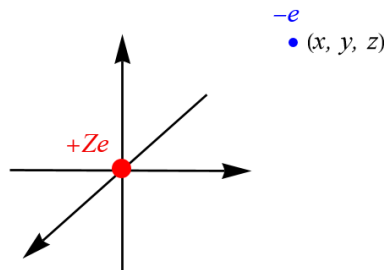


Problem 4.19

A **hydrogenic atom** consists of a single electron orbiting a nucleus with Z protons. ($Z = 1$ would be hydrogen itself, $Z = 2$ is ionized helium, $Z = 3$ is doubly ionized lithium, and so on.) Determine the Bohr energies $E_n(Z)$, the binding energy $E_1(Z)$, the Bohr radius $a(Z)$, and the Rydberg constant $\mathcal{R}(Z)$ for a hydrogenic atom. (Express your answers as appropriate multiples of the hydrogen values.) Where in the electromagnetic spectrum would the Lyman series fall, for $Z = 2$ and $Z = 3$? *Hint:* There's nothing much to *calculate* here—in the potential (Equation 4.52) $e^2 \rightarrow Ze^2$, so all you have to do is make the same substitution in all the final results.

Solution

The goal in this problem is to analyze a hydrogenic atom, which has Z protons and one electron. Because a proton is roughly 2000 times more massive than an electron, the protons' motion can be neglected to a good approximation. As such, let the protons lie at the origin of space. Ignore spin for now.



The electron is somewhere around the nucleus; solve the Schrödinger equation to determine its wave function.

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m_e} \nabla^2 \Psi + V(x, y, z) \Psi(x, y, z, t)$$

The potential energy function $V(x, y, z)$ is determined from

$$\mathbf{F} = -\nabla V,$$

where \mathbf{F} is given by Coulomb's law.

$$\frac{1}{4\pi\epsilon_0} \frac{(-e)(Ze)}{r^2} \hat{\mathbf{r}} = -\nabla V,$$

Since the force is only dependent on the spherical coordinate $r = \sqrt{x^2 + y^2 + z^2}$, the potential energy function is as well.

$$-\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^2} = -\frac{dV}{dr}$$

Multiply both sides by -1 and then integrate both sides from ∞ to r .

$$\int_{\infty}^r \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_0^2} dr_0 = \int_{\infty}^r \frac{dV}{dr}(r_0) dr_0$$

Evaluate the integrals.

$$-\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_0} \Big|_{\infty}^r = V(r) - \underbrace{V(\infty)}_{=0}$$

As a result,

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

and Schrödinger's equation becomes

$$\begin{aligned} i\hbar \frac{\partial \Psi}{\partial t} &= -\frac{\hbar^2}{2m_e} \nabla^2 \Psi + V(r) \Psi(r, \phi, \theta, t) \\ &= -\frac{\hbar^2}{2m_e} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \Psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \Psi}{\partial \phi^2} \right] + V(r) \Psi(r, \phi, \theta, t). \end{aligned}$$

The aim is to solve for $\Psi = \Psi(r, \theta, \phi, t)$ in all of space ($0 \leq r < \infty$, $0 \leq \theta \leq \pi$, $0 \leq \phi \leq 2\pi$) for $t > 0$. Assuming a product solution of the form $\Psi(r, \theta, \phi, t) = R(r)\Theta(\theta)\xi(\phi)T(t)$ and plugging it into the PDE yields the following system of ODEs (see Problem 4.4).

$$\left. \begin{aligned} i\hbar \frac{T'(t)}{T(t)} &= E \\ \frac{1}{R(r)} \frac{d}{dr} \left(r^2 R'(r) \right) - \frac{2m_e r^2}{\hbar^2} [V(r) - E] &= F \\ \frac{\sin \theta}{\Theta(\theta)} \frac{d}{d\theta} \left(\Theta'(\theta) \sin \theta \right) + F \sin^2 \theta &= G \\ -\frac{\xi''(\phi)}{\xi(\phi)} &= G \end{aligned} \right\}$$

The normalized products of angular eigenfunctions $\Theta(\theta)\xi(\phi)$ are called the spherical harmonics and are denoted by $Y_\ell^m(\theta, \phi)$. Solutions only exist if $F = \ell(\ell + 1)$, where $\ell = 0, 1, 2, \dots$, and if $G = m^2$ is an integer.

