05 - Hydrogenic Atoms

- <u>Aim of Section</u>:
    - Investigation of bound energy eigenstates of hydrogenic atoms: i.e., atoms with single electron, such as H, He^+, Li^{++}, etc.

Hamiltonian - I

- Non-relativistic Hamiltonian of point particle is sum of operators representing kinetic and potential energies:

$$H = K + V.$$

- By analogy with classical physics, kinetic energy of particle of mass m, moving in three dimensions, is

$$K = \frac{p^2}{2m} \equiv \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m},$$

where p_x is quantum mechanical operator that represents x-momentum, etc.

Hamiltonian - II

- In a hydrogenic atom, classical potential energy takes form $V = V(r)$, where $r = (x^2 + y^2 + z^2)^{1/2}$. Such a potential is termed a central potential (because it only depends on radial distance, r, from origin).

- Assume that quantum mechanical potential energy is same function of operators representing Cartesian components of position that classical potential is of Cartesian coordinates.

- Hamiltonian of point particle moving in central potential becomes

$$H = \frac{p^2}{2m} + V(r). \qquad (1)$$

- Wish to find bound energy eigenstates of system. These are square-integrable solutions of time-independent Schrödinger equation:

$$H\psi = E\psi. \qquad (2)$$

Derivation of Radial Equation - I

▶ Cartesian components of momentum, **p**, are represented as

$$p_i = -\mathrm{i}\,\hbar\,\frac{\partial}{\partial x_i}$$

for $i = 1, 2, 3$, where $x_1 \equiv x$, etc.

▶ Radial component of momentum can be represented as (Hw. 3, Q. 4)

$$p_r \equiv \frac{\mathbf{x} \cdot \mathbf{p}}{r} = \frac{x_i\, p_i}{r} = -\mathrm{i}\,\hbar\,\frac{x_i}{r}\,\frac{\partial}{\partial x_i} = -\mathrm{i}\,\hbar\,\frac{\partial}{\partial r}. \qquad (3)$$

▶ Here, have made use of Einstein summation convention: $x_i\, p_i \equiv \sum_{i=1,3} x_i\, p_i$.

Derivation of Radial Equation - II

- Angular momentum vector, **L**, is defined

$$\mathbf{L} = \mathbf{x} \times \mathbf{p}. \tag{4}$$

- Previous expression can also be written:

$$L_i = \epsilon_{ijk} \, x_j \, p_k,$$

  where $\epsilon_{ijk} = +1$ if i, j, k cyclic permutation of $1, 2 \; 3$; $\epsilon_{ijk} = -1$ if anti-cyclic permutation; $\epsilon_{ijk} = 0$ otherwise.

- L^2 is equivalent to $L_i \, L_i$. Thus, we obtain

$$L^2 = \epsilon_{ijk} \, x_j \, p_k \, \epsilon_{ilm} \, x_l \, p_m = \epsilon_{ijk} \, \epsilon_{ilm} \, x_j \, p_k \, x_l \, p_m.$$

- Note that we are able to shift position of ϵ_{ilm} because its elements are just numbers, and, therefore, commute with all of the x_i and the p_i.

Derivation of Radial Equation - III

▶ Easily demonstrated that

$$\epsilon_{ijk}\,\epsilon_{ilm} \equiv \delta_{jl}\,\delta_{km} - \delta_{jm}\,\delta_{kl},$$

where $\delta_{ij} = 1$ if $i = j$; $\delta_{ij} = 0$ otherwise.

▶ Previous two equations yield

$$L^2 = x_i\,p_j\,x_i\,p_j - x_i\,p_j\,x_j\,p_i. \tag{5}$$

▶ Here, we have made use of result $\delta_{ij}\,a_i\,b_j \equiv a_i\,b_i$. We have also been careful to preserve order of various terms on right-hand side of previous expression, because the x_i and the p_i do not necessarily commute with one another.

Derivation of Radial Equation - IV

▶ Now need to rearrange order of terms on right-hand side of (5).

