

EMA601: Quantum Engineering with Atoms and Photons

University of Wisconsin - Madison

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Practice Set 3

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Question 1: Numerical Solutions of the Schrodinger equation

- a. The radial wave equation $R(r)$ for an electron in a spherically symmetric, coulomb potential $V(r)$ is given by the expression:

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR(r)}{dr} \right) + \frac{2\mu}{\hbar^2} (E - V(r)) R(r) = \frac{l(l+1)}{r^2} R$$
$$\frac{d^2 R(r)}{dr^2} + \frac{2}{r} \frac{dR(r)}{dr} + R(r) \left\{ \frac{2\mu}{\hbar^2} (E - V(r)) - \frac{l(l+1)}{r^2} \right\} = 0$$

We substitute radius as $r = xa_o$ and replace $\mu \approx m$, where m is the mass of electron.

$$\frac{d^2 R(x)}{dx^2} + \frac{2}{x} \frac{dR(x)}{dx} + R(x) \left\{ \frac{2ma_o^2 E}{\hbar^2} - \left(\frac{2ma_o^2 V(x)}{\hbar^2} + \frac{l(l+1)}{x^2} \right) \right\} = 0$$
$$\tilde{E} = \frac{2ma_o^2 E}{\hbar^2}$$
$$\tilde{V}(x) = \frac{2ma_o^2 V(x)}{\hbar^2} + \frac{l(l+1)}{x^2}$$
$$\frac{d^2 R(x)}{dx^2} + \frac{2}{x} \frac{dR(x)}{dx} + R(x) [\tilde{E} - \tilde{V}(x)] = 0$$

In the central-field approximation, for $r > r_c$ (or $x > x_c$), $Z_{eff} = 1$, hence:

$$a_o = \frac{4\pi\epsilon_o \hbar^2}{me^2} \quad \text{and}$$
$$\tilde{V}(x) = \frac{2ma_o^2}{\hbar^2} \left(\frac{-e^2}{4\pi\epsilon_o a_o x} \right) + \frac{l(l+1)}{x^2}$$
$$\tilde{V}(x) = -\frac{2me^2}{\hbar^2 x (4\pi\epsilon_o)} \left(\frac{4\pi\epsilon_o \hbar^2}{me^2} \right) + \frac{l(l+1)}{x^2}$$
$$\tilde{V}(x) = -\frac{2}{x} + \frac{l(l+1)}{x^2}$$

and for \tilde{E} :

$$\tilde{E} = \frac{2m}{\hbar^2} \left(\frac{4\pi\epsilon_o \hbar^2}{me^2} \right)^2 E$$
$$\tilde{E} = \frac{8\pi\epsilon_o a_o}{e^2} E$$

Hence, \tilde{E} is scaled by 13.6 eV.

- b. Keeping the second-order differential term same, we can modify the first order differential term as:

$$\frac{dR(x)}{dx} = \frac{R(x + \delta x) - R(x - \delta x)}{2\delta x}$$

We use these in the given expression in part (a). For simplification, we're substituting \tilde{E} as E and $\tilde{V}(x)$ as V :

$$\begin{aligned} \frac{R(x + \delta x) + R(x - \delta x) - 2R(x)}{\delta x^2} + \frac{2}{x} \frac{R(x + \delta x) - R(x - \delta x)}{2\delta x} + (E - V)R(x) &= 0 \\ \frac{xR(x + \delta x)}{x\delta x^2} + \frac{\delta x R(x + \delta x)}{x\delta x^2} &= \frac{2R(x) - R(x - \delta x)}{\delta x^2} + \frac{R(x - \delta x)}{x\delta x} + (V - E)R(x) \\ \frac{R(x + \delta x)}{\delta x^2} \left(1 + \frac{\delta x}{x}\right) &= \frac{2R(x) - R(x - \delta x)}{\delta x^2} + \frac{R(x - \delta x)}{x\delta x} + (V - E)R(x) \\ \frac{R(x + \delta x)}{\delta x^2} \left(1 + \frac{\delta x}{x}\right) &= \frac{2xR(x) - xR(x - \delta x) + \delta x R(x - \delta x)}{x\delta x^2} + (V - E)R(x) \\ R(x + \delta x) \left(1 + \frac{\delta x}{x}\right) &= \frac{2xR(x) - R(x - \delta x)(x - \delta x)}{x} + (V - E)R(x)\delta x^2 \\ R(x + \delta x) \left(1 + \frac{\delta x}{x}\right) &= 2R(x) - R(x - \delta x) \left(1 - \frac{\delta x}{x}\right) + (V - E)R(x)\delta x^2 \\ R(x + \delta x) &= \frac{2R(x) + (V - E)R(x)\delta x^2 - R(x - \delta x) \left(1 - \frac{\delta x}{x}\right)}{\left(1 + \frac{\delta x}{x}\right)} \end{aligned}$$

- c. This is a very interesting question since there can be several methods to approach it, and has a subtle point to illustrate that under the central field approximation, the electron orbitals of a "larger" atom also look like hydrogen orbitals, since in our potential term in part (a), $\tilde{V}(x)$, we have assumed $Z_{eff} = 1$.

