

Chapter 2

Schrödinger equation for central potentials

In this chapter we extend the concepts and methods introduced in the previous chapter for a one-dimensional problem to a specific and very important class of three-dimensional problems: a particle of mass m under a central potential $V(r)$, i.e. depending only upon the distance r from a fixed center. The Schrödinger equation we are going to study in this chapter is thus

$$H\psi(\mathbf{r}) \equiv \left[-\frac{\hbar^2}{2m}\nabla^2 + V(r) \right] \psi(\mathbf{r}) = E\psi(\mathbf{r}). \quad (2.1)$$

The problem of two interacting particles via a potential depending only upon their distance, $V(|\mathbf{r}_1 - \mathbf{r}_2|)$, e.g. the Hydrogen atom, reduces to this case, with m equal to the reduced mass of the two particles.

The general solution proceeds via the separation of the Schrödinger equation into an angular and a radial part. In this chapter we consider the numerical solution of the radial Schrödinger equation. A non-uniform grid is introduced and the radial Schrödinger equation is transformed to an equation that can still be solved using Numerov's method introduced in the previous chapter.

2.1 Variable separation

Let us introduce a polar coordinate system (r, θ, ϕ) , where θ is the polar angle, ϕ the azimuthal one, and the polar axis coincides with the z Cartesian axis. After some algebra, one finds the Laplacian operator in polar coordinates:

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \quad (2.2)$$

It is convenient to introduce the operator $L^2 = L_x^2 + L_y^2 + L_z^2$, the square of the angular momentum vector operator, $\mathbf{L} = -i\hbar\mathbf{r} \times \nabla$. Both \vec{L} and L^2 act only on angular variables. In polar coordinates, the explicit representation of L^2 is

$$L^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]. \quad (2.3)$$

The Hamiltonian can thus be written as

$$H = -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{L^2}{2mr^2} + V(r). \quad (2.4)$$

The term $L^2/2mr^2$ has a classical analogous: the radial motion of a mass having classical angular momentum L_{cl} can be described by an effective radial potential $\hat{V}(r) = V(r) + L_{cl}^2/2mr^2$, where the second term (the ‘‘centrifugal potential’’) takes into account the effects of rotational motion. For high L_{cl} the centrifugal potential ‘‘pushes’’ the equilibrium position outwards.

In the quantum case, both L^2 and one component of the angular momentum, for instance L_z :

$$L_z = -i\hbar \frac{\partial}{\partial \phi} \quad (2.5)$$

commute with the Hamiltonian, so L^2 and L_z are conserved and H , L^2 , L_z have a (complete) set of common eigenfunctions. We can thus use the eigenvalues of L^2 and L_z to classify the states. Let us now proceed to the separation of radial and angular variables, as suggested by Eq.(2.4). Let us assume

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi). \quad (2.6)$$

After some algebra we find that the Schrödinger equation can be split into an angular and a radial equation. The solution of the angular equations are the *spherical harmonics*, known functions that are eigenstates of both L^2 and L_z :

$$L_z Y_{\ell m}(\theta, \phi) = m\hbar Y_{\ell m}(\theta, \phi), \quad L^2 Y_{\ell m}(\theta, \phi) = \ell(\ell + 1)\hbar^2 Y_{\ell m}(\theta, \phi) \quad (2.7)$$

($\ell \geq 0$ and $m = -\ell, \dots, \ell$ are integer numbers).

The radial equation is

$$-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R_{n\ell}}{\partial r} \right) + \left[V(r) + \frac{\hbar^2 \ell(\ell + 1)}{2mr^2} \right] R_{n\ell}(r) = E_{n\ell} R_{n\ell}(r). \quad (2.8)$$

In general, the energy will depend upon ℓ because the effective potential does; moreover, for a given ℓ , we expect to find bound states with discrete energies and we have indicated with n the corresponding index.