▶ Can achieve this goal by making use of fundamental commutation relation for the x_i and the p_i:

$$[x_i, p_j] = i\,\hbar\,\delta_{ij}.$$

▶ Thus,

$$L^2 = x_i\,(x_i\,p_j - [x_i, p_j])\,p_j - x_i\,p_j\,(p_i\,x_j + [x_j, p_i])$$
$$= x_i\,x_i\,p_j\,p_j - i\,\hbar\,\delta_{ij}\,x_i\,p_j - x_i\,p_j\,p_i\,x_j - i\,\hbar\,\delta_{ij}\,x_i\,p_j$$
$$= x_i\,x_i\,p_j\,p_j - x_i\,p_i\,p_j\,x_j - 2\,i\,\hbar\,x_i\,p_i.$$

▶ Here, we have made use of fact that $p_j\,p_i = p_i\,p_j$, because the p_i commute with one another.

Derivation of Radial Equation - V

▶ Next,

$$L^2 = x_i \, x_i \, p_j \, p_j - x_i \, p_i \, (x_j \, p_j - [x_j, p_j]) - 2 \, i \, \hbar \, x_i \, p_i.$$

▶ Now,

$$[x_j, p_j] \equiv [x_1, p_1] + [x_2, p_2] + [x_3, p_3] = 3 \, i \, \hbar.$$

▶ Hence, we obtain

$$L^2 = x_i \, x_i \, p_j \, p_j - x_i \, p_i \, x_j \, p_j + i \, \hbar \, x_i \, p_i.$$

▶ When expressed in more conventional vector notation, previous expression becomes

$$L^2 = r^2 \, p^2 - (\mathbf{x} \cdot \mathbf{p})^2 + i \, \hbar \, \mathbf{x} \cdot \mathbf{p}. \qquad (6)$$

▶ If we had attempted to derive previous expression directly from (4), using standard vector identities, then we would have missed final term on right-hand side. This term originates from lack of commutation between x_i and p_i operators in quantum mechanics.

- (6) can be rearranged to give

$$p^2 = r^{-2} \left[(\mathbf{x} \cdot \mathbf{p})^2 - \mathrm{i}\,\hbar\,\mathbf{x} \cdot \mathbf{p} + L^2 \right].$$

- Now,

$$\mathbf{x} \cdot \mathbf{p} = r\,p_r = -\mathrm{i}\,\hbar\,r\,\frac{\partial}{\partial r},$$

  where use has been made of (3).

- Hence, we obtain

$$p^2 = -\hbar^2 \left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\,\frac{\partial}{\partial r} \right) + \frac{1}{r}\frac{\partial}{\partial r} - \frac{L^2}{\hbar^2\,r^2} \right].$$

- Finally, previous equation can be combined with (1) to give following expression for Hamiltonian:

$$H = -\frac{\hbar^2}{2\,m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{L^2}{\hbar^2\,r^2} \right) + V(r). \qquad (7)$$

Derivation of Radial Equation - VII

- Let us now consider whether previous Hamiltonian commutes with angular momentum operators L_z and L^2.

- Recall that L_z and L^2 are represented as differential operators that depend solely on angular spherical coordinates, θ and ϕ, and do not contain radial coordinate, r.

- Thus, any function of r, or any differential operator involving r (but not θ and ϕ), will automatically commute with L^2 and L_z.

- Moreover, L^2 commutes both with itself, and with L_z.

- It is, therefore, clear that previous Hamiltonian commutes with both L_z and L^2.

Derivation of Radial Equation - VIII

- If two operators commute with one another then they possess simultaneous eigenstates.

- Conclude that, for a particle moving in a central potential, eigenstates of Hamiltonian are simultaneous eigenstates of L_z and L^2.

- Have already found simultaneous eigenstates of L_z and L^2—they are spherical harmonics, $Y_l^m(\theta, \phi)$.

