Physics 468: Computing Project 3

February 1, 2012

Monte Carlo Estimation of e-e interaction in a neutral Helium atom

In homework 5.11 you performed the folioing integral analytically:

$$\left\langle \frac{1}{|r_1 - r_2|} \right\rangle = \left(\frac{8}{\pi a^3}\right)^2 \int\int \frac{e^{-4(r_1+r_2)/a}}{|\vec{r}_1 - \vec{r}_2|}\, d^3r_2\, d^3r_1 = \frac{5}{4a} \tag{1}$$

The result was produced after many lines of difficult math. It's actually amazing that it was doable at all! There are many integrals from quantum physics that are much harder, and not analytically solvable. How can we handle such situations? You guessed it! (Did you read the title?) We're going to apply the strategy we worked out last time to this, more difficult, but much more rewarding, problem.

The basic idea is very similar to computing project 2 except that we're now working in 3 dimensions and the coordinates are a bit more complicated. Computing the expectation value of the RMS distance between electrons can be done by simply generating random $\vec{r}_1$ and $\vec{r}_2$, with probability distributions that match the wavefunction, and then simply computing the average value of the distance between the two electrons at those random locations. The trick is to get the random distributions right!

Moving to 3D

We can think of the probability densities of the two electrons independently. For the first electron the probability must satisfy:

$$\left(\frac{8}{\pi a^3}\right) \int e^{-4r_1/a} d^3r_1 = 1 \tag{2}$$

But if you expand all the variables, that looks like:

$$\left(\frac{8}{\pi a^3}\right)\int_0^\infty r_1^2 e^{-4r_1/a} dr_1 \int_0^\pi \sin\theta_1 d\theta_1 \int_0^{2\pi} d\phi_1 = 1 \tag{3}$$

The R direction

Note that the r_1 distribution is *not* a simple exponential due to the differential volume element (Jacobian Determinant if you learned that in vector calculus!) So, in order to use the monte-carlo approach to solve this integral, we'll need a distribution of r_1s that goes like

$$P_r(r_1) = \left(\frac{2^5}{a^3}\right) r_1^2\, e^{-4r_1/a} \tag{4}$$

This turns out to the nothing other than the *gamma distribution* (you can check the normalization yourself):

`http://en.wikipedia.org/wiki/Gamma_distribution`

which has a probability density of:

$$f(x; k, \theta) = \frac{1}{\theta^k}\frac{1}{\Gamma(k)} x^{k-1} e^{-\frac{x}{\theta}} \text{ for } x \geq 0 \text{ and } k, \theta > 0 \tag{5}$$

Where $\Gamma(k)$ is the *gamma function* (closely related to the factorial. $\Gamma(k) = (k-1)!$ if k is integral.), k is the *shape* parameter and θ is the *scale* parameter. For our application the shape would be 3, and the scale would be $a/4$.

In python we can generate random numbers with this distribution using the built-in gamma function:

```
from pylab import *

a=1.0           # set a to one unit
shape = 3.0     # from our wavefunction
scale = a/4     # since Z=2 our probability density
                # goes like exp(-4.0*r/a) -> theta = a/4.

N = 1000        # generate 1000 random 'r's

r1 = gamma(shape, scale, N)
hist(r1, bins=20)
show()
```

The θ direction

In the θ direction you can see by the same argument that the angles are distributed like $\sin(\theta)$. If you compute the CDF and invert it you'll see that $\cos(\theta)$ is uniformly distributed between -1 and +1:

$$
\begin{aligned}
r &= CDF(\theta) && (6)\\
r &= \frac{1}{2}(1-\cos\theta) && (7)\\
2r-1 &= -\cos\theta && (8)\\
1-2r &= \cos\theta && (9)\\
\theta &= \cos^{-1}(1-2r) && (10)
\end{aligned}
$$

Note that Eq 9 indicates that $\cos\theta$ is a random number equal to $1-2r$, but that's clearly a random number chosen between -1 and +1, so it's easy! In the code, where you need a random $\cos\theta$, just pick a uniformly distributed random number between -1 and +1, no need to actually get θ nor compute its cosine!

The ϕ direction

The normalization integral (Eq 3) shows that ϕ is simply uniformly distributed between 0 and 2π. But the expectation value we're computing Eq 1, doesn't depend on ϕ at all. Note that:

$$|\vec{r}_1-\vec{r}_2| = \sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta} \tag{11}$$

So while in principle we should be generating one random ϕ for each r_1, r_2 and θ since the expectation value doesn't actually depend on ϕ at all, we can skip it.

Wrapping things up

So that's it... use the gamma function twice to compute randomly distributed r_1 and r_2 values, get random $\cos\theta$ values uniformly distributed between -1 and +1, then compute $1.0/|\vec{r}_1-\vec{r}_2|$ for each set. The average of these values *should* be the correct expectation value you worked out analytically in problem 5.11 in Griffiths.

Questions

Please answer these questions at the end of your report.

1) How would you have to change your program to find the e-e repulsion energy for an excited state of Helium?

2) Later (chapter 7) we'll learn that there's another approach to improving our calculation (the Variational Method). The idea is to assume that the effective nuclear charge that each electron sees is somewhat diminished due to the presence of the other electron. How would you modify the program to take this effect into account?