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## Worksheet 1: Schrödinger equation

For nearly the rest of the semester, we will be studying a famous equation and its solutions because they are very important for chemistry. This equation, the Schrödinger equation, is a differential equation. In this worksheet, we explore the meaning of the Schrödinger equation and nature of its solutions. We are not concerned with how to solve the equation or with complicated mathematics. The goal is to begin to understand what the equation means and what its solutions have to do with the physical world.

To keep things simple, we will stick to one dimension. There are two forms of the Schrödinger equation, and in one dimension they are:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \quad (1) \qquad -\frac{\hbar^2}{2m} \frac{d^2\Psi(x,t)}{dx^2} + V(x)\Psi(x,t) = i\hbar \frac{\partial\Psi(x,t)}{\partial t} \quad (2)$$

### Critical Thinking Questions

1. How are the two equations alike? How are they different? We use different names for the two equations. What are they (check the text)?
2. The  $\hbar$  is just a constant. Figure out what it is (look in your text or Google “h bar”).
3. E represents the total energy, and V(x) represents the potential energy. Why do we write V(x)? What would it mean if we wrote V(x,t)? (That is actually possible, but we won't encounter a time-dependent V in our problems.)
4. What do you think the unknowns usually are in the two equations?
5. Think of an example from the physical world that illustrates the difference between  $\psi(x)$  and  $\Psi(x, t)$ . Hint: think of waves on the ocean.
6. What properties of a particle depend on time? What properties are independent of time? (You might picture the moon orbiting the earth, but imagine moon and earth to be very small. The moon would represent a “particle.”)
7. What properties of a wave are independent of time? What properties depend on time? Try to draw a sketch that illustrates a “time-independent wave” (think “frozen wave”), and a sketch that illustrates a “time-dependent wave” (think wave traveling across the ocean).
8. Electrons are responsible for many of the properties of atoms and molecules. Think for example of the electrons surrounding the nucleus, or in covalent bonds. What properties of the electrons is it important to know if you want to understand the properties of an atom or molecule? What properties of the electrons do you not really need to know?

9. If  $E\psi(x)$  represents total energy times  $\psi(x)$ , and  $V(x)\psi(x)$  represents potential energy times  $\psi(x)$ , what do you think  $-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2}$  represents? What, if anything, about your answer is weird or confusing?

10. The classical equation for a wave can be written:

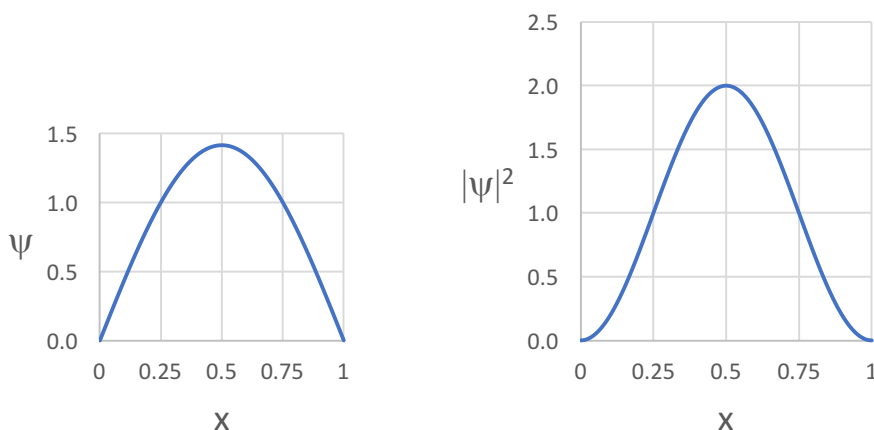
$$c^2 \frac{d^2 u(x, t)}{dx^2} = \frac{d^2 u(x, t)}{dt^2}$$

You can see several differences between this and eq. (2) at the top. If you had to identify one of the difference as the most significant one, which would it be? Why?

