Chem 30324, Spring 2018, Homework 8

Due April 4, 2018

Variations on the hydrogen atom

The *variational principle* allows us to develop approximate solutions to the Schrodinger equation numerically. Here you will apply the variational principle to the H atom. For this problem it is easiest to work in atomic units. In these units, $\hbar$, a_0, and $4\pi\epsilon_0$ are all equal to 1 and the unit of energy is the Hartree, equivalent to 27.212 eV. In atomic units the H atom Schrodinger equation is written:

$$\left\{ -\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r}\frac{d}{dr} - \frac{1}{r} + \frac{l(l+1)}{2r^2} \right\} R(r) = ER(r)$$

1. Normalize the true 1s wavefunction, $R_{10}(r) = e^{-r}$. Do not forget to include the r^2 integration factor.

$\tilde{R}_{10}(r) = Ce^{-r}$, solve normalization constant C by

$$\int_0^\infty r^2 C^2 e^{-2r}\, dr = 1$$

```
In [8]:  from sympy import *

         r = symbols('r')
         I = integrate(r**2*exp(-2*r),(r,0,oo))
         print(sqrt(1/I)) # normalization constant

         2
```

So the normalized 1s wavefunction is $\tilde{R}_{10}(r) = 2e^{-r}$.

2. Is this 1s wavefunction an eigenfunction of the hydrogen Schrodinger equation? What is the eigenvalue? Recall that your answer will be in Hartree.

1s orbital: n = 1, l = 0:

$$\hat{H} = -\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r}\frac{d}{dr} - \frac{1}{r}$$

$$\hat{H}\tilde{R}_{10}(r) = -e^{-r} = (-\frac{1}{2})\tilde{R}_{10}(r)$$

So, this 1s wavefunction is an eigenfunction of the hydrogen Schrodinger equation, the eigenvalue is $-\frac{1}{2}$ Ha.

3. Suppose in a fit of panic you forget the 1s radial function when asked on an exam. Now wanting to leave the answer blank, you decide to guess something, and liking bell-shaped curves, you guess $R_{10}(r) = e^{-r^2}$. Normalize this guess.

```
In [9]:  I = integrate(r**2*exp(-2*r**2),(r,0,oo))
         pprint(sqrt(1/I))
```

$$\frac{2 \cdot \sqrt[4]{2} \cdot \sqrt{2}}{\sqrt[4]{\pi}}$$

So the normalized 1s wavefunction is $\tilde{R}_{10}(r) = (\frac{128}{\pi})^{1/4}e^{-r^2}$.

4. Calculate the expectation value of the energy of your normalized guess. Is it greater or less than the true value?

$$\hat{H} = -\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r}\frac{d}{dr} - \frac{1}{r}$$

$$\frac{d}{dr}e^{-r^2} = -2re^{-r^2}$$

$$\frac{d^2}{dr^2}e^{-r^2} = -2e^{-r^2} + 4r^2e^{-r^2}$$

$$\hat{H}\tilde{R}_{10}(r) = C[-\frac{1}{2}(-2e^{-r^2} + 4r^2e^{-r^2}) - \frac{1}{r}(-2re^{-r^2}) - \frac{1}{r}e^{-r^2}]$$

$$= C(-2r^2 + 3 - 1/r)e^{-r^2}$$

The expectation value of the energy:

$$\langle E \rangle = \int_0^\infty \tilde{R}_{10}(r)\hat{H}\tilde{R}_{10}(r)r^2dr =$$

$$\int_0^\infty C^2(-2r^4 + 3r^2 - r)e^{-2r^2}dr$$

```
In [10]:  E = 1/I*integrate((-2*r**4+3*r**2-r)*exp(-2*r**2),(r,0,oo))
          print(E)
```

```
8*sqrt(2)*(-1/4 + 3*sqrt(2)*sqrt(pi)/32)/sqrt(pi)
```

```
In [22]:  import numpy as np
          print('The expectation value of the energy is {0:.3f} Ha. It is greater than t
          he true value.'.format(8*np.sqrt(2)*(-1/4 + 3*np.sqrt(2)*np.sqrt(np.pi)/32)/np
          .sqrt(np.pi)))
```

```
The expectation value of the energy is -0.096 Ha. It is greater than the true
value.
```

5. What does the variational principle say about the expectation value of the energy of your guess as you vary a parameter γ in your guess, $R_{10} = e^{-\gamma r^2}$? Suggest a strategy for determining the "best" γ.

