Chapter 1

Time Independent Schrödinger Equation

1.1 Revision of the Schrödinger equation

The Schrödinger equation is a *time-dependent partial differential equation*. In this introductory lecture, we will not consider the time dependence (that will come in lecture 3), and so we will instead consider the simpler case of the *time independent* version. We can sometimes restrict things even more by considering just one spatial dimension, in which case, we only have a reasonably straightforwards ordinary differential equation to solve, subject to some set of boundary conditions. This is exactly the type of problem that you have solved analytically in the past.

We start by rewriting the time independent Schrödinger equation

$$-\frac{\hbar^2}{2m_e}\nabla^2\psi\left(\mathbf{r}\right)+V\left(\mathbf{r}\right)\psi\left(\mathbf{r}\right)=E\psi\left(\mathbf{r}\right) \tag{1.1}$$

in atomic units, that is $\hbar = m_e = e = 4\pi\varepsilon_0 = 1$ [so from now on we shall always work in energy units of Hartrees ($27.2eV$) and in length units of Bohr radii ($a_0 = 0.529$ Å)] and so :

$$-\frac{1}{2}\nabla^2\psi+V\psi=E\psi \tag{1.2}$$

or in terms of the Hamiltonian operator $\widehat{H}$,

$$\widehat{H}\psi=E\psi \tag{1.3}$$

We know that this is an example of an *eigenvalue equation*, and that for a given potential $V\left(\mathbf{r}\right)$ and boundary conditions, there will in general be a number of different possible solutions, corresponding to different *eigenenergies* E_i with corresponding *eigenfunctions* ψ_i .

The first term in equation 1.1 corresponds to the kinetic energy of the state, and so we see that a smoothly varying wavefunction (small $\nabla^2\psi$) will generally be a lower energy state than a rapidly varying one. This can also be related to the number of nodes (zero crossings) in the wavefunction - a smooth wavefunction will have less nodes than a rapidly varying one.

Example 1 - particle in infinite square well

As an example, we can consider the simple case of a quantum particle moving in one dimension in an infinitely deep square well:

$$\begin{array}{rcll} V(x) & = & 0 & -a \leq x \leq a \\ & \rightarrow & \infty & otherwise \end{array} \tag{1.4}$$

which then gives the general solution of equation 4.1 as

$$\psi(x) = A\cos(kx) + B\sin(kx) \tag{1.5}$$

with A and B being constants given by the boundary conditions and

$$k = \sqrt{2E} \tag{1.6}$$

If we now apply the boundary conditions that $\psi(-a) = \psi(a) = 0$ then

$$k = n\pi/2a \tag{1.7}$$

where n is an integer. For odd n we get $\cos(ka) = 0$ and hence $A = 0$ whilst for even n we get $\sin(ka) = 0$ and hence $B = 0$. As the well is infinitely deep, then all solutions are bound states. As usual, bound states have quantized energies, given in this case by

$$E_n = \frac{\pi^2 n^2}{8a^2} \tag{1.8}$$

Note that as the potential has a definite *parity* then so do the eigenfunctions. Note also that the ground state wavefunction has no nodes, whilst the first excited state has one node, and successive excited states have more nodes. See figure 1.1 for a simple sketch of the three lowest energy solutions.

We can also solve analytically problems such as the finite square well, or the harmonic oscillator, or the spherical well, etc. Remember that these can be used to demonstrate the existence of zero-point motion, tunnelling into classically forbidden regions and the Heisenberg Uncertainty Principle.