## Worksheet 2: Born Interpretation

One postulate of quantum mechanics is that the wave function,  $\psi$ , contains all the dynamical information about the system. Probably the most important piece of information is position: where is the “system” located (one of the simplest systems is a single particle, so just picture a particle)? Born hypothesized that the probability that the system is located at position  $x$  is proportional to  $|\psi(x)|^2$ , which is called the probability density. This worksheet explores what  $|\psi(x)|^2$  means and how it is used to describe location.

Consider the graphs of  $\psi$  and  $|\psi|^2$  show below.



According to the Born postulate, the probability of finding the particle described by  $\psi$  within an infinitesimally small region of length  $dx$  and centered about the point  $x$  is  $|\psi|^2 dx$ .

### Critical Thinking Questions

1. How many times as likely is it to find the particle at the point  $x = 0.50$  compared to the point  $x = 0.25$ ? Estimate by reading off the appropriate graph.
2. Explain in grammatical English why  $|\psi(x)|^2$  is called a “probability density.” Why is the term “density” used? Can you make an analogy with other physical quantities?
3. Why did Born postulate this particular relationship? That is, why would he use the absolute value, and why would he use the power of two? Remember that this was a postulate; Born did not derive the relationship from “first principles.”

### Exercises

1. For the graphs shown above, the equation for  $\psi(x)$  is:  $\psi(x) = (2)^{1/2} \sin(\pi x)$ . The following simple calculations should help you understand the Born postulate better:

- (a) Determine a simple, approximate expression for the probability of finding the particle within a very short line segment centered about  $x = 0.25$  and having length  $\delta x$  (we use  $\delta$  to mean very small but not necessarily infinitesimal).
- (b) Show that your answer for C.T.Q. 1 was correct by comparing the probability of finding the particle in a tiny line segment centered about  $x = 0.50$  with the probability you found in part (a) for a tiny line segment centered about  $x = 0.25$ . You should assume, of course, that the line segments have the same length.
- (c) The particle has to be found somewhere, and in this example, it is confined to the region between 0 and 1. Show that the total probability of finding the particle anywhere within this region is exactly one. What does it mean for the probability to be one?
- (d) Calculate the probability of finding the particle within the region  $x = 0.25$  and  $x = 0.75$ .

### Worksheet 3: Constraints on allowable wavefunctions

The Born interpretation puts a constraint on allowable wavefunctions (i.e. wavefunctions that can describe actual, physical systems):

$$\int_{\text{all space}} |\psi|^2 d\tau = 1 \quad \text{or} \quad \int_{-\infty}^{+\infty} |\psi|^2 dx = 1$$

(in general)

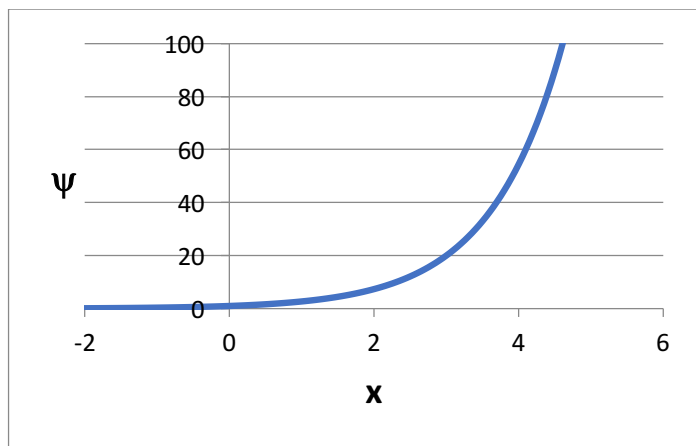
(for a real wavefunction in one dimension:  
we will think about these for simplicity)

The curious thing is that if a particular wavefunction ( $\psi_1$ ) solves the Schrödinger equation, so does any multiple of this wavefunction ( $\psi_2 = N\psi_1$ ) (test this out). But there is only one value of  $N$  that makes  $\int_{-\infty}^{+\infty} |\psi_2|^2 dx = 1$ . Only this value of  $N$  gives a  $\psi_2$  that can describe an actual, physical system. In other words, most of the solutions of the Schrödinger equation do not describe actual, physical systems! After we obtain a solution, we have to determine the value of  $N$  needed to describe an actual, physical system. This process is called “normalization.”