Finally, the complete wave function will be

$$\psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r)Y_{\ell m}(\theta, \phi) \quad (2.9)$$

The energy does not depend upon m . As already observed, m classifies the projection of the angular momentum on an arbitrarily chosen axis. Due to spherical symmetry of the problem, the energy cannot depend upon the orientation of the vector \mathbf{L} , but only upon his modulus. An energy level $E_{n\ell}$ will then have a *degeneracy* $2\ell + 1$ (or larger, if there are other observables that commute with the Hamiltonian and that we haven't considered).

2.1.1 Radial equation

The probability $p(r)dr$ to find the particle at a distance between r and $r + dr$ from the center is given by the integration over angular variables only of the wavefunction squared:

$$p(r)dr = \int_{\Omega} |\psi_{n\ell m}(r, \theta, \phi)|^2 r d\theta r \sin \theta d\phi dr = |R_{n\ell}|^2 r^2 dr = |\chi_{n\ell}|^2 dr \quad (2.10)$$

where we have introduced an auxiliary function $\chi(r)$, sometimes called *orbital* wavefunction,

$$\chi(r) = rR(r) \quad (2.11)$$

and exploited the normalization of the spherical harmonics:

$$\int_0^{2\pi} d\phi \int_0^\pi d\theta |Y_{\ell m}(\theta, \phi)|^2 \sin \theta = 1 \quad (2.12)$$

As a consequence the normalization condition for χ is

$$\int_0^\infty |\chi_{n\ell}(r)|^2 dr = 1 \quad (2.13)$$

The function $|\chi(r)|^2$ can thus be directly interpreted as the radial probability density. Let us re-write the radial equation for $\chi(r)$ instead of $R(r)$. Its is straightforward to find that Eq.(2.8) becomes

$$-\frac{\hbar^2}{2m} \frac{d^2\chi}{dr^2} + \left[V(r) + \frac{\hbar^2 \ell(\ell+1)}{2mr^2} - E \right] \chi(r) = 0. \quad (2.14)$$

We note that this equation has the same form as the one-dimensional Schrödinger equation, Eq.(1.1), for a particle under an effective potential and $r \geq 0$:

$$\hat{V}(r) = V(r) + \frac{\hbar^2 \ell(\ell+1)}{2mr^2}. \quad (2.15)$$

As already explained, the second term is the centrifugal potential. The same methods used to find the solution of Eq.(1.1), and in particular, Numerov's method, can be used to find the radial part of the eigenfunctions of the energy.

2.2 Coulomb potential

The most important and famous case is when $V(r)$ is the Coulomb potential:

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}, \quad (2.16)$$

where $e = 1.6021 \times 10^{-19}$ C is the electron charge, Z is the atomic number (number of protons in the nucleus), $\epsilon_0 = 8.854187817 \times 10^{-12}$ in MKSA units. Physicists tend to prefer the CGS system, in which the Coulomb potential is written as:

$$V(r) = -Zq_e^2/r. \quad (2.17)$$

In the following we will use $q_e^2 = e^2/(4\pi\epsilon_0)$ so as to fall back into the simpler CGS form.

It is often practical to work with *atomic units* (a.u.): assuming that $\hbar = 1$, $m_e = 1/2$, $q_e^2 = 2$, the length is expressed in units of *Bohr radii* (or simply, "Bohr"), a_0 :

$$a_0 = \frac{\hbar^2}{m_e q_e^2} = 0.529177 \text{ \AA} = 0.529177 \times 10^{-10} \text{ m}, \quad (2.18)$$

while energies are expressed in units of *Rydberg* (Ry):

$$1 \text{ Ry} = \frac{m_e q_e^4}{2\hbar^2} = 13.6058 \text{ eV}. \quad (2.19)$$

when $m_e = 9.11 \times 10^{-31}$ Kg is the electron mass, not the reduced mass of the electron and the nucleus.