- Follows that spherical harmonics are also eigenstates of Hamiltonian. This observation leads us to try following separable form for stationary wavefunction:

$$\psi(r, \theta, \phi) = R(r)\, Y_l^m(\theta, \phi). \tag{8}$$

▶ Immediately follows from properties of Y_l^m, and fact that L_z and L^2 both obviously commute with $R(r)$, that

$$L_z \, \psi = m \, \hbar \, \psi, \tag{9}$$

$$L^2 \, \psi = l \, (l+1) \, \hbar^2 \, \psi. \tag{10}$$

▶ Recall that l is non-negative integer, and m is integer lying in range $-l \le m \le +l$.

▶ Finally, making use of (2), (7), and (10), we obtain following differential equation which determines radial variation of stationary wavefunction:

$$-\frac{\hbar^2}{2m} \left[\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{l \, (l+1)}{r^2} \right] R_{n,l} + V(r) \, R_{n,l} = E \, R_{n,l}. \tag{11}$$

- Here, have labeled function $R(r)$ by two quantum numbers, n and l.
- Second quantum number, l, is related to eigenvalue of L^2. [Note that azimuthal quantum number, m, does not appear in previous equation, and, therefore, does not influence either function $R(r)$ or energy, E.]
- First quantum number, n, is determined by constraint that radial wavefunction be square-integrable.

Normalization of Radial Equation - I

- A hydrogenic atom consists of an electron, of change $-e$ and mass m_e, and a nucleus of charge $+Z\,e$, and mass $m_n = A\,m_p$.
- Here, Z and A are atomic number and mass number of atom, respectively. Moreover, m_p is proton mass.
- Potential energy of atom is

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

  where $r = |\mathbf{x}|$, and $\mathbf{x}$ is position vector of electron relative to nucleus.
- As in classical physics, two-body problem can be converted into equivalent one-body problem in which particle of mass

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

  moves in central potential

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

Normalization of Radial Equation - II

- $V(r) \to 0$ as $r \to \infty$, so bound state has negative energy.
- Given that $m_e/m_p \simeq 1/1836$, fractional difference between m_e and μ is less than 5.4×10^{-4}. However, relativistic corrections to electron mass are larger than this. (See later.) Hence, it does not make sense to make a distinction between m_e and μ in non-relativistic quantum mechanics.
- Conclude that appropriate version of radial equation, (11), for hydrogenic atom is

$$-\frac{\hbar^2}{2m_e}\left[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{l\,(l+1)}{r^2}\right]R_{n,l} - \frac{Z\,e^2}{4\pi\epsilon_0\,r}\,R_{n,l} = E\,R_{n,l}.$$

Normalization of Radial Equation - III

▶ Previous equation can be rearranged to give

$$\frac{d^2 R_{n,l}}{dr^2} + \frac{2}{r}\frac{dR_{n,l}}{dr} + \frac{2m_e}{\hbar^2}\left[E + \frac{Z\,e^2}{4\pi\epsilon_0\,r} - \frac{\hbar^2\,l\,(l+1)}{2m_e\,r^2}\right]R_{n,l} = 0.$$

▶ Convenient to rewrite radial equation in terms of dimensionless energy and dimensionless radial coordinate.

▶ Let a be characteristic length-scale of hydrogenic atom.

▶ Dimensionless radial coordinate is

$$\rho = \frac{r}{a}. \tag{12}$$

▶ Follows that

$$\frac{1}{a^2}\frac{d^2 R_{n,l}}{d\rho^2} + \frac{1}{a^2}\frac{2}{\rho}\frac{dR_{n,l}}{d\rho} + \frac{2m_e}{\hbar^2}\left[E + \frac{Z\,e^2}{4\pi\epsilon_0\,a\,\rho} - \frac{\hbar^2\,l\,(l+1)}{2m_e\,a^2\,\rho^2}\right]R_{n,l} = 0.$$

Normalization of Radial Equation - IV

- Multiplying by a^2, obtain

$$\frac{d^2 R_{n,l}}{d\rho^2} + \frac{2}{\rho} \frac{dR_{n,l}}{d\rho} + \left[\frac{2m_e \, a^2 \, E}{\hbar^2} + \frac{m_e \, Z \, e^2}{4\pi\epsilon_0 \, \hbar^2} \frac{2 \, a}{\rho} - \frac{l \, (l+1)}{\rho^2} \right] R_{n,l} = 0.$$

- Terms inside square bracket on right-hand side of previous equation are dimensionless.

