Exact QM solution in one-electron atoms.

McMurry Ch 7.1 and 7.2. SP Ch 2.1, Foot Ch 2.
Exercises: 12 - 15. (H4 and H5)

$SE: \left(-\frac{\hbar^2}{2\mu} \nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}\right)\Psi = E\Psi$

$E_n = -R_M \cdot \frac{Z^2}{n^2}$

$\Psi_{n,\ell,m}(r, \theta, \varphi) = R_{n,\ell}(r) \cdot Y_{\ell,m}(\theta, \varphi)$

$\int_0^{2\pi} \int_0^\pi \int_0^\infty \left| R_{n,\ell}(r) \cdot Y_{\ell,m}(\theta, \varphi) \right|^2 r^2 \sin \theta dr d\theta d\varphi = 1$

$R(\rho) = \rho^\ell \cdot e^{-\rho} \cdot c_0 \cdot (1 + \sum_{k=0}^{n-\ell-1} \frac{c_k \cdot \rho^k}{c_0 \cdot \rho^k})$, $\rho = \frac{Z}{na_0} \cdot r$

$c_0 \neq 0$ determined from the normalization condition.

$c_{k+1} = -2c_k \frac{n-(\ell+k+1)}{(\ell+k+2)(\ell+k+1) - \ell(\ell+1)}$, $k = 0, 1, ..., n-\ell-1$

$\langle r_{n\ell} \rangle = \int R^*(r) \cdot r \cdot R(r) \cdot r^2 dr = \frac{1}{2Z} [3n^2 - \ell(\ell+1)]$
One-electron atoms in spherical coordinates

\[ L_x = i\hbar (\sin \varphi \frac{\partial}{\partial \theta} + \frac{\cos \varphi}{\tan \theta} \frac{\partial}{\partial \varphi}), \]

\[ L_y = i\hbar (-\cos \varphi \frac{\partial}{\partial \theta} + \frac{\sin \varphi}{\tan \theta} \frac{\partial}{\partial \varphi}), \]

\[ L_z = -i\hbar \frac{\partial}{\partial \varphi} \]

\[ L^2 = -\hbar^2 \left( \frac{\partial^2}{\partial \theta^2} + \frac{1}{\tan \theta} \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right) \]

\[ H = -\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{Ze^2}{4\pi \varepsilon_0 \cdot r} \]

\[ = -\frac{\hbar^2}{2\mu} \left[ \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{1}{r^2} \left( \frac{\partial^2}{\partial \theta^2} + \frac{1}{\tan \theta} \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right) \right] - \frac{Ze^2}{4\pi \varepsilon_0 \cdot r} \]

\[ = -\frac{\hbar^2}{2\mu} \cdot \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{L^2}{2\mu \cdot r^2} - \frac{Ze^2}{4\pi \varepsilon_0 \cdot r} \]
In atomic physics the value of $\ell$ is always given as a letter: $\ell = 0 \rightarrow s$, $1 \rightarrow p$, $2 \rightarrow d$, $3 \rightarrow f$, $4 \rightarrow g, h, i, (j), k, l, \ldots$. 

A p electron with an energy of $-5 \text{ eV}$ is classically constrained to oscillate between $1.4 < r < 4 \ a_0$ whereas with an energy of about $-6.8 \text{ eV}$ it can only move in a circular orbit with a radius of $2a_0$.

Note, only s-electrons can move close to the nucleus. Very important later on!!
Series solution of the radial differential equation.

\[ f'' - 2 f' - \left( \frac{\ell(\ell + 1)}{\rho^2} - \frac{2Z}{a_0 \rho^\ell} \right) f = 0 \quad (8) \]

Ansatz:

\[ f(\rho) = \rho^s \sum_{k=0}^{\infty} c_k \rho^k \quad c_0 \neq 0. \]

Calculate the derivatives and collect terms with similar powers in (8)

\[ \sum_{k=0}^{\infty} c_k [(s+k)(s+k-1) - \ell(\ell + 1)] \rho^{s+k-2} + \sum_{k=0}^{\infty} c_k \left[ \frac{2Z}{a_0 \rho^\ell} - 2(s+k) \right] \rho^{s+k-1} = 0 \]

The lowest order term arises from the first sum with \( k = 0 \). If we write that term separately the first sum will start with \( k = 1 \) and both sums will be in powers of \( s + k - 1 \). If we change summation index in the first sum from \( k \) to \( k + 1 \) we can write everything as a single summation:

\[ c_0 \left( s(s-1) - \ell(\ell + 1) \right) \rho^{s-2} + \sum_{k=0}^{\infty} [c_{k+1} \cdot ((s+k+1)(s+k) - \ell(\ell + 1))] \rho^{s+k-1} + 2c_k \cdot \left[ \frac{Z}{a_0 \rho^\ell} - (s+k) \right] \rho^{s+k-1} = 0 \]

If the polynomial is zero for all values of \( \rho \) then each coefficient must be zero individually.