Example 2 - the hydrogen atom

In order to solve the Schrödinger equation for the hydrogen atom, we need to deal with a 3D equation in spherical polar coordinates. However, because

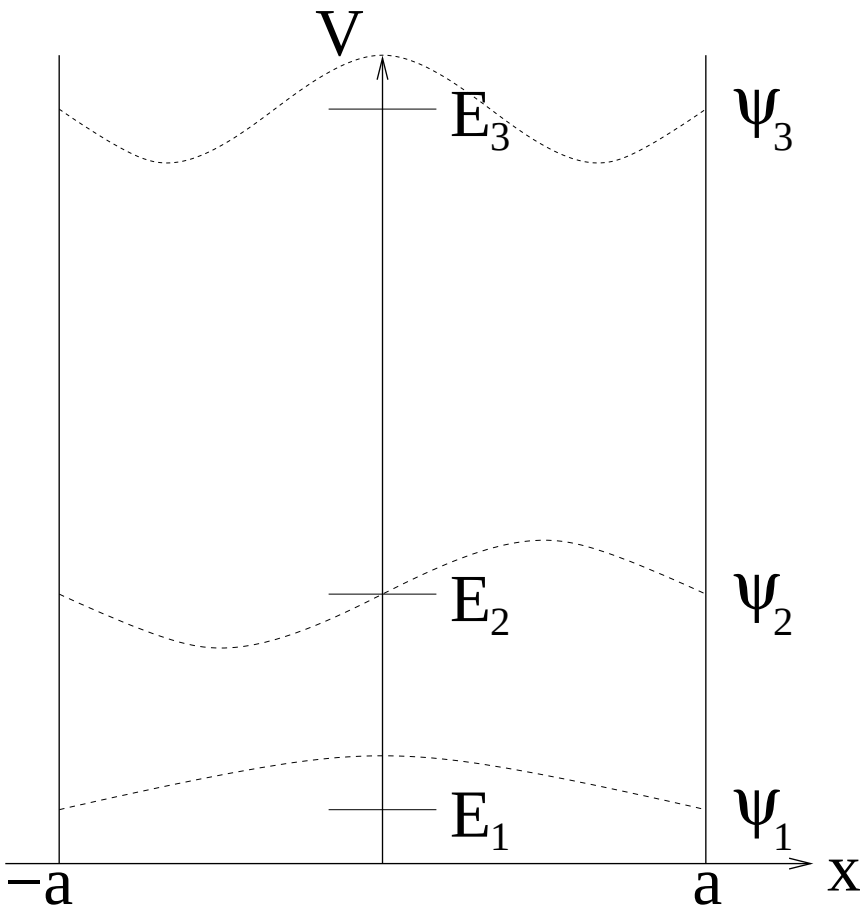

Figure 1.1: Sketch of infinite square well, showing lowest three eigenvalues and corresponding eigenfunctions.

of the spherical symmetry of the Coulomb potential, we can separate the solution into a radial and an angular part:

$$\psi(\mathbf{r}) = \psi(r,\theta,\phi) = R_{nl}(r)\,Y_{lm}(\theta,\phi) \tag{1.9}$$

where $\{n,l,m\}$ are *quantum numbers* (integers) which characterise the solution. If we substitute equation 1.9 into equation 4.1 and apply the *method of separation of variables*, we get two equations - a 2D angular equation, whose solution is given in terms of *spherical harmonics* and a 1D *radial equation:*

$$-\frac{1}{2}\frac{d^2\chi_{nl}(r)}{dr^2} + \left[V(r) + \frac{l(l+1)}{2r^2}\right]\chi_{nl}(r) = E\chi_{nl}(r) \tag{1.10}$$

where the substitution

$$\chi_{nl}(r) = rR_{nl}(r) \tag{1.11}$$

is used both to simplify the equation and ease its interpretation. Remember that the probability of finding the particle in a small volume d^3r is

$$\begin{aligned} P\left(\mathbf{r} \to \mathbf{r} + d^3r\right) &= |\psi(\mathbf{r})|^2 d^3r \\ &= |\psi(\mathbf{r})|^2 r^2 dr \cdot \sin(\theta)\, d\theta d\phi \\ &= |\chi(r)|^2 dr \cdot Y_{lm}^2(\theta,\phi)\sin(\theta)\, d\theta d\phi \end{aligned} \tag{1.12}$$

