

Smith College  
Chemistry 331, Fall 2011  
Mr. Linck

## Exercises, Set Two

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### Schroedinger' s Equation and some Simple Solutions, Including the POP and the Harmonic Oscillator

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20.

20.1. Find the value of A for the function

$$\psi(x, t) = A \text{Exp}[-q x^2] \text{Exp}[-i \omega t]$$

that normalizes the function; A, q and  $\omega$  are real and positive constants. Do so at  $t = 0$ . Show that this value is the same at  $t = 10$ . HINT : The function is valid over the range  $-\infty$  to  $\infty$ .

20.2. Show that the function in 20.1. has a probability that is independent of time.

20.3. Let  $q = 0.3$  and  $\omega = 1$ ; find the probability that the particle described by the wave function in 20.1. will be found between  $x = -0.1$  and  $x = 0.1$ .

20.4. You measure the position of the particle described by the wave function in 20.1. and find it to have a negative value of x. Therefore if you make another measurement on an identically prepared system you will find the particle to have a positive value of x since the probability that the particle is to be found between  $x = -\infty$  and  $x = 0$  is 0.5. Comment on these sentences.

20.5. With  $q = 0.3$  and  $\omega = 1$ , calculate the expectation value of  $x$  for the wave function in problem 20.1.

20.6. How do you make sense of that number?

20.7. Using the same parameters, calculate the expectation value of  $x^2$  for the wave function in 20.1.

20.8. How do you make sense of that number?

20.9. Calculate the expectation value of  $-\hbar^2 d^2/dx^2$  for the wave function in 20.1 with the same values of the parameters as in 20.5.

## 21.

21.1. Consider a classical case where the total energy is less than the potential energy. What is the consequence of this? HINT : Total energy is “potential energy plus ..” ?

21.2. This problem isn't hard. Just rewrite SE as instructed! Consider the one dimensional time independent Schrödinger equation. Rewrite the equation so that the only term on the left hand side is the second derivative of  $\psi$  with respect to  $x$ . Now examine a region of space where  $V(x)$  is greater than  $E$  and where  $\psi(x)$  is positive. What can you say about the sign of  $d^2\psi/dx^2$ ?

21.3. If the second derivative of  $\psi$  is positive where  $\psi$  is positive, that means that the change in the slope,  $d\psi/dx$ , is getting larger as  $x$  get larger. If this is true, what, therefore, happens to the magnitude of  $\psi$ ?

21.4. What can you say about normalizing  $\psi$  under the conditions outlined in 21.3.? HINT: Remember normalization gets the area under the product function equal to unity. NOTE: There is a way out of this problem: have  $\psi = 0$  in the stated region.

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**22.**

22.1. Plot the POP wave function for  $n = 2$  and for  $n = 4$  on a pole of length 1.

22.2. Use Mathematica to show that the two wave functions that satisfy the parve on a pole problem,  $\psi_2(x)$  and  $\psi_4(x)$ , are orthogonal to each other.

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**23.**

23.1. Consider a particle (a parve) on a ring with no potential energy. Given that kinetic energy is  $m/(2 v^2)$ , show that the energy can be written as

$$\ell^2/(2 m r^2)$$

where  $\ell$  is the angular momentum, namely  $m^2 v^2 r^2$ .

23.2. If the Schrodinger operator for  $\ell$  is  $(\hbar/i) / \varphi$ , use the expression for the kinetic energy in terms of  $\ell$  to find the operator for the kinetic energy.

23.3. Show that  $\text{Sin}[a \varphi]$  is a solution to Schrodinger' s equation.

23.4. Show that  $\text{Cos}[a \varphi]$  is also a solution.

23.5. For a solution to be suitable (acceptable), the boundary conditions must be satisfied. Show that  $\text{Sin}[a \varphi]$  is a suitable solution if  $a = 1, 2, 3, \dots$  HINT : You will need the relationship that  $\text{Sin}[q + r] = \text{Sin}[q] \text{Cos}[r] + \text{Sin}[r] \text{Cos}[q]$ .