- Evident that characteristic length-scale is

$$a = \frac{4\pi\epsilon_0 \, \hbar^2}{m_e \, Z \, e^2}. \tag{13}$$

- Characteristic energy scale is $\hbar^2/(2m_e \, a^2)$.

- Define dimensionless energy parameter,

$$\gamma^2 = -E \bigg/ \left(\frac{\hbar^2}{2m_e \, a^2} \right). \tag{14}$$

- Note that $E < 0$ for bound state. Hence, $\gamma^2 > 0$. Can chose positive root without loss of generality.

- Radial equation becomes

$$\frac{d^2 R_{n,l}}{d\rho^2} + \frac{2}{\rho} \frac{dR_{n,l}}{d\rho} + \left[-\gamma^2 + \frac{2}{\rho} - \frac{l\,(l+1)}{\rho^2} \right] R_{n,l} = 0. \quad (15)$$

- Normalization condition for radial wavefunction is

$$\int_0^\infty r^2 \left[R_{n,l}(r) \right]^2 dr = a^3 \int_0^\infty \rho^2 \left[R_{n,l}(\rho) \right]^2 d\rho = 1. \quad (16)$$

Solution of Radial Equation - I

- Consider large-ρ limit of (15) in which $1/\rho$ and $1/\rho^2$ terms are negligible.

- Equation reduces to

$$\frac{d^2 R_{n,l}}{d\rho^2} - \gamma^2 R_{n,l} \simeq 0.$$

- Solutions are $R_{n,l} = \mathrm{e}^{\pm\gamma\rho}$. However, $\mathrm{e}^{+\gamma\rho}$ solution is not compatible with normalization condition (16).

- Conclude that

$$R_{n,l}(\rho) \sim \mathrm{e}^{-\gamma\rho}$$

at large ρ.

Solution of Radial Equation - II

- Consider small-ρ limit of (15) in which $1/\rho^2$ term dominates.
- Equation reduces to

$$\frac{d^2 R_{n,l}}{d\rho^2} + \frac{2}{\rho} \frac{dR_{n,l}}{d\rho} - \frac{l(l+1)}{\rho^2} R_{n,l} \simeq 0.$$

- Search for power-law solution of form $R(\rho) = \rho^q$. Obtain

$$q(q-1) + 2q - l(l+1) = q(q+1) - l(l+1) = 0.$$

- Solutions are $q = l$ and $q = -l - 1$. Latter solution not compatible with physical constraint that wavefunction finite at origin.
- Conclude that

$$R_{n,l}(\rho) \sim \rho^l$$

at small ρ.

Solution of Radial Equation - III

- Previous analysis suggest that we search for a solution of radial equation (15) that has form

$$R_{n,l}(\rho) = e^{-\gamma \rho} \rho^l H(\rho). \qquad (17)$$

- (15) transforms to give (Hw. 3, Q. 5)

$$\rho \frac{d^2 H}{d\rho^2} + 2(l + 1 - \gamma \rho) \frac{dH}{d\rho} + 2(1 - \gamma - \gamma l) H = 0. \qquad (18)$$

- Search for power-law solution of form

$$H(\rho) = \sum_{j=0,\infty} c_j \rho^j. \qquad (19)$$

- Solution automatically satisfies correct boundary condition at small ρ.

Solution of Radial Equation - IV

- Previous two equations lead to recursion relation (Hw. 3, Q. 6)

$$c_{j+1} = \frac{2\,\gamma\,(1+j+l) - 2}{(j+1)\,(j+2\,l+2)}\,c_j. \qquad (20)$$

- In large-j limit, obtain

$$c_{j+1} \simeq \frac{2\,\gamma}{j}\,c_j.$$

- But series

$$e^{2\,\gamma\,\rho} = \sum_{j=0,\infty} \frac{(2\,\gamma)^j}{j!}\,\rho^j$$

has same large-j recursion relation.