My method involves fixing a value of l , and making a plot of $R(x)$ vs x , for various values of \tilde{E} . The qualification criteria for a legit solution is that it should look similar to the Hydrogen atom radial solution (for the specific value of l) **and** that $R(x)$ goes to 0 asymptotically for a sufficiently large x .

I've arbitrarily chosen a "small" value for δx , referred to as dx in my code. And defined the initial values of $R(x)$ as 1. The radial wavefunction is stored as a 2-D array in my code with one column corresponding to \tilde{E} and the other x , and is referred to as $R_range(E,x)$. A code snippet to illustrate this:

```
dx=0.00001;
x_range=dx:dx:20; %x starts from dx and goes up to 20 and x=r/a_o

R_range = zeros(length(Et_range), length(x_range));
R_range(:,1)=1;
R_range(:,2)=1;
```

To evaluate the numerical expression for $R_range(E,x)$, I'm using the following logic:

```

for i=1:1:length(Et_range)
    for j=1:1:(length(x_range)-2)
        R_range(i,j+2) = (2*R_range(i,j+1)
        +(1*(1+1)/x_range(j+1)^2-2/x_range(j+1)
        -Et_range(i))*R_range(i,j+1)*dx^2
        -(1-dx/x_range(j+1))*R_range(i,j)) / (1+dx/x_range(j+1));
    end
end
end

```

I'm making my scaled, eigen-energy term, \tilde{E} , dependent on the effective quantum number n^* by using the relation $\tilde{E} = \frac{1}{(n^*)^2}$

For my method to work, the primary assumption is that the quantum defect is a small quantity, hence I'm only looking for n^* (referred as `n_range` in code) values that are near actual (integer) n values. That also restricts the values of \tilde{E} (referred as `Et_range` in code) that go in the numerical expression.

Hence, I choose a pair of quantum number values, for example, $n = 2$; $l = 1$, and plot the radial wave equations for a range of n^* centered at the chosen n value. A code snippet to illustrate this:

```

l=1; %angular wave number
n=2; %target radial wave number

n_range=linspace(n-0.02,n+0.02,100); %effective radial wave number

Et_range= -1./(n_range.^2); %E tilde range

Energy_range = 13.6.*Et_range; %actual energy range

```

This leads to a hundred solutions, corresponding to each n^* value:

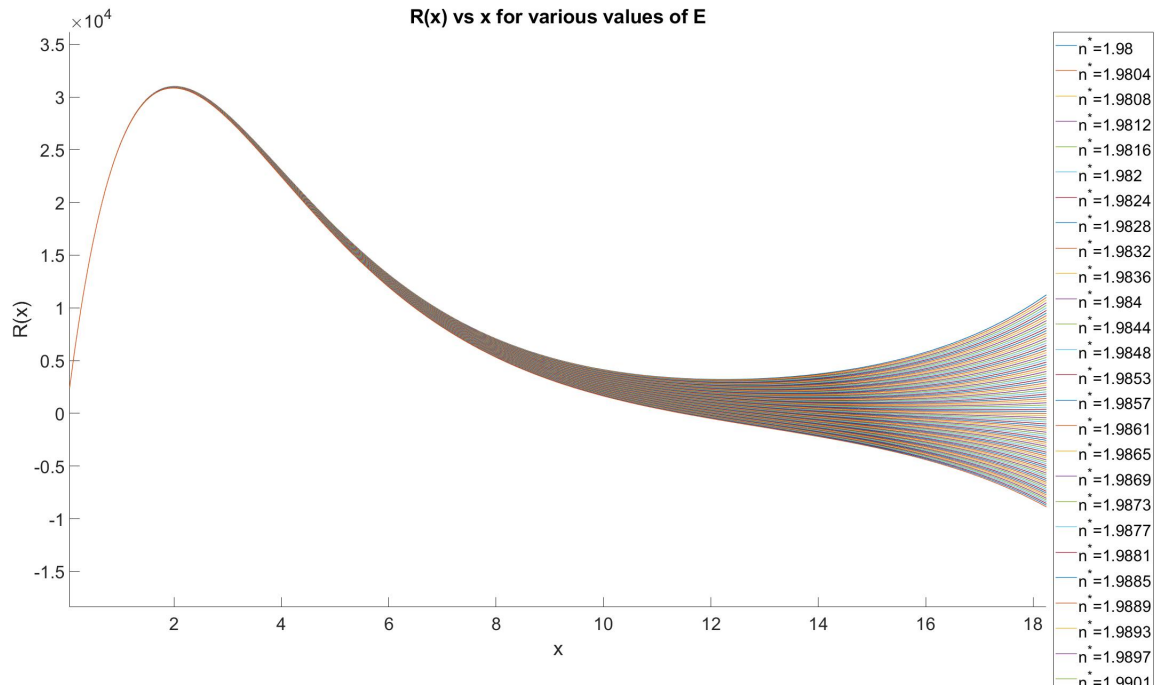


Figure 1: $R(x)$ vs x plot for various values of n^*

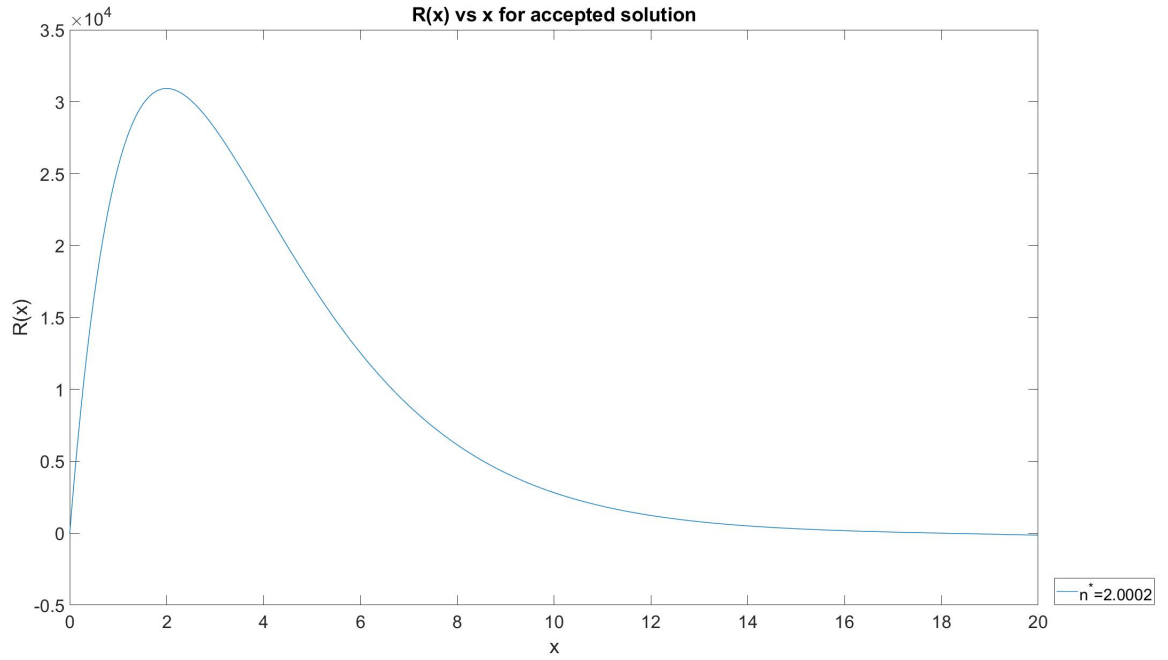
For the initial values of x , all of them "look" similar to the hydrogen radial wavefunction for $n = 2$; $l = 1$, but not all of them approach 0 asymptotically as x increases. So, we need to come up with a criteria to "handpick" the wavefunction that's closest to 0 for the highest value of x .

I do this by scanning through all the "end" values of x (presumed to be infinity) and find the solution that's closes to 0. Here's a code snippet to illustrate this:

```
diff=1e10;
E_choice=0;

for k=1:length(Et_range)
    if abs(R_range(k,end)) <= diff
        diff = abs(R_range(k,end));
        E_choice=k;
    end
end
```