and so we see that the normalisation of χ_{nl} and Y_{lm} can be chosen such that

$$\int_0^\infty |\chi(r)|^2 dr = 1 \tag{1.13}$$

i.e. $|\chi(r)|^2$ is the *radial probability density.*

Note that the second term in equation 1.10 looks very like a potential energy term in the standard time independent Schrödinger equation, and so is known as the *effective potential:*

$$V_{eff}(r) = V(r) + \frac{l(l+1)}{2r^2} \tag{1.14}$$

and the $\frac{l(l+1)}{2r^2}$ term is known as the *centrifugal barrier.*

What can we deduce about the general form of $\chi(r)$? Well, we know the form of the Coulomb potential and so as long as $V(r) \to -\infty$ as $r \to 0$ no more quickly than r^{-1} we get

$$\frac{d^2\chi}{dr^2} = \frac{l(l+1)}{r^2}\chi \tag{1.15}$$

which gives a non-divergent solution as

$$\begin{aligned} \chi(r \to 0) &\sim r^{l+1} \\ \Rightarrow R_l(r \to 0) &\sim r^l \end{aligned} \tag{1.16}$$

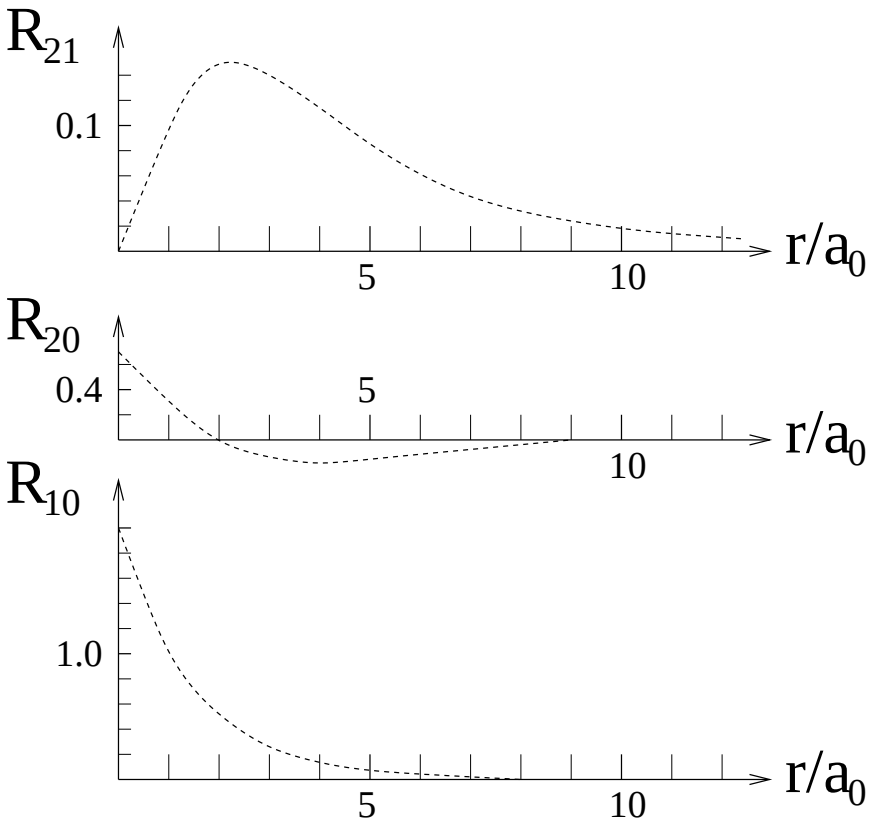

Figure 1.2: Sketch of first three radial eigenfunctions for the hydrogen atom.