23.6. Show that  $\text{Cos}[a \varphi]$  is a suitable solution if  $a = 0, 1, 2, 3, \dots$  HINT : You will need the relationship that  $\text{Cos}[q + r] = \text{Sin}[q] \text{Cos}[r] - \text{Sin}[r] \text{Cos}[q]$ .

23.7. Normalize your solutions.

23.8. From your solutions, find the expectation value of  $\ell$ .

23.9. Are the eigenfunctions of the energy operator also eigenfunctions of  $\ell$ ?

23.10. Make the following linear combination of eigenfunctions of the energy operator :

$$\psi_1 = (1/\text{Sqrt}[2]) (\text{Sqrt}[1/\pi]) (\text{Sin}[n \varphi] + \text{Cos}[n \varphi])$$

$$\psi_2 = (1/\text{Sqrt}[2]) (\text{Sqrt}[1/\pi]) (\text{Sin}[n \varphi] - \text{Cos}[n \varphi])$$

Show that these linear combinations are eigenfunctions of the energy operator.

23.11. Show that the linear combinations from problem 23.10. are also eigenfunctions of  $\ell$  also.

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**24.**

24.1. We use integration by parts quite often in quantum mechanics. This is based on the relationship of the total differential

$$d(uv) = u dv + v du$$

or

$$u dv = d(uv) - v du$$

which, when integrated gives

$$\int u dv = uv - \int v du$$

where for most cases each integral is a definite integral and the quantity  $uv$  is evaluated as

$$u v (\text{final state}) - u v (\text{initial state})$$

By hand, not with Mathematica, find the integral of  $\ln(x) dx$  between  $x = 1$  and  $x = 2$ .

24.2. Use Mathematica to find the value of the integral from exercise 24.1.

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**25.**

For the parve on a pole problem, show symbolically that two different wave functions (two different  $n$  values) are orthogonal to each other in the parve on a pole problem. HINT : Use an expansion for the product  $\sin(a) \sin(b)$ ; this is not a *Mathematica* problem.

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**26.**

Find the probability that a parve (in the parve on a pole system) is between  $0.4 L$  and  $0.6 L$ , where  $L$  is the length of the pole, if  $n = 1$ ; if  $n = 4$ ; if  $n = 15$ . What is the classical probability?

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**27.**

Evaluate  $\langle x \rangle$ ,  $\langle x^2 \rangle$ ,  $\sigma_x$ ,  $\langle p \rangle$ ,  $\langle p^2 \rangle$ ,  $\sigma_p$ , and the product  $\sigma_x \sigma_p$  for  $n = 7$  for the parve on a pole system.

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**28.**

Solve the parve on a pole problem when the pole is defined to start at  $x = -L/2$  and to end at  $x = L/2$ . HINTS : (1.) As is true in many problems, all the  $\psi$ ' s won' t have the same form. (2.) In contrast to the pole defined from zero to L, one boundary condition won' t reveal daylight; it will take both. (3.) If you get stuck, use your knowledge of the answer—which must be independent of OUR choice of zero to sketch the answers and see if that helps.

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**29.**

29.1. A parve on a pole (of length one, running from  $x = 0$  to  $x = 1$ ) has a potential such that the wavefunction is

$$\psi = (1 - x) \text{Sin}[4 \pi x]$$

A bunch of these systems are prepared; all of them have the potential suddenly removed (to zero). Express  $\psi$  is terms of the eigenfunctions of a parve on a pole with zero potential. HINT : This is the superposition principle in action.

29.2. What is the energy of the system immediately after the potential is removed?

29.3. What is the probability that an energy of  $9 \hbar^2 \pi^2 / (2 m)$  will be measured after the potential is removed?

