Dr. Hawker

Chem 108

Solving the 1D Schrodinger Equation

*Adapted from K. Closser based on materials by M. Lopez del Puerto, "Using the Finite-Difference Approximation and Hamiltonians to solve 1D Quantum Mechanics Problems," Published in the PICUP Collection, May 2017.*

Submit answers to the attached questions. You will need the MATLAB live script provided in Canvas, but you do not need to submit it with your results.

***Background***

The time-independent Schrödinger equation is a powerful and fundamental component of quantum mechanics.

Solutions to the equation are the wavefunctions (which give all properties of a system) and energies. However, there are only a few situations where the Schrödinger equation can be solved directly. In most cases, it must be solved numerically using a computer. In this problem set, you will explore some simple 1D problems and compare the numerical solutions to the exact solutions.

***Particle in a Box***

The simplest problem where the Schrödinger equation can be applied is for a system known as the particle in a box. The particle can move along the line in one dimension, and the potential energy is 0 within the box and infinite everywhere else.



Shape of the Potential Energy Well

The Hamiltonian for this system is thus purely kinetic energy within the region of the box and has the form of a second derivative

The wavefunctions that satisfy this equation have the general form (with *A*, *B* and *k* constants):

In order for the wavefunction to be valid, it must be finite and go to 0 at each of the boundaries, thus

And

If *A* were to equal 0, this would be trivial, and the particle would not actually exist, so assuming this is not the case, we must have and thus, or where *n* is an integer.

Thus, the solution becomes

The constant *A* is arbitrary, and can be chosen for the wavefunction to be normalized (meaning that

Thus, the final normalized wavefunction is

1. Show that the eigenvalues for this wavefunction are . Apply the Hamiltonian to the normalized wavefunction and solve for the multiplier. Note .
2. Determine exact energies for the first 5 states of a 1 nm box and report them here. Hint: It will be easier to answer the rest of the questions if you compute them as prompted in MATLAB.
3. How do the energy levels change as *n* increases? Include a sketch.
4. How do the energy levels change as the size of the box decreases? Include a sketch.

When solving the Schrödinger equation numerically, functions must be discretized (turned into a set of x values, and the function computed for these). Don’t worry too much about how this is done, but consider how the results are affected by using different numbers of points.

1. What is the percent error in the energy of the first state when the number of points used is 10, 100 and 1000? How many points are needed to have an error < 1%?
2. Consider the resulting wavefunctions as well, what happens to the approximate wavefunctions as the number of points *N* is increased?
3. What is the most probable position for a particle in the ground state (*n*=1--note this is different from *N*)? Sketch the probability curve.
4. What effect does increasing the quantum number *n* have on the wavefunction? What happens to the probability in the limit of very high values for *n*? Sketch the curve.
5. Define a node. What is the relationship between the number of nodes in the wavefunction and the quantum number *n*?
6. Although crude, the particle in a box model can be applied to conjugated bond systems to approximate their energy levels. Explain why the particle in a box is a reasonable approximation for a conjugated system (use organic chemistry knowledge). How does the number of conjugated bonds affect the energy?

***Particle in a parabolic well***

Solutions are also included in the MATLAB script for the particle in a parabolic well. Here the Hamiltonian has the form

Where the potential energy . This model is also exactly solvable, but the solutions are somewhat more complicated a special class of polynomials that will be discussed further in class. The energy levels are found to be

1. How do the energy levels in this system differ from those of a particle in a box (especially consider the spacing).
2. How do the wavefunctions differ from those of a particle in a box? Do you notice anything odd about them?
3. How do the energy levels change asthe width of the parabola decreases? Include a sketch.
4. The lowest energy state is known as the ground state. Can this system ever have an energy of 0? If so under what circumstances? If not, explain why not.