The variational principle says true wavefunction energy is always lower bound on energy of any trial wavefunction. We can get the "best" γ by optimizing the wavefunction with respect to variational parameter:

$$\frac{\partial \langle E \rangle}{\partial \gamma} = 0$$

6. *Extra credit*: Determine the best value of γ. Show and carefully justify your work to receive credit.

Normalize R_{10}: $\int_0^\infty r^2 C^2 e^{-2\gamma r^2} dr = 1$

$\langle E \rangle = \int_0^\infty \tilde{R}_{10}(r) \hat{H} \tilde{R}_{10}(r) r^2 dr =$
$\int_0^\infty C^2(-2\gamma^2 r^4 + 3\gamma r^2 - r)e^{-2\gamma r^2} dr$

```
In [17]:  gamma = symbols('gamma',positive=True)
          C_squared = 1/integrate(r**2*exp(-2*gamma*r**2),(r,0,oo)) # normalization cons
          tant squared
          E_guess = C_squared*integrate((-2*gamma**2*r**4+3*gamma*r**2-r)*exp(-2*gamma*r
          **2),(r,0,oo)) # expectation value of energy
          print(E_guess)
          print('The best value of gamma is ')
          print(solve(diff(E_guess,gamma),gamma)) # solve dE/dgamma = 0
```

```
8*sqrt(2)*gamma**(3/2)*(-1/(4*gamma) + 3*sqrt(2)*sqrt(pi)/(32*sqrt(gamma)))/s
qrt(pi)
The best value of gamma is
[8/(9*pi)]
```
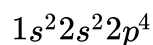
```
In [18]: gamma = 8/(9*np.pi)
         print('The expectation value of the energy is {0:.3f} Ha.'.format(8*np.sqrt(2)
         *gamma**(3/2)*(-1/(4*gamma) + 3*np.sqrt(2)*np.sqrt(np.pi)/(32*np.sqrt(gamma)))
         /np.sqrt(np.pi)))
```

The expectation value of the energy is -0.424 Ha.

Many-electron atoms:

Oxygen (O) is the eighth atom on the periodic table and has 6 valence electrons.

7. Write the ground state atomic configuration of oxygen.

$1s^2 2s^2 2p^4$

8. Provide *one possible set* of quantum numbers (n, l, m_l, m_s) for each of the valence electrons in the atom. What is the ground state *spin multiplicity* of O?

One possible set of quantum numbers:

n	l	m_l	m_s
1	0	0	+1/2
1	0	0	-1/2
2	0	0	+1/2
2	0	0	-1/2
2	1	0	+1/2
2	1	0	-1/2
2	1	-1	+1/2
2	1	1	+1/2

We know that the spin of an atom is calculated by summing up the values of ms over the entire atom. We find that the ground state oxygen atom has a spin of 1. We can then determine the multiplicity by multiplying the spin by 2, and adding 1 to it. Therefore the ground state spin multiplicity of an oxygen atom is 3 (this will always be equal to the number of unpaired electrons +1).

9. *Qualitatively* compare the energies necessary to remove a 1s electron from O and from sulfur (S), one row below O in the periodic table. Explain your answer. (Note that the measurement of these energies is the basis of X-ray core-level spectroscopy.)

It will require much more energy to remove the 1s electron from the sulfur atom than from an oxygen atom. This is due to the great increase in the coulomb potential by increasing the number of protons in the nucleus. Additionally, since we are explicitly considering the 1s orbital, which is not shielded, the electrons will feel the full effect of the extra charge in the nucleus, while the effect will be decreased in further out orbitals due to shielding (i.e. the difference in the energy levels of the 2p orbitals will not be as great as the difference in the 1s orbitals).

10. *Qualitatively* compare the ionization energies (energies to remove a valence p electron) from O and from S, one row below O in the periodic table. Explain your answer.