29.4. What is the energy you get from your expanded wavefunction? How close is it to the initial energy?

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**30.**

30.1. Is the wave function below an acceptable one with respect to the boundary conditions of a parve on a pole of length  $a$ ?

$$\psi(x) = x(a - x)^2$$

30.2. Plot the function.

30.3. What is  $\langle E \rangle$  ?

30.4. Remember in quantum mechanics, as we shall prove when we get to the postulates, any arbitrary function can be expanded as a linear combination of the eigenfunctions of an operator. If  $\varphi_i$  is the  $i$ th eigenfunction, and  $\psi$  is the arbitrary function, we write:

$$\psi = \sum_i c_i \varphi_i$$

Now because the integral of  $\varphi_i \varphi_j$  is zero unless  $i = j$ , the  $c_i$  are given by the integral of  $\varphi_i \psi$ . Write the function of 30.1. as a sum involving the first 10 eigenfunctions of the energy operator for the parve on a pole.

30.5. Plot your expansion to see how close it is to the original function.

30.6. Given this expansion, what is the probability that a measurement will yield a value of the energy of  $\hbar^2 \pi^2 / (2m)$ ? of  $16 \hbar^2 \pi^2 / (2m)$ ?

**31.**

We want to evaluate the expectation value of the energy for a time independent function that is expanded in terms of the eigenfunctions of the Schrödinger equation (for a parve on a pole) with coefficients  $c_n$ . Show that  $\langle H \rangle$  is given by:

$$\sum_n c_n^2 E_n$$

where  $E_n$  are the energies of the wave functions in the expansion.

**32.**

Imagine the time independent wave function for a system is give by the equation

$$\psi = A \text{Exp}[-a r]$$

where  $A$  and  $a$  are constants and  $r$  is the variable. What does the time dependent function look like? Answer this question generally, not specifically.

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**33.**

33.1. If you have  $d\psi/dx = -6x$  and a condition that  $\psi$  at  $x = 0$  is 3, what does the function  $\psi$  look like between  $x = 0$  and  $x = 1$ ? HINT : This is an old fashion integration problem.

33.2. *Mathematica* has a function that solves differential equation problems numerically. It is called NDSolve. It was topic 15 in our introduction to M. Show that it works on the equations in 33.1.

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**34.**

34.1. Use NDSolve to make a graph of the solution to a parve on a pole with  $\hbar = 1$ ,  $L = 1$ , and  $m = 1$  for the ground state. HINT: Your NDSolve system should include Schrodinger' s equation for the system as well as the two starting conditions,  $\psi[x = 0]$  equals something and  $\psi' [x = 0]$  equals something. This problem is important because we will use the procedure in lots of cases this semester.

34.2. Try the same for an energy in excess of 100 in the units with  $\hbar = 1$  etc.

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**35.**

35.1. A “ pole”(starting at  $x = 0$  and going to  $x = \text{Infinity}$ ) has a potential that raises smoothly from  $x = 0$  according to the law:

$$V = 2x$$

Find the lowest level wave function for this situation using numerical methods. HINT: Continue to use the atomic units of  $\hbar = 1$ ,  $m = 1$ .

35.2. For the potential in 35.1., find some excited level wavefunction and its energy. HINT : I tried something in the range of 25 for energy, which was a too high.

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**36.**

36.1. You have a potential defined by the equation:

$$V = (5 (1 + \text{Exp}[-x])) + \text{Exp}[-3 x] - .778141$$

with  $V = 0$  at  $x < 0$ . Find the lowest energy level using numerical techniques with  $\hbar$  and  $m = 1$ . NOTE : The term at the end is just to make the lowest potential energy value equal to zero. HINTS : What must be true of  $\psi(x)$  at  $x = 0$ ? Use an  $x$  range of 0 to 10 as the barrier on the right hand side is rather small.

36.2. Find the expectation value of  $x$  for your answer to 36.1.

36.3. Find the value of  $x$  for which  $V$  is a minimum.

36.4. Why do your answers for 36.2. and 36.3.differ?

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**37.**

We have a parve on a pole with length = 1.0 in which the potential energy is zero from  $x = 0$  to  $x = 0.8$ . For  $0.8 \leq x \leq 1.0$  the potential is  $V$ . Find the first three energy levels for  $V = 0$  (trivial), 5, 20, and 80 units (when  $\hbar$  and  $m$  are set equal to unity) -- that is, you have to do nine problems: Feel free to work with others on this problem as there are lots of very similar calculations; but be sure each one in your group can do any given part of the problem. Be able to give a verbal account of what your wave functions look like.