By assuming instead $\hbar = 1$, $m_e = 1$, $q_e = 1$, we obtain another set of atomic units, in which the *Hartree* (Ha) is the unit of energy instead of the Ry:

$$1 \text{ Ha} = 2 \text{ Ry} = \frac{m_e q_e^4}{\hbar^2} = 27.212 \text{ eV}. \quad (2.20)$$

Beware! Never talk about "atomic units" without first specifying *which ones*. In the following, the first set ("Rydberg" units) will be occasionally used.

We note first of all that for small r the centrifugal potential is the dominant term in the potential. The behavior of the solutions for $r \rightarrow 0$ will then be determined by

$$\frac{d^2\chi}{dr^2} \simeq \frac{\ell(\ell+1)}{r^2}\chi(r) \quad (2.21)$$

yielding $\chi(r) \sim r^{\ell+1}$, or $\chi(r) \sim r^{-\ell}$. The second possibility is not physical because $\chi(r)$ is not allowed to diverge.

For large r instead we remark that bound states may be present only if $E < 0$: there will be a classical inversion point beyond which the kinetic energy becomes negative, the wave function decays exponentially, only some energies can yield valid solutions. The case $E > 0$ corresponds instead to a problem of electron-nucleus scattering, with propagating solutions and a continuum energy spectrum. Here we deal with bound states; unbound states are the subject of the next chapter.

The asymptotic behavior of the solutions for large $r \rightarrow \infty$ will thus be determined by

$$\frac{d^2\chi}{dr^2} \simeq -\frac{2m_e}{\hbar^2}E\chi(r) \quad (2.22)$$

yielding $\chi(r) \sim \exp(\pm kr)$, where $k = \sqrt{-2m_e E}/\hbar$. The + sign must be discarded as nonphysical. It is thus sensible to assume for the solution a form like

$$\chi(r) = r^{\ell+1} e^{-kr} \sum_{n=0}^{\infty} A_n r^n \quad (2.23)$$

which guarantees in both cases, small and large r , a correct behavior, as long as the series does not diverge exponentially.

2.2.1 Energy levels

The radial equation for the Coulomb potential can then be solved along the same lines as for the harmonic oscillator, Sec.1.1. The expansion of Eq.(2.23) is introduced into Eq.(2.14), a recursion formula for coefficients A_n is derived, one finds that the series in general diverges like $\exp(2kr)$ unless it is truncated to a finite number of terms, and this happens only for some particular values of E :

$$E_n = -\frac{Z^2 m_e q_e^4}{n^2 2\hbar^2} = -\frac{Z^2}{n^2} \text{Ry} \quad (2.24)$$

where $n \geq \ell + 1$ is an integer known as *main quantum number*. For a given ℓ we find solutions for $n = \ell + 1, \ell + 2, \dots$; or, for a given n , possible values for ℓ are $\ell = 0, 1, \dots, n - 1$.

Although the effective potential appearing in Eq.(2.14) depends upon ℓ , and the angular part of the wave function also strongly depends upon ℓ , the energies, Eq.(2.24) depend only upon n . We have thus a degeneracy on the energy levels with the same n and different ℓ , in addition to the one due to the $2\ell + 1$ possible values of the quantum number m (as implied in Eq.(2.8) where m does not appear). The total degeneracy (not considering spin) for a given n is thus

$$\sum_{\ell=0}^{n-1} (2\ell + 1) = n^2. \quad (2.25)$$

2.2.2 Radial wave functions

Finally, the solution for the radial part of the wave functions is

$$\chi_{n\ell}(r) = \sqrt{\frac{(n - \ell - 1)! Z}{n^2 [(n + \ell)!]^3 a_0^3}} x^{\ell+1} e^{-x/2} L_{n-1}^{2\ell+1}(x) \quad (2.26)$$

where

$$x \equiv \frac{2Z}{n} \frac{r}{a_0} = 2\sqrt{-\frac{2m_e E_n}{\hbar^2}} r \quad (2.27)$$

and $L_{n-1}^{2\ell+1}(x)$ are *Laguerre polynomials* of degree $n - \ell - 1$. The coefficient has been chosen in such a way that the following orthonormality relations hold:

$$\int_0^\infty \chi_{n\ell}(r) \chi_{n'\ell}(r) dr = \delta_{nn'}. \quad (2.28)$$

The ground state has $n = 1$ and $\ell = 0$: $1s$ in “spectroscopic” notation ($2p$ is $n = 2, \ell = 1$, $3d$ is $n = 3, \ell = 2$, $4f$ is $n = 4, \ell = 3$, and so on). For the Hydrogen atom ($Z = 1$) the ground state energy is -1Ry and the binding energy of the electron is 1 Ry (apart from the small correction due to the difference between electron mass and reduced mass). The wave function of the ground state is a simple exponential. With the correct normalization:

$$\psi_{100}(r, \theta, \phi) = \frac{Z^{3/2}}{a_0^{3/2} \sqrt{\pi}} e^{-Zr/a_0}. \quad (2.29)$$

The dominating term close to the nucleus is the first term of the series, $\chi_{n\ell}(r) \sim r^{\ell+1}$. The larger ℓ , the quicker the wave function tends to zero when approaching the nucleus. This reflects the fact that the function is “pushed away” by the centrifugal potential. Thus radial wave functions with large ℓ do not appreciably penetrate close to the nucleus.

At large r the dominating term is $\chi(r) \sim r^n \exp(-Zr/na_0)$. This means that, neglecting the other terms, $|\chi_{n\ell}(r)|^2$ has a maximum about $r = n^2 a_0/Z$. This gives a rough estimate of the “size” of the wave function, which is mainly determined by n .

In Eq.(2.26) the polynomial has $n - \ell - 1$ degree. This is also the number of nodes of the function. In particular, the eigenfunctions with $\ell = 0$ have $n - 1$ nodes; those with $\ell = n - 1$ are node-less. The form of the radial functions can be seen for instance on the Wolfram Research site¹ or explored via the Java applet at Davidson College²

2.3 Code: hydrogen_radial

The code `hydrogen_radial.f90`³ or `hydrogen_radial.c`⁴ solves the radial equation for a one-electron atom. It is based on `harmonic1`, but solves a slightly different equation on a logarithmically spaced grid. Moreover it uses a more sophisticated approach to locate eigenvalues, based on a perturbative estimate of the needed correction.

The code uses atomic (Rydberg) units, so lengths are in Bohr radii ($a_0 = 1$), energies in Ry, $\hbar^2/(2m_e) = 1$, $q_e^2 = 2$.

2.3.1 Logarithmic grid

The straightforward numerical solution of Eq.(2.14) runs into the problem of the singularity of the potential at $r = 0$. One way to circumvent this difficulty is to work with a variable-step grid instead of a constant-step one, as done in the previous chapter. Such grid becomes denser and denser as we approach the origin. Real-life solutions of the radial Schrödinger equation in atoms, especially heavy one, invariably involve such kind of grids, since wave functions close to the nucleus vary on a much smaller length scale than far from the nucleus. A detailed description of the scheme presented here can be found in chap.6 of *The Hartree-Fock method for atoms*, C. Froese Fischer, Wiley, 1977.

Let us introduce a new integration variable x and a constant-step grid in x , so as to be able to use Numerov’s method without changes. We define a mapping between r and x via

$$x = x(r). \tag{2.30}$$

The relation between the constant-step grid spacing Δx and the variable-step grid spacing is given by

$$\Delta x = x'(r)\Delta r. \tag{2.31}$$

¹<http://library.wolfram.com/webMathematica/Physics/Hydrogen.jsp>

²http://webphysics.davidson.edu/physlet_resources/cise_qm/html/hydrogenic.html

³http://www.fisica.uniud.it/%7Egiannozz/Didattica/MQ/Software/F90/hydrogen_radial.f90

⁴http://www.fisica.uniud.it/%7Egiannozz/Didattica/MQ/Software/C/hydrogen_radial.c

We make the specific choice

$$x(r) \equiv \log \frac{Zr}{a_0} \quad (2.32)$$

(note that with this choice x is adimensional) yielding

$$\Delta x = \frac{\Delta r}{r}. \quad (2.33)$$

The $\Delta r/r$ ratio remains thus constant on the grid of r so defined. This kind of grid is usually called *logarithmic grid*, but some people see the thing the other way round and call it *exponential*!

There is however a problem: by transforming Eq.(2.14) in the new variable x , a term with first derivative appears, preventing the usage of Numerov's method (and of other integration methods as well). The problem can be circumvented by transforming the unknown function as follows:

$$y(x) = \frac{1}{\sqrt{r}} \chi(r(x)). \quad (2.34)$$

It is easy to verify that by transforming Eq.(2.14) so as to express it as a function of x and y , the terms containing first-order derivatives disappear, and by multiplying both sides of the equation by $r^{3/2}$ one finds

$$\frac{d^2 y}{dx^2} + \left[\frac{2m_e}{\hbar^2} r^2 (E - V(r)) - \left(\ell + \frac{1}{2} \right)^2 \right] y(x) = 0 \quad (2.35)$$

where $V(r) = -Zq_e^2/r$ for the Coulomb potential. This equation no longer presents any singularity for $r = 0$, is in the form of Eq.(1.22), with

$$g(x) = \frac{2m_e}{\hbar^2} r(x)^2 (E - V(r(x))) - \left(\ell + \frac{1}{2} \right)^2 \quad (2.36)$$

and can be directly solved using the numerical integration formulae Eqs.(1.32) and (1.33) and an algorithm very similar to the one of Sec.1.3.2.

Subroutine `do_mesh` computes and stores the values of r , \sqrt{r} , r^2 for each grid point. The potential is also calculated and stored in `init_pot`. The grid is calculated starting from a minimum value, set in the code to $x = -8$, corresponding to $Zr_{\min} \simeq 3.4 \times 10^{-3}$ Bohr radii. Note that the grid in r does not include $r = 0$: this would correspond to $x = -\infty$. The known analytical behavior for $r \rightarrow 0$ and $r \rightarrow \infty$ are used to start the outward and inward recurrences, respectively.

2.3.2 Improving convergence with perturbation theory

A few words are needed to explain this section of the code:

```
i = icl
ycusp = (y(i-1)*f(i-1)+f(i+1)*y(i+1)+10.d0*f(i)*y(i)) / 12.d0
dfcusp = f(i)*(y(i)/ycusp - 1.d0)
! eigenvalue update using perturbation theory
de = dfcusp/ddx12 * ycusp*ycusp * dx
```

whose goal is to give an estimate, to first order in perturbation theory, of the difference δe between the current estimate of the eigenvalue and its final value.

Reminder: `ic1` is the index corresponding to the classical inversion point. Integration is made with forward recursion up to this index, with backward recursion down to this index. `ic1` is thus the index of the matching point between the two functions. The function at the right is rescaled so that the total function is continuous, but the first derivative dy/dx will be in general discontinuous, unless we have reached a good eigenvalue.

In the section of the code shown above, `y(ic1)` is the value given by Numerov's method using either `ic1-1` or `ic1+1` as central point; `ycusp` is the value predicted by the Numerov's method using `ic1` as central point. The problem is that `ycusp` \neq `y(ic1)`.

What about if our function is the *exact solution*, but for a *different problem*? It is easy to find what the different problem could be: one in which a delta function, $v_0\delta(x-x_c)$, is superimposed at $x_c \equiv \mathbf{x}(\text{ic1})$ to the potential. The presence of a delta function causes a discontinuity (a "cusp") in the first derivative, as can be demonstrated by a limit procedure, and the size of the discontinuity is related to the coefficient of the delta function. Once the latter is known, we can give an estimate, based on perturbation theory, of the difference between the current eigenvalue (for the "different" potential) and the eigenvalue for the "true" potential.

