Chem 30324, Spring 2017, Homework 4

Due February 22, 2017

In a "1-dimensional hydrogen atom", an electron is confined to the positive x axis and attracted to a proton at the origin. The potential felt by the electron can be written as

$$V(x) = \begin{cases} -C\frac{1}{x} & \text{if x} > 0 \\ \infty & \text{if x} \le 0 \end{cases}$$

where $c = \dfrac{e^2}{4\pi\epsilon_0} = \dfrac{\hbar^2}{m_e a_0}$ **is a bunch of constants with units energy times distance. In particular, m_e is the electron mass and a_0 is the bohr radius, a convenient unit of length equal to 0.529 Å. It's easiest to solve the problems below using the second set of constants. Further, the following equations are often of use in solving problems related to this system:**

$$\int_0^\infty x^n e^{-ax}\, dx = \frac{n!}{a^{n+1}}, \quad \frac{d}{dx}x e^{-ax} = e^{-ax}(1-ax), \quad \frac{d^2}{dx^2}x e^{-ax} = a e^{-ax}(ax-2)$$

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).

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, $\int_0^\infty \phi(x) * \phi(x)dx = \infty$, $\phi(x)$ is not square-integrable and it can not be normalized.

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 .)

In [8]:
```python
import numpy as np
import matplotlib.pyplot as plt

hbar = 1.05457e-34 #J*s
me = 9.109e-31 # kg
a0 = 0.529e-10 # m

x = np.linspace(0.1,10,200)
Psi_1 = x*np.exp(-x) # replace x/a0 by x
V = -hbar**2/me/a0**2/x # replace x/a0 by x

plt.plot(x,Psi_1)
plt.xlabel('$x/a_0$')
plt.ylabel('$\Psi_1(x)$')
plt.show()
plt.plot(x,V)
plt.xlabel('$x/a_0$')
plt.ylabel('$V(x)(J)$')
plt.show()
```
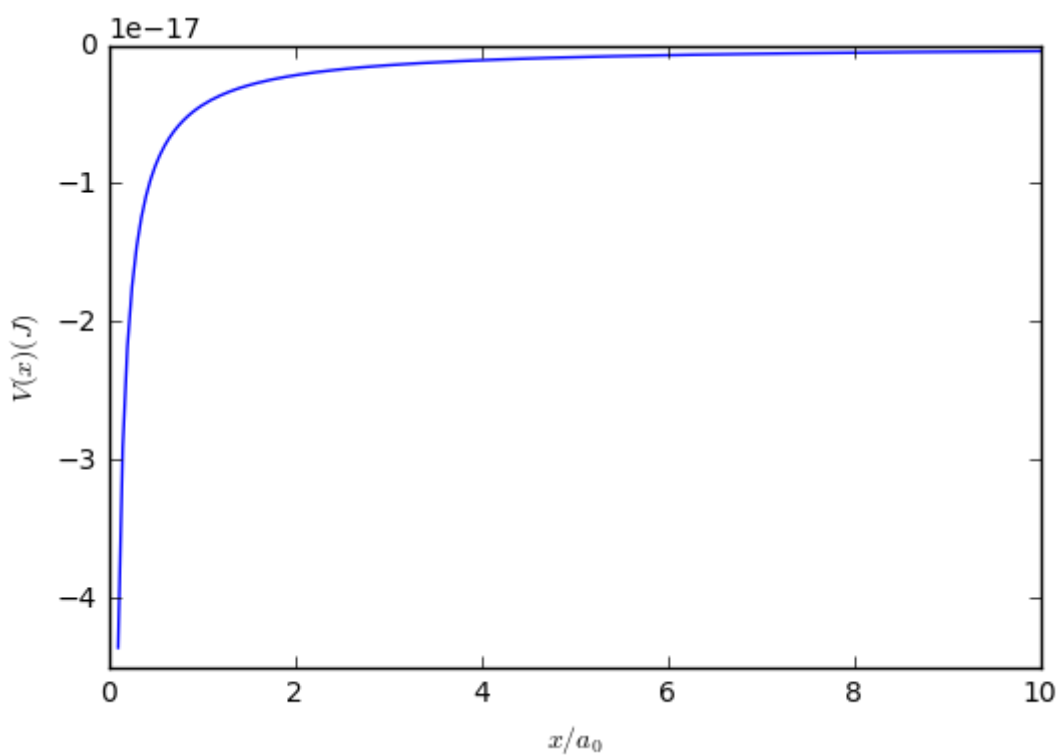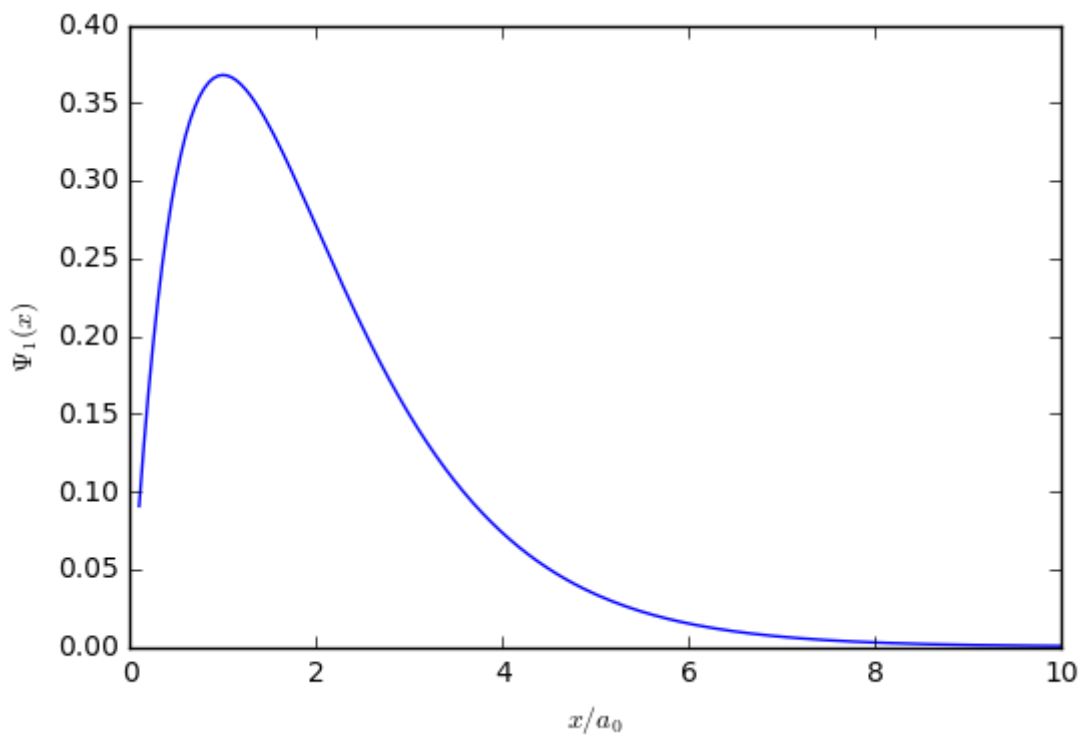
4. Is $\Psi_1(x)$ normalized? If not, construct the normalized $\tilde{\Psi}_1(x)$. It is ok to express you answer in terms of fundamental constants.

```
In [9]: from sympy import * # import sympy for symbolic mathematics
        x = symbols('x')
        a0 = symbols('a0',positive=True)
        a = integrate(((x/a0*exp(-x/a0))**2),(x,0,oo)) # integrate the square of
         wavefunction
        print (sqrt(1/a)) # normalization coefficient
```

```
2/sqrt(a0)
```

