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1.9 The normalized wavefunction $\tilde{\Psi}_2(x) = \frac{x}{\sqrt{2}a_0^{3/2}}(1 - \frac{x}{2a_0})e^{-x/2a_0}$ is an eigenfunction of the one-dimensional H atom Schrödinger equation with eigenvalue $E_2 = -\frac{\hbar^2}{8m_e a_0^2}$. Plot $\tilde{\Psi}_2(x)$. Are $\tilde{\Psi}_1(x)$ and $\tilde{\Psi}_2(x)$ orthogonal? (Be sure to justify your answer!) 5

1.10 Suppose an electron is in a superposition state described by $\xi(x) = \frac{1}{\sqrt{3}}(\tilde{\Psi}_1(x) + \sqrt{2}\tilde{\Psi}_2(x))$. If you measure the total energies of many electrons, all with the same wavefunction $\xi(x)$, will you get the same answer every time? What will you get on average? It is ok to express you answer in terms of fundamental constants. 6

1.11 The uncertainties in the positions of an electron described by $\tilde{\Psi}_1(x)$ and $\tilde{\Psi}_2(x)$ can be shown to be $2^{1/2}a_0$ and $6^{1/2}a_0$, respectively. Contrast the uncertainties in their linear speeds. 7

1 Chem 30324, Spring 2018, Homework 4 Solution

1.1 Write down the time-independent Schrödinger equation for the 1-D H atom. Remember to include the domain of the equation.

The time-independent Schrödinger equation is $\hat{H}\Psi = E\Psi$.
In a "1-dimensional hydrogen atom",

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} - \frac{c}{x}, (x > 0).$$

So the time-independent Schrödinger equation of this system is

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\Psi - \frac{c}{x}\Psi = E\Psi, (x > 0).$$

1.2 Would $\phi(x) = e^{ikx}$ be an acceptable wavefunction for this system? Why or why not?

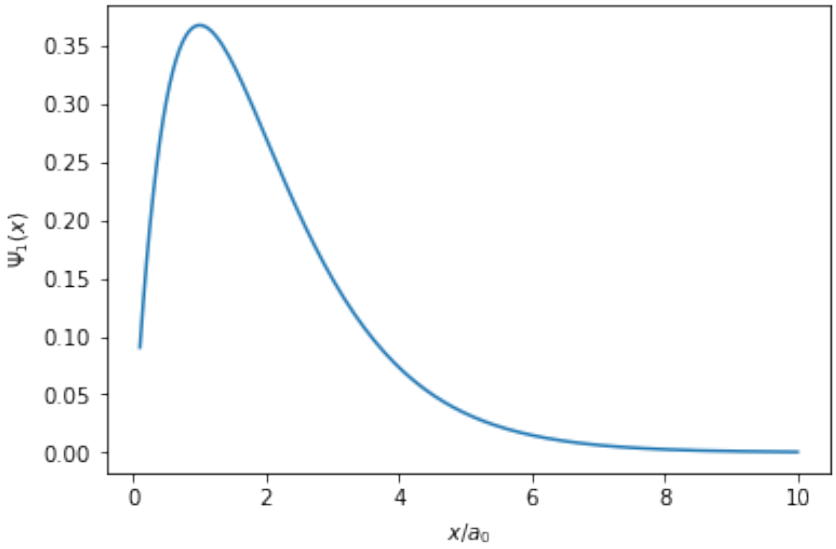
$\phi(x) = e^{ikx}$ is not an acceptable wavefunction for this system.
According to Postulate 1 of Quantum Mechanics, a wavefunction is required to be square-integrable. In this case,