$$Y_\ell^m(\theta, \phi) = \sqrt{\frac{(2\ell + 1)(\ell - m)!}{4\pi(\ell + m)!}} e^{im\phi} P_\ell^m(\cos \theta), \quad \begin{cases} \ell = 0, 1, 2, \dots \\ m = -\ell, -\ell + 1, \dots, -1, 0, 1, \dots, \ell - 1, \ell \end{cases}$$

With these results the equation for $R(r)$ becomes

$$\begin{aligned} \frac{1}{R(r)} \frac{d}{dr} \left(r^2 R'(r) \right) - \frac{2m_e r^2}{\hbar^2} \left(-\frac{Ze^2}{4\pi\epsilon_0 r} - E \right) &= \ell(\ell + 1) \\ \frac{d}{dr} \left[r^2 \frac{dR}{dr}(r) \right] + \left[2 \left(\frac{Zm_e e^2}{4\pi\epsilon_0 \hbar^2} \right) r + \frac{2m_e r^2}{\hbar^2} E \right] R(r) - \ell(\ell + 1)R(r) &= 0. \end{aligned} \quad (1)$$

Note that since we're interested in the bound states of the hydrogenic atom (protons and an electron paired together), $E < 0$. Also, the grouping of constants in parentheses is $1/a$, where $a = a(Z)$ is the hydrogenic Bohr radius.

$$a(Z) = \frac{4\pi\epsilon_0 \hbar^2}{Zm_e e^2} = \frac{a_0}{Z}$$

Make the change of variables,

$$s = \kappa r, \quad \text{where } \kappa = \frac{\sqrt{-8m_e E}}{\hbar}.$$

Consequently, equation (1) turns into

$$\frac{ds}{dr} \frac{d}{ds} \left[\left(\frac{s}{\kappa} \right)^2 \frac{ds}{dr} \frac{d}{ds} R \left(\frac{s}{\kappa} \right) \right] + \left[\frac{2}{a} \left(\frac{s}{\kappa} \right) + \frac{2m_e s^2}{\hbar^2 \kappa^2} E \right] R \left(\frac{s}{\kappa} \right) - \ell(\ell+1) R \left(\frac{s}{\kappa} \right) = 0.$$

Use a new dependent variable,

$$w(s) = R \left(\frac{s}{\kappa} \right),$$

and simplify the left side.

$$\begin{aligned} \kappa \frac{d}{ds} \left[\left(\frac{s^2}{\kappa^2} \right) \kappa \frac{dw}{ds} \right] + \left[\frac{2}{a} \left(\frac{s}{\kappa} \right) + \frac{2m_e s^2}{\hbar^2} \left(-\frac{\hbar^2}{8m_e} \right) \right] w(s) - \ell(\ell+1)w(s) &= 0 \\ \frac{d}{ds} \left(s^2 \frac{dw}{ds} \right) + \left[\frac{2s}{a\kappa} - \frac{s^2}{4} - \ell(\ell+1) \right] w(s) &= 0 \end{aligned}$$

Make another change of variables.

$$w(s) = s^\ell e^{-s/2} u(s)$$

As a result,

$$\begin{aligned} 0 &= \frac{d}{ds} \left\{ s^2 \frac{d}{ds} [s^\ell e^{-s/2} u(s)] \right\} + \left[\frac{2s}{a\kappa} - \frac{s^2}{4} - \ell(\ell+1) \right] s^\ell e^{-s/2} u(s) \\ &= \frac{d}{ds} \left\{ s^2 \left[\ell s^{\ell-1} e^{-s/2} u(s) + s^\ell \left(-\frac{1}{2} \right) e^{-s/2} u(s) + s^\ell e^{-s/2} \frac{du}{ds} \right] \right\} + \left[\frac{2s}{a\kappa} - \frac{s^2}{4} - \ell(\ell+1) \right] s^\ell e^{-s/2} u(s) \\ &= \frac{d}{ds} \left(\ell s^{\ell+1} e^{-s/2} u(s) - \frac{1}{2} s^{\ell+2} e^{-s/2} u(s) + s^{\ell+2} e^{-s/2} \frac{du}{ds} \right) + \left[\frac{2s}{a\kappa} - \frac{s^2}{4} - \ell(\ell+1) \right] s^\ell e^{-s/2} u(s) \\ &= \left[\cancel{\ell(\ell+1) s^\ell e^{-s/2} u(s)} + \ell s^{\ell+1} \left(-\frac{1}{2} \right) e^{-s/2} u(s) + \ell s^{\ell+1} e^{-s/2} \frac{du}{ds} \right] \\ &\quad - \frac{1}{2} \left[\cancel{(\ell+2) s^{\ell+1} e^{-s/2} u(s)} + \cancel{s^{\ell+2} \left(-\frac{1}{2} \right) e^{-s/2} u(s)} + s^{\ell+2} e^{-s/2} \frac{du}{ds} \right] \\ &\quad + \left[(\ell+2) s^{\ell+1} e^{-s/2} \frac{du}{ds} + s^{\ell+2} \left(-\frac{1}{2} \right) e^{-s/2} \frac{du}{ds} + s^{\ell+2} e^{-s/2} \frac{d^2 u}{ds^2} \right] \\ &\quad + \frac{2}{a\kappa} s^{\ell+1} e^{-s/2} u(s) - \frac{1}{4} \cancel{s^{\ell+2} e^{-s/2} u(s)} - \cancel{\ell(\ell+1) s^\ell e^{-s/2} u(s)} \\ &= s^{\ell+2} e^{-s/2} \frac{d^2 u}{ds^2} + (2\ell+2-s) s^{\ell+1} e^{-s/2} \frac{du}{ds} + \left(\frac{2}{a\kappa} - \ell - 1 \right) s^{\ell+1} e^{-s/2} u(s). \end{aligned}$$