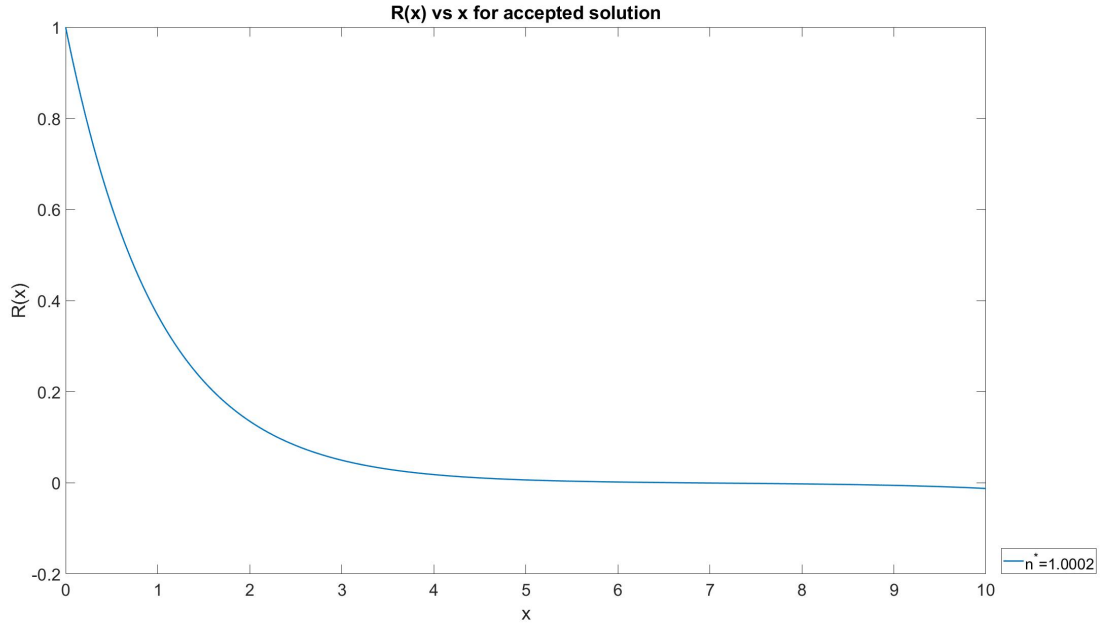
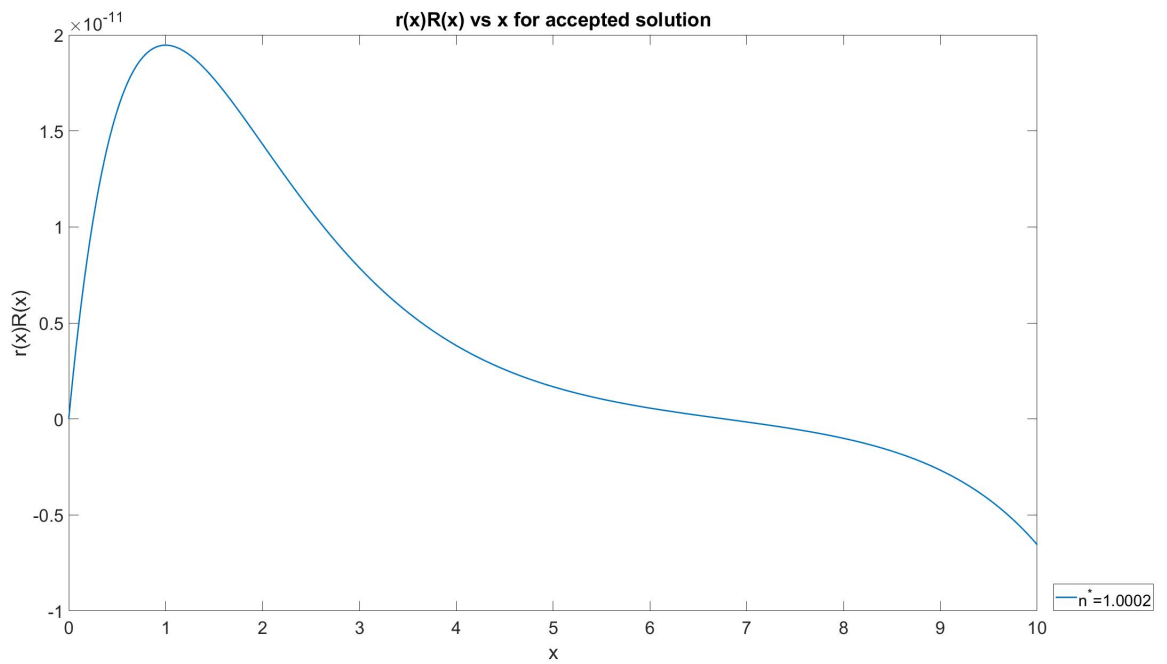
By doing this, we obtain a single solution of the radial wavefunction, that corresponds to a single \tilde{E} and hence a single n^* .