The process of normalizing a solution of the Schrödinger equation is covered elsewhere. It is a straightforward mathematical process. Here we want to consider the kinds of solutions of the Schrödinger equation that can be used to describe actual, physical systems. One criterion, obviously, is that it must be possible to normalize the solution. But that is not the only criterion. Here we explore all the criteria. As you consider the questions, let logic be your guide.

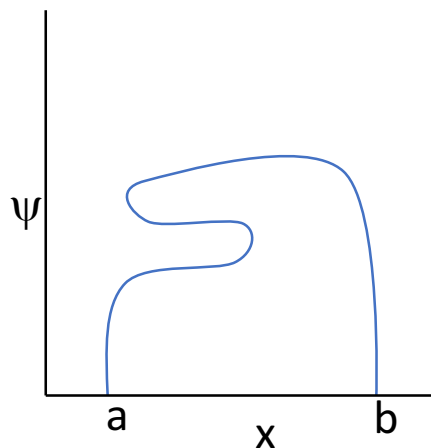
A note on usage: in practice, scientists often use  $\psi(x)$  to mean any solution to the Schrödinger equation, and yet they ALSO use  $\psi(x)$  to mean a normalized solution to the Schrödinger equation that can represent an actual, physical system. Scientists don't usually bother to write  $\psi_1(x)$  for the unnormalized wavefunction and  $\psi_2(x)$  for the normalized wavefunction. They just figure it is obvious what they mean by  $\psi(x)$  from the context. We will usually do the same thing in this class, so you will need to figure out whether we are talking about an unnormalized or a normalized  $\psi(x)$  from the context.

### Critical Thinking Questions



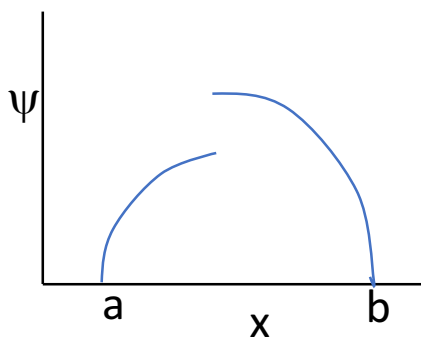
$$\psi(x) = e^x \text{ and the range is } -\infty \leq x \leq +\infty$$

1. Consider the function shown above. Suppose it solves the Schrödinger equation. Can it be normalized to represent an actual, physical system? Why or why not?



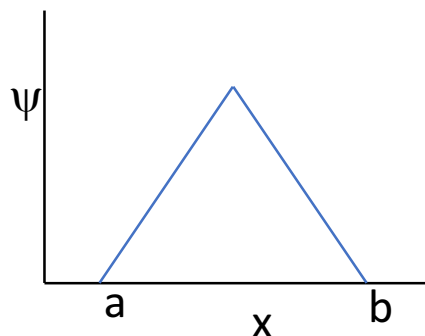
a and b can be any convenient numbers,  $\psi = 0$  for  $x < a$  and  $x > b$ ,  
and the scale is arbitrary

2. Consider the function shown above. Suppose it solves the Schrödinger equation. Can it represent an actual, physical system? Why or why not?



a and b can be any convenient numbers,  $\psi = 0$  for  $x < a$  and  $x > b$ ,  
and the scale is arbitrary

3. Consider the function shown above. Can it solve the Schrödinger equation and represent an actual, physical system? Why or why not?



$a$  and  $b$  can be any convenient numbers,  $\psi = 0$  for  $x < a$  and  $x > b$ ,  
and the scale is arbitrary

4. Consider the function shown above. Can it solve the Schrödinger equation and represent an actual, physical system? Why or why not?
5. Based on the examples you just considered, construct a list of rules that describe the kinds of functions that can describe actual, physical systems (assuming the functions also solve the Schrödinger equation).



