and in turn the truncation of the sum on page 11, corresponds to the fact that **the H atom can be ionized**.

- Before Bohr, the energy spectrum of H was measured accurately by Johannes Rydberg to be $E_n = -Ry/n^2$, $n = 1, 2, 3, \ldots$, where $Ry = 2.18 \times 10^{-11}$ erg $= 13.6$ eV. Bohr's triumph was in showing – much differently than we just did – that *Ry* is a product of more fundamental constants $\left(m_e e^4/\hbar^2\right)$, rather than being an independent physical constant.

The wavefunction of hydrogen

- Furthermore, $\kappa = \frac{m_e e^2}{\hbar^2}\frac{1}{n} \equiv \frac{1}{na}$, $\boxed{a = \frac{\hbar^2}{m_e e^2}}$. $\left[\frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} \text{ in SI units}\right]$ **Bohr radius**

- Finally, we can write out the wavefunction, by undoing all our various substitutions and abbreviations:

$$\psi_{n\ell m}(r,\vartheta,\varphi) = R_{n\ell}(r)Y_\ell^m(\vartheta,\varphi) \quad ,$$

$$R_{n\ell}(r) = \frac{u(r)}{r} = \frac{1}{r}\rho^{\ell+1}e^{-\rho}v(\rho) = \boxed{\frac{1}{na}\left(\frac{r}{na}\right)^\ell e^{-r/na}v_{n\ell}\left(\frac{r}{na}\right)} \quad ,$$

where v is a polynomial in ρ given by the terminated sum on page 11:

$$v_{n\ell}(\rho) = \sum_{j=0}^{n-\ell-1} c_j\rho^j \quad , \text{ where } \quad c_{j+1} = \frac{2(\ell+j+1)-\rho_0}{(j+1)(j+2\ell+2)}c_j \quad .$$

Normalization of the ground-state H wavefunction

- The lowest energy (ground) state of H has $n=1, \ell=m=0$. From the past few pages above, and from the discussion of spherical harmonics in Lecture 14,

$$\left.\begin{aligned}
&P_0(\cos\vartheta)=\frac{1}{2^0 0!}\left(\frac{d}{d(\cos\vartheta)}\right)^0\left(\cos^2\vartheta-1\right)^0=1 \quad ;\\
&P_0^0(\cos\vartheta)=(-1)^0\left(1-x^2\right)^0\left(\frac{d}{dx}\right)^0 P_0(x)=1 \quad ;\\
&Y_0^0(\vartheta,\varphi)=\sqrt{\frac{(0+1)(0)!}{4\pi(0)!}}\,e^{i0}P_0^0(\cos\vartheta)=\sqrt{\frac{1}{4\pi}} \quad ;\\
&R_{10}(r)=\frac{1}{a}\left(\frac{r}{a}\right)^0 e^{-r/a}v_{10}\left(\frac{r}{a}\right)=\frac{c_0}{a}e^{-r/a} \quad .
\end{aligned}\right\}
\left\{\begin{aligned}
1&=\int\psi_{100}^*\psi_{100}\,d\tau=\frac{1}{4\pi}\frac{|c_0|^2}{a^2}\int_0^{2\pi}\int_0^{\pi}\sin\vartheta\,d\vartheta\,d\varphi\int_0^{\infty}e^{-2r/a}r^2dr\\
&=\frac{1}{4\pi}\frac{|c_0|^2}{a^2}(4\pi)\left(\frac{a}{2}\right)^3\int_0^{\infty}e^{-u}u^2du=\frac{|c_0|^2}{a^2}\left(\frac{a}{2}\right)^3(2!)=\frac{|c_0|^2a}{4}\\
&\boxed{c_0=\frac{2}{\sqrt{a}}}\ \Rightarrow\ \boxed{\psi_{100}(r,\vartheta,\varphi)=\frac{1}{\sqrt{\pi a^3}}e^{-r/a}}\quad .
\end{aligned}\right.$$

Associated Laguerre functions

- All the other coefficients in $v_{n\ell}(\rho)=\sum_{j=0}^{n-\ell-1} c_j\rho^j$ come from this value of c_0, and $c_{j+1}=\frac{2(\ell+j+1)-\rho_0}{(j+1)(j+2\ell+2)}c_j$.
- An applied mathematician would recognize the expression $v_{n\ell}(\rho)$ and c_{j+1}/c_j. They would write it as

$$v_{n\ell}(\rho)=L_{n-\ell-1}^{2\ell+1}(2\rho) \quad , \quad \text{where} \quad L_q^p(x)=(-1)^p\left(\frac{d}{dx}\right)^p L_{p+q}(x)$$