$\Psi_1(x)$ is not normalized, the factor is $\frac{2}{a_0}$, $\tilde{\Psi}_1(x) = \frac{2x}{a_0^{3/2}}e^{-x/a_0}$.

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

```
In [10]: print(solve(diff((2*x/a0**(3/2)*exp(-x/a0))**2,x),x)) # make the fist de
         rivative of wavefunction squared equal to 0, then solve x
```

```
[0.0, a0]
```

There are two solutions, x = 0 is meaningless, x = a_0 is the most probable distance.

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

```
In [11]: a0 = 0.529e-10 # m
         Psi_1 = 2*x/a0**(3/2)*exp(-x/a0) # normalized wavefunction
         probability = integrate(Psi_1**2,(x,a0,oo))
         print("The probability of finding the electron further than a0 from the
          proton is {:.3f}.".format(probability))
```

```
The probability of finding the electron further than a0 from the proton
 is 0.677.
```

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 $\hat{p}_x = -i\hbar\frac{d}{dx}$.

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

We cannot write the result in the form of constant*$\tilde{\Psi}_1(x)$, so $\tilde{\Psi}_1(x)$ is not an eigenfunction of $\hat{p}_x$. We will not get the same answer every time.

```
In [12]:  from sympy import * # import sympy for symbolic mathematics
          x = symbols('x')
          i,hbar,a0 = symbols('i,hbar,a0',positive=True)
          Psi_1 = 2*x/a0**(3/2)*exp(-x/a0)
          pPsi_1 = -i*hbar*2/a0**(3/2)*(1-x/a0)*exp(-x/a0)
          print("The average of momentum is {}.".format(integrate(Psi_1*pPsi_1,
          (x,0,oo))))
```

          The average of momentum is 0.

Makes sense. If average momentum was anything but 0, the particle would have to be moving towards infinity.

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

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

The result is in the form of constant*$\tilde{\Psi}_1(x)$, so $\tilde{\Psi}_1(x)$ is the eigenfunction of $\hat{H}$, we can get the same answer every time. The average is the constant $-\frac{\hbar^2}{2m_e a_0^2}$, which is called the eigenvalue of $\tilde{\Psi}_1(x)$ of the operator $\hat{H}$.