## Worksheet 4: Operators and eigenvalue equations

[This worksheet should be preceded by a short lecture on operators and eigenvalue equations.]

Operator notation provides a convenient way to represent various mathematical operations and to combine them. We usually represent an operator by a variable with a circumflex, e.g.  $\hat{\Omega}$  or  $\hat{x}$ . An operator “operates” on a function via some mathematical operation, and we get to define just what it is for our operator. Here are a few examples:

<u>Operator symbol</u>	<u>Operation</u>	<u>Definition</u>	<u>Result of operator acting on function <math>f(x)</math></u>
$\hat{\Omega}_1$	$5 \cdot$	multiplication by 5	$5f(x)$ $[\hat{\Omega}_1 f(x) \rightarrow 5f(x)]$
$\hat{\Omega}_2$	$x \cdot$	multiplication by $x$	$xf(x)$ $[\hat{\Omega}_2 f(x) \rightarrow xf(x)]$
$\hat{\Omega}_3$	$\frac{d}{dx}$	differentiation wrt <sup>1</sup> $x$	$\frac{df}{dx}$ $[\hat{\Omega}_3 f(x) \rightarrow \frac{df}{dx}]$
$\hat{\Omega}_4$	$\sqrt{\quad}$	square root	$\sqrt{f(x)}$ $[\hat{\Omega}_4 f(x) \rightarrow \sqrt{f(x)}]$

We need to define how operators “associate.” Here are the definitions:

$$\text{Addition: } (\hat{A} + \hat{B})f(x) = \hat{A}f(x) + \hat{B}f(x)$$

$$\text{Multiplication: } \hat{A}\hat{B}f(x) = \hat{A}(\hat{B}f(x))$$

### Critical Thinking Questions

1. Suppose  $f(x) = e^{2x}$ . Evaluate  $\hat{\Omega}_1 f(x)$  and  $\hat{\Omega}_3 f(x)$ .
2. Again, suppose  $f(x) = e^{2x}$ . Does  $\hat{\Omega}_1 \hat{\Omega}_2 f(x) = \hat{\Omega}_2 \hat{\Omega}_1 f(x)$ ? Does  $\hat{\Omega}_2 \hat{\Omega}_3 f(x) = \hat{\Omega}_3 \hat{\Omega}_2 f(x)$ ? (Evaluate all the expressions to decide.)
3. If  $\hat{A}\hat{B}f(x) = \hat{B}\hat{A}f(x)$ , we say that  $\hat{A}$  and  $\hat{B}$  “commute.” What do you conclude about the operators  $\hat{\Omega}_1$ ,  $\hat{\Omega}_2$  and  $\hat{\Omega}_3$ ?
4. If it is true that  $\hat{\Omega}(f(x) + g(x)) = \hat{\Omega}f(x) + \hat{\Omega}g(x)$ , we say that the operator is “linear.” Consider  $\hat{\Omega}_1$ ,  $\hat{\Omega}_2$ ,  $\hat{\Omega}_3$  and  $\hat{\Omega}_4$ : which are linear operators and which are nonlinear? [In this course, we will mainly be considering linear operators.]

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<sup>1</sup> wrt means “with respect to”

## Worksheet 5: Eigenvalue equations

An eigenvalue equation is a special kind of equation involving operators:

$$\widehat{\Omega}f(x) = \omega f(x)$$

where  $\omega$  is a number. That is,  $\omega$  is not a function of  $x$ , but rather just a number, that is, some fixed value. If  $\omega$  is not just a number, the equation is not an eigenvalue equation. When  $\omega$  **is** a number,  $f(x)$  is a special kind of function that, in a sense, goes together with the operator  $\widehat{\Omega}$  and the eigenvalue  $\omega$ . We call  $f(x)$  an eigenfunction of the operator  $\widehat{\Omega}$ , and we say that  $\omega$  is the eigenvalue of  $\widehat{\Omega}$  that corresponds to the eigenfunction  $f(x)$ . (If  $\omega$  is not a number,  $f(x)$  is not an eigenfunction.) We will see that eigenvalue equations are very important for quantum mechanics. Right now, the goal is just to understand to get used to them.