Figure 2: $R(x)$ vs x plot for the chosen solution

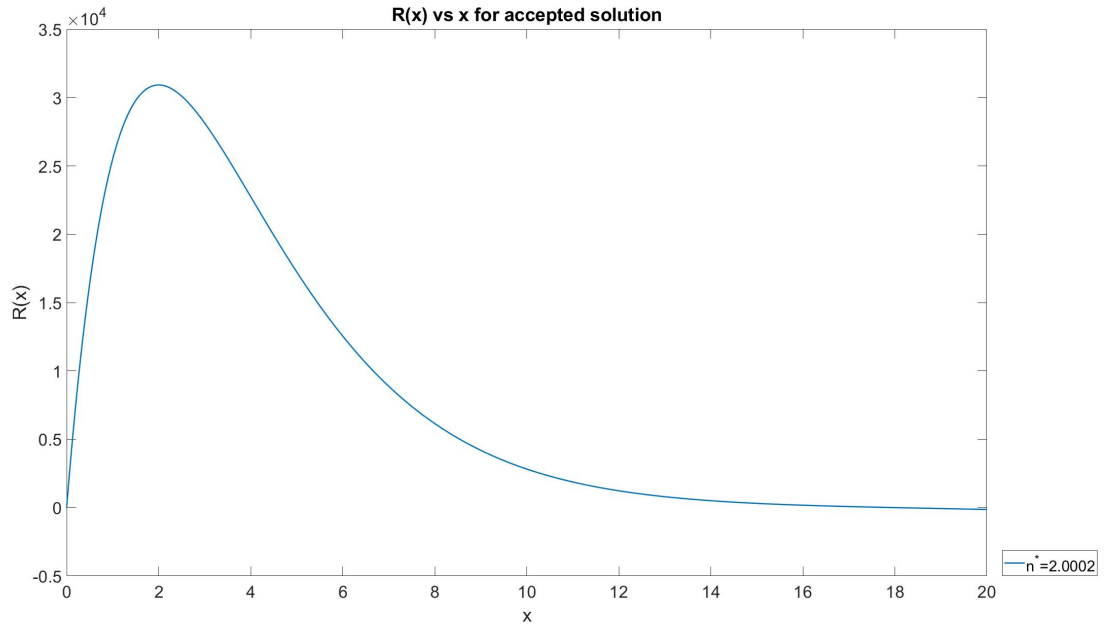
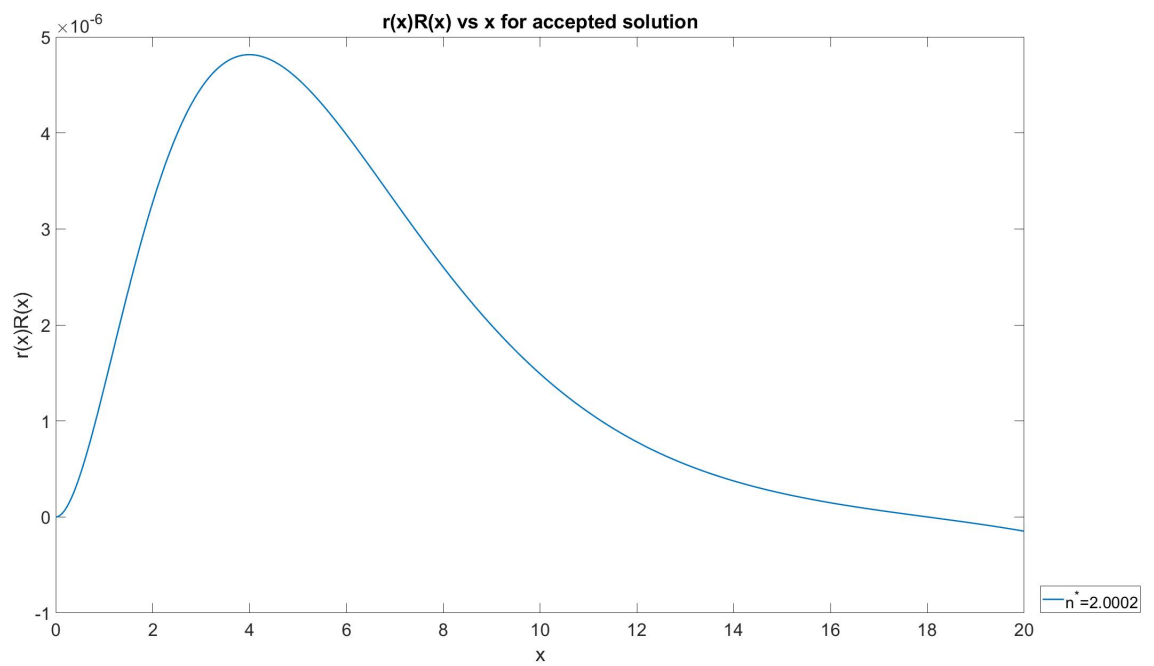
Using this method, I calculated the Eigen-energies and effective quantum numbers for the given values if $l = 0, 1, 2$

n, l	Eigenenergy ($13.6 * \tilde{E}$) [eV]	n^*
$n = 1, l = 0$	-13.5945	1.0002
$n = 2, l = 0$	-3.3993	2.0002
$n = 2, l = 1$	-3.3993	2.0002
$n = 3, l = 0$	-1.4912	3.0200
$n = 3, l = 1$	-1.4912	3.0200
$n = 3, l = 2$	-1.4912	3.0200