Solution of Radial Equation - V

- Conclude from (17) and (19) that $R_{n,l}(\rho) \sim \rho^l\,e^{\gamma\,\rho}$ at large-ρ, which is is not compatible with normalization condition (16).

- Only way to prevent this unacceptable behavior is if series (19) terminates at a finite value of j.

- Suppose that maximum power of ρ in series solution (19) is $\rho^{j_{\max}}$.

- In order for the series to terminate, we require $c_{j_{\max}+1} = 0$ when $c_{j_{\max}} \neq 0$.

- Follows from recursion relation (20) that

$$2\,\gamma\,(1 + j_{\max} + l) - 2 = 0.$$

- Let

$$n = j_{\max} + l + 1.$$

Evident that $n \geq l + 1$ is positive integer (because $j_{\max} \geq 0$).

- From previous two equations, allowed values of energy parameter are

$$\gamma = \frac{1}{n}. \tag{21}$$

- Here, n is termed principle quantum number of hydrogenic atom.

- Note that the power-law solution (19) contains $n - l$ terms.

Useful Quantities - I

- Helpful to define Bohr radius:

$$a_0 = \frac{4\pi\epsilon_0 \, \hbar^2}{m_e \, e^2} = 5.29177 \times 10^{-11} \, \text{m}. \qquad (22)$$

- Also helpful to define hydrogen ground-state energy:

$$E_0 = -\frac{\hbar^2}{2m_e \, a_0^2} = -\frac{e^2}{8\pi\epsilon_0 \, a_0} = -13.6 \, \text{eV}. \qquad (23)$$

- In terms of these quantities

$$a = \frac{a_0}{Z}. \qquad (24)$$

- Energy of hydrogenic atom associated with principle quantum number n is

$$E_n = \frac{Z^2 \, E_0}{n^2}. \qquad (25)$$

- Ratio of magnitude of hydrogen ground-state energy to electron rest mass energy is

$$\frac{|E_0|}{m_e \, c^2} = \frac{\alpha^2}{2},$$

where

$$\alpha = \frac{e^2}{4\pi\epsilon_0 \, \hbar \, c} \simeq \frac{1}{137} \tag{26}$$

is dimensionless fine-structure constant.

- Fact that $\alpha \ll 1$ justifies non-relativistic treatment of problem.

Radial Wavefunctions - I

- Laguerre polynomials (warning: this is math definition—see Wikipedia), $L_q(x)$, defined as follows:

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

  where q is a non-negative integer.

- Associated Laguerre polynomials, $L_q^p(x)$, defined as follows:

$$L_q^p(x) = (-1)^p \frac{d^p}{dx^p} L_{q+p}(x),$$

  where p is a non-negative integer.

- Given that $L_q(x)$ are polynomials of degree q, follows that $L_q^p(x)$ are also polynomials of degree q.

Radial Wavefunctions - II

▶ Associated Laguerre polynomials are solutions of following differential equation:

$$x \frac{d^2 L_q^p}{dx^2} + (p + 1 - x) \frac{dL_q^p}{dx} + q \, L_q^p = 0.$$

▶ (18) and (21) yield

$$x \frac{d^2 H}{dx^2} + [2(l + 1) - x] \frac{dH}{dx} + (n - 1 - l) H = 0,$$

where $x = 2\rho/n$.

▶ Previous two equations imply that

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

Radial Wavefunctions - III

- From (17), (21), radial wavefunction becomes

$$R_{n,l}(\rho) = A_{n,l}\, e^{-\rho/n}\, \rho^l\, L_{n-l-1}^{2l+1}(2\,\rho/n).$$

- $A_{n,l}$ determined from normalization condition (16).
- From (12), (24),

$$A_{n,l}^2 \left(\frac{a_0}{Z}\right)^3 \int_0^\infty \rho^2\, e^{-2\,\rho/n}\, \rho^{2\,l} \left[L_{n-l-1}^{2l+1}(2\rho/n)\right]^2 d\rho = 1.$$

- This yields

$$A_{n,l}^2 \left(\frac{a_0}{Z}\right)^3 \left(\frac{n}{2}\right)^{2l+3} \int_0^\infty x^{2\,(l+1)}\, e^{-x} \left[L_{n-l-1}^{2l+1}(x)\right]^2 dx = 1,$$

where $x = 2\,\rho/n$.

