Aim of Section:
- Investigation of bound energy eigenstates of **hydrogenic atoms**: i.e., atoms with single electron, such as H, He\(^+\), Li\(^{++}\), etc.
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.
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
\[ H = \frac{p^2}{2m} + V(r). \]  

Wish to find bound energy eigenstates of system. These are square-integrable solutions of time-independent Schrödinger equation:
\[ H \psi = E \psi. \]
Derivation of Radial Equation - I

- Cartesian components of momentum, \( p \), are represented as
  \[ p_i = -i \hbar \frac{\partial}{\partial x_i} \]
  for \( i = 1, 2, 3 \), where \( x_1 \equiv x \), etc.

- Radial component of momentum can be represented as
  \( p_r \equiv \frac{x \cdot p}{r} = \frac{x_i p_i}{r} = -i \hbar \frac{x_i}{r} \frac{\partial}{\partial x_i} = -i \hbar \frac{\partial}{\partial r}. \)  \( \text{(3)} \)

- 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, $\mathbf{L}$, is defined

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

- Previous expression can also be written:

$$L_i = \epsilon_{ijk} \times j \ p_k,$$

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

$$L^2 = \epsilon_{ijk} \times j \ p_k \epsilon_{ilm} \times l \ p_m = \epsilon_{ijk} \epsilon_{ilm} \times j \ p_k \times l \ p_m.$$

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

Easily demonstrated that

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

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,

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

- 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,

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

- Now,

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

- 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

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

Now,
\[ \mathbf{x} \cdot \mathbf{p} = r p_r = -i \hbar r \frac{\partial}{\partial r}, \]
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:
\[ H = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{L^2}{\hbar^2 r^2} \right) + V(r). \]
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, $\theta$ and $\phi$, and do not contain radial coordinate, $r$.

Thus, any function of $r$, or any differential operator involving $r$ (but not $\theta$ and $\phi$), 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 $L^2$. 
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, $Y_{lm}(\theta, \phi)$.

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

$$\psi(r, \theta, \phi) = R(r) \ Y_{lm}(\theta, \phi).$$  \hspace{1cm} (8)
Immediately follows from properties of $Y^m_l$, and fact that $L_z$ and $L^2$ both obviously commute with $R(r)$, that

\[ L_z \psi = m \hbar \psi, \quad (9) \]
\[ L^2 \psi = l(l+1) \hbar^2 \psi. \quad (10) \]

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

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

\[ -\frac{\hbar^2}{2m} \left[ \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{l(l+1)}{r^2} \right] R_{n,l} + V(r) R_{n,l} = E R_{n,l}. \quad (11) \]
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.
A hydrogenic atom consists of an electron, of charge $-e$ 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

$$V(r) = -\frac{Z \, e^2}{4\pi\varepsilon_0 \, r},$$

where $r = |x|$, and $x$ 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

$$V(r) = -\frac{Z \, e^2}{4\pi\varepsilon_0 \, r}.$$
V(r) → 0 as r → ∞, so bound state has negative energy.

Given that \( m_e/m_p \simeq 1/1836 \), fractional difference between \( m_e \) and \( \mu \) is less than \( 5.4 \times 10^{-4} \). 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 \( \mu \) in non-relativistic quantum mechanics.

Conclude that appropriate version of radial equation, (11), for hydrogenic atom is

\[
- \frac{\hbar^2}{2m_e} \left[ \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{l(l+1)}{r^2} \right] R_{n,l} - \frac{Ze^2}{4\pi\varepsilon_0 r} R_{n,l} = E R_{n,l}.
\]
Normalization of Radial Equation - III

- Previous equation can be rearranged to give

\[
\frac{d^2 R_{n,l}}{dr^2} + \frac{2}{r} \frac{dR_{n,l}}{dr} + \frac{2m_e}{\hbar^2} \left[ E + \frac{Ze^2}{4\pi\varepsilon_0 r} - \frac{\hbar^2 l(l+1)}{2m_e r^2} \right] R_{n,l} = 0.
\]

- 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

\[
\rho = \frac{r}{a}.
\]  

(12)

- Follows that

\[
\frac{1}{a^2} \frac{d^2 R_{n,l}}{d\rho^2} + \frac{1}{a^2} \frac{2}{\rho} \frac{dR_{n,l}}{d\rho} + \frac{2m_e}{\hbar^2} \left[ E + \frac{Ze^2}{4\pi\varepsilon_0 a \rho} - \frac{\hbar^2 l(l+1)}{2m_e a^2 \rho^2} \right] R_{n,l} = 0.
\]
Multiplying by \( a^2 \), obtain
\[
\frac{d^2 R_{n,l}}{d\rho^2} + \frac{2}{\rho} \frac{dR_{n,l}}{d\rho} + \left[ \frac{2m_e a^2 E}{\hbar^2} + \frac{m_e Z e^2}{4\pi\varepsilon_0 \hbar^2} \frac{2a}{\rho} - \frac{l(l+1)}{\rho^2} \right] R_{n,l} = 0.
\]

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

Evident that characteristic length-scale is
\[
a = \frac{4\pi\varepsilon_0 \hbar^2}{m_e Z e^2}.
\]  \hspace{1cm} (13)

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

Define dimensionless energy parameter,
\[
\gamma^2 = -E \left( \frac{\hbar^2}{2m_e a^2} \right).
\]  \hspace{1cm} (14)

Note that \( E < 0 \) for bound state. Hence, \( \gamma^2 > 0 \). Can chose positive root without loss of generality.
Normalization of Radial Equation - V

- 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

$$\int_0^{\infty} r^2 [R_{n,l}(r)]^2 dr = a^3 \int_0^{\infty} \rho^2 [R_{n,l}(\rho)]^2 d\rho = 1. \quad (16)$$
Consider large-$\rho$ 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 $R_{n,l} = e^{\pm \gamma \rho}$. However, $e^{+\gamma \rho}$ solution is not compatible with normalization condition (16).