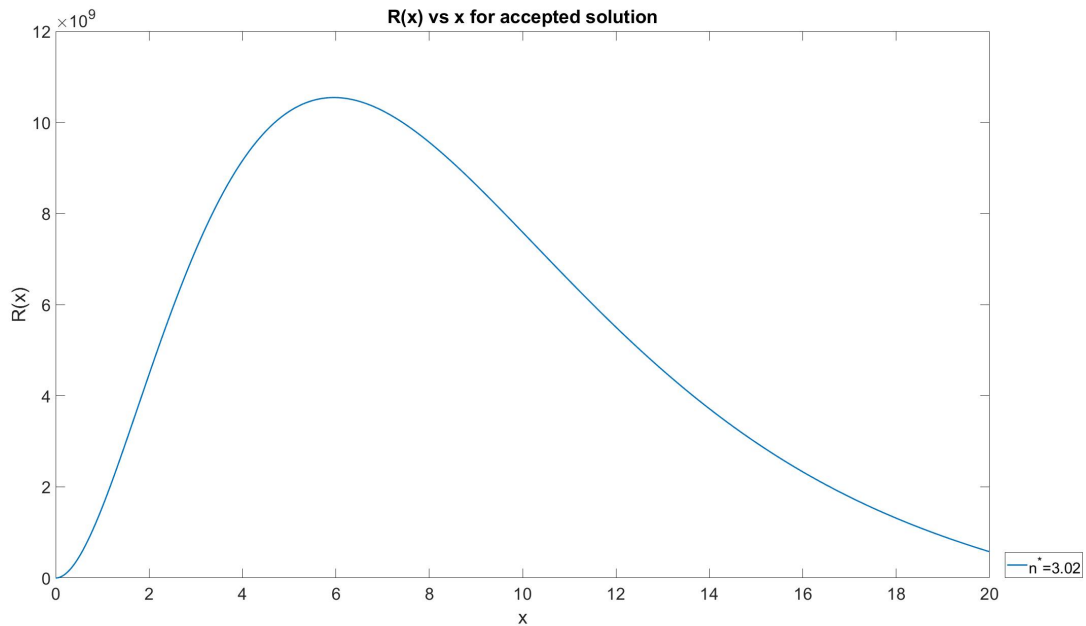
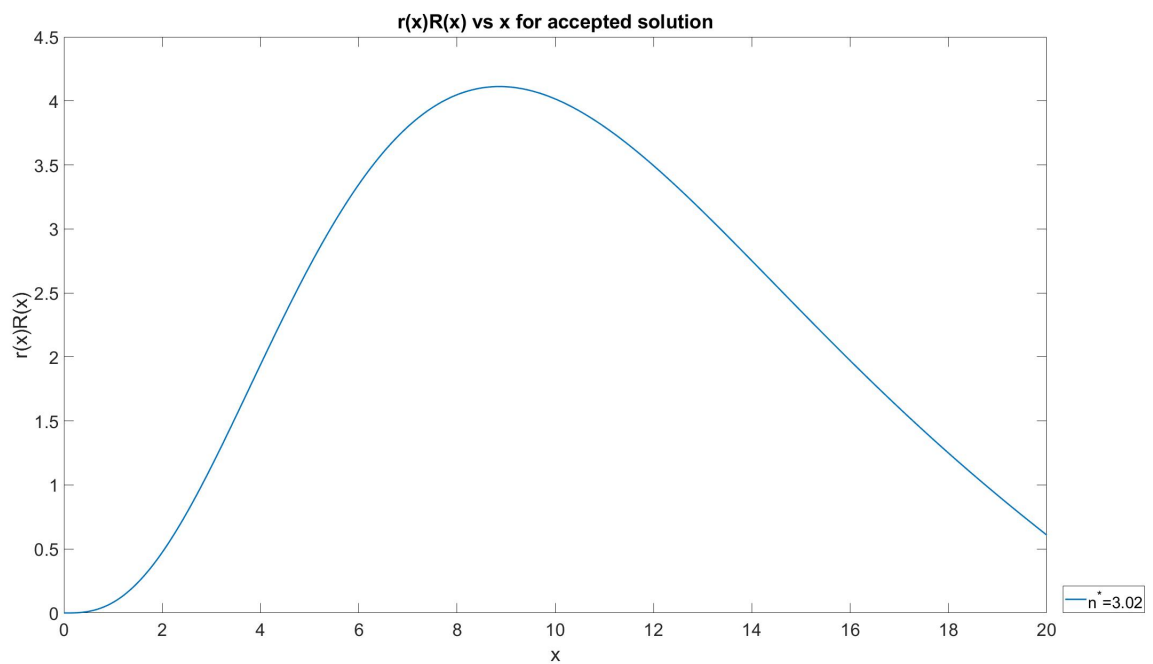
- d. We use the above table to find the lowest eigenenergies corresponding to an l value.
- i. Lowest eigenenergy for $l = 0$ is -13.5945 eV. Hence, the corresponding radial wavefunction plots are:

Figure 3: $R(x)$ vs x plot for $n=1, l=0$ Figure 4: $r(x)R(x)$ vs x plot for $n=1, l=0$

- ii. Lowest eigenenergy for $l = 1$ is -3.993 eV. Hence, the corresponding radial wave-function plots are:

Figure 5: $R(x)$ vs x plot for $n=2, l=1$ Figure 6: $r(x)R(x)$ vs x plot for $n=2, l=1$

- iii. Eigenenergy for $l = 2$ is -1.4912 eV. Hence, the corresponding radial wavefunction plots are:

Figure 7: $R(x)$ vs x plot for $n=3, l=2$ Figure 8: $r(x)R(x)$ vs x plot for $n=3, l=2$

The general shapes of $R(x)$ vs x plots of all l values are similar to the ones observed in a hydrogen atom. It's difficult to compare the y-axis since it isn't normalised, but the general shapes have a strong similarity with the hydrogen atom radial functions, for the corresponding quantum numbers.

Since in part (a) itself, we started off with the assumption of $Z_{eff} = 1$, it is no surprise that our n^* values are very close to the actual n values, indicating the

there is a minimal quantum defect in this case.

The eigenenergy values derived here are within ± 0.02 eV range of actual eigenenergies of hydrogen atom.

Problem 3:

- a. The ground state of the valence electron in Rb-87: $5^2S_{1/2}$
- b. For the lower energy level, we see 3 Zeeman splittings, corresponding to $F=1$ ($m_F = -1, 0, 1$)
 For the upper energy level, we see 5 Zeeman splittings, corresponding to $F=2$ ($m_F = -2, -1, 0, 1, 2$)
 For the ground state valence electron, we know $J = 1/2$. And we know that $I \pm J = F$

$$I + \frac{1}{2} = 2$$

$$I = \frac{3}{2} \text{ and}$$

$$I - \frac{1}{2} = 1$$

$$I = \frac{3}{2}$$

Hence, $I = 3/2$ satisfies both equations.