Similarly, as $r \to \infty$ we get

$$\frac{d^2\chi}{dr^2} = -2E\chi(r) \tag{1.17}$$

which gives two classes of solution:

$$\begin{array}{rcll} \chi(r) & \sim & e^{-\sqrt{2|E|}r} & E<0 \quad (bound\ states) \\ \chi(r) & \sim & e^{\pm i\sqrt{2E}r} & E>0 \quad (continuum) \end{array} \tag{1.18}$$

For intermediate values of r we can either use more elaborate mathematics (which is possible for hydrogen but not for more complex atoms) or turn to numerical solutions. We can therefore use this known asymptotic behaviour to test our numerical solutions - every bound state solution, corresponding to an eigenenergy E_n, should tend to zero as $r \to \infty$, and for $r \to 0$ should either tend to zero (for non-zero l) or tend to a cusp (for $l = 0$). See figure 1.2 for a sketch of the three lowest eigenenergy solutions which demonstrates this behaviour. We now turn to the problem of how to solve differential equations numerically.

1.2 Revision of solving ordinary differential equations numerically

Unfortunately, the number of cases where we can solve the Schrödinger equation exactly are rather small. More usually, we are faced with the problem of trying to find numerical solutions. As the Schrödinger equation is a linear second-order differential equation, this should not pose too much difficulty. We therefore begin by revising what we already know about solving ordinary differential equations, before going on to explore particular techniques that are suitable for the Schrödinger equation.

Most methods are designed for first-order differential equations of the general form

$$\frac{dy}{dx} = f\left(y\left(x\right), x\right) \tag{1.19}$$

Second-order equations of the general form

$$\frac{d^2y}{dx^2} = f\left(y\left(x\right), x\right) \tag{1.20}$$

can be transformed into a pair of coupled first-order equations using

$$\begin{aligned} \frac{dy}{dx} &= z\left(x\right) \\ \frac{dz}{dx} &= f\left(y\left(x\right), x\right) \end{aligned} \tag{1.21}$$

and then solved using the same techniques.

Most methods then proceed to use an approximation to the derivative, such as the *forward difference*:

$$\frac{dy}{dx} \approx \frac{y\left(x+\delta x\right) - y\left(x\right)}{\delta x} \tag{1.22}$$

the *backwards difference*:

$$\frac{dy}{dx} \approx \frac{y\left(x\right) - y\left(x-\delta x\right)}{\delta x} \tag{1.23}$$

or the *centred difference*:

$$\frac{dy}{dx} \approx \frac{y\left(x+\delta x\right) - y\left(x-\delta x\right)}{2\delta x} \tag{1.24}$$

A straightforwards implementation of this approach results in the *Euler method*:

$$y_{n+1} \approx y_n + f\left(y_n, x_n\right) h \tag{1.25}$$

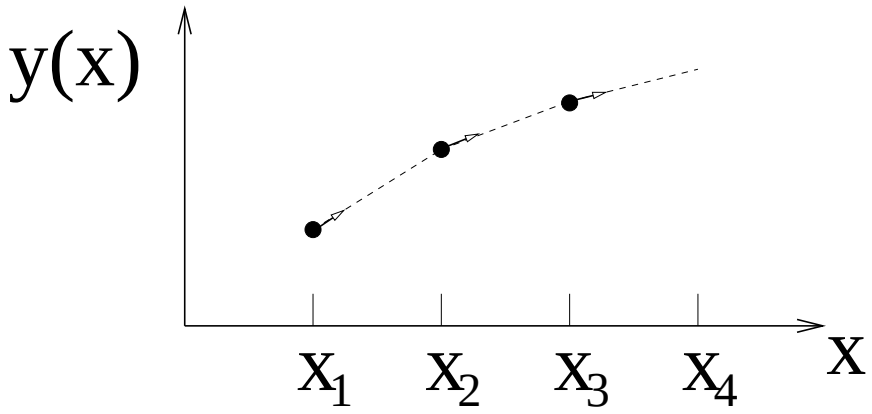

Figure 1.3: Illustration of Euler's method - the derivative at each point x_n is extrapolated over the whole step length h to form the next point.

where the solution advances from x_n to $x_{n+1} = x_n + h = x_n + \delta x$ and h is the step size. See figure 1.3 for an illustration of the method. Comparison to the Taylor series shows that this method has an error $O\left(h^2\right)$ and hence is called a *first-order method* (an n^{th}-order method has an error term $O\left(h^{n+1}\right)$). Whilst the Euler method is the theoretical basis of most schemes, and as such is important, it should not be used as it stands as it suffers from large errors and is unstable. However, it can be improved upon to form the schemes we shall discuss below.

