Quantum Physics III (8.06) Spring 2005
Assignment 7

March 29, 2005 **Due Tuesday April 5, 2005**

Readings

The reading assignment for this problem set and the first part of the next one is:

- Griffiths Chapter 7.
- Cohen-Tannoudji Chapter XI, Complements E,F,G.
- Griffiths Chapter 8

Problem Set 7

1. **Variational bound on the ground state in an exponential potential (12 points)**

   Unlike in one dimension, an attractive potential in three dimensions does not always have a bound state. A simple variational guess can give us an estimate of how strong a potential must be in order to have a bound state, even though the exact solution would require solving the Schrödinger equation numerically.

   Consider a particle of mass m moving in three dimensions under a central force derived from an exponential potential,

$$V(r) = -\alpha e^{-2\mu r} ,$$

   where α and μ are positive. Take a simple exponential variational *ansatz* for the ground state wavefunction:

$$\psi_\lambda(r) = Ce^{-\lambda r} . \tag{1}$$

(a) Find the constant C by demanding that $\int d^3r|\psi_\lambda(r)|^2 = 1$.

(b) Compute the variational estimate of the energy of ψ, as a function of λ.

Hint: Once you have normalized the wave function, the variational estimate is given by

$$E(\lambda) = \int d^3r \left\{ \frac{\hbar^2}{2m} \left| \frac{d\psi_\lambda(r)}{dr} \right|^2 + V(r) \, |\psi_\lambda(r)|^2 \right\} \tag{2}$$

Hint: The only integral needed is $\int_0^\infty dx x^n e^{-x} = n!$.
Answer: $E(\lambda) = \frac{\lambda^2}{2m} - \alpha(\frac{\lambda}{\mu+\lambda})^3$.

(c) Show that for small α, the minimum value of $E(\lambda)$ is zero and is obtained for $\lambda = 0$. Interpret this result (for example, where is the particle found when $\lambda = 0$?).

(d) Lets scale out some of the dimensionful parameters to make this problem easier to analyze. Consider $\mathcal{E} = \frac{mE}{\mu^2}$. Show that $\mathcal{E}$ can be written as a function of $x = \lambda/\mu$ and a scaled strength of the potential, $\kappa = \alpha m/\mu^2$. Rewrite the result of part (b) as $\mathcal{E}(\kappa, x)$. Analyze this equation graphically or numerically and find the minimum value of κ for which a bound state exists. What is the value of x at this value of κ.

(e) Does the result of the previous section give you a minimum value of α (for fixed m and μ) required for a bound state, or a maximum, or neither? Explain.

2. Several proofs constructed via the variational method (10 points)

The variational method allows us to prove some important properties of wavefunctions in one dimensional and quasi-one dimensional problems.

(a) Suppose $\psi_0(x)$ is the (normalizable) ground state of the Schrödinger equation in one dimension with a potential $V(x)$. Prove that $\psi_0(x)$ has no nodes.

[Hint: The proof proceeds by contradiction. Assume $\psi_0(x)$ is the ground state and has a node at x_0. Then consider the trial function $\psi(x) = |\psi_0(x)|$. It's easy to see that $E[\psi] = E[\psi_0]$. $\psi(x)$ has a cusp where $\psi_0(x)$ had a node. Smooth out the cusp and you'll have a new trial function with no node and even lower energy. The trick is to find a way to smooth out the cusp and still estimate the energy. Of course there may be other ways to prove the theorem too.]

(b) Prove the following corollary to (a): in the absence of spin, the ground state in one dimension is not degenerate.

(c) You do not need to have completed parts (a) and (b) to do part (c). Consider a potential in one-dimension, $V(x)$, which vanishes for $x < x_1$ and $x > x_2$, and is everywhere negative for $x_1 < x < x_2$. Prove that the Schrödinger equation with this potential has at least one bound state. Hint: try $\psi(x) \propto e^{-\lambda(|x-|x_0||)}$ where $x_0 = \frac{1}{2}(x_1 + x_2)$.

3. **The Hydrogen Molecular Ion (20 points)**

One of the classic applications of the variational method is the evaluation of the ground state energy of the hydrogen molecular ion, H_2^+. This is described in some detail in Griffiths section 7.3. We will not have time to do this example in lecture, but I want you to work through it. Hence, this problem.

The Hamiltonian is (using cgs units; Griffiths does not; set Griffiths' $4\pi\epsilon_0$ to 1)

$$H = -\frac{\hbar^2}{2m}\nabla^2 - e^2\left(\frac{1}{r_1} + \frac{1}{r_2}\right) , \qquad (3)$$

where r_1 and r_2 are the distances to the electron from the respective protons. The protons are separated by a distance R. See Griffiths' Figure 7.5.

In this problem, R is the variational parameter.

Our main interest here is to determine whether this system bonds. If we can find a trial wave function for which the energy is less than that of a neutral hydrogen atom plus a free proton, we shall learn that there *is* a bound state. A better trial function can only make the bonding even stronger.