- c. The levels are grouped according to the value of F in the low-field (anomalous Zeeman) regime and m_J in the strong-field (hyperfine Paschen-Back) regime.
 (Ref: <https://steck.us/alkalidata/rubidium87numbers.1.6.pdf>)

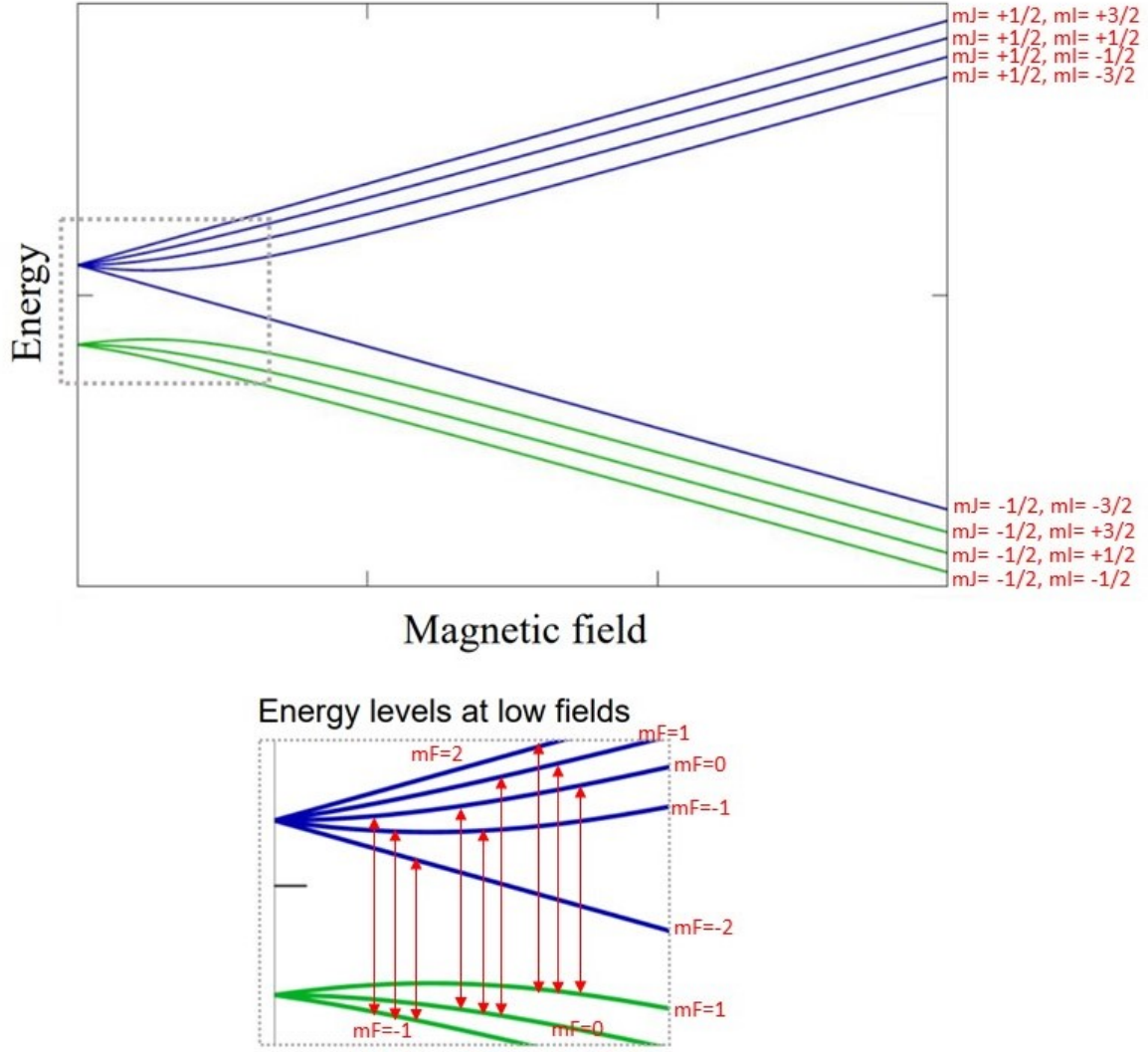


Figure 9: Quantum numbers and allowed transitions for ground state of Rb-87 in Magnetic Field. Transitions only illustrated in high-fields plot

- d. The clock transition should be insensitive to magnetic fields, hence the $m_F = 0$ to $m_F = 0$ transition is the "clock" transition.