1.2.1 The Runge-Kutta method

The Runge-Kutta method is a common class of methods used for solving many differential equations. The simplest version improves upon the Euler method by doing it twice: we evaluate y_n using a single Euler step of length h and also using a midpoint step as follows:

$$\begin{aligned} k_1 &= f\left(x_n, y_n\right) h \\ k_2 &= f\left(x_n + \frac{h}{2}, y_n + \frac{k_1}{2}\right) h \\ y_{n+1} &= y_n + k_2 + O\left(h^3\right) \end{aligned} \tag{1.26}$$

which is known as the *second-order Runge-Kutta* or *midpoint method*. It has the advantage of being more stable than the Euler method, and so can be used with a larger step size, and so requires less steps to span a given interval. Unfortunately, the cost for this higher order method is that it requires two function evaluations of $f\left(x\right)$ per step. Often, this is the most time consuming part of the calculation. See figure 1.4 for an illustration of this method.

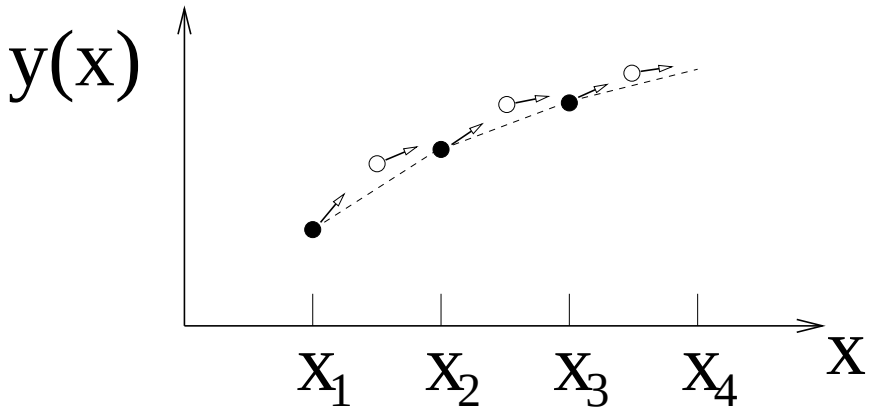

Figure 1.4: Second-order Runga-Kutta method - the derivative at the start of the step is used to find a point half-way across the interval h and this midpoint value is then used to improve the calculation of the final point at the end of the step. The filled circles represent final values which are of interest, whilst open circles are intermediate values k_i which are discarded at the end of each step.

This method can be extended to arbitrarily high orders. In practice, it is often found that the fourth-order method is the most efficient, in that higher order methods require many more function evaluations without bringing significant improvements in stability or step size. Note that a higher-order method does not always have higher accuracy! The *fourth-order Runge-Kutta method* is:

$$\begin{aligned} k_1 &= f(x_n, y_n)\, h \\ k_2 &= f\left(x_n + \frac{h}{2}, y_n + \frac{k_1}{2}\right) h \\ k_3 &= f\left(x_n + \frac{h}{2}, y_n + \frac{k_2}{2}\right) h \\ k_4 &= f(x_n + h, y_n + k_3)\, h \\ y_{n+1} &= y_n + \frac{k_1}{6} + \frac{k_2}{3} + \frac{k_3}{3} + \frac{k_4}{6} + O\left(h^5\right) \end{aligned} \tag{1.27}$$

A significant advantage of the Runge-Kutta method is that it can be used with a variable step size: at each step, an estimate of the error in the solution can be made, and the step size reduced if the error is larger than some prescribed tolerance, or the step size may be increased if a larger error can be accepted. In this way, more attention is paid to those regions where the solution is rapidly varying, whilst not paying an unnecessarily high price of using an unnecessarily small step size where the function is slowly changing. This variable step size is achieved by evaluating y_{n+1} twice, once

using a step size of h and then again using a step size of $\frac{h}{2}$. If the difference in y_{n+1} for the two different step sizes is Δ, then it can be shown that for the fourth order method, the required step size $h^{'}$ to keep the prescribed error to within δ is given by

$$h^{'} = \frac{15}{16} h \left| \frac{\delta}{\Delta} \right|^{\frac{1}{5}} \tag{1.28}$$

as the error term is $O\left(h^5\right)$. That is, if $h^{'} < h$ we must repeat the current step with the smaller step size, whilst if $h^{'} \geq h$ we may use $h^{'}$ as the new step size for the next step. There is, of course, some freedom in how to choose δ depending on the type of problem being solved - this may either be an absolute error, a fractional error, or an accumulated fractional error since the start of the calculation.

The fourth-order Runge-Kutta method, with variable step size, is perhaps the most widely used and trusted general purpose method for integrating ordinary differential equations. It has the advantage of being a self-starting method, that is, does not require knowledge of previous values to complete each step. However, it does not exploit any particular properties of the Schrödinger equation, and so in this instance there may be more specialised integration methods that can outperform it. We shall now consider one such method.

1.2.2 The Numerov method

The Numerov method is a specialised method for solving a restricted set of differential equations - those that can be written in the form:

$$\frac{d^2 y}{dx^2} = f(x)\, y(x) \tag{1.29}$$

which includes the time independent Schrödinger equation. The method exploits the special structure of this equation to produce a method that has fifth-order accuracy but only requires two function evaluations per step!

We can derive the method by expanding both $y(x \pm h)$ and $\left.\frac{d^2 y}{dx^2}\right|_{x \pm h}$ in Taylor series up to powers of h^4 and combining terms. There is a perfect cancellation of all odd-powers of h due to the symmetry of equation 1.29 and so the resulting method is accurate to order h^6. The result is

$$z(x+h) = 2z(x) - z(x-h) + h^2 f(x)\, y(x) + O\left(h^6\right) \tag{1.30}$$

where

$$z(x) = \left[1 - \frac{h^2}{12} f(x)\right] y(x) \tag{1.31}$$

The advantage of this method is that it has an error $O\left(h^6\right)$ which is an order of magnitude better than 4th-order Runge-Kutta and only requires two (rather than four) function evaluations per step. Hence it is the preferred method for solving the Schrödinger equation. However, it does have a drawback in that it is not self-starting due to the $z\left(x-h\right)$ term - that is, it requires another method to generate the first step, whereupon the Numerov method can be used. This feature of the method will also give problems if there are any discontinuities in the potential whereas the single-step Runga-Kutta method will be OK.

1.2.3 Singularities

There is a problem as to what to do at singularities. For example, in the hydrogen atom both the Coulomb potential and the centrifugal barrier diverge at the origin. However, for the hydrogen atom we have a known analytic result for $\chi\left(r=0\right)$ and so this can be substituted instead. But what about the general case of a singularity with non-zero l? Well, as long as the divergence is not too fast, then χ will still be well behaved, and we can do a Taylor series expansion for $\chi\left(r\right)$ around the singularity:

$$\chi\left(r\right)=\sum_{s=0}^{\infty}a_s r^{s+l+1} \tag{1.32}$$

from which it can be shown that

$$a_s=\frac{2}{s\left(s+2l+1\right)}\left(rV_{eff}a_{s-1}+\left(\frac{d\left(rV_{eff}\right)}{dr}-E\right)a_{s-2}\right) \tag{1.33}$$

with $a_0=1$ (unless $l=0$) and $a_{-1}=0$. Therefore we can generate all the terms for χ, with an arbitrary normalisation that can be fixed later.

