

4. Energy Levels

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4.1 Bound problems

In the previous chapter we studied stationary problems in which the system is best described as a (time-independent) wave, “scattering” and “tunneling” (that is, showing variation on its intensity) because of obstacles given by changes in the potential energy.

Although the potential determined the space-dependent wavefunction, there was no limitation imposed on the possible wavenumbers and energies involved. An infinite number of *continuous* energies were possible solutions to the time-independent Schrödinger equation.

In this chapter, we want instead to describe systems which are best described as particles confined inside a potential. This type of system well describe atoms or nuclei whose constituents are bound by their mutual interactions. We shall see that because of the particle confinement, the solutions to the energy eigenvalue equation (i.e. the time-independent Schrödinger equation) are now only a *discrete* set of possible values (a discrete set of energy levels). The energy is therefore **quantized**. Correspondingly, only a discrete set of eigenfunctions will be solutions, thus the system, if it's in a stationary state, can only be found in one of these allowed eigenstates.

We will start to describe simple examples. However, after learning the relevant concepts (and mathematical tricks) we will see how these same concepts are used to predict and describe the energy of atoms and nuclei. This theory can predict for example the discrete emission spectrum of atoms and the nuclear binding energy.

4.1.1 Energy in Square infinite well (particle in a box)

The simplest system to be analyzed is a particle in a box: classically, in 3D, the particle is stuck inside the box and can never leave. Another classical analogy would be a ball at the bottom of a well so deep that no matter how much kinetic energy the ball possess, it will never be able to exit the well.

We consider again a particle in a 1D space. However now the particle is no longer free to travel but is confined to be between the positions 0 and L . In order to confine the particle there must be an infinite force at these boundaries that repels the particle and forces it to stay only in the allowed space. Correspondingly there must be an infinite potential in the forbidden region.

Thus the potential function is as depicted in Fig. 20: $V(x) = \infty$ for $x < 0$ and $x > L$; and $V(x) = 0$ for $0 \leq x \leq L$. This last condition means that the particle behaves as a free particle inside the well (or box) created by the potential.

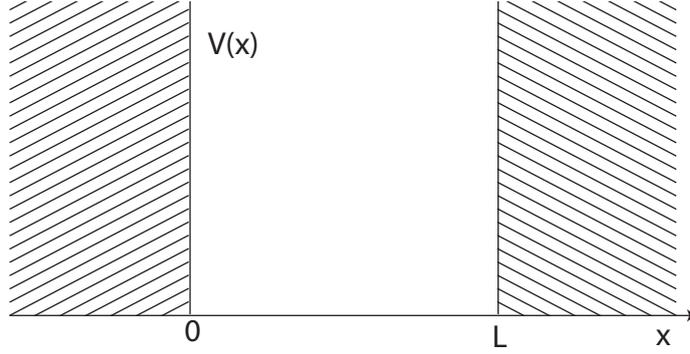


Fig. 19: Potential of an infinite well

We can then write the energy eigenvalue problem inside the well:

$$\mathcal{H}[w_n] = -\frac{\hbar^2}{2m} \frac{\partial^2 w_n(x)}{\partial x^2} = E_n w_n(x)$$

Outside the well we cannot write a proper equation because of the infinities. We can still set the values of $w_n(x)$ at the boundaries $0, L$. Physically, we expect $w_n(x) = 0$ in the forbidden region. In fact, we know that $\psi(x) = 0$ in the forbidden region (since the particle has zero probability of being there)⁶. Then if we write any $\psi(x)$ in terms of the energy eigenfunctions, $\psi(x) = \sum_n c_n w_n(x)$ this has to be zero $\forall c_n$ in the forbidden region, thus the w_n have to be zero.

At the boundaries we can thus write the boundary conditions⁷:

$$w_n(0) = w_n(L) = 0$$

We can solve the eigenvalue problem inside the well as done for the free particle, obtaining the eigenfunctions

$$w'_n(x) = A' e^{ik_n x} + B' e^{-ik_n x},$$

with eigenvalues $E_n = \frac{\hbar^2 k_n^2}{2m}$.

It is easier to solve the boundary conditions by considering instead:

$$w_n(x) = A \sin(k_n x) + B \cos(k_n x).$$

We have:

$$w_n(0) = A \times 0 + B \times 1 = B = 0$$

Thus from $w_n(0) = 0$ we have that $B = 0$. The second condition states that

$$w_n(L) = A \sin(k_n L) = 0$$

The second condition thus does not set the value of A (that can be done by the normalization condition). In order to satisfy the condition, instead, we have to set

$$k_n L = n\pi \quad \rightarrow \quad k_n = \frac{n\pi}{L}$$

for integer n . This condition then in turns sets the allowed values for the energies:

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 \pi^2}{2mL^2} n^2 \equiv E_1 n^2$$

where we set $E_1 = \frac{\hbar^2 \pi^2}{2mL^2}$ and n is called a **quantum number** (associated with the energy eigenvalue).

