

# Physics 468: Computing Project 5

January 24, 2020

## Helium Atom Ground State, Revisited

In CP3 we estimated a difficult, but not impossible, integral using a Monte Carlo strategy with a known exact result. The idea was to test the technique on a problem that is possible to work out analytically so we can get some confidence that the strategy has merit and can be successfully employed in other context where we can't solve the problem directly. This week we're more or less doing a similar thing, but this time, we're employing the Variational Principle along with our Monte Carlo approach to find an improved ground state energy for Helium.

### What are we varying?

The idea here is to guess that the two electrons don't see the "full" charge of the nucleus. The suspicion is that they effectively shield one another from the nucleus so that instead of two protons they each see  $Z$  protons (where  $Z < 2$ ) most of the time.

The idea is to imagine that the corrected wavefunction might have a different  $r$  coefficient so we replace the '2' with an arbitrary factor  $Z$  that we can vary to minimize the expectation value of the Hamiltonian. Including the new normalization factor we get Griffiths' Eq. 7.27:

$$\psi(r_1, r_2, Z) = \frac{Z^2}{\pi a^3} e^{-Z(r_1+r_2)/a} \quad (1)$$

where  $Z$  is a free parameter. We want to evaluate the expectation value of the *physical* Hamiltonian  $\hat{H}$  using this *made up* wavefunction to see if we can get a lower energy than the one we got effectively by using first order perturbation theory in CP3. What is the physical Hamiltonian? For this exercise let's use:

$$\hat{H} = \hat{K}_1 + \hat{K}_2 - \frac{e^2}{4\pi\epsilon_0} \left( \frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|r_1 - r_2|} \right) \quad (2)$$

Note that we can divide this up into two parts:

$$\hat{H}_A = \hat{K}_1 + \hat{K}_2 - \frac{e^2}{4\pi\epsilon_0} \left( \frac{Z}{r_1} + \frac{Z}{r_2} \right) \quad (3)$$

and what's left over:

$$\hat{H}_B = -\frac{e^2}{4\pi\epsilon_0} \left( \frac{2-Z}{r_1} + \frac{2-Z}{r_2} - \frac{1}{|r_1 - r_2|} \right) \quad (4)$$

and fixing up some signs

$$\hat{H}_B = \frac{e^2}{4\pi\epsilon_0} \left( \frac{Z-2}{r_1} + \frac{Z-2}{r_2} + \frac{1}{|r_1 - r_2|} \right) \quad (5)$$

What's the point of that? Well..  $\hat{H}_A$  is just the Hamiltonian for the problem we solved in chapter 5, but with a nuclear charge of  $Z$ , so our proposed wavefunction is an *eigenfunction* of this part of the Hamiltonian. In other words we can just write down the expectation value of this part of the Hamiltonian, since it's just the corresponding eigenvalue:  $2Z^2E_1$  rather than  $8E_1$  (see Eq. 5.31 and problem 4.16). Putting all this in we see that  $\langle H \rangle$  will be:

$$\langle H \rangle = 2Z^2E_1 + \frac{e^2}{4\pi\epsilon_0} \left( 2(Z-2) \left\langle \frac{1}{r} \right\rangle + \left\langle \frac{1}{|r_1 - r_2|} \right\rangle \right) \quad (6)$$

Note that

$$\frac{e^2}{4\pi\epsilon_0} = -2aE_1 \quad (7)$$

So Eq. 6 becomes:

$$\langle H \rangle = 2Z^2E_1 + -2aE_1 \left( 2(Z-2) \left\langle \frac{1}{r} \right\rangle + \left\langle \frac{1}{|r_1 - r_2|} \right\rangle \right) \quad (8)$$

$$\langle H \rangle = 2E_1 \left( Z^2 - 2(Z-2) \left\langle \frac{a}{r} \right\rangle - \left\langle \frac{a}{|r_1 - r_2|} \right\rangle \right) \quad (9)$$

So.. that's it. We can just vary  $Z$ , evaluate  $\langle H \rangle$  using the MC integration and then check to see if it goes down! Since we *know* that  $\langle H \rangle$  is minimized for the exact ground state, we can tell if things are improving. What's more, since Griffiths worked out the value of  $Z$  that minimizes the hamiltonian analytically, we can check our numerical approach against his analytical solution.

Since all we care about is the *value* of  $Z$  when  $\langle H \rangle$  is minimized what we really need is just a function that computes:

$$\langle H \rangle / |2E_1| = - \left( Z^2 - 2(Z - 2) \left\langle \frac{a}{r} \right\rangle - \left\langle \frac{a}{|r_1 - r_2|} \right\rangle \right) \quad (10)$$

When I run a QMC integration for the two expectation values in Eq. 10 for 30  $Z$  values between  $Z = 1.4$  and  $Z = 2.0$  I get the following graph:

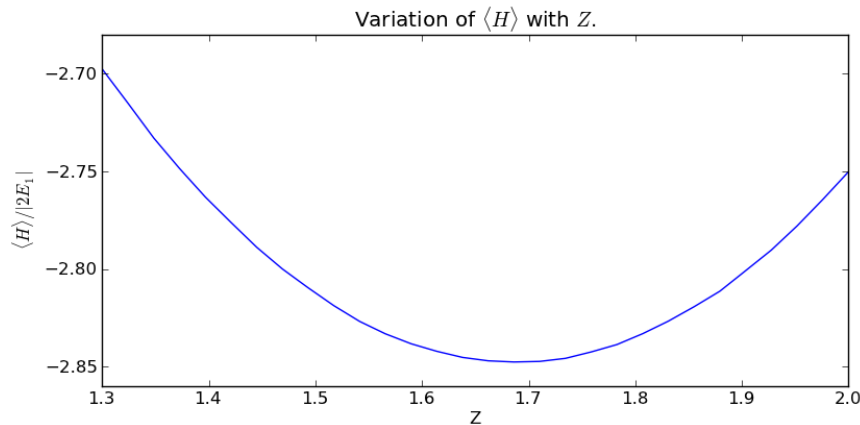


Figure 1: Eq. 10 value at 30  $Z$  values from  $Z = 1.4$  to  $Z = 2.0$  with  $10^7$  samples each.

You should get a graph similar to this one. Since Griffiths' solution gives a  $Z = 1.69$  it looks like we're on the right track.

## Questions

Please answer these questions at the end of your report.

- 1) What energy do you find for the minimum? Does this compare reasonably with Griffiths' value?
- 2) If we hadn't picked a wavefunction that happened to be an eigenstate of part of our Hamiltonian, how could we proceed with this calculation? What would have to change in the code?
- 3) What would you have to change to apply this idea to the Hydrogen molecular ion described in section 7.3?