$$\int_0^\infty \phi(x) * \phi(x) dx = \infty$$

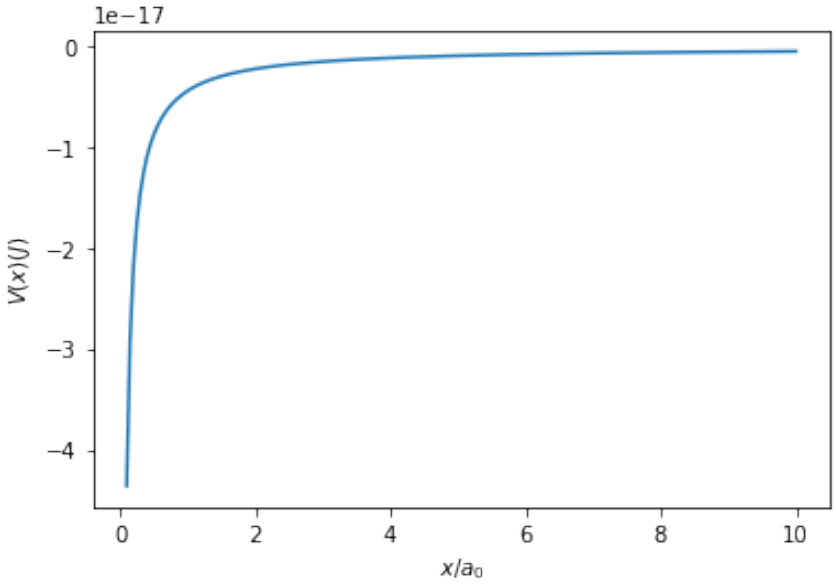
So $\phi(x)$ is not square-integrable and it can not be normalized.

1.3 Consider the candidate wavefunction $\Psi_1(x) = \frac{x}{a_0}e^{-x/a_0}$. Plot $V(x)$ and $\Psi_1(x)$. Be sure to label axes appropriately. (*Hint*: it is convenient to work in units of a_0. That is, make your plots against x/a_0 .)

The plot of $\Psi_1(x)$ looks like



The plot for $V(x)$ looks like



1.4 Is $\Psi_1(x)$ normalized? If not, construct the normalized $\tilde{\Psi}_1(x)$. It is ok to express you answer in terms of fundamental constants.

If we integrate the square of the wave function from 0 to infinity:

$$\int_0^\infty |\Psi_1(x)|^2 = \frac{\sqrt{a_0}}{2}$$

Hence, the normalized wave function is given by:

$$\tilde{\Psi}_1(x) = \frac{2x}{a_0^{3/2}} e^{-x/a_0}$$

1.5 What is the most probable distance of the electron from the proton, in units of a_0?

To get the most probable distance, we set the condition:

$$\frac{d|\Psi_1(x)|^2}{dx} = 0$$

Two values of x satisfy the condition, 0 and a_0. Since a = 0 is meaningless, x = a_0 is the most probable distance.

1.6 What is the probability of finding the electron further than a_0 from the proton?

To get this probability, we evaluate:

$$\int_{a_0}^\infty |\tilde{\Psi}_1(x)|^2$$

The probability comes out to be 0.677.

1.7 If you measure the linear momentum of many electrons, all with the same wavefunction $\tilde{\Psi}_1(x)$, will you get the same answer every time? What will you get on average? It is ok to express you answer in terms of fundamental constants.

Linear momentum operator is $\hat{p}_x = -i\hbar\frac{d}{dx}$.

$$\hat{p}_x\tilde{\Psi}_1(x) = -i\hbar\frac{d}{dx}\frac{2x}{a_0^{3/2}}e^{-x/a_0} = -i\hbar\frac{2}{a_0^{3/2}}(1 - \frac{x}{a_0})e^{-x/a_0}$$

As can be seen, the above result can't be written in terms of an eigenvalue times $\tilde{\Psi}_1(x)$.
Hence, we will not get the same answer every time. To get the average, we need to evaluate:

$$< \tilde{\Psi}_1(x)|\hat{p}_x|\tilde{\Psi}_1(x) >$$

In other words, this messy integral:

$$\int_0^\infty dx \frac{2x}{a_0^{3/2}} e^{-x/a_0} - i\hbar \frac{2}{a_0^{3/2}}(1 - \frac{x}{a_0})e^{-x/a_0}$$

The average is 0. If it were non-zero, particle would move to infinity.