▶ However,

$$\int_0^\infty x^{2\,(l+1)}\,e^{-x}\,\left[L_{n-l-1}^{2l+1}(x)\right]^2\,dx = \frac{2n\,(n+l)!}{(n-l-1)!}.$$

▶ Hence,

$$A_{n,l} = \left\{\left(\frac{2\,Z}{n\,a_0}\right)^3\,\frac{(n-l-1)!}{2n\,(n+l)!}\right\}^{1/2}\,\left(\frac{2}{n}\right)^l.$$

▶ Properly normalized radial wavefunctions become

$$R_{n,l}(r) = \left\{\left(\frac{2\,Z}{n\,a_0}\right)^3\,\frac{(n-l-1)!}{2n\,(n+l)!}\right\}^{1/2}\,\exp\left(-\frac{Z\,r}{n\,a_0}\right)\,\left(\frac{2\,Z\,r}{n\,a_0}\right)^l$$

$$\times\,L_{n-l-1}^{2l+1}\left(\frac{2\,Z\,r}{n\,a_0}\right). \tag{27}$$

Radial Wavefunctions - V

- First few associated Laguerre polynomials as follows:

$$L_0^0(x) = 1, \qquad\qquad L_0^1(x) = 1,$$

$$L_0^2(x) = 1, \qquad\qquad L_0^3(x) = 1,$$

$$L_1^0(x) = 1 - x, \qquad\qquad L_1^1(x) = 2 - x,$$

$$L_1^2(x) = 3 - x, \qquad\qquad L_1^3(x) = 4 - x,$$

$$L_2^0(x) = 1 - 2x + x^2/2, \qquad L_2^1(x) = 3 - 3x + x^2/2,$$

$$L_2^2(x) = 6 - 4x + x^2/2, \qquad L_2^3(x) = 10 - 5x + x^2/2.$$

Radial Wavefunctions - VI

- First few radial wavefunctions as follows:

$$R_{1,0}(r) = 2 \left(\frac{Z}{a_0} \right)^{3/2} e^{-Z\,r/a_0},$$

$$R_{2,0}(r) = 2 \left(\frac{Z}{2\,a_0} \right)^{3/2} \left(1 - \frac{Z\,r}{2\,a_0} \right) e^{-Z\,r/2\,a_0},$$

$$R_{2,1}(r) = \frac{1}{\sqrt{3}} \left(\frac{Z}{2\,a_0} \right)^{3/2} \frac{Z\,r}{a_0} e^{-Z\,r/2\,a_0},$$

$$R_{3,0}(r) = 2 \left(\frac{Z}{3\,a_0} \right)^{3/2} \left(1 - \frac{2\,Z\,r}{3\,a_0} + \frac{2\,Z^2\,r^2}{27\,a_0^2} \right) e^{-Z\,r/3\,a_0},$$