Consider a trial wave function of the form (Griffiths 7.37)

$$\psi = A\left[\psi_g(r_1) + \psi_g(r_2)\right] \qquad (4)$$

where $\psi_g(r)$ is the ground state wave function for a single hydrogen atom with radial coordinate r. This method is called the method of linear combinations of atomic orbitals.

(a) Normalize the trial wave function. That is, follow Griffiths and show how to evaluate the normalization factor A in terms of the variational parameter R and the Bohr radius a. [In parts (a) and (b) of this problem, you should feel free to use Mathematica or MatLab or equivalent to help you with doing integrals.]

(b) Evaluate $\langle H \rangle$. The calculation is set up in Griffiths, and you should present his argument, but you must also fill in the gaps. In particular, you must evaluate the quantities D and X, defined in Griffiths 7.45 and 7.46. (That is, I am asking you to do Griffiths Problem 7.8.) Show, finally, that the total energy of the system is given by (13.6 eV)$F(R/a)$ where the function $F(x)$ is given in Griffiths 7.51.

(c) From the fact that $F(x)$ goes below -1, shown in Griffiths plot (Fig. 7.7), we learn that the energy is less than that of the neutral atom plus a free proton (to wit, -13.6 eV). Minimize $F(x)$ numerically. Hence, estimate the equilibrium separation between the two protons in a hydrogen molecular ion and estimate (give an upper bound on) the binding energy.

[Note: you will find that Figure 7.7 is not drawn very accurately.]

(d) Evaluate the second derivative of F at the equilibrium point. You should do this evaluation numerically.

Relate d^2F/dx^2 to $V'' \equiv d^2V/dR^2$.

You can now use V'' at the equilibrium point to estimate the natural frequency of vibration ω of the two protons in the hydrogen molecular ion, via the relation $m\omega^2 = V''$. Think carefully about what the appropriate m is here, and then evaluate ω, the vibrational frequency.

Estimate how many bound vibrational levels there are.

(e) Suppose that we used a minus sign in our trial wave function:

$$\psi = A\left[\psi_g(r_1) - \psi_g(r_2)\right] \ . \tag{5}$$

Without doing any new integrals (ie just changing the signs in front of some integrals you've already done) find the new function $F(x)$. Plot this $F(x)$ and show that there is no evidence of bonding. Ie there is no R for which $F(r/a) < -1$. [This does not prove that there is no bonding, since the variational method only gives an upper bound, but it certainly does not look promising.]

4. **Tunnelling and the Stark Effect (18 points)**

When we discussed the Stark effect — the physics of an atom in an electric field — we noticed that turning on an electric field meant that the electron in an atom can tunnel out of the atom, making the atomic bound states unstable. I claimed that this was an extremely small effect, which could be neglected. Let us check this, in a simpler one-dimensional analog problem.

Supose an electron is trapped in a one-dimensional square well of depth V_0 and width d:

$$\begin{aligned} V(x) &= -V_0 \text{ for } |x| < d/2 \\ &= 0 \quad \text{for } |x| \geq d/2 \ . \end{aligned}$$

Suppose a weak constant electric field in the x-direction with strength $\mathcal{E}$ is turned on. That is $V \rightarrow (V - e\mathcal{E}x)$. Assume throughout this problem that $e\mathcal{E}d \ll \hbar^2/2md^2 \ll V_0$.

(a) Set $\mathcal{E} = 0$ in this part of the problem. Estimate the ground state energy (ie the amount by which the ground state energy is above the bottom of the potential well) by pretending that the well is infinitely deep. (Because $\hbar^2/2md^2 \ll V_0$, this is a good approximation.) Use this estimate of the ground state energy in subsequent parts of the problem.

[Aside: the true ground state energy is lower than what you've estimated. (You can show this, but that's optional.) This means that the tunnelling lifetime you estimate below is an underestimate.]

(b) Sketch the potential with $\mathcal{E} \neq 0$ and explain why the ground state of the $\mathcal{E} = 0$ potential is no longer stable when $\mathcal{E} \neq 0$.

(c) Use the semiclassical approximation to calculate the barrier penetration factor for the ground state. [You should use the fact that $e\mathcal{E}d \ll \hbar^2/2md^2$ to simplify this part of the problem.]

(d) Use classical arguments to convert the barrier penetration factor into an estimate of the lifetime of the bound state.

(e) Now, lets put in numbers. Calculate the lifetime for $V_0 = 20$ eV, $d = 2 \times 10^{-8}$ cm and an electric field of 7×10^4 V/cm. Compare the lifetime you estimate to the age of the universe.

(f) Show that the lifetime goes like $\exp 1/\mathcal{E}$, and explain why this result means that this "instability" could not be obtained in any finite order of perturbation theory, treating $\mathcal{E}$ as a perturbation to the Hamiltonian.