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**38.**

We want to find the probability that a particle will be between  $0.4 L$  and  $0.6 L$  in the ground state and in the second excited state (two separate calculations) for the following potential energy situation:  $V$  is infinity for  $x < 0$  and  $x > L$ .  $V$  is 0 for  $0 < x < 0.4 L$  and  $0.6 L < x < L$ . For the intermediate area,  $0.4 L < x < 0.6 L$ ,  $V$  is 250. Let  $\hbar = 1$  and  $m = 1$ . Before you quit Mathematic after doing this problem, remember that doing problem 39. in the same sitting is useful. HINT: Remember to make “conditionalplots” we use the underscore definitions in M. See original hints sheet, number 13.

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**39.**

Let's look at the consequences of the barrier in the last problem. You have the energies (and therefore the numerical wavefunctions) for the first two levels. [HINT : In Mathematica, you might want to name these differently, say  $\psi[x]$ , and  $z[x]$ , although since we have to refer to them by their " Out[#] anyway, it is not absolutely necessary.] I worked out the energies for the next two : 97.292 and 99.13 in the units of the last problem. You can therefore find these numerical wavefunctions; name them differently from the first two. So you have four wavefunctions on your machine, located at various " Out[76] type locations. [HINT : you have to do this problem in one sitting; closing Mathematica deletes these numerical values.] Here's the problem: Write an analytical solution for a parve trapped in the left side of the box at time zero. You can expand that in terms of the four numerical functions at time zero. [HINT: Be careful of your limits on integration.] Now look at the probability distribution generated by that wavefunction at zero time. Add the appropriate time dependency to each of the functions to get an approximation to the time dependent wavefunction (Why just an approximation?) and look to see what happens to the probability as a function of time. HINT: Take 1, 2, and 4 as your time intervals, remembering that we have defined  $\hbar = 1$ .

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**40.**

40.1. Consider a potential **well** running from - 1 to 1. Solve the system for the right side ( $x = 0$  to  $x = 1$ ) for even functions (i.e.,  $\psi$  some positive number at  $x = 0$ ) of this potential well numerically (using NDSolve). Let  $m = 1$ ,  $\hbar = 1$ , and  $V = -100$ . HINT: you know the answers from class. Also, think carefully about the boundary conditions that you put on the problem.

40.2. Is there tunneling?

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**41.**

Let a particle of mass  $m$  start on the left half of a pole of length  $L$  with a wave function at  $t = 0$  in which the probability is constant between 0 and  $L/2$ . Find  $\psi(x, t) = \psi(x, 0)$ , normalize it, and obtain the probability that a measurement of the energy would yield a value of  $\pi^2 \hbar^2 / (2 m L^2)$

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42.

For a free particle determine the relative probability of finding the particle between  $x = -11$  and  $x = -10$  compared to finding it in the region  $x = 0$  to  $x = 1$ .

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43.

For the step potential ( $V = 0$  when  $x < 0$  and  $V = V_+$  for  $x > 0$ ), and  $E$  of the incoming free particle less than  $V_+$  determine the wave function valid in the region  $x > 0$ . How does this compare to the classical situation?

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44.

For the parve in a finite potential well (potential =  $-V$  for  $-a \leq x \leq a$ ; potential equal to zero otherwise; and since the parve is in the well,  $E < 0$ ) determine the equations that need to be solved to find the solutions for the odd functions. You don't have to solve them.

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45.

Plot the function  $\psi = \text{Exp}[-x^2/2]$ .

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46.

Use numerical techniques to plot the wavefunction for a harmonic oscillator in the first excited level. HINTS : Use the S.E. in "q" form and solve for  $E/(\hbar \omega)$ .

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47.

