

Astrophysical Exercises: The Energy Levels of the Hydrogen Atom

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1. Physical Background

To interpret the spectra of stars, gaseous nebulae, galaxies, and quasars, to compute the structure and evolution of the stars and nebulae, detailed knowledge of the structure of the atoms and ions are necessary, which the cosmic gas consists of. The atomic structure is governed by quantum mechanics, which permits the computation of the wavefunction(s) of the various states which the system can attain. This is the basic task to be done, as all the other quantities, such as probabilities for the transitions between states and interaction cross sections may be computed from the wavefunctions.

In our program, we shall treat the simplest atom — hydrogen — in order to study the principles of such a calculation. We solve Schrödinger's equation, and try to find all the energy states of hydrogen. Using the wave functions, we shall compute the transition probabilities for the spectral lines of hydrogen. By changing the expression for the potential energy, the program can also compute the energy levels for other systems, such as the harmonic oscillator.

2. The Equation

We are interested in the states that the electron in an hydrogen atom can attain. Since we shall not deal with the time evolution of states, we need to find the stationary states. These are described by Schrödinger's eigenvalue equation:

$$\mathbf{H}\Psi = E\Psi \tag{1}$$

Thus our aim is to find all those functions Ψ which obey the equation, and whose normalization integral

$$\int_{-\infty}^{+\infty} \Psi^* \Psi d^3x$$

is finite. Also we wish to find the corresponding energies E .

\mathbf{H} is the Hamilton operator, the sum of kinetic and potential energy of the particle. If the latter is only due to the central electrostatic field caused by the nucleus of charge Ze , we get

$$-\frac{\hbar^2}{8\pi^2 m_e} \nabla^2 \Psi - \frac{Ze^2}{4\pi\epsilon_0 r} \Psi = E\Psi \quad (2)$$

This problem is best dealt with in a spherical coordinate system centered in the nucleus, so the Laplacian operator has the form

$$\begin{aligned} \nabla^2 &= \frac{1}{r^2} \left(\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \right) \\ &+ \frac{1}{r^2 \sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial}{\partial \vartheta} \right) \\ &+ \frac{1}{r^2 \sin^2 \vartheta} \frac{\partial^2}{\partial \varphi^2} \end{aligned} \quad (3)$$

As you may remember from your quantum mechanics course, one can split up the wavefunction into the product of a function $R(r)$ that depends on radius only and an angle dependent function $Y(\vartheta, \varphi)$. The latter is the spherical harmonic function Y_m^l

$$Y(\vartheta, \varphi) = Y_{lm} = \sqrt{\frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}} e^{im\varphi} P_{l|m|}(\cos \vartheta) \quad (4)$$

which depends on the quantum number l for the orbital angular momentum and $m = -l, \dots, +l$ for its z component. Note that it is the product of two functions that depend on ϑ and φ separately. The P_{lm} are the associated Legendre functions. In the following table the first few are listed.

Associated Legendre Functions

$P_{00} = 1$	
$P_{10} = x$	$P_{11} = \sqrt{1-x^2}$
$P_{20} = \frac{1}{2}(3x^2 - 1)$	$P_{21} = 3\sqrt{1-x^2}x$
$P_{22} = 3(1-x^2)x$	
$P_{30} = \frac{1}{2}(5x^3 - 3x)$	$P_{31} = \frac{3}{2}\sqrt{1-x^2}(5x^2 - 1)x$
$P_{32} = 15x(1-x^2)x$	$P_{33} = 15(1-x^2)^{3/2}x$

The spherical harmonic functions are the eigenfunctions of the angular part of the Laplacian with the eigenvalues $l(l+1)$. Thus for the radially dependent part one has:

$$-\frac{\hbar^2}{8\pi^2 m_e} \left(\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{l(l+1)}{r^2} \right) R(r) - \frac{Ze^2}{4\pi\epsilon_0 r} R(r) = ER(r) \quad (5)$$

As you may remember, this gives a set of eigenfunctions R_n numbered by the principal quantum number n , and the condition for the orbital quantum number $l = 0, \dots, (n-1)$.

2.1 How to Compute it

The search for the radial eigenfunctions $R(r)$ is done this way: Starting at the centre with an estimate for the wavefunction's value there, and a guess value for the energy E , we integrate Eq. (5) towards greater radii r . Because a genuine eigenfunction must be normalizable, i.e. the integral

$$\int_0^\infty R^*(r)R(r)dr$$

must be finite, a condition which is met if the function is bounded. Depending on how R behaves for large r , we can judge how to adjust the energy estimate, and try again. Once the change in energy becomes smaller than a given tolerance, we accept it and its corresponding wavefunction.

It is convenient to convert this second order differential equation into a system of two first-order ones, and to isolate the derivatives:

$$\frac{df(r)}{dr} = -\frac{2}{r}f(r) + \left(\frac{l(l+1)}{r^2} - \frac{8\pi^2 m_e}{\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0 r} + E \right) \right) R(r) \quad (6a)$$

$$\frac{dR(r)}{dr} = f(r) \quad (6b)$$

These equations are solved numerically: This means that one does not deal with a function $g(x)$ itself, but only with the values $g_i = g(x_i)$ at discrete values x_i of the independent variable. This "grid" of x could be fixed and equispaced, or adjustable during the computations. Integrals then are sums, and derivatives are represented by the difference quotients.

We proceed in the following manner: Given the values R_i and $f_i = R'(r_i)$ at any radius point r_i , we compute how much the functions change, if one goes to the next radius r_{i+1} further out. This is first done for f :

$$f_{i+1} = f_i + \left(-\frac{2}{r_i}f_i + \left(\frac{l(l+1)}{r_i^2} - \frac{8\pi^2 m_e}{\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0 r_i} + E \right) \right) R_i \right) (r_{i+1} - r_i) \quad (7a)$$

Note that we assumed that the value of the derivative (right hand sides of Eq. (6a)) computed at the "old" radius r_i remains constant between i and $i+1$. This is called

an "explicit" method, since in computing the derivatives one makes use of information that already is available at the "old" grid points.

If takes also information of the function at the "new" radius (which is yet to be computed), one speaks of an "implicit" scheme. We use of this for the second equation:

$$R_{i+1} = R_i + \frac{f_i + f_{i+1}}{2}(r_{i+1} - r_i) \quad (7b)$$

Thus, some information about the wavefunction at the new radius is taken into account. Here, only information about the derivative of R is used. In a fully implicit scheme, one makes use of the new function value, too. Since this makes it necessary to perform iterations for the new function value, implicit methods are usually more complex and more difficult to program. They do have advantages.

Our method is of first order, because we represent the derivatives by a first-order difference quotient. Higher order schemes, that offer a higher accuracy for the same grid spacing, are possible, but are not only more complex to program but also may be difficult to "tame", e.g. to prevent from producing rapidly oscillating solutions.

2.2 The Radial Grid

The accuracy of the numerical solution depends on how well the derivatives and integrals are approximated, i.e. on the spacing ($r_{i+1} - r_i$) of the grid. To obtain results close enough to the true solutions, it must be made as fine as possible. However, a finer grid needs more computing time. The best way to find out, how to obtain sufficiently accurate results within reasonable time, is to make test calculations.

The simplest choice for the radial grid is one with constant intervals. Since the typical dimension of an atom is one Ångström (10^{-10} m), and probably 100 grid points should be a good choice to replace an integral by a sum, $\Delta r = 0.01$ Å is a good starter. By looking at the wavefunction or plotting it, you can see how to modify it.

If you like, you can try to make an adaptive grid, which adjusts itself to match the spacing to the change of the functions to be integrated. Thus, at every radial point, one computes the stepwidth $\Delta r = r_{i+1} - r_i$ based on some criterion. One possibility is: Estimate from the points i and $i - 1$ by linear extrapolation, how large Δr ought to be, if one allows the functions R and f to change by a given factor ξ , say ten percent:

$$\Delta r = \xi \frac{r_i - r_{i-1}}{|R_i| - |R_{i-1}|} |R_i| \quad (8)$$

Similar with f , and then take the minimum stepwidth. There are many other possible schemes. Try out what serves you best.

2.3 Checks of the Method

Before one applies one's program to the real problem, one must check whether it really does what it was designed to do. The ideal way is to run it for problems that have an analytical solution. For example:

1. Exchange Eq. (6a) by a very simple differential equation: $df/dr = a = \text{const.}$, $f(0) = b$ and $R(0) = c$. Then the program must turn out $f(r) = ar + b$ and $R(r) = ar^2/2 + br + c$. Any deviation from the analytical results indicates the accuracy of the integration method.
2. Check also more complicated equations, which resemble the character of the real one, but which you can easily solve analytically.

2.4 How to Find the Eigensolutions

The eigenfunctions are found by a trial and error method: We first guess a value for E , then start the integration of the wave function at the atom's centre. The initial value for R is not important, because the Schrödinger equation is homogeneous, that is the solution can be multiplied with any arbitrary normalization constant. So let's assume $R(0) = 1$. For the derivative $f(0)$ you are invited to try out any value. You will find that it really does not matter much, since after a couple of radial steps, the wave function will be the same for any value of $f(0)$. So let's take $f(0) = 0$.

Now, try it out manually: Compute the wave function for several values of E . You will find that for larger r it will either grow rapidly towards positive values, or towards negative ones. Since this growth is the same, even if you use a finer radial grid, it must be genuine. If you vary the energy appropriately, you can make the divergence happen at larger radii. If you have done this a few times, you will notice that the necessary adjustments to E are rapidly becoming smaller. Then the level energy is known within a certain accuracy, and you might stop your effort.

This can be programmed as an automatic procedure: Just observe how you proceed to make the adjustments to E . Probably what you did was:

- (a) At first, try out randomly or systematically the whole probable range of E values, to find how the wave function behaves.
- (b) Whenever there was a change of the sign towards where the function grew, one suspects an eigenvalue, which is investigated more closely:
- (c) If $R(r)$ becomes larger than a positive threshold value, stop the integration, and perhaps raise E , and try again.
- (d) If it becomes smaller than a negative threshold value, stop, and change E in the opposite way. Try again.
- (e) The more adjustments you make, or the farther away in radius r the wave function exceeds the threshold values, the smaller is the necessary change in E .

2.5 The Eigensolutions of Hydrogenic Atoms

Fortunately, we can check the results from the program directly with the analytical solutions of the equations. Introducing the Bohr radius

$$a = \frac{h^2 \epsilon_0}{\pi m_e e^2}$$

and the scaled radial coordinate $\rho = Zr/a$ the radial parts of the first few wave functions for the electron in the field of positive charge Ze are listed in the following table (from Schpolski, Atomic Physics):

n	l	$R_{nl}(r)$
1	0	$2(Z/a)^{3/2} \exp(-\rho)$
2	0	$1/(2\sqrt{2})(Z/a)^{3/2}(2 - \rho) \exp(-\rho/2)$
2	1	$1/(2\sqrt{6})(Z/a)^{3/2} \rho \exp(-\rho/2)$
3	0	$2/(81\sqrt{3})(Z/a)^{3/2}(21 - 18\rho + 2\rho^2) \exp(-\rho/3)$
3	1	$2\sqrt{2}/273(Z/a)^{3/2}(6 - 18\rho) \exp(-\rho/3)$
3	2	$\sqrt{2}/(81\sqrt{15})(Z/a)^{3/2} \rho^2 \exp(-\rho/3)$

3. General Remarks, Hints, and Kinks

0. Before actually writing the program, do make a flow chart diagram in order to understand the sequence of what is computed; a diagram of the program structure and the data structure to find out, how the loops and iterations are nested, which data from earlier parts you need at each section, which kind of vectors and arrays you are going to need. This may seem bureaucratic, boring or even old fashioned, but **don't start typing anything, before you are absolutely clear about what you plan to do**. Otherwise you may really end up wasting much time in trying to find the logical errors, loopholes, and cul-de-sacs of your hasty programming. Save yourself the frustration, disappointment, and anger!
1. General Program Planning: It is a good idea to lay out the program as general as possible. This makes it easier to include other effects, or to try out other situations. E.g. keep the number of radial points and the upper limits as parameters which are given values in the main program, rather than being specified everywhere the grid is used. Checking the program for other kinds of stars can thus

- be done easily at any time. Or the grid parameters can be changed, whenever a model with high accuracy is to be computed.
2. **Modular Construction:** It is also a good idea to break up the program into mathematically or physically sensible units. This allows a better testing of these individual modules — and most of the time is spent in tracing an error — a more flexible use of them for other purposes, and their exchange against improved or alternative methods, improved data, other physical processes, etc. For example, if the optical depth integration is contained in a separate unit, one simply exchanges this against a more sophisticated method, if need arises, but without the trouble of having to change the program at a dozen places. For testing, a simple main program has to be written which supplies the necessary input data to this unit. When adapting the program to a different problem, one merely re-arranges the modules. The main program may then be just a control program to call the subprograms in the particular order, and gets and supplies data from and to each part.
 3. **Check Everything by Hand:** Often, we underestimate our ingenuity to make small logical mistakes or simple typing errors, which may cause faulty results. The worst kind of mistakes are those which produce results that look as one would expect them to be. Do take the trouble of check everything the program does, until you are sure it does only what you want it to do. In programs about physical things, basic physics must be obeyed: conservation of particles, energy, etc. Also, all the simple and limiting cases which we do understand, must be reproduced accurately.
 4. **Provide Error Messages and Tracing:** Especially during testing, you will print out everything that is useful to judge on what the program does and what decisions it makes. For example, the radial step width, if you compute it automatically, or just the values of f and R at every radius.... It is recommendable to define one or more variables that can be used to switch on these print-outs. In this way, one can always check every part of the program, even after it has been considered finished. If you later want to try out some modification, and the results are either complete rubbish (because you made some error) or you just want to understand how the solution behaves, this option is very useful. Provide written messages if something goes not normal, e.g. if the automatic stepwidth goes below or above specified values. This become more important as the program grows in size and complexity.
 5. **Take Time For Comments:** Don't be lazy with putting comments into the program. Not only for the general description what each subprogram does, what data it needs, and what variables it changes. But also if you change just a line for a test. Often one forgets after a few days about it, and is quite surprised about the results. Save yourself the panic! Plenty of comments are vital, if you find some time later that you might use it for something, but you can't remember about its inner workings. Don't wait for them after "the program is finished". It never happens, or you won't have the time.
 6. **Be highly skeptic of anything the program produces.**

7. When you are making tests, and later running the program for various situations and parameters, try to keep a careful written record of what you do, noting input parameters and results. This will make it easier for you later to compare results with earlier ones, in case you have to hunt for an error that has crept in yesterday when you “just changed a few things, almost nothing — but the program doesn’t work any more”.

4. The Hydrogen Levels

If you consider hydrogen ($Z = 1$), you should get the well known formula for the energy levels:

$$E_n = E_H \left(1 - \frac{1}{n^2}\right) \quad (9)$$

where $n = 1, 2, 3, \dots$ is the principal quantum number and

$$E_H = \frac{m_e e^4}{8h^2 \epsilon_0^2} = 13.56 \text{ eV}$$

is the energy of the ionization threshold. The level energy does not depend on the orbital quantum number l : the levels are said to be degenerated, i.e. in each level n the electron can be in any of the n^2 states of different orbit angular momentum, all at the same energy.

5. Transition Probabilities of Hydrogen Lines

To derive from the absorption line spectrum of a star the conditions in its atmosphere, such as temperature, surface gravity, and the abundances of the elements, one needs to know the transition probabilities of all the lines. These are obtained from the matrix elements of the particular transition, i.e. one must know the wave functions of the initial and the final state. The Einstein A -value — or inverse lifetime — of a line produced by emission of electric dipole radiation from the higher level i to the lower f is:

$$A_{if} = \frac{3h^4 c^3}{64\pi^4 (E_i - E_f)^3} |r_{if}|^2 \quad (10)$$

The modulus of the matrix element r_{if} is the expectation value

$$|r_{if}|^2 = \int \Psi_i^* e \hat{r} \Psi_f d^3x \quad (11)$$

of the electric dipole operator

$$\hat{r} = \begin{Bmatrix} x/r \\ y/r \\ z/r \end{Bmatrix} = \begin{Bmatrix} \cos \vartheta \cos \varphi \\ \cos \vartheta \sin \varphi \\ \sin \vartheta \end{Bmatrix} \quad (12)$$

To evaluate the integral, we use spherical coordinates. Because the wave functions for our particular problem happen to be products of three functions each of which depends on only one coordinate, the triple integral breaks up into the product of three single ones:

$$\begin{aligned} \int \Psi_i^* e^{\hat{r}} \Psi_f d^3x &= e \int_0^\infty R_{nl}(r) R_{n'l'}(r) r^2 dr \\ &\cdot \frac{1}{2\pi} \int_0^{2\pi} e^{-im\varphi} \begin{Bmatrix} \cos \varphi \\ \sin \varphi \\ 1 \end{Bmatrix} e^{im'\varphi} d\varphi \\ &\cdot N_{lm} N_{l'm'} \int_0^\pi P_{lm}(\cos \vartheta) \begin{Bmatrix} \cos \vartheta \\ \cos \vartheta \\ \sin \vartheta \end{Bmatrix} P_{l'm'}(\cos \vartheta) \sin \vartheta d\vartheta \quad (13) \end{aligned}$$

The N_{lm} are the normalization factors in Eq. (4). Since the levels are degenerated in l and m , we must sum over all possible transitions $(n, l, m) \rightarrow (n', l', m')$: To evaluate this complete sum over all possible transition channels may be a rather stupid way to evaluate this integral, since you may remember that there there are selection rules for the transitions. The ones you probably are familiar with:

$$\Delta l = 0, \pm 1$$

$$\Delta m = 0, \pm 1$$

are valid for "permitted" lines, those of electric dipole nature. For the hydrogen atom we already know the angular functions, so in principle we could evaluate those integrals analytically, like

$$\int_0^{2\pi} e^{i(m'-m)\varphi} \begin{Bmatrix} \cos \varphi \\ \sin \varphi \\ 1 \end{Bmatrix} d\varphi = \begin{cases} 1/2 \\ 1/2 \\ 1 \end{cases} \text{ if } m' - m = \begin{cases} \pm 1 \\ \pm 1 \\ 0 \end{cases}$$

For any other than the value of $\Delta m = m' - m$ given, the integral is zero. Because we had made the assumption of dipole radiation, these selection rules for Δm are valid for this case only. The ϑ -dependent part could also be dealt with analytically, and yields the other selection rule. But we shall pretend that we do not know about the special properties of the Legendre functions, and evaluate the integral numerically. Thus the program should "find" the selection rules.

There are a number of numerical integration prescriptions, with various accuracies, such as Simpson's rule or Gauss' formulae, or more sophisticated ones, usually

available from software packages. However, the trapezoidal rule is simple to use, reliable even with strange functions, and accurate, if the function is given at a sufficient large number of grid points, i.e. if the grid is fine enough. Then the integral is replaced by a sum

$$\int_a^b f(x)dx = \sum_{i=1}^n f(x_i)w_i \quad (14a)$$

over the function given at the n grid points x_i — which need not necessarily be equally spaced — multiplied by the integration weights

$$w_i = \begin{cases} 0.5(x_2 - x_1) & \text{for } i = 1 \\ (x_i - x_{i-1}) & \text{for } 1 < i < n \\ 0.5(x_n - x_{n-1}) & \text{for } i = n \end{cases} \quad (14b)$$

If one later wishes to take a different scheme, one changes the prescription for the integration weights.

Transition probabilities, computed in this way or measured, can be found in data collections (Wiese, National Bureau of Standards) and data banks. For the hydrogen Balmer lines they are

Line	n_f	n_i	A_{if}
H α	2	3	4.410 10^7
H β	2	4	8.419 10^6
H γ	2	5	2.530 10^6
Units			sec $^{-1}$

6. Other Potentials

Once the program has been checked to perform the integrations of the Schrödinger equation correctly, it can also be applied to other systems. Especially so, if it is able to find the eigenfunctions automatically.

One example is the harmonic oscillator with the potential energy $E_{pot} = Cr^2$ which has energy levels equally spaced. This model is used to compute the rotational levels in molecules, which are very important in the atmospheres of cool stars, and interstellar space. Likewise you may try to treat the behaviour of an electron trapped by walls of higher potential. The thinner the wall is, the greater is the probability that the electron escapes by the "tunnel effect". Finally, compute the wave function for the free electron, i.e. with the potential set to zero. How many eigenvalues can you find?