One may wonder how to deal with a delta function in numerical integration. In practice, we assume the delta to have a value only in the interval Δx centered on `y(ic1)`. The algorithm used to estimate its value is quite sophisticated. Let us look again at Numerov's formula, Eq.(1.33): note that the formula actually provides only the product `y(ic1)f(ic1)`. From this we usually extract `y(ic1)` since `f(ic1)` is assumed to be known. Now we suppose that `f(ic1)` has a different and unknown value `fcusp`, such that our function satisfies Numerov's formula also in point `ic1`. The following must hold:

$$\text{fcusp} * \text{ycusp} = \text{f}(\text{ic1}) * \text{y}(\text{ic1})$$

since this product is provided by Numerov's method (by integrating from `ic1-1` to `ic1+1`), and `ycusp` is that value that the function `y` must have in order to satisfy Numerov's formula also in `ic1`. As a consequence, the value of `dfcusp` calculated by the program is just `fcusp-f(ic1)`, or δf .

The next step is to calculate the variation δV of the potential $V(r)$ appearing in Eq.(2.35) corresponding to δf . By differentiating Eq.(2.36) one finds $\delta g(x) = -(2m_e/\hbar^2)r^2\delta V$. Since $f(x) = 1 + g(x)(\Delta x)^2/12$, we have $\delta g = 12/(\Delta x)^2\delta f$, and thus

$$\delta V = -\frac{\hbar^2}{2m_e} \frac{1}{r^2} \frac{12}{(\Delta x)^2} \delta f. \quad (2.37)$$

First-order perturbation theory gives then the corresponding variation of the eigenvalue:

$$\delta e = \langle \psi | \delta V | \psi \rangle = \int |y(x)|^2 r(x)^2 \delta V dx. \quad (2.38)$$

Note that the change of integration variable from dr to dx adds a factor r to the integral:

$$\int_0^\infty f(r)dr = \int_{-\infty}^\infty f(r(x))\frac{dr(x)}{dx}dx = \int_{-\infty}^\infty f(r(x))r(x)dx. \quad (2.39)$$

We write the above integral as a finite sum over grid points, with a single non-zero contribution coming from the region of width Δx centered at point $x_c = \mathbf{x}(\mathbf{ic1})$. Finally:

$$\delta e = |y(x_c)|^2 r(x_c)^2 \delta V \Delta x = -\frac{\hbar^2}{2m_e} \frac{12}{(\Delta x)^2} |y(x_c)|^2 \Delta x \delta f \quad (2.40)$$

is the difference between the eigenvalue of the current potential (i.e. with a superimposed Delta function) and that of the true potential. This expression is used by the code to calculate the correction \mathbf{de} to the eigenvalue. Since in the first step this estimate may have large errors, the line

```
e = max(min(e+de,eup),elw)
```

prevents the usage of a new energy estimate outside the bounds $[\mathbf{elw}, \mathbf{eip}]$. As the code proceeds towards convergence, the estimate becomes better and better and convergence is very fast in the final steps.

2.3.3 Laboratory

- Examine solutions as a function of n and ℓ ; verify the presence of accidental degeneracy.
- Examine solutions as a function of the nuclear charge Z .
- Compare the numerical solution with the exact solution, Eq.(2.29), for the $1s$ case (or other cases if you know the analytic solution).
- Slightly modify the potential as defined in subroutine `init_pot`, verify that the accidental degeneracy disappears. Some suggestions: $V(r) = -Zq_e^2/r^{1+\delta}$ where δ is a small, positive or negative, number; or add an exponential Yukawa damping, $V(r) = -Zq_e^2 \exp(-Qr)/r$, where Q is a number of the order of 0.05 a.u..
- Calculate the expectation values of r and of $1/r$, compare them with the known analytical results.

Possible code modifications and extensions:

- Consider a different mapping: $r(x) = r_0(\exp(x) - 1)$, that unlike the one we have considered, includes $r = 0$. Which changes must be done in order to adapt the code to this mapping?