1.2.4 Other methods of solution

There are other methods that can be used to solve differential equations. For example, we might choose to discretize space and solve the equation on a grid, replacing differentials by appropriate sums over neighbouring grid points, and successively iterating to self-consistency. This is known as the finite-difference approach. It can be incorporated in various ways, such as with a single fixed grid, or with a hierarchy of grid sizes, or with a grid that adapts to the solution (e.g. putting more points in the regions where the function is rapidly changing). Such methods can be very successful and an example will be considered in a later lecture.

There are also indirect methods that can be used to produce information about the solution without directly solving the equation. Such methods exploit special properties of the equation, for example, that it has particular

symmetries, or is an eigenvalue equation, or can be expressed in terms of a variational principle, etc. This will form a very important theme to later lectures in this course.

1.2.5 Errors

In general, when solving any differential equation numerically, there will be two dominant sources of error:

- truncation error
  - this is caused by the truncation of the Taylor series and represents the fundamental limit to the accuracy of a given algorithm. In general the error in a solution caused by truncation error can be reduced by using a smaller step size h.
- rounding error
  - this is caused by the finite representation of numbers within a digital computer. For example, when using single precision arithmetic in a typical modern computer, all *floating point numbers* will be accurate to about 8 significant figures, and when using double precision arithmetic they will be accurate to around 16 significant figures. In general, the error in the final solution caused by rounding error can be reduced by using fewer integration steps so that there is less accumulation of error, corresponding to a larger step size h.

It can be seen then that there is a competition between these two sources of error. Usually truncation error dominates, especially when using double precision arithmetic (which is essential for any kind of scientific computing). So when computing any solution, it is always a good idea to repeat the calculation with a smaller step size and see if there is any significant change in the solution. If there is, then the calculation must be repeated again with an even smaller step size, etc. until there is no significant change. However, if the step size is reduced too much, then rounding error will start to become signifcant and accuracy will be lost again.

1.3 Application to the Schrödinger equation

How then shall we use either the Runge-Kutta or Numerov method to solve the Schrödinger equation for any particular problem? If we are interested in finding the bound states, i.e. the eigenenergies and eigenfunctions, then we must:

- choose a particular angular momentum (value of l)
- choose a trial energy (value of E_{trial})
- starting from $r = 0$ integrate the radial equation up to some appropriate large value of $r = r_{max}$
- examine the behaviour of the solution - in particular $\chi(r \to \infty)$
- if $\chi(r) \to \pm\infty$ then E_{trial} does not correspond to a bound state so adjust E_{trial} and repeat

This process of tuning E_{trial} can of course be automated, resulting in a variant of the "shooting method".

Note that the ground state solution will have no nodes. A general solution will have integer values for $\{n, l, m\}$ - but we will get no information on m from the radial equation and we have chosen l at the outset - so by counting the number of nodes we can deduce the value of n:

$$n = (number\ of\ nodes) + l + 1$$

1.4 Final comments

A few final points to highlight:

- The Schrödinger equation can often be written as an ordinary differential equation and solved using standard numerical techniques.
- Bound states should have a vanishing wavefunction in the long-range limit.
- The Numerov method is much more efficient than fourth-order Runga-Kutta for solving the Schrödinger equation.
- Different algorithms have different characteristic features, such as the ability to handle discontinuities or variable step sizes.
- A higher-order algorithm in general has a smaller truncation error than a lower-order one (but it depends on the unknown prefactor!)
- Rounding error will dominate if the step size is made too small.

1.5 Further reading

- TISE in any undergraduate Quantum Mechanics textbook
- Numerov method discussed in "Computational Physics" by J.M. Thijssen, appendix A7