Since we assumed \( c_0 \neq 0 \) the first term gives \( s = \ell + 1 \) or \( s = -\ell \). The last possibility must be ignored since it leads to a non-normalizable function \( P(\rho) \) when \( \rho \to 0 \).

To make everything within the curly brackets equal to zero in the remaining summation the \( c \)-coefficients must satisfy the recursion relation (using \( s = \ell + 1 \))

\[ c_{k+1} = -2c_k \frac{(Z/a_0 \kappa) - (\ell + k + 1)}{(\ell + k + 2)(\ell + k + 1) - \ell(\ell + 1)} \]

For large \( k \) the ratio of the coefficients will be \( c_{k+1} / c_k = 2k/k^2 = 2/k \). This ratio is the same as that between successive terms in the expansion of

\[ e^{2\rho} = 1 + \frac{2\rho}{1!} \rho^2 + \frac{2^2}{2!} \rho^3 + \ldots + \frac{2^{k-1}}{(k-1)!} \rho^{k-1} + \frac{2^k}{k!} \rho^k + \ldots \]

Hence, for large \( \rho \) the two functions behave similar and \( P(\rho) \approx e^{-\rho} \cdot e^{2\rho} \to \infty \) when \( \rho \to \infty \).

Thus it is not normalizable and the series must be \textit{truncated}, i.e. for some \( k = N = 0, 1, 2, \ldots \)

\[ (Z/a_0 \kappa) - (\ell + N + 1) = 0 \]

Introducing the main quantum number \( n = \ell + N + 1 = 1, 2, 3, \ldots \) we obtain finally \( \kappa = Z/a_0 n \) and hence a quantized energy:

\[ E_n = -\frac{\hbar^2}{2\mu a_0} \frac{Z^2}{n^2}. \]

Thus the reasonable demand that the wavefunction is normalizable leads to a quantized energy!!
3.2 Energy-level diagram for atomic hydrogen.
Table 2.2 Radial hydrogenic wavefunctions $R_{n,l}$ in terms of the variable $\rho = Zr/ (na_0)$, which gives a scaling that varies with $n$. The Bohr radius $a_0$ is defined in eqn 1.40.

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

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

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

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

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

\[
R_{3,2} = \left( \frac{Z}{3a_0} \right)^{3/2} \frac{2\sqrt{2}}{3\sqrt{5}} \rho^2 e^{-\rho}
\]

Normalisation: $\int_0^\infty R_{n,l}^2 r^2 \, dr = 1$
Note:
1. Only $R_{3s}(0) \neq 0$
2. Number of zero crossings ($r > 0$) is $n-\ell-1$. 
Radial probability distribution in H.

For 1s, 2p, 3d,... i.e.
\[ n, \ell = n - 1 \]
the most probable distance \( r_n \) is given by:
\[ r_n = a_0 \frac{n^2}{Z} \]
i.e. the same result as in the Bohr model!

Number of minima:
\[ N = n - \ell - 1 \]
Summary one-electron atoms.

Bohr:

\[ r_n = a_0 \cdot \frac{n^2}{Z}, \quad a_0 = 0.529 \, \text{Å}. \]

\[ v_n = \alpha \cdot c \cdot \frac{Z}{n}, \quad \alpha = \frac{1}{137} \]

\[ E_n = -R_M \cdot \frac{Z^2}{n^2}, \quad R_M = \frac{m}{M + m} \cdot 109737 \, \text{cm}^{-1} \]

Quantum mechanics

\[ (-\frac{\hbar^2}{2\mu} \nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r})\Psi = E\Psi \]

\[ E_n = -R_M \cdot \frac{Z^2}{n^2} \quad (E \text{ in cm}^{-1}) \]

Only for the Coulomb potential is \( E \) independent of \( \ell \).

\( n = 1, 2, 3 \ldots \) \quad \( \ell = 0, 1, 2, \ldots (n-1) \) \quad \( m = -\ell, -\ell + 1, \ldots, \ell \)

\[ \Psi_{n,\ell,m}(r, \theta, \varphi) = R_{n,\ell}(r)Y_{\ell,m}(\theta, \varphi) \]

\[ R(\rho) = \rho^{\ell} \cdot e^{-\rho} \cdot c_0 \cdot (1 + \sum_{k=1}^{n-\ell-1} \frac{c_k}{c_0} \cdot \rho^k), \quad \rho = \frac{Z}{a_0 n} \cdot r \]

\( c_0 \neq 0 \) determined from the normalization condition.

\( R(\rho) \) has \( n - \ell - 1 \) zeros for \( r > 0 \)

\[ \int_0^\infty \int_0^{2\pi} \int_0^{\pi} |R_{n,\ell}(r) \cdot Y_{\ell,m}(\theta, \varphi)|^2 r^2 \sin \theta dr d\theta d\varphi = 1 \]

\[ <r_{n\ell}> = \int R^*(r) \cdot r \cdot R(r) \cdot r^2 dr = \frac{1}{2Z} [3n^2 - \ell(\ell + 1)] \]