This homework covers two sets of approximation techniques: { week 8: variational principle } and { week 9: the sudden and adiabatic approximations }.

Problem 1 : On the nature of Helium, Screening, and Effective Charge

Griffiths' section §7.2 goes through the most CLASSIC application of the variational principle: finding the ground state energy of the <u>helium atom</u> including the mutual <u>Coulomb repulsion</u> between the two electrons. When we discussed **screening** in our atomic structure section, we advertised that we would come back to the concept of an effective nuclear charge $< Z$ and calculate one when we had more tools. Well here we are!

First, here is a summary of Griffiths §7.2. The Hamiltonian used for the helium atom is :

$$H(\vec{r}_1, \vec{r}_2) = -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|\vec{r}_1 - \vec{r}_2|}\right)$$

No spin-dependent forces here, just the Coulomb attraction of each electron to the $Z_{He}=2$ nucleus and the electron-electron repulsion term (which we call V_{ee} for short). The trial wavefunction used for this classic problem is essentially the product of two hydrogen wavefunctions, one for each of helium's electrons:

$$\psi(\vec{r}_1, \vec{r}_2) = \frac{Z^3}{\pi a_0^3} e^{-Z(r_1+r_2)/a_0} \quad \text{where } a_0 \text{ is the Bohr radius (see 486 formula sheet).}$$

"Wait", you remark, "if a_0 is the Bohr radius, that trial wavefunction has no <u>variable parameter</u>, I thought we were always supposed to include at least one in order to minimize our ground-state energy as much as possible?" You are correct … and there *is* a variable parameter: it is Z. "But $Z = 2$ for Helium!", you exclaim, "I can't play around with the truth!" True … but the idea behind this trial wavefunction is to introduce an **effective Z** that will come out *less* than $Z_{He} = 2$ because the effect of the V_{ee} term is to partially **screen the nuclear charge**. To understand, imagine you are one of the two electrons and that your name is Ivan. You are attracted to the positively-charged $Z_{He} = 2$ nucleus, which sits at the center of your probabilistic cloud of spherically-symmetric *s*-shell existence ... but you are repelled by the other electron, named Juan, which is probabilistically splattered through space the same way you are. If you think about Juan using your mastery of Gauss' Law from PHYS 212 (footnote available[1]), you will realize the following: if you, Ivan, are momentarily located a distance r_{ivan} away from the nucleus, the *only* portion of Juan's probability cloud that affects you is the part that is <u>closer to the nucleus than you are</u>, i.e. the part with $r_{juan} < r_{ivan}$. Juan is negatively charged, as are you, so the electric field you see at your location is due to attraction from the charge $+Z_{He}$ nucleus & repulsion from a portion of Juan's charge -1 cloud. Thus, Juan **screens** part of the $+Z_{He}$ nuclear charge from you. Our hope is that introducing an effective = screened charge Z as a variational parameter will provide a good approximation to the full effect of the V_{ee} term.

As you see in Griffiths, the best values obtained for the He ground state using the "(hydrogen)²-with-screening" trial function are $Z = 1.69$ (which is less than 2, so yes, the helium nucleus is screened in this model) and $E_{gs} = -77.5$ eV. This is absurdly close to the experimental value of **–79 eV**. You may recall that in a previous homework, you used 1st order perturbation theory to calculate the very same thing – the effect of V_{ee} on the

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helium ground state energy – and you obtained $E_{gs} = -75$ eV. That's not quite as good, but of course with perturbation theory, you can keep going, to 2nd order, 3rd order, etc with enough time/energy/processors.

(a) The "(hydrogen)²-with-screening" trial function does NOT do such a good job in obtaining the ground state of the **H⁻ ion**, i.e. a hydrogen nucleus surrounded by two electrons in a closed 1s² shell. Using the trial wavefunction described above, calculate the approximate ground state energy of the H⁻ ion with V_{ee} repulsion included.

▶ To shorten this problem, you may use any result from Griffiths §7.2, just give the equation number.

▶ FYI: It is very common in atomic calculations, such as this one, to need $<1/r>$ and/or $<1/r^2>$ for hydrogenic wavefunctions ψ_{nlm}. The answers are equations 6.55 and 6.56 in Griffiths, and you are free to use them, but I do want you to know that there is a very <u>fast way</u> to get the first one. You use the super-useful Virial Theorem, which is true in both QM and CM: $<V> = -2<T>$ for a particle bound in a $1/r$ potential. Since you know $<E> = <T+V>$ for the hydrogenic wavefunctions (well, it's on your formula sheet) and $V \sim 1/r$, $<1/r>$ is easily obtained! This is problem 6.12 in Griffiths; the calculation of $<1/r^2>$ is addressed in problem 6.33 & 6.32, which is a bit of a project.