1.8 If you measure the total energies of many electrons, all with the same wavefunction $\tilde{\Psi}_1(x)$, will you get the same answer every time? What will you get on average? (Hint: It will help to express $V(x)$ in terms of a_0 , $\hbar$, and m_e .)

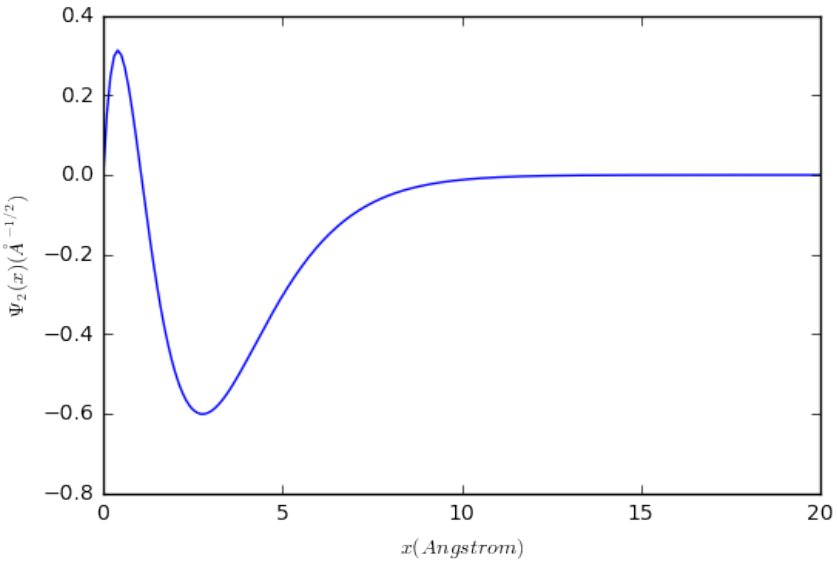
Total energy operator is $\hat{H} = -\frac{\hbar^2}{2m_e}\frac{d^2}{dx^2} - \frac{\hbar^2}{m_e a_0 x}$.

$$\hat{H}\tilde{\Psi}_1(x) = -\frac{\hbar^2}{2m_e}\frac{d^2}{dx^2}\tilde{\Psi}_1(x) - \frac{\hbar^2}{m_e a_0 x}\tilde{\Psi}_1(x) = -\frac{\hbar^2}{2m_e a_0^2}\frac{2x}{a_0^{3/2}}e^{-x/a_0}$$

As it turns out, the result is in terms of an eigenvalue times $\tilde{\Psi}_1(x)$. Thus, if we measure the energy we will get the same value everytime.
The average is same as the eigenvalue, which is $-\frac{\hbar^2}{2m_e a_0^2}$

1.9 The normalized wavefunction $\tilde{\Psi}_2(x) = \frac{x}{\sqrt{2}a_0^{3/2}}(1 - \frac{x}{2a_0})e^{-x/2a_0}$ is an eigenfunction of the one-dimensional H atom Schrödinger equation with eigenvalue $E_2 = -\frac{\hbar^2}{8m_e a_0^2}$. Plot $\tilde{\Psi}_2(x)$. Are $\tilde{\Psi}_1(x)$ and $\tilde{\Psi}_2(x)$ orthogonal? (Be sure to justify your answer!)

The plot of $\tilde{\Psi}_2(x)$ looks like:



To find out if $\tilde{\Psi}_1(x)$ and $\tilde{\Psi}_2(x)$
are orthogonal, we have to evaluate:

$$\langle\tilde{\Psi}_1(x)|\tilde{\Psi}_2(x)\rangle$$

Basically, the integral:

$$\int_0^\infty dx \frac{2x}{a_0^{3/2}} e^{-x/a_0} \frac{x}{\sqrt{2}a_0^{3/2}}(1-\frac{x}{2a_0})e^{-x/2a_0}$$

This turns out to be zero, meaning the wavefunctions are orthogonal.