Conclude that

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

at large $\rho$. 
Consider small-$\rho$ 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 $\rho$. 
Previous analysis suggest that we search for a solution of radial equation (15) that has form

\[ R_{n,l}(\rho) = e^{-\gamma \rho} \rho^l H(\rho). \]  

(17)

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

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

(18)

Search for power-law solution of form

\[ H(\rho) = \sum_{j=0,\infty} c_j \rho^j. \]  

(19)

Solution automatically satisfies correct boundary condition at small \( \rho \).
Previous two equations lead to recursion relation (Hw. 3, Q. 6)

\[ c_{j+1} = \frac{2 \gamma (1 + j + l) - 2}{(j + 1)(j + 2l + 2)} c_j. \] (20)

In large-\(j\) limit, obtain

\[ c_{j+1} \approx \frac{2 \gamma}{j} c_j. \]

But series

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

has same large-\(j\) recursion relation.
Conclusion from (17) and (19) that $R_{n,l}(\rho) \sim \rho^l e^{\gamma \rho}$ at large-$\rho$, which 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 $\rho$ in series solution (19) is $\rho^{j_{\text{max}}}$.

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

Follows from recursion relation (20) that

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

Let

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

Evident that $n \geq l + 1$ is positive integer (because $j_{\text{max}} \geq 0$).
From previous two equations, allowed values of energy parameter are

\[ \gamma = \frac{1}{n}. \]  \hspace{1cm} (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**:

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

- Also helpful to define **hydrogen ground-state energy**:

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

- In terms of these quantities

  \[ a = \frac{a_0}{Z}. \]  
  \[ (24) \]

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

  \[ E_n = \frac{Z^2 E_0}{n^2}. \]  
  \[ (25) \]
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

\[
\alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c} \sim \frac{1}{137}
\]

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:

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

where \( q \) is a non-negative integer.

- Associated Laguerre polynomials, \( L^p_q(x) \), defined as follows:

\[
L^p_q(x) = (-1)^p \frac{d^p}{dx^p} L_{q+p}(x),
\]

where \( p \) is a non-negative integer.

- Given that \( L_q(x) \) are polynomials of degree \( q \), follows that \( L^p_q(x) \) are also polynomials of degree \( q \).
Radial Wavefunctions - II

- Associated Laguerre polynomials are solutions of following differential equation:

\[ x \frac{d^2 L_p^q}{dx^2} + (p + 1 - x) \frac{dL_p^q}{dx} + q L_p^q = 0. \]

- (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

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

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

This yields

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

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,

\[ A_{n,l} = \left\{ \left( \frac{2Z}{na_0} \right)^3 \frac{(n-l-1)!}{2n(n+l)!} \right\}^{1/2} \left( \frac{2}{n} \right)^l. \]

Properly normalized radial wavefunctions become

\[ R_{n,l}(r) = \left\{ \left( \frac{2Z}{na_0} \right)^3 \frac{(n-l-1)!}{2n(n+l)!} \right\}^{1/2} \exp \left( -\frac{Zr}{na_0} \right) \left( \frac{2Zr}{na_0} \right)^l \times L_{n-l-1}^{2l+1} \left( \frac{2Zr}{na_0} \right). \] (27)
First few associated Laguerre polynomials as follows:

\begin{align*}
L_0^0(x) &= 1, \\
L_0^1(x) &= 1, \\
L_0^2(x) &= 1, \\
L_1^0(x) &= 1 - x, \\
L_1^1(x) &= 2 - x, \\
L_1^2(x) &= 3 - x, \\
L_1^3(x) &= 4 - x, \\
L_2^0(x) &= 1 - 2x + x^2/2, \\
L_2^1(x) &= 3 - 3x + x^2/2, \\
L_2^2(x) &= 6 - 4x + x^2/2, \\
L_2^3(x) &= 10 - 5x + x^2/2.
\end{align*}
First few radial wavefunctions as follows:

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

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

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

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

\[ R_{3,1}(r) = \frac{4 \sqrt{2}}{3} \left( \frac{Z}{3 a_0} \right)^{3/2} \frac{Z r}{a_0} \left( 1 - \frac{Z r}{6 a_0} \right) e^{-Z r/3 a_0}, \]

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

$R_{3,0}$

$R_{3,1}$

$R_{3,2}$
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 - I
Energy Eigenstates - II

- Quantum number $n$ takes values

  \[ n = 1, 2, 3, \ldots \]

- 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

  \[ -l \leq m \leq +l. \]
The $n$th energy level is $2n^2$-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:

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

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

\[
\langle \frac{1}{r} \rangle = \frac{Z}{a_0 n^2},
\]

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

\[
\langle \frac{1}{r^3} \rangle = \frac{Z^3}{a_0^3 n^3 l(l + 1/2)(l + 1)}.
\]