In low-fields (ignoring any higher order B terms), we can write the Breit-Rabi formula for $m_F = 0$ states and $I = 3/2$ as:

$$E_{m_F}^{\pm} = \frac{-A(3/2 + 1/2)}{2(2 \times 3/2 + 1)} \pm \frac{A(3/2 + 1/2)}{2}$$

Hence, the difference between the two states is $E_{m_F}^{+} - E_{m_F}^{-} = 2A$.

$$A = h * 3.417 \text{ GHz}$$

$$\Delta E_{\text{clock}} = 2 * 3.417 * h \text{ GHz}$$

$$\Delta E_{\text{clock}} = 6.834 * h \text{ GHz}$$

$$\Delta \nu_{\text{clock}} = 6.834 \text{ GHz}$$

Using the Breit-Rabi formula for $m_F = 0$ states, and considering the second-order

B-term, we can write:

$$E_{m_F}^{\pm} = \frac{-A(I + 1/2)}{2(2I + 1)} \pm \frac{A(I + 1/2)}{2}(1 + x^2)^2$$

$$\Delta E_{clock} = A\left(I + \frac{1}{2}\right) \left[1 + \left(\frac{(g_J - g_I)\mu_B B}{A(I + \frac{1}{2})}\right)^2\right]^{1/2}$$

Using Taylor Series Expansion for small B field:

$$\Delta E_{clock} = A\left(I + \frac{1}{2}\right) \left[1 + \frac{1}{2}\left(\frac{(g_J - g_I)\mu_B B}{A(I + \frac{1}{2})}\right)^2\right]$$

$$\Delta \nu_{clock} = 6.834 \left[1 + \frac{1}{2}\left(\frac{1.0014975\mu_B B}{A}\right)^2\right] \text{ GHz}$$

e. The following transitions are first-order independent in the crossover regime:

$$m_F = 0 \text{ to } m_F = 0$$

$$m_F = -1 \text{ to } m_F = -1$$

$$m_F = +1 \text{ to } m_F = +1$$

f. Using the weak and strong field regimes covered in class (Lecture 17 slide 3). I equated the Zeeman, hyperfine splittings in both the regimes, and calculated the g_F value. I arbitrarily chose the $m_F = 1$ level in the lower (green) hyperfine level for doing this.

$$g_F = \frac{5}{16}g_j \text{ and}$$

$$\mu_B B(g_F m_F + g_I m_I - g_j m_j) = A m_I m_j$$

$$B = \frac{3.417 \times h \times (3/2) \times (-1/2)}{\mu_B [(5/16) \times 2.002 + (-0.000995) \times (3/2) - 2.002 \times (-1/2)]}$$

$$B \approx 1.12669 \times 10^{-10} \text{ T}$$

MATLAB Scripts

Problem 1:

```
%EMA601 PS3
%MATLAB Code for numerical analysis of schrodinger equation

clear all

l=2; %angular wave number
n=3; %target radial wave number

n_range=linspace(n-0.02,n+0.02,100); %effective radial wave number

Et_range= -1./(n_range.^2); %E tilde range, corresponding to each radial wave number

Energy_range = 13.6.*Et_range; %actual energy range

dx=0.00001;
x_range=dx:dx:20; %x starts from dx and goes up to 100 and x=r/a_o

R_range = zeros(length(Et_range), length(x_range));
R_range(:,1)=1;
R_range(:,2)=1;

for i=1:1:length(Et_range)
    for j=1:1:(length(x_range)-2)
        R_range(i,j+2) = (2*R_range(i,j+1) + (l*(l+1)/x_range(j+1)^2-2/x_range(j+1)-Et_range(i))*R_range(i,j));
    end
end

%function to plot all R(x) values over the n* range
%clf(ffigure(1),'reset')
%for k=1:1:length(Et_range)
%    figure(1)
%    hold on
%    plot(x_range,R_range(k,:), 'DisplayName', append('n^*=', num2str(n_range(k))), 'LineStyle', 'solid');
%end
%legend('Location', 'southeastoutside')
%title('R(x) vs x for various values of E')
%xlabel('x')
%ylabel('R(x)')
%ax = gca;
%ax.FontSize = 25;

diff=1e10;
E_choice=0;

for k=1:1:length(Et_range)
```

```

        if abs(R_range(k,end)) <= diff
            diff = abs(R_range(k,end));
            E_choice=k;
        end
    end
end

n_range(E_choice) %effective n for the chosen solution
Energy_range(E_choice) %actual eigenenergy for the chosen solution

%function to plot the accepted R(x) solution
clf(ffigure(2),'reset')
figure(2)
plot(x_range,R_range(E_choice,:), 'DisplayName',append('n^*=',num2str(n_range(E_choice)))
legend('Location', 'southeastoutside')
title('R(x) vs x for accepted solution')
xlabel('x')
ylabel('R(x)')
ax = gca;
ax.FontSize = 25;

%function to plot the accepted rR(x) solution
r_range = 5.29177e-11.*x_range;
rR_range = r_range.*R_range(E_choice,:);
clf(ffigure(3),'reset')
figure(3)
plot(x_range,rR_range,'DisplayName',append('n^*=',num2str(n_range(E_choice))), 'Linewidth',2)
legend('Location', 'southeastoutside')
title('r(x)R(x) vs x for accepted solution')
xlabel('x')
ylabel('r(x)R(x)')
ax = gca;
ax.FontSize = 25;

```