PHYSNET

MISN-0-245

NUMERICAL DEMONSTRATION
OF ENERGY QUANTIZATION
FOR ATOMIC HYDROGEN

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by
Peter Signell

Title: **Numerical Demonstration of Energy Quantization for Atomic Hydrogen**

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Input Skills:

1. Vocabulary: ground state, energy quantization (MISN-0-215), Bohr energy, Bohr radius (MISN-0-309), boundary conditions (MISN-0-232), radial probability density (MISN-0-250), coulomb potential (MISN-0-116).
2. State the finite difference approximation for the second derivative. (MISN-0-4).
3. Sketch the energy levels of atomic hydrogen, roughly to scale (MISN-0-215).

Output Skills (Knowledge):

K1. Vocabulary: normalization, normalization factor, normalized wave function, radial Schrödinger equation, radial wave function, 3-point recurrence relation, net-point notation.

K2. Given the general radial Schrödinger equation for zero angular momentum, derive a 3-point recurrence relation for the radial wave function.

K3. State the boundary conditions on the radial wave function at the origin and at infinity and give the reasons for them.

Output Skills (Project):

P1. Use your own computer output and pre-prepared graphs to illustrate that the radial wave function satisfies the boundary conditions on it only at isolated energies.

External Resources (Required):

1. A microcomputer with BASIC (see attached Local Guide); graph paper.

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1. Introduction

1a. Numerical Solutions Are the Rule. Numerical solutions to the powerful Schrödinger equation form the backbone of atomic and molecular physics, virtually all of theoretical chemistry, most of nuclear and solid-state physics, and some of elementary particle physics. Formal mathematical solutions are known for only a few simple cases, but computer-generated numerical solutions are now covering a wide variety of cases. The range of applicability and the accuracy achieved have depended upon both the power of the computers and upon the ingenuity and insight which have gone into devising the numerical-solution algorithms (recipes).

1b. The Solution Gives All Observable Properties. Once the Schrödinger equation has been set up and solved for a particular system, all observable (measurable) properties of the system can be calculated from that solution. For example, the hydrogen atom solution is all one needs in order to calculate atomic hydrogen's electric susceptibility and dielectric constant, as well as the electron's spatial distribution within the atom.

1c. The "Closeness" Criterion. The requirement that the hydrogen atom's electron must be somewhere near the proton is a powerful condition on the physical acceptability of various radial Schrödinger equation solutions, $u(r)$.[1] Here r is the radial distance of the electron from the proton. Any solution, $u(r)$, is called a "radial wave function." From it we can compute the radial probability density, $|u(r)|^2$. For energies not at the values that occur in nature, the wave functions $u(r)$ produce an infinite probability that the electron is an infinite distance from the proton and this certainly violates the "near the proton" requirement! The situation is typically as shown in Fig. 1, where we show solutions u and the associated probability densities $|u(r)|^2$ at a series of energies. In the

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[1]See "Quantum Tunneling Through a Barrier: Pictures, Probability, Flow, Personal Reaction" (MISN-0-250) and "The Schrödinger Equation in One Dimension: Quantization of Energy" (MISN-0-242).
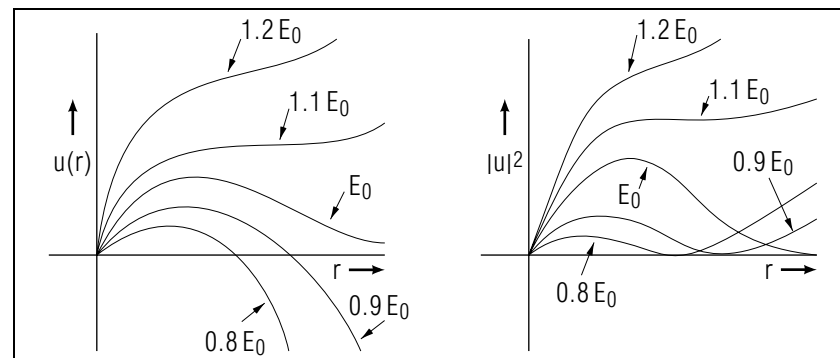
Figure 1. A rough sketch of solutions u to the Schrödinger equation for the hydrogen atom at a number of nearby energies. Also shown is the probability density function $|u(r)|^2$.

small energy range shown, only at the precise energy E_0 does the density not approach infinity as the radius approaches infinity. Only at that energy can the electron be said to be "near" the proton. That energy is the only one observed for hydrogen, in that energy range, in the chemistry lab. It is called a "physical energy." Experiment and theory agree!