Sulfur has a lower first ionization energy than oxygen. Ionization is easiest from the highest energy orbitals, and the n = 3 p orbitals of sulfur are higher in energy than the n = 2 p orbitals of oxygen.

11. *Qualitatively* compare the ionization energies (energies to remove a valence p electron) from O and from fluorine (F), one column to the right of O in the periodic table. Explain your answer.

The first ionization energy of fluorine is greater than oxygen. Fluorine has one more proton and one more 2p electron than oxygen. Electrons in the same subshell are ineffective at shielding each other, so the 2p electrons in fluorine feel a greater effective nuclear charge than do those in oxygen.

12. Show that a 2s hydrogenic orbital approaches closer to the nucleus than the 2p, by comparing the probability of finding either electron within 1 atomic unit of the nucleus. In atomic units, the 2s and 2p radial wavefunctions are given by:

$$R_{2,0} = \frac{1}{\sqrt{2}}(1 - r/2)e^{-r/2}$$

$$R_{2,1} = \frac{1}{2\sqrt{6}}re^{-r/2}$$

Remember to construct the radial probability functions correctly.

$$P_{2s} = \int_0^1 r^2 R_{2,0}^2 dr = \int_0^1 \frac{r^2}{2}(1 - r/2)^2 e^{-r} dr$$

$$P_{2p} = \int_0^1 r^2 R_{2,1}^2 dr = \int_0^1 \frac{1}{24} r^4 e^{-r} dr$$

```
In [19]:  r = symbols('r')
          P_1 = integrate(r**2/2*(1-r/2)**2*exp(-r),(r,0,1))
          P_2 = integrate(1/24*r**4*exp(-r),(r,0,1))
          print(P_1,P_2)
```

```
-21*exp(-1)/8 + 1 -2.70833333333333*exp(-1) + 1.0
```

```
In [21]:  print('The probability of finding electron within 1 atomic unit of the nucleus
           of 2s orbital is {0:.3f}, the probability of 2p orital is {1:.3f}.'.format(-2
          1*np.exp(-1)/8 + 1, -2.70833333333333*np.exp(-1) + 1.0))
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The probability of finding electron within 1 atomic unit of the nucleus of 2s
orbital is 0.034, the probability of 2p orital is 0.004.
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Therefore, an electron in a 2s orbital is much more likely to be within 1 bohr radius of the nucleus, than an electron in a 2p orbital.

Multi-electron atoms and the self-consistent field.

Modern calculations on atom and molecules take advantage of the variational principle and are made with sophisticated computer programs that solve the many-electron Schrödinger equation. *Density functional theory* (DFT) is the most common set of approximations for the electron-electron interactions used today. In this problem you'll do a DFT calculation using the *Gaussian* program (http://www.gaussian.com (http://www.gaussian.com)).

Now, let's set up your calculation (you may do this with a partner if you choose):

1. Log into the Webmo server https://www.webmo.net/demoserver/cgi-bin/webmo/login.cgi (https://www.webmo.net/demoserver/cgi-bin/webmo/login.cgi) using "guest" as your username and password.
2. Select New Job-Creat New Job.
3. Use the available tools to draw an argon (Ar) atom on the screen.
4. Use the right arrow at the bottom to proceed to the Computational Engines.
5. Choose Gaussian
6. Select "Molecular Orbitals" for the Calculation type, "B3LYP" for theory, "Minimal" for the basis set, "0" for the charge, and "Singlet" for the multiplicity.
7. Select the right arrow to run the calculation.
8. From the job manager window choose the completed calculation to view the results.

13. Write down the energies of the occupied molecular orbitals and identify them by their shell ($n = 1, 2, \ldots$) and subshell (s, p, d, ...). For fun, click on the Magnifying Glass icons to see the molecular orbitals in 3-D. You may have to play around with the Display Settings and Preferences to get good views.

Orbital	Energy (Hartree)
1s	-113.791
2s	-10.826
2p	-8.425
3s	-0.8497
3p	-0.3178

You are welcome to play around with other atoms. For anything other than the noble gases, be sure to set the Multiplicity to a sensible value.