$$R_{3,1}(r) = \frac{4\sqrt{2}}{3} \left(\frac{Z}{3\,a_0} \right)^{3/2} \frac{Z\,r}{a_0} \left(1 - \frac{Z\,r}{6\,a_0} \right) e^{-Z\,r/3\,a_0},$$
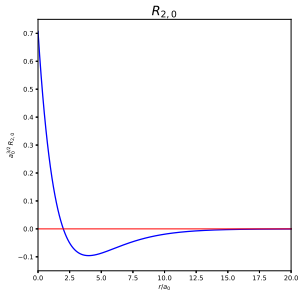
$$R_{3,2}(r) = \frac{2\sqrt{2}}{27\sqrt{5}} \left(\frac{Z}{3\,a_0} \right)^{3/2} \left(\frac{Z\,r}{a_0} \right)^2 e^{-Z\,r/3\,a_0}.$$
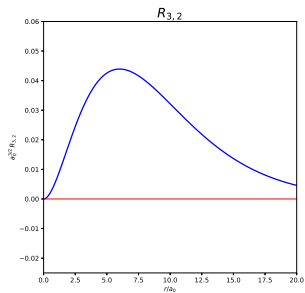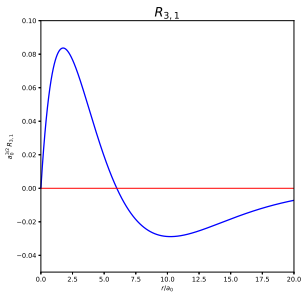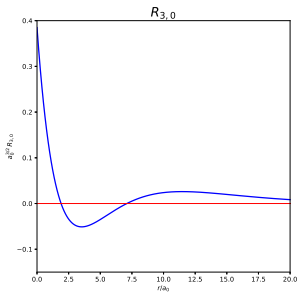
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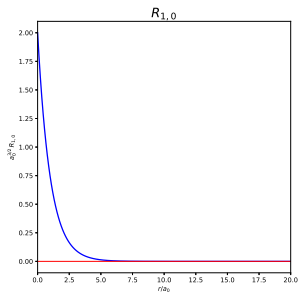
$n = 2$ Radial Wavefunctions
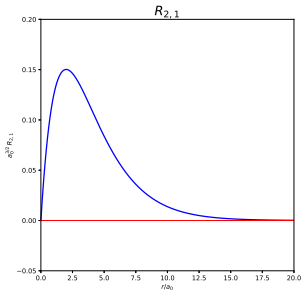
$n = 3$ Radial Wavefunctions

Energy Eigenstates - I

- Taking electron spin into account, energy eigenstates of hydrogenic atom can be written

$$\psi_{n,l,m,\pm} = R_{n,l}(r)\, Y_l^m(\theta, \phi)\, \chi_\pm.$$

- States are orthonormal:

$$\int_0^\infty r^2\, R_{n,l}(r) R_{n',l}(r)\, dr = \delta_{nn'},$$

$$\oint Y_l^{m*}(\theta, \phi)\, Y_{l'}^{m'}(\theta, \phi)\, d\Omega = \delta_{ll'}\, \delta_{mm'},$$

$$\chi_s^\dagger \chi_{s'} = \delta_{ss'},$$

where $s = \pm$.

Energy Eigenstates - II

- Quantum number n takes values

$$n = 1, 2, 3, \cdots.$$

- Energy eigenvalues are

$$E_n = \frac{Z^2 E_0}{n^2},$$

  where $E_0 = -13.6 \, \text{eV}$.

- Quantum number l takes values

$$0 \leq l < n.$$

- Quantum number m takes values

$$-l \leq m \leq +l.$$

- nth energy level is $2\,n^2$-fold degenerate. That is, there are two $n = 1$ states, eight $n = 2$ states, eighteen $n = 3$ states, etc.
- As we shall see later, this degeneracy is lifted, to some extent, by relativistic corrections. In fact,

$$E_n \simeq \frac{Z^2\,E_0}{n^2} + \frac{Z^4\,\alpha^2\,E_0}{n^4}\left(\frac{n}{j + 1/2} - \frac{3}{4}\right),$$

where j is quantum number associated with total angular momentum.

Properties of Hydrogenic Wavefunctions

▶ Hydrogenic wavefunctions have following useful properties:

$$\langle r \rangle = \frac{a_0}{2\,Z}\left[3\,n^2 - l\,(l+1)\right],$$

$$\langle r^2 \rangle = \frac{a_0^2\,n^2}{2\,Z^2}\left[5\,n^2 + 1 - 3\,l\,(l+1)\right],$$

$$\left\langle \frac{1}{r} \right\rangle = \frac{Z}{a_0\,n^2},$$

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{Z^2}{a_0^2\,n^3\,(l+1/2)},$$

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{Z^3}{a_0^3\,n^3\,l\,(l+1/2)\,(l+1)}.$$