### Critical Thinking Questions

1. Suppose  $\widehat{\Omega}_1 = \frac{d}{dx}$  and  $f(x) = e^{2x}$ . What is the eigenvalue of  $\widehat{\Omega}_1$  that corresponds to the function  $f(x)$ ?
2. Suppose again that  $\widehat{\Omega}_1 = \frac{d}{dx}$ . Consider the function  $g(x) = \sin(x)$ . Is  $g(x)$  an eigenfunction of  $\widehat{\Omega}_1$ ?
3. Consider your answers to CTQs 1 and 2. What do you conclude about operators and functions?
4. Consider the operator  $\widehat{\Omega}_2 = \frac{d^2}{dx^2}$ . Are  $f(x)$  and  $g(x)$  eigenfunctions of  $\widehat{\Omega}_2$ ? If so, what are the corresponding eigenvalues?
5. Consider your answer to CTQ 4. What do you conclude about operators, eigenfunctions, and eigenvalues? List as many things as you can.

## Worksheet 6: Quantum mechanical operators and observables

Observables are properties that can be measured. One of the postulates of quantum mechanics is that each observable corresponds to a quantum mechanical operator. The two fundamental operators are:

<u>Observable</u>	<u>Operator symbol</u>	<u>Operation</u>	<u>Description</u>
Position	$\hat{x}$	$x \cdot$	Multiplication by $x$
Momentum	$\hat{p}_x$	$\frac{\hbar}{i} \frac{d}{dx}$	$\frac{\hbar}{i}$ times derivative with respect to $x$

Operators corresponding to other observables can be created from these. The way to do so is to write the classical form of the observable in terms of position and momentum, and then substitute the quantum mechanical operators above for the classical position and momentum.

For more dimensions, form corresponding operators by analogy. For example, the operator for position along the  $y$ ,  $\hat{y}$ , represents the operation  $y \cdot$  (multiplication by  $y$ ).

If the wavefunction is an eigenfunction of the operator in question, a measurement of the corresponding observable will return an eigenvalue of the operator. (Sometimes the wavefunction is not an eigenfunction of the operator; we will deal with such situations later).

### Critical Thinking Questions

1. Explain the difference between the variable  $x$  and the operator  $\hat{x}$  in plain English.
2. Suppose the wavefunction for the system is  $\psi(x) = e^{ikx}$ . If the momentum is measured, what value will be found, in terms of  $k$ ? For an electron traveling at one tenth the speed of light,  $k = 2.6 \times 10^{11} \text{ m}^{-1}$ . What is momentum of the electron?
3. The classical expression for kinetic energy (in one dimension, which we call  $x$ ),  $T_x$ , is  $T_x = \frac{1}{2}mv_x^2$ . Show that  $T_x$  can be rewritten as  $T_x = \frac{p_x^2}{2m}$  and determine the operator for kinetic energy,  $\hat{T}_x$ .
4. If the system is in the same state as in CTQ 2 (i.e. using the same wavefunction), and the kinetic energy is measured, what value will be observed? Does this make sense, given the value for momentum from CQT 2?
5. What is the operator for the total kinetic energy,  $\hat{T}$ , in two dimensions,  $x$  and  $y$ ?
6. For rotation in the  $xy$  plane, the angular momentum is represented as a vector pointing in the  $z$  direction. The classical value for  $J_z$  is  $J_z = xp_y - yp_x$ . What is the quantum mechanical operator for angular momentum,  $\hat{J}_z$ ? ( $J_z$  and  $\hat{J}_z$  can also be written in polar coordinates, but we will do that later.)

**Looking Ahead**

1. Suppose the system is in a state corresponding to the wavefunction  $\psi(x) = \sin(kx)$ . Can we predict the result of measuring the momentum,  $p_x$ ? If this confusing, why is it?