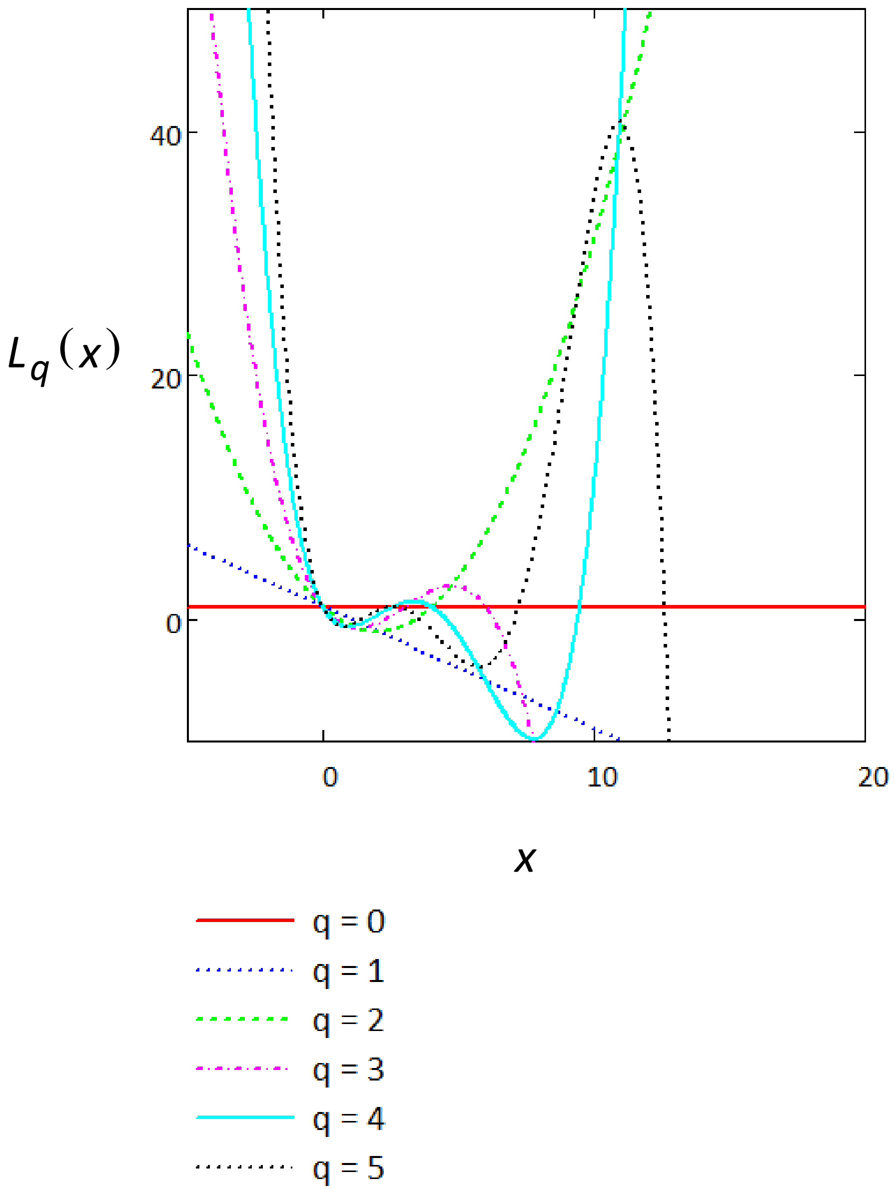
is called the **associated Laguerre function**, and where

$$L_q(x)=\frac{e^x}{q!}\left(\frac{d}{dx}\right)^q\left(x^q e^{-x}\right)$$

is the (qth) **Laguerre polynomial**. A few of each are listed in the next pages, which we show to prevent fear that they are dangerous beasts: they are, after all, polynomials. It doesn't – or shouldn't – scare you to perform any mathematical operation on a polynomial.

Laguerre polynomials

q	$L_q(x)$
0	1
1	$-x+1$
2	$\frac{1}{2}(x^2-4x+2)$
3	$\frac{1}{6}(-x^3+9x^2-18x+6)$
4	$\frac{1}{24}(x^4-16x^3+72x^2-96x+24)$
5	$\frac{1}{120}(-x^5+25x^4-200x^3+600x^2-600x+120)$
$\vdots$	$\vdots$
q	$\frac{1}{q!}((-x)^q+q^2(-x)^{q-1}+\cdots+\left(\frac{q!}{p!(q-p)!}\right)^2 p!(-x)^{q-p}+\cdots+q(q!)(-x)+q!)$



Normalized H wavefunctions

- In all, the H wavefunctions are

$$\boxed{\psi_{n\ell m}(r,\vartheta,\varphi)=\sqrt{\left(\frac{2}{na}\right)^3\frac{(n-\ell-1)!}{2n(n+\ell)!}}\,e^{-r/na}\left(\frac{2r}{na}\right)^{\ell}L_{n-\ell-1}^{2\ell+1}\left(\frac{2r}{na}\right)Y_\ell^m(\vartheta,\varphi)\quad .}$$

- And, as we are getting used to, they are orthonormal:

$$\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}\psi_{n\ell m}^*\psi_{n'\ell'm'}\,r^2dr\sin\vartheta d\vartheta d\varphi=\delta_{nn'}\delta_{\ell\ell'}\delta_{mm'}\quad .$$

- They are quite a chore to visualize, though. See G&S page 153 for some monochrome attempts, but don’t neglect to search the web for color-coded renditions which may make more sense to you. Page 1, for example.

- Next time: example use of the H wavefunctions