1d. The Normalization Condition. The energies between the physical ones for the hydrogen atom have an infinite probability density for finding the electron at infinity and that implies an infinite probability for finding the electron somewhere in all of space. That is clearly ridiculous: the probability for finding a real electron somewhere in all of space is one (100%).[1] Therefore the mathematical solutions corresponding to energies between the physical ones are ruled out by this so-called "normalization" condition. Our procedure thus breaks down into three steps:

1. finding mathematical solutions;

2. rejecting solutions that cannot meet the normalization requirement; and

3. noting that the remaining "physical" solutions are only at discrete energies which in fact agree with experiment.

Figure 2. Values of $u(n\Delta)$ obtained from Eq. (1), connected by a smooth curve.

2. The General Method

2a. Recurrence Relation Method. The general approach we will use is to start from zero radius, where all mathematical solu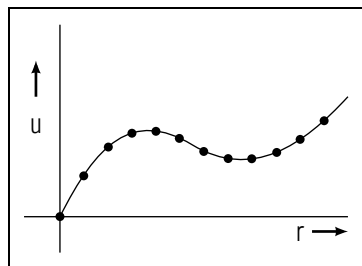tions are the same, and use our Schrödinger equation with some guessed-at energy to form the solution as we move outward radially. The movement outward from the origin is in small radial steps Δ. We move outward step by step, with step size Δ, using a 3-point "recurrence" relation (meaning a recurring mathematical relation):

$$u(r + \Delta) = g(r)\, u(r) - u(r - \Delta), \qquad (1)$$

where $g(r)$ contains the information from the Schrödinger equation.

Using Eq. (1), and given the solution u at $r = 0$ and $r = \Delta$, we can find it at $r = 2\Delta$. Then, knowing it at Δ and 2Δ, we can find it at 3Δ, etc. The end result of this iterative process is values for u at evenly spaced values of r. We plot these values on a graph of u versus r. We number the radial points in order from the origin and call them "radial net points." We draw a smooth curve connecting the u values at these points and the solution is finished (see Fig. 2). We then choose a new value of E and repeat the whole process to get another solution. After a number of solutions have been plotted, we examine them to see which ones do and which ones do not obey the normalization condition.

2b. A Computer does the Boring Part. A computer program is used to calculate $g(r)$ of Eq. (1) at any one radial net point, then use that $g(r)$, plus $u(r)$ and $u(r - \Delta)$, to calculate the solution $u(r + \Delta)$ at the next radial net point, then iterate the process outward automatically. The program must be given:

1. appropriate starting values for $u(0)$ and $u(\Delta)$;

2. instructions on how to calculate $g(r)$ from the Schrödinger equation;

3. instructions to print or display the solution at each net-point; and

4. when to stop.

We have already constructed such a program for you. You need only push a few keys, but you can do more than that if you wish.

2c. Rejecting Solutions Means Rejecting Energies. Each mathematical solution to the radial Schrödinger equation is for a specific value of energy: rejecting solutions which do not obey the normalization condition means rejecting the energies used in generating those solutions. The energies and solutions that remain constitute a series of "allowed" energies and solutions: these will be the only ones actually observed in nature or in the chemistry lab. The only allowed solutions are found to be at isolated points along the energy scale. The (continuous) energies between these points are all forbidden since their corresponding mathematical solutions are not normalizable. These forbidden energies are not found in real hydrogen atoms.

The allowed energies form a discrete set and so the energy is said to be "quantized." We are demonstrating how the phenomenon of quantization arises in the solving atomic theory. Finding the entire set of energies for an atom, using numerical methods, is discussed elsewhere.[2]

3. The Algorithm

3a. The 3-Point Recurrence Relation: Derivation. We are trying to solve the radial Schrödinger equation as a function of the electron-proton distance r in a single hydrogen atom. This is really a two-body problem, so the mass going into the radial Schrödinger equation should be given by $m = m_p m_e/(m_p + m_e)$.[3] However, m is quite accurately given by the electron mass because that mass is very small compared to the proton mass. After removing the angular dependence from the Schrödinger equation and specializing to the case of zero angular momentum, one is left with the "zero angular momentum radial Schrödinger equation:"

$$-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}u_E(r) + E_p(r)u_E(r) = Eu_E(r).$$

Here r is the distance from proton to electron, m is the system's reduced mass,[3] $E_p(r)$ is the attractive Coulomb potential between the electron

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[2]See "Locating All Schrödinger Equation Bound States" (MISN-0-253).
[3]See "Two-Body Kinematics and Dynamics" (MISN-0-45).

and the proton,

$$E_p(r) = -k_e \frac{e^2}{r} \equiv -\frac{b}{r},$$

where $\hbar$ is Plank's Constant divided by 2π, $b = 1.4400\,\text{eV nm}$, and E is the total energy of the electron-proton system. For the ground state of the hydrogen atom, $E = -13.6\,\text{eV}$.

In order to simplify the equation we define a function

$$f(r) \equiv -\frac{2m}{\hbar^2}\left[E - E_p(r)\right]$$

and then the radial Schrödinger equation can be written as:

$$u''(r) = f(r)u(r)$$

where the primes indicate derivatives. We now replace u'' by the finite difference approximation to it,[4]

$$u''(r) \simeq \left[u(r+\Delta) - 2u(r) + u(r-\Delta)\right]/\Delta^2$$

to produce:

$$u(r+\Delta) = \left[2 + \Delta^2 f(r)\right]u(r) - u(r-\Delta). \tag{2}$$

This is our "3-point recurrence relation"; it is called that because it relates u at three successive radial net points.

3b. Value at the First Net Point. Unless the potential is pathological at zero radius, any radial Schrödinger solution must be zero there:

$$u(0) = 0.$$

This is so because otherwise u would not be a solution to the full 3-dimensional Schrödinger equation at the origin. The point is that in going from the full 3-dimensional equation to the radial one we lose information about behavior near the origin. This information must be put back in as the zero-value-at-zero-radius requirement on the radial solution u.

3c. Value at the Second Net Point. The value of the solution at the second net point can be any value one chooses. We usually choose:

$$u(\Delta) = 1.$$

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[4]See "Taylor's Series for the Expansion of a Function About a Point" (MISN-0-4).

The reason that the value is immaterial is due to the homogeneity of the Schrödinger equation; the fact that, mathematically, any constant times a solution is also a solution. However, all solutions that differ only by a multiplicative constant are really the same solution as far as the physics is concerned. Each such solution must be multiplied by a normalization factor N,

$$u_N(r) = N\,u(r), \tag{3}$$

defined by the requirement that the total (integrated) probability of finding the electron somewhere in all of space is unity:

$$1 = \int_0^\infty |u_N(r)|^2\,dr. \tag{4}$$

In practice, a solution $u(r)$ is obtained and then, if a normalized solution is desired, N is computed from

$$N^{-1/2} = \int_0^\infty |u(r)|^2\,dr.$$

Thus the set of all solutions which differ only by multiplicative constants reduces, under normalization, to a single normalized solution. Until one actually calculates N, any member of the set is as good as any other. The value we pick for $u(\Delta)$ merely determines which member one gets and which value of N one will then find in obtaining the unique normalized solution.

Note that the "normalizability requirement" on a mathematical solution $u(r)$ can be stated this way: one must be able to find a value of N such that Eqs. (3) and (4) are satisfied or the solution is not a physical one. Solutions that go to infinity as r goes to infinity cannot satisfy this requirement.

3d. A BASIC Program. Here is a simple BASIC program that runs on most microcomputers (you may have to modify it slightly for your micro if you have one). On University PC's the universal BASIC is called QBASIC. Just type it into some micro and then run it.

The Description:
REM LENGTH UNITS ARE NM, ENERGY EV.
REM D=DELTA R; RX=MAXIMUM RADIUS; E=ENERGY.

The Program:

```
D=0.01
RX=0.20
E=−13.6
A=−26.232
U=0
UP=1
B=2+D^2*A*E
C=1.4400*D^2*A
FOR R=D TO RX STEP D
UM=U: U=UP
UP=(B+C/R)*U−UM
PRINT R,U
NEXT R
END
```

Vary D to obtain whatever accuracy you desire (but see Sect/5a). Use your own values for RX, etc. Suppose you don't have a printer and the numbers go by on the screen too fast for you to write them down. For this case we suggest you obtain the u's for the larger values of r by making multiple runs, each time increasing the value of RX so that the last screenful displayed on each run is one screenful farther along (in radius) than was the last screenful of the previous run.

4. Hand-Plotting Computer Output

All line shapes that you make from your computer output must be justified by the data points.

The graphs in Fig. 3 are not acceptable because there are not enough data points to justify the shapes of the lines.

For contrast, the curves in Fig. 4 *are* justified by the points shown.

Finally, Fig. 5 shows the case where one point falls off a smooth curve. In such a case, first check to see if perhaps the point is merely misplotted. If not, then the vicinity of the odd point should be filled in with points
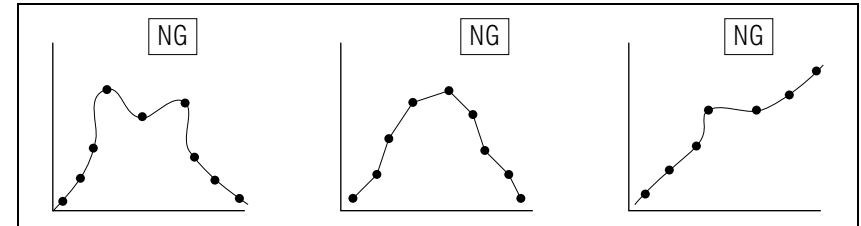
Figure 3. .

in order to ascertain the curve's true shape there.

5. Computer Run Details

5a. Accuracy: Making the Step Size Smaller. The main method of checking one's numerical accuracy is to reduce the step size used in the algorithm until the desired digit in the solution has stabilized. Here is an example of an accuracy table:

Δ	u(.6)/u(.2)
0.2000	2.062
0.1000	2.024
0.0500	2.014
0.0250	2.012
0.0125	2.012

Reducing the step size Δ makes the solution more accurate by decreasing the error incurred in using the finite difference approximation for the second derivative.

Too small a Δ may cause the Schrödinger equation input to be lost by the computer. For example, suppose you make $\Delta = 10^{-4}$ and you
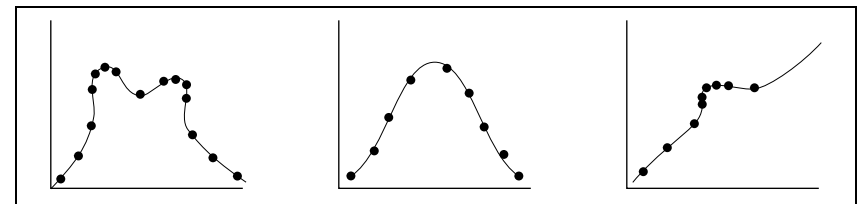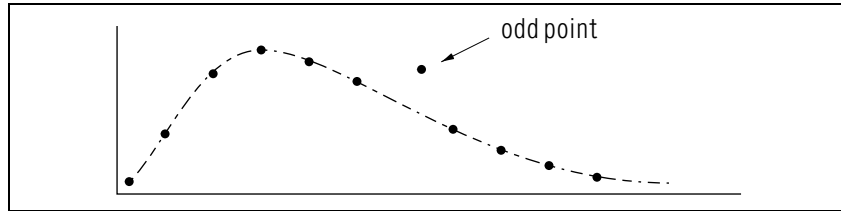

Figure 4. .

Figure 5. .

use a computer that keeps only 6 digits in any number. You might find something like this happening:

$$2 + \Delta^2 f_n \quad = \quad 2.00000$$
$$+0.00000152293$$
$$= \quad 2.00000$$

The $\Delta^2 f_n$ term has been lost in the addition process and hence the "solution" produced would be a straight line. Such an error would show up explicitly in an accuracy table.

5b. No Perfect Wave Functions. It is not possible to find the exact solution with this computer method because:

1. Use of a finite step introduces an error that makes the numerical-solution energy different from the correct one. The numerical-solution energy approaches the correct answer as the step size approaches zero (up to a point; see the next item).

2. Even the numerical-solution energy, which is not precisely the correct energy, is not obtainable because the computer only carries a finite number of digits of accuracy. Thus the numerical-solution energy will generally fall between two successive numbers realizable on the computer.

The consequence of the above argument is that every wave function you get will eventually, as you go outward in radius, go to either plus or minus infinity. The closer you are to the numerical-solution energy, the farther out you can go in radius before the wave function takes off for plus or minus infinity. The only way out of this dilemma is to use a different numerical recipe for solving the equation (see the Appendices if interested).

A: How to Plot Infinity on a Graph

(for those interested)

For a process in which we are interested in the behavior of a function as its independent variable approaches infinity, we would sometimes like to plot that behavior on a piece of graph paper of finite extent. Then a mapping technique will be a necessity.

The problem is to graph a function of r over the interval $0 \leq r \leq \infty$. We will denote the actual measured distance along the graph paper, while r goes from 0 to ∞, by the variable x. Then we will make the correspondence:

$$x = 0 \text{ when } r = 0$$

$$x = 1 \text{ when } r = \infty$$

Here x is the mapped variable. The maximum value of x is set to 1 here but could equally well be set to any other finite number. One mapping which satisfies these conditions is:

$$r = \frac{x}{1 - x},$$

and its inverse,

$$x = \frac{r}{r + 1}.$$

With this mapping, a function of $r(0, \infty)$ can be plotted as a function of $x(0, 1)$. Fig. 6 shows a comparison of the two scales. Notice that this scale is highly non-linear in r, but it fulfills the requirements of allowing us to plot previously unseeable information. Finally, in Fig. 7, we have used this technique in both of the graphical dimensions to plot all of $u = r^2$.
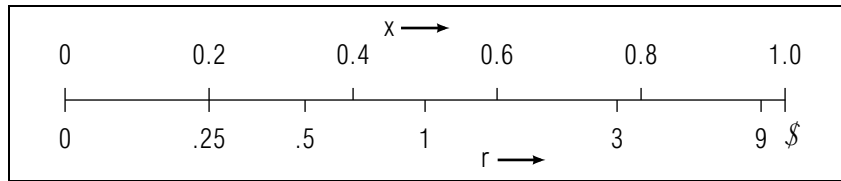
Figure 6. .

B. A Better but "Canned" Recipe

(for those interested)

If you prefer, you can use a "canned" computer program called ERWIN which avoids the infinities inherent in the method described in the present module. The program ERWIN solves the Schrödinger equation in the mapped space described in Appendix A, so it covers the entire range of radius from zero to infinity.

Here, infinite radius is just a point at a finite mapped distance. The program takes advantage of this and starts the "integration" there, at infinity, with the wave function properly set to zero, and works its way inward toward the origin. Now the wave function will never become infinite.
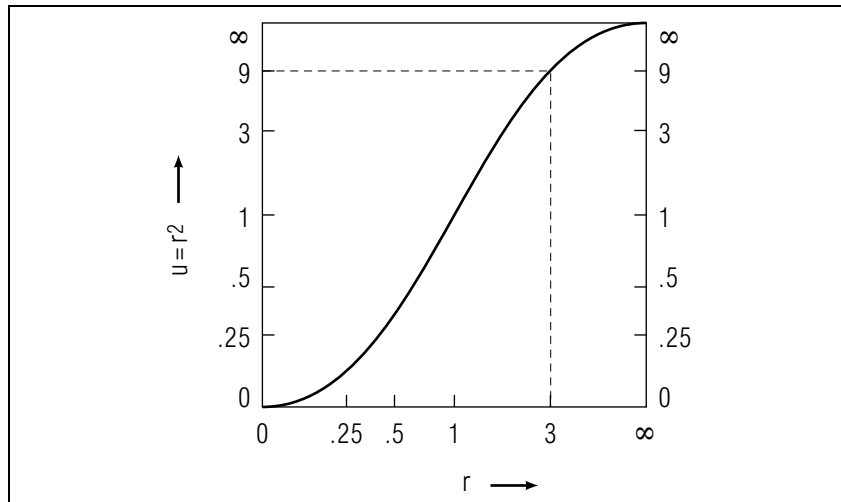

Figure 7. .

With ERWIN, your job is to find the energy (or energies) at which the wave function turns out to be (properly) zero at the origin.

You must run "ERWIN.EXE" from a file server in a University Micro Lab: ask a CBI Consultant for a copy of "document 8-100."

Be sure you understand the mapping described in Appendix A before you try to use ERWIN.

All radial wave functions, physical or not, must be zero at the origin because otherwise they would not satisfy the full three-dimensional Schrödinger equation from which the radial Schrödinger equation is derived. To be very specific: the three-dimensional Schrödinger equation has a Laplacian operator. When this operates on a wave function whose component radial wave function is non-zero at the origin, it produces a 3-dimensional delta function at the origin. With this term in it, the three-dimensional Schrödinger equation can only be satisfied if there is another similar term to cancel it. The only place where this could occur is in the inter-particle potential, and almost no inter-particle potential contains a delta function at the origin. Thus the term is not allowed and so the radial wave function which is non-zero at the origin is not allowed.[2]

LOCAL GUIDE

We don't care what microcomputer you use, but we only provide help in using MSU IBM-PC clones. You can use such clones in the campus Microcomputer Laboratories without charge.

If you do not know where the campus Microcomputer Labs are, or which ones contain IBM-PC clones, you can find out by calling the Computer Laboratory.

If you do not know how to use BASIC on micros, go to the CBI Consulting Room during your class's regular hours and get a copy of "CBI on University Micros": ask any Consultant for it as "document 8-100." Ignore the parts about "canned" (pre-stored) CBI programs. This document also lists the locations of the campus Micro Labs which contain PC clones.

If you have never used a micro before, we urge you to get a more experienced friend to go with you and help you the first time. Have the friend show you what to do, then reset everything and watch while you do it all from scratch. If you have no such friend, then get help from the Attendant in the Micro Lab when you get there.

MODEL EXAM

1. See Output Skills K1-K3 on this module's *ID Sheet*. The actual exam may contain one or more of these skills, or none.

Examinee:

On your computer output sheet(s):

(i) Mark page numbers in the upper right corners of all sheets.

(ii) Label all output, including all axes on all graphs.

On your Exam Answer Sheet(s), for each of the following parts of items (below this box), show:

(i) a reference to your annotated output; and

(ii) a blank area for grader comments.

When finished, staple together your sheets as usual, but include the original of your annotated output sheets just behind the Exam Answer Sheet.

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2. Attach one or more graphs which you or the computer plotted with an explanation, in writing on the graph, of how the graph illustrates that the radial wave function satisfies the correct boundary conditions *only at isolated energies.*

3. Attach the computer output for all curves plotted on the graph(s). Make sure each computer run is hand-annotated by you to show the reader how to find the graph curve correspoinding to that run's data.

INSTRUCTIONS TO THE GRADER

Grader! The student must have attached:
• the ORIGINAL of his/her computer output, and
• the ORIGINAL of his/her wave function graph(s).
If the student handed in a copy, not an original, of either one, then **immediately give the student a grade of zero** on this exam. Write the reason on the Exam Answer Sheet and grade no further.