Multiply both sides by $e^{s/2}$.

$$s^{\ell+2} \frac{d^2 u}{ds^2} + (2\ell+2-s) s^{\ell+1} \frac{du}{ds} + \left(\frac{2}{a\kappa} - \ell - 1 \right) s^{\ell+1} u(s) = 0$$

Divide both sides by $s^{\ell+1}$.

$$s \frac{d^2 u}{ds^2} + [(2\ell+1) + 1 - s] \frac{du}{ds} + \left(\frac{2}{a\kappa} - \ell - 1 \right) u(s) = 0, \quad 0 < s < \infty$$

This is the generalized Laguerre differential equation. Normalizable solutions exist only if the quantity in parentheses multiplying $u(s)$ is a nonnegative integer $(0, 1, 2, \dots)$. It's this fact that allows us to determine the eigenenergies of the bound states of a hydrogenic atom. Let N be the nonnegative integer.

$$\frac{2}{a\kappa} - \ell - 1 = N \quad \rightarrow \quad \frac{2}{a\kappa} = N + \ell + 1$$

The number on the right side is a positive integer $(1, 2, \dots)$ and is denoted by n .

$$\frac{2}{a\kappa} = n \quad \rightarrow \quad 2 \left(\frac{Zm_e e^2}{4\pi\epsilon_0 \hbar^2} \right) \left(\frac{\hbar}{\sqrt{-8m_e E}} \right) = n$$

Solve for $E = E_n(Z)$ and write it in terms of E_n , the eigenenergies of the bound states of the hydrogen atom.

$$E_n(Z) = -\frac{Z^2 m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2} = -Z^2 \left[\frac{m_e}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} = \frac{Z^2 E_1}{n^2} = Z^2 E_n, \quad n = 1, 2, \dots$$

The binding energy is obtained by setting $n = 1$.

$$E_1(Z) = Z^2 E_1$$

If the electron transitions from an initial stationary state with $n = n_i$ to a final stationary state with $n = n_f$ in which $n_i > n_f$, then a photon will be emitted with energy ΔE .

$$\Delta E = E_{n_i}(Z) - E_{n_f}(Z)$$

$$h\nu = -\frac{Z^2 m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n_i^2} + \frac{Z^2 m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n_f^2}$$

$$(2\pi\hbar) \left(\frac{c}{\lambda} \right) = \frac{Z^2 m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

Divide both sides by $2\pi\hbar c$.

$$\begin{aligned} \frac{1}{\lambda} &= \frac{Z^2 m_e e^4}{64\pi^3 \epsilon_0^2 \hbar^3 c} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \\ &= \mathcal{R}(Z) \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \end{aligned}$$

$\mathcal{R}(Z)$ is the hydrogenic Rydberg constant, and $\mathcal{R} \approx 1.09737 \times 10^7 \text{ m}^{-1}$ is the Rydberg constant for the hydrogen atom.

$$\mathcal{R}(Z) = \frac{Z^2 m_e e^4}{64\pi^3 \epsilon_0^2 \hbar^3 c} = Z^2 \left[\frac{m_e}{4\pi c \hbar^3} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] = Z^2 \mathcal{R}$$