(b) Let's leave the H⁻ ion alone for a moment and jargon-bust the word **ionization**. It means "the freeing of an electron from an atomic bound state". Remember that to **free** a bound particle means to elevate its total energy from a negative value (its bound-state energy) to ZERO, at which point it is able to reach ∞ = a place free of influence from any other forces ($V=0$) with just enough kinetic energy to be physical ($T=0$).
Consider the **He⁺ ion** = a helium atom with one electron removed. As noted above, a He atom has ground state energy –79 eV; calculate the **ionization energy** required to free one electron from a ground-state He atom and turn it into a ground-state He⁺ ion.

▶ Massive hints: (i) consult the 486 formula sheet, and (ii) this is a very short problem.

(c) Back to the H⁻ ion. Compare the ground state energy of the H⁻ ion that you got in part (a) to the ground state energy of the H atom that you got in 486. We will shortly derive something that you instinctively know or suspect already:

> Quantum systems that are in <u>excited states</u> are, in general, **unstable** as they will spontaneously decay / transition to available <u>lower-energy states</u> with some characteristic lifetime.

So: suppose an astronomer tells you that the H⁻ ion is totally stable, and is called "hydride", and is commonly found in the atmosphere of stars. Does your calculation from (a) support this information? Why or why not?

FYI: The solution to the wonky value of the H⁻ energy is in problem 7.18. Do read the problem, the concept is very nice! But the solution requires many integrals … we'll skip it.

Problem 2 : An Infinite Well ™ of Changing Size   *Qual Problem*

A particle of mass M bounces elastically between two infinite, parallel plane walls separated by a distance D. The particle is in its lowest possible energy state.

(a) What is the energy of this state?

(b) The separation between the walls is slowly (i.e., adiabatically) increased to 2D.

   (i) How does the expectation value of the energy change?

   (ii) Compare this energy change with the result obtained classically from the mean force exerted on a wall by the bouncing ball?

(c) Now assume that the separation between the walls is increased rapidly, with one wall moving at a speed $\gg$ $(E/M)^{1/2}$. Classically, there is no change in the particle's energy since the wall is moving faster than the particle and cannot be struck by the particle while the wall is moving.

(i) What happens to the expectation value of the energy quantum-mechanically?

(ii) Compute the probability that the particle is left in its lowest possible energy state.

Problem 3 : A 1D SHO with a Suddenly Applied Electric Field *Qual Problem*

A particle of mass m experiences a simple-harmonic potential in one dimension, so the particle's Hamiltonian is

$$H_0 = \frac{p^2}{2m} + \frac{m\omega^2 x^2}{2} \, .$$

(a) You are told that the form of the ground state wavefunction is $\psi_0(x) = Ne^{-\alpha^2 x^2/2}$.
Calculate the constants N and α **WITHOUT using the 1D SHO reference section of our formula sheets.**
(A bit of review of basic things is always good.)

(b) What is the energy of the ground state? Again please derive the result **WITHOUT using the 1D SHO reference section of our formula sheets.**

(c) At time $t = 0$, a constant, uniform electric field of magnitude E is switched on, adding this new term to the Hamiltonian:

$$H' = e\,E\,x$$

Despite the notation "H_0" and "H'" from perturbation theory, **you may NOT assume that the perturbing electric potential is small compared to the harmonic-oscillator potential!** Calculate the <u>exact</u> ground state energy of the new hamiltonian $H_0 + H'$.
▶ HINT: Complete the square.

(d) Assuming that the field is switched on <u>instantaneously</u>, what is the probability that the particle stays in the ground state?

(e) Obviously one cannot turn on anything "instantaneously", that is just code for "fast enough that we can use the sudden approximation". Well, how fast is fast? Fill in the following sentence with an order-of-magnitude quantity (i.e. we don't care about factors of 2 or 5 or whatever) :

"In order to use the sudden approximation in part (d), the electric field must be switched on over a time interval that is much shorter than _____".

▶ HINT: Have a peek at the relevant lecture slide