47.1. Show that for the function  $f = a_0 + a_1 q + a_2 q^2 + a_3 q^3 + \dots$  that

$$q \, df/dq = \sum_n n a_n q^n$$

47.2. Also show that

$$d^2f/dq^2 = \sum_{n=2} n(n-1) a_n q^{n-2}$$

**48.**

- 48.1. Find the relative coefficients of the  $q$ ,  $q^3$ , and  $q^5$  terms for  $K = 11$  in the Hermite polynomials.
- 48.2. Write an appropriate (non - normalized if you wish) wave function for the harmonic oscillator for  $E = (11/2) (\hbar \omega)$ .
- 48.3. Plot the function.

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**49.**

- 49.1. Normalize the function for the harmonic oscillator in the second excited state (with  $n = 2$ ) for which the Hermite polynomial is  $(4 q^2 - 2)$ .
- 49.2. Plot the normalized  $\psi$  versus  $q$ .
- 49.3. Plot the probability distribution.
- 49.4. What is the expectation value that the oscillator will be found with a value of  $q$  between  $- 0.125$  and  $0.125$ ?
- 49.5. What is the expectation value that the oscillator will be found with a value of  $q$  between  $0.5$  and  $0.75$ ?
- 49.6. Do your answers to exercises 49.4. and 49.5 make sense? Explain.

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**50.**

50.1. The harmonic oscillator system we have been working with has the mass of the object in it; one object. When dealing with two atoms, the appropriate mass is called the reduced mass, defined by

$$1/\mu = 1/m_1 + 1/m_2$$

If the force constant for the C - O bond in CO is  $1.1 \times 10^3$  N/m, evaluate  $\omega$ . HINT : Don' tforget 12 g/mole is not 12 g/molecule.

50.2. Find the value of the classical turning point for the  $n = 2$  level for CO.

50.3. Calculate the wave number for the transition from  $n = 0$  to  $n = 1$  for CO.

50.4. Compute the value of  $q$  for the turning point from your data in exercise 50.2.

50.5. Find the probability of the CO molecule being outside the classical turning point region; that is, stretched or compressed past the classical turning points.

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**51.**

You have an analytically derived solution for  $\psi$  with  $n = 4$  for the harmonic oscillator. Find  $\psi_4$  numerically. Normalize both and show that the integral of their product is unity, establishing that they are the same function.

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**52.**

Use the wave function for the harmonic oscillator,  $n = 3$ , derived with the dummy variable  $q$  and find the  $\langle x \rangle$ ,  $\langle x^2 \rangle$ ,  $\langle p \rangle$ ,  $\langle p^2 \rangle$ ,  $\sigma_x$ , and  $\sigma_p$  for CO — See exercise 50. Also determine the product  $\sigma_x \sigma_p$  and verify the uncertainty principle. HINT : For  $n = 3$ , we have the un - normalized function

$$\psi = (8 q^3 - 12q) \text{Exp}[-q^2/2]$$

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**53.**

Find  $\langle p^2 \rangle$  for a harmonic oscillator in the  $n = 0$  and  $n = 2$  (two separate calculations, which, if I were you, I would use Mathematica to do). Comment on any differences that you find.

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**54.**

54.1. A Morse potential is a more realistic potential curve than that of the harmonic oscillator. The Morse curve is given by

$$V = p (1 - \text{Exp}[-a (x - x_0)])^2$$

Plot this function for a value of  $p = 30,000 \text{ cm}^{-1}$ ,  $x_0 = 1.45 \text{ \AA}$  and  $a = 2.5 \text{ \AA}^{-1}$ .

54.2. Qualitatively, how would you expect the energies and the wave functions for this system to differ from those of the harmonic oscillator?

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**55.**

We have two harmonic oscillators of the same reduced mass. One with a  $k$  of 350 N/m, the other with a  $k$  of 720 N/m. How do the potential energy curves differ? What can you say about the energy levels of the two oscillators? Solve this by thought, not with Mathematica or, indeed, with mathematics.