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!)

```
In [25]:  import numpy as np
          import matplotlib.pyplot as plt

          a0 = 0.529 # angstrom

          x = np.linspace(0,20,200)
          Psi_2 = x/2**0.5/a0**(3/2)*(1-x/2/a0)*np.exp(-x/2/a0) # normalized wavef
          unction
          plt.plot(x,Psi_2) # plot the orinqinal wavefunction
          plt.xlabel('$x(Angstrom)$')
          plt.ylabel('$\Psi_2(x)(\AA^{-1/2})$')
          plt.show()
```
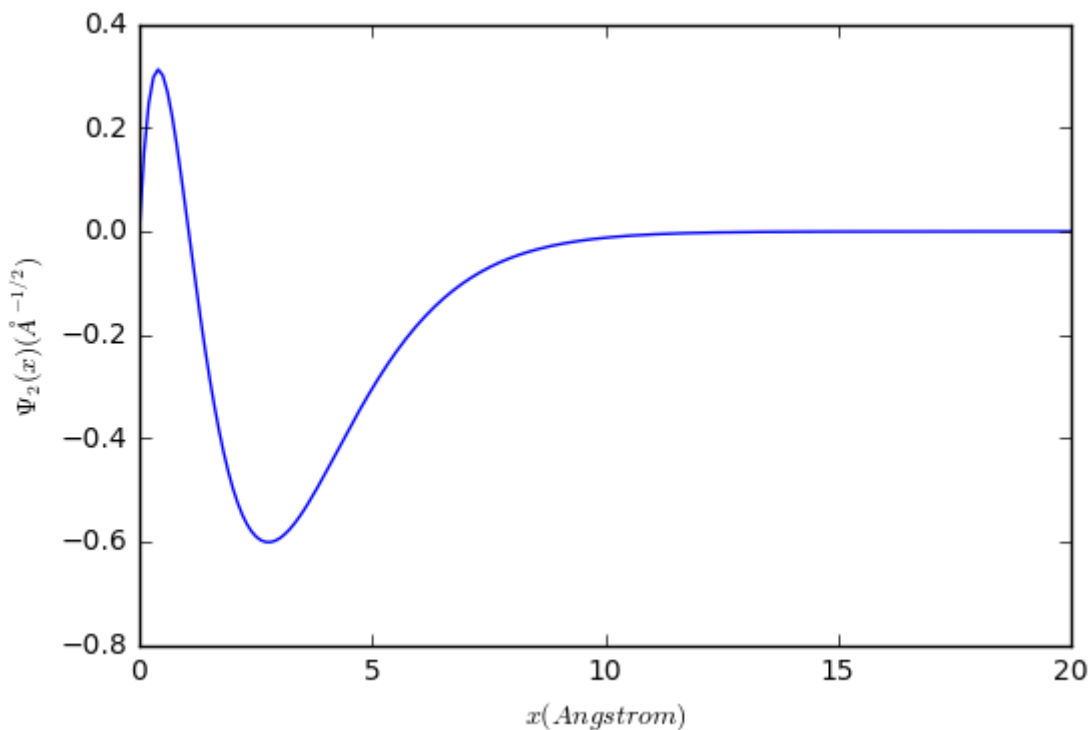


```
In [26]:  from sympy import * # import sympy for symbolic mathematics
          x = symbols('x')
          a0 = symbols('a0',positive=True)
          Psi_1 = 2*x/a0**(3/2)*exp(-x/a0)
          Psi_2 = x/2**0.5/a0**(3/2)*(1-x/2/a0)*exp(-x/2/a0)
          print(integrate(Psi_1*Psi_2,(x,0,oo)))
```

          0

The integral $\langle \tilde{\Psi}_1(x)|\tilde{\Psi}_2(x)\rangle$ is equal to 0, which means the two wavefunctions are orthogonal.

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.**

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 $\langle H \rangle$.

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

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

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

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

1/3 of the time we will measure E_1, 2/3 of the time E_2.

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 uncertainty principle is $\Delta x \Delta p \geq \frac{\hbar}{2}$. We also know $\Delta x_1 = 2^{1/2}a_0$, $\Delta x_2 = 6^{1/2}a_0$. The relationship between the uncertainties in linear speeds and the uncertainties in linear momentums is $\Delta p = m\Delta v$. So $\Delta v \geq \frac{\hbar}{2m\Delta x}$.

```
In [15]: hbar = 1.05457e-34 #J*s
         me = 9.109e-31 # kg
         a0 = 0.529e-10 # m
         dx1 = 2**0.5*a0 # m
         dx2 = 6**0.5*a0 # m
         dv1 = hbar/2/me/dx1 # m/s
         dv2 = hbar/2/me/dx2 # m/s
         print("The uncertainties in their linear speeds are {0:.3E} m/s and {1:.
         3E} m/s.".format(dv1,dv2))
```

The uncertainties in their linear speeds are 7.738E+05 m/s and 4.467E+0
5 m/s.

$\Delta x_1 < \Delta x_2$, according to the uncertainty principle, we get $\Delta v_1 > \Delta v_2$.

In [ ]: