

23. The Hydrogen Atom

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The most important example of a spherically symmetric potential energy is the *Coulomb potential*,

$$V(r) = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r}, \quad (1)$$

between two point charges q_1 and q_2 separated by a distance r . If one of the two charges is a heavy atomic nucleus and the other is a much lighter electron, then to a good approximation we can treat the nucleus as a fixed center of force and apply quantum mechanics only to the electron's motion (see Problem 5.1 in Griffiths if you want to know how accurate this approximation is). In terms of the fundamental unit of charge,

$$e = 1.602 \times 10^{-19} \text{ C}, \quad (2)$$

the electron's charge is $-e$ and the nuclear charge is Ze , where Z is the number of protons. For now we'll consider only the hydrogen atom, with $Z = 1$, so the potential energy is

$$V(r) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r}. \quad (3)$$

Given this potential energy function, we can immediately write down the effective potential,

$$V_{\text{eff}}(r) = \frac{\hbar^2 l(l+1)}{2mr^2} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r}, \quad (4)$$

where m is the electron's mass, and then use this V_{eff} in the (reduced) radial Schrödinger equation,

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + V_{\text{eff}}(r) \right] u(r) = E u(r). \quad (5)$$

Natural units

It looks like the TISE for the hydrogen atom involves four different constants: e , ϵ_0 , m , and $\hbar$. But they occur in only two different combinations,

$$\frac{e^2}{4\pi\epsilon_0} \quad \text{and} \quad \frac{\hbar^2}{m}, \quad (6)$$

and you can immediately see from equation 4 that these combinations have dimensions of energy times distance and energy times distance squared, respectively. We can therefore divide the latter by the former to obtain a natural unit of distance,

$$a_0 = \frac{\hbar^2/m}{e^2/(4\pi\epsilon_0)} = 0.529 \times 10^{-10} \text{ m}, \quad (7)$$

called the *Bohr radius* (after Niels Bohr). And then we can divide $e^2/(4\pi\epsilon_0)$ by a_0 to obtain a natural unit of energy,

$$E_h = \frac{e^2}{4\pi\epsilon_0 a_0} = \frac{\hbar^2}{ma_0^2} = \left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{m}{\hbar^2} = 27.2 \text{ eV}, \quad (8)$$

called the *hartree* (after Douglas Hartree, who made important early contributions to theoretical atomic physics).

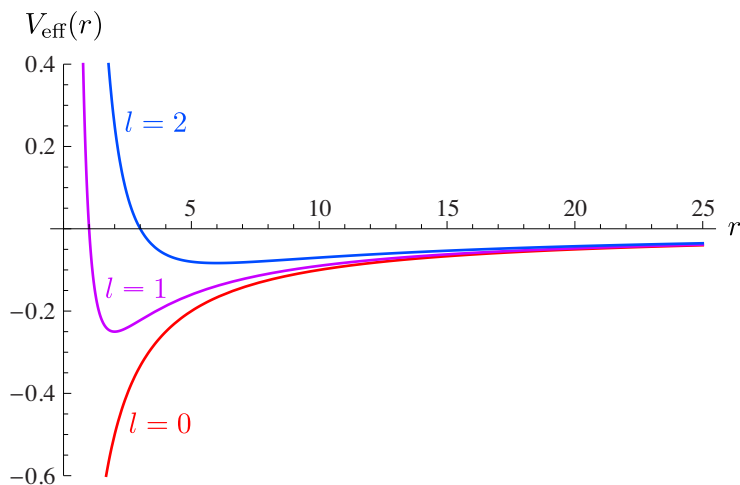
These natural units are called *atomic units*, often abbreviated a.u. (not to be confused with AU for astronomical units!). Actually, the atomic unit system sets all four of the constants m , $\hbar$, e , and $1/(4\pi\epsilon_0)$ equal to 1. (Sometimes you might encounter a competing atomic unit system in which some factors of 2 are absorbed into some of the units so the energy unit comes out half as large, 13.6 eV. That energy unit is called the *rydberg*, and you can distinguish the two systems by saying *Hartree atomic units* or *Rydberg atomic units*. In this class we will use only Hartree atomic units.)

With the understanding that all distances are measured in units of a_0 and all energies are measured in units of E_h , the radial Schrödinger equation becomes

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} - \frac{1}{r} \right] u(r) = E u(r). \quad (9)$$

Qualitative solutions

Here is a plot of the effective potential, for $l = 0, 1$, and 2 , with the scales on both axes measured in atomic units:



As you can see, the attractive Coulomb potential always dominates at large r , but when $l > 0$ the repulsive centrifugal term sends V_{eff} to $+\infty$ as $r \rightarrow 0$. The competition between the two terms leads to a local minimum, which you can easily

show to lie at $r = l(l + 1)$, at which point $V_{\text{eff}} = -1/(2l(l + 1))$ (check this on the graph!). Any solutions to the Schrödinger equation must have energies at least a little above this minimum, that is, above $-1/4$ for $l = 1$, above $-1/12$ for $l = 2$, and so on. Meanwhile, in order for the electron to be bound to the nucleus (that is, in order to have a hydrogen *atom* rather than an *ion*), its energy must be negative.

With these limits in mind, it's an instructive exercise to simply *guess* some energy levels, draw them on the graph to determine the associated classical turning points, and then sketch tentative graphs of the one-bump wavefunction, the two-bump wavefunction, and so on, just as you would do if this were a one-dimensional problem. There is a separate set of solutions for each l value, and these “wavefunctions” will actually be $u(r)$, which you have to divide by r to obtain $R(r)$. The widths of the “bumps” will grow as you go outward (away from the minimum of V_{eff}), and the centrifugal term pushes the wavefunctions farther and farther out as l increases. It's not obvious what happens near the origin in the case $l = 0$, but it's reasonable to guess that even then the *reduced* wavefunction must go to zero as $r \rightarrow 0$, and this guess turns out to be correct.

One other thing that isn't obvious is how *many* bound states this system has for each l value. On one hand the potential wells for $l > 0$ don't look especially deep, so you might guess that there aren't very many bound states. But on the other hand, for values of E that are only slightly negative there is a great deal of horizontal space in which to fit plenty of bumps. It turns out that this second effect dominates, so the number of bound states is actually *infinite* for each l value, no matter how large.

Numerical solutions

The matrix diagonalization method isn't well suited to the Coulomb potential, because the wavefunctions extend out to rather large r values, forcing you to use a wide “box” to enclose them, and for such a wide box you need to use a lot of sine waves (large `nmax`) to accurately fit the short-wavelength, small- r portions of the wavefunctions. You can still get a few of the lowest-energy states, but it's computationally inefficient.

The shooting method, on the other hand, works just fine. For this purpose it's a little easier to solve the radial equation for d^2u/dr^2 :

$$\frac{d^2u}{dr^2} = -2\left(E - \frac{l(l+1)}{2r^2} + \frac{1}{r}\right)u(r). \quad (10)$$

Because of the r 's in the denominators, you need to start the integration a little away from the origin, say at $r_{\text{min}} = 0.0001$. For $l = 0$ the functions $u(r)$ turn out to be linear near the origin, so it works well to use the boundary conditions $u(r_{\text{min}}) = r_{\text{min}}$ and $u'(r_{\text{min}}) = 1$. For $l > 0$ the functions $u(r)$ die out more rapidly near the origin, so it's best to set $u(r_{\text{min}}) = 0$ and $u'(r_{\text{min}}) = r_{\text{min}}$ (or any other

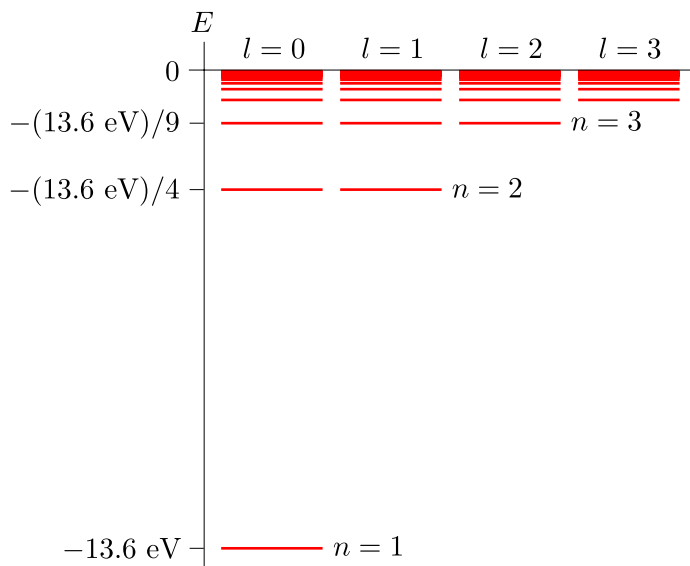
small value). You'll find that you need to use surprisingly large maximum values of r .

You probably won't be surprised to learn that the energy eigenvalues follow a simple pattern. For $l = 0$, still using natural units, they are $-1/2$, $-1/8$, $-1/18$, $-1/32$, and so on, that is, $-1/(2n^2)$, where $n = 1, 2, 3, \dots$ is the number of bumps. Then an amazing (though perhaps familiar) thing happens for $l = 1$: The energy values turn out to be exactly the same, except that the list omits $-1/2$ and instead starts at $-1/8$, so the one-bump $l = 1$ wavefunction is degenerate with the *two*-bump $l = 0$ wavefunction, while the two-bump $l = 1$ wavefunction is degenerate with the *three*-bump $l = 0$ wavefunction, and so on. And the list of energies for $l = 2$ is similarly degenerate with the others, but starting with $-1/18$. Please recall that there is *no* such degeneracy for the other central force problems we've explored, such as the spherical infinite well and the linear (constant-force) potential. The degeneracy seems like a total coincidence! Of course it's not a coincidence, but the reason for it is rather difficult to understand so I won't go into it here.

Because of this degeneracy, it's conventional to define the quantum number n so that the energy formula $-1/(2n^2)$ works even for $l > 0$. In conventional units,

$$E_n = -\frac{E_h}{2n^2} = -\frac{13.6 \text{ eV}}{n^2}. \quad (11)$$

This definition of n is confusing, because it means (for instance) that the wavefunction with $l = 1$ and $n = 2$ has only *one* bump (in the r direction). In general, the number of bumps in $u(r)$ equals $n - l$. Here is an energy-level diagram with the values of l and n (but not the number of bumps) labeled:



Of course it's also important to remember that for any given n and l values, there are still $2l + 1$ degenerate states with different values of the quantum number m (also

called m_l when a plain m would be ambiguous). So in the figure on the previous page, each $l = 1$ state is actually triply degenerate, each $l = 2$ state is five-fold degenerate, and so on.

Analytic solutions

As with the one-dimensional harmonic oscillator, the existence of a simple formula for the energy eigenvalues is a sure sign that it must be possible to solve the TISE analytically. For the full analytic solution (via the power-series method) I'll refer you to Griffiths, Section 4.2. Here I'll focus on the general form of the solutions and the specific formulas for a few of the simplest ones.

One key observation is that in the limit of large r , both $V(r)$ and the centrifugal term go to zero so the radial equation becomes simply

$$\frac{d^2 u}{dr^2} = -2E u(r) = \frac{1}{n^2} u(r), \quad (12)$$

where in the last expression I've used the formula $E = -1/(2n^2)$ that we inferred from the pattern of the numerical solutions. The solutions to this differential equation are exponential functions, $e^{r/n}$ and $e^{-r/n}$, but the former isn't normalizable so we're left with the latter.

The (reduced) wavefunctions must also go to zero at $r = 0$, and most of them have multiple bumps and nodes. The simplest functions that have these properties are polynomial functions of r , so it's reasonable (and correct) to guess that the general formula for $u(r)$ is a polynomial in r times $e^{-r/n}$. There can be no constant terms in these polynomials, because they must go to zero at the origin.

The next thing to notice is that the $l = 0$ reduced wavefunctions are approximately linear near the origin (as you can see from the numerical solutions), so in these cases the polynomial must have a linear r^1 term. For the ground state this term is sufficient, while each additional node requires a term in the polynomial with the next-higher power of r .

For $l = 1$ the wavefunctions are concave-up near the origin, so a reasonable guess is that $u(r)$ begins with an r^2 term, again adding a term with the next-higher power of r for each additional node. For $l = 2$, the $u(r)$ functions begin with r^3 , and so on. This pattern is actually easier to remember for the *unreduced* radial wavefunctions, $R(r) = u(r)/r$, which begin with the power r^l .

Of course you can verify this pattern, at least for the one-bump wavefunctions, by simply plugging the formula into the radial Schrödinger equation and showing that it works. For the two-bump wavefunctions, you can make up a letter for the coefficient of the next polynomial term, plug in the formula, and solve for the value of the coefficient that works. To work out the polynomials for wavefunctions with more than two bumps is rather tedious, so at that point you're probably better off just plowing through the full power-series solution in Griffiths.

These polynomials have names, by the way: After factoring out the overall powers of r , the remaining polynomials (suitably normalized) are called *associated Laguerre polynomials*. You can work out their coefficients using recursion relations, or look them up in tables, or invoke them with Mathematica. (Be careful: Griffiths and Mathematica use different normalization conventions for the associated Laguerre polynomials.) I usually find it easier, though, to simply work from a table of the radial wavefunctions themselves, and Griffiths conveniently provides one (for the *unreduced* functions $R(r)$) that goes up to $n = 4$. This table also includes the normalization coefficients, which are straightforward but tedious to work out.