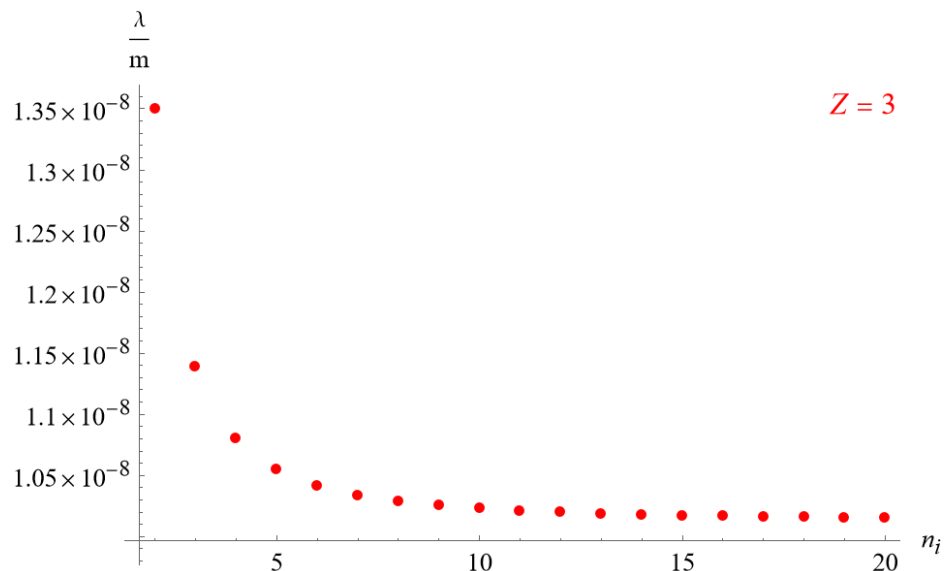
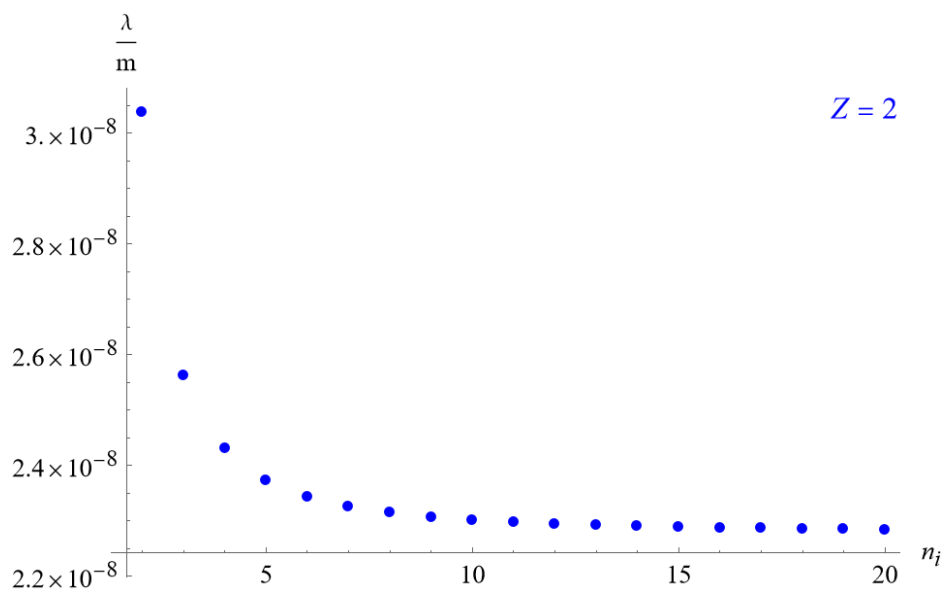
Transitions in which $n_f = 1$ are collectively known as the Lyman series.

$$\begin{aligned}\frac{1}{\lambda} &= \mathcal{R}(Z) \left(1 - \frac{1}{n_i^2}\right), \quad n_i = 2, 3, 4, \dots \\ &= Z^2 \mathcal{R} \left(\frac{n_i^2 - 1}{n_i^2}\right)\end{aligned}$$

Invert both sides to get the wavelength.

$$\lambda = \frac{1}{Z^2 \mathcal{R}} \left(\frac{n_i^2}{n_i^2 - 1}\right), \quad n_i = 2, 3, 4, \dots$$

Below are plots of λ (in meters) versus n_i for $Z = 2$ and $Z = 3$.



Photons with a wavelength of roughly 10^{-8} meters lie in the ultraviolet region.