1.10 Suppose an electron is in a superposition state described by $\xi(x) = \frac{1}{\sqrt{3}}(\tilde{\Psi}_1(x) + \sqrt{2}\tilde{\Psi}_2(x))$. If you measure the total energies of many electrons, all with the same wavefunction $\xi(x)$, will you get the same answer every time? What will you get on average? It is ok to express you answer in terms of fundamental constants.

The total energy operator is $\hat{H}$.

$$\hat{H}\xi(x) = \hat{H}[\frac{1}{\sqrt{3}}(\tilde{\Psi}_1(x) + \sqrt{2}\tilde{\Psi}_2(x))]$$

$$= \frac{1}{\sqrt{3}}\hat{H}\tilde{\Psi}_1(x) + \frac{\sqrt{2}}{\sqrt{3}}\hat{H}\tilde{\Psi}_2(x)$$

$$= \frac{1}{\sqrt{3}}E_1\tilde{\Psi}_1(x) + \frac{\sqrt{2}}{\sqrt{3}}E_2\tilde{\Psi}_2(x)$$

$$= \frac{1}{\sqrt{3}}(-\frac{\hbar^2}{2m_e a_0^2})\tilde{\Psi}_1(x) + \frac{\sqrt{2}}{\sqrt{3}}(-\frac{\hbar^2}{8m_e a_0^2})\tilde{\Psi}_2(x)$$

The result is not in the form of constant*$\xi(x)$, so $\xi(x)$ is not the eigenfunction of $\hat{H}$, we can't get the same answer every time.
We can use "braket" notation to calculate the average value $\langle H \rangle$.

$$\langle H \rangle = \langle \xi(x)|\hat{H}|\xi(x)\rangle = \langle \frac{1}{\sqrt{3}}(\tilde{\Psi}_1(x) + \sqrt{2}\tilde{\Psi}_2(x))|\hat{H}|\frac{1}{\sqrt{3}}(\tilde{\Psi}_1(x) + \sqrt{2}\tilde{\Psi}_2(x))\rangle$$

$$= \frac{1}{3}\langle\tilde{\Psi}_1(x)|\hat{H}|\tilde{\Psi}_1(x)\rangle + \frac{\sqrt{2}}{3}\langle\tilde{\Psi}_1(x)|\hat{H}|\tilde{\Psi}_2(x)\rangle + \frac{\sqrt{2}}{3}\langle\tilde{\Psi}_2(x)|\hat{H}|\tilde{\Psi}_1(x)\rangle + \frac{2}{3}\langle\tilde{\Psi}_2(x)|\hat{H}|\tilde{\Psi}_2(x)\rangle$$

$$= \frac{1}{3}E_1 + \frac{2}{3}E_2$$

$$= -\frac{\hbar^2}{4m_e a_0^2}$$

We thus measure E_1 1/3 of the time, and E_2 2/3 of the time.

1.11 The uncertainties in the positions of an electron described by $\tilde{\Psi}_1(x)$ and $\tilde{\Psi}_2(x)$ can be shown to be $2^{1/2}a_0$ and $6^{1/2}a_0$, respectively. Contrast the uncertainties in their linear speeds.

The uncertainity principle is given by:

$$\Delta x \Delta p \geq \frac{\hbar}{2}$$

Given that $\Delta x_1 = 2^{1/2}a_0$, $\Delta x_2 = 6^{1/2}a_0$
Thus, by uncertainity relationship:

$$\Delta v \geq \frac{\hbar}{2m\Delta x}$$

Hence, we get the uncertainities as Δ v_1 = 7.738E+05 m/s,
Δ v_2 = 4.467E+05 m/s
It follows that Δ v_1 > Δ v_2