From this, we see that only some values of the energies are allowed. There are still an infinite number of energies, but now they are not a continuous set. We say that the energies are **quantized**. The quantization of energies (first

⁶ Note that this is true because the potential is infinite. The energy eigenvalue function (for the Hamiltonian operator) is always valid. The only way for the equation to be valid outside the well it is if $w_n(x) = 0$

⁷ Note that in this case we cannot require that the first derivative be continuous, since the potential becomes infinity at the boundary. In the cases we examined to describe scattering, the potential had only discontinuity of the first kind.

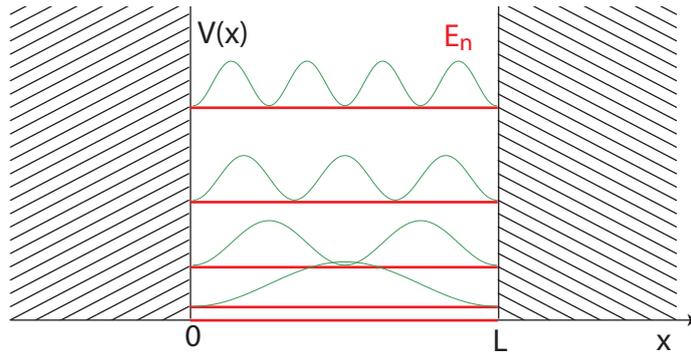


Fig. 20: Quantized energy levels (E_n for $n = 0 - 4$) in red. Also, in green the position probability distribution $|w_n(x)|^2$

the photon energies in black-body radiation and photo-electric effect, then the electron energies in the atom) is what gave *quantum* mechanics its name. However, as we saw from the scattering problems in the previous chapter, the quantization of energies is not a general property of quantum mechanical systems. Although this is common (and the rule any time that the particle is *bound*, or confined in a region by a potential) the quantization is always a consequence of a particular characteristic of the potential. There exist potentials (as for the free particle, or in general for unbound particles) where the energies are not quantized and do form a continuum (as in the classical case).

Finally we calculate the normalization of the energy eigenfunctions:

$$\int_{-\infty}^{\infty} dx |w_n|^2 = 1 \rightarrow \int_0^L A^2 \sin^2(k_n x) dx = \frac{L}{2} A^2 = 1 \rightarrow A = \sqrt{\frac{2}{L}}$$

Notice that because the system is bound inside a well defined region of space, the normalization condition has now a very clear physical meaning (and thus we must always apply it): if the system is represented by one of the eigenfunctions (and it is thus stationary) we know that it must be found somewhere between 0 and L . Thus the probability of finding the system somewhere in that region must be one. This corresponds to the condition $\int_0^L p(x) dx = 1$ or $\int_0^L |\psi(x)|^2 dx = 1$.

Finally, we have

$$w_n(x) = \sqrt{\frac{2}{L}} \sin k_n x, \quad k_n = \frac{n\pi}{L}, \quad E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2$$

Now assume that a particle is in an energy eigenstate, that is $\psi(x) = w_n(x)$ for some n : $\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$. We plot in Fig. 21 some possible wavefunctions.

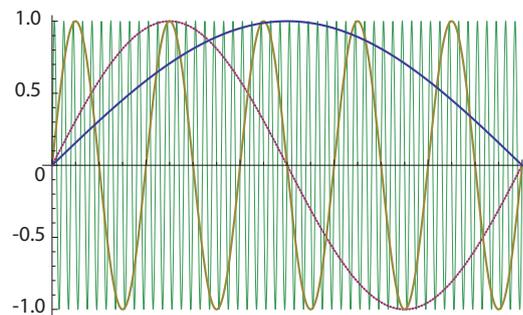


Fig. 21: Energy eigenfunctions. Blue: $n=1$, Mauve $n=2$, Brown $n=10$, Green $n=100$

Consider for example $n = 1$.

? **Question:** What does an energy measurement yield? What is the probability of this measurement?

($E = \frac{\hbar^2 \pi^2}{2m}$ with probability 1)

? **Question:** what does a position measurement yield? What is the probability of finding the particle at $0 \leq x \leq L$ and at $x = 0, L$?

? **Question:** What is the difference in energy between n and $n + 1$ when $n \rightarrow \infty$? And what about the position probability $|w_n|^2$ at large n ? What does that say about a possible classical limit?

In the limit of large quantum numbers or small deBroglie wavelength $\lambda \propto 1/k$ on average the quantum mechanical description recovers the classical one (*Bohr correspondence principle*).

4.1.2 Finite square well

We now consider a potential which is very similar to the one studied for scattering (compare Fig. 15 to Fig. 22), but that represents a completely different situation. The physical picture modeled by this potential is that of a bound particle. Specifically if we consider the case where the total energy of the particle $E_2 < 0$ is negative, then classically we would expect the particle to be trapped inside the potential well. This is similar to what we already saw when studying the infinite well. Here however the height of the well is finite, so that we will see that the quantum mechanical solution allows for a finite penetration of the wavefunction in the classically forbidden region.

? **Question:** What is the expected behavior of a classical particle? (consider for example a snowboarder in a half-pipe. If she does not have enough speed she's not going to be able to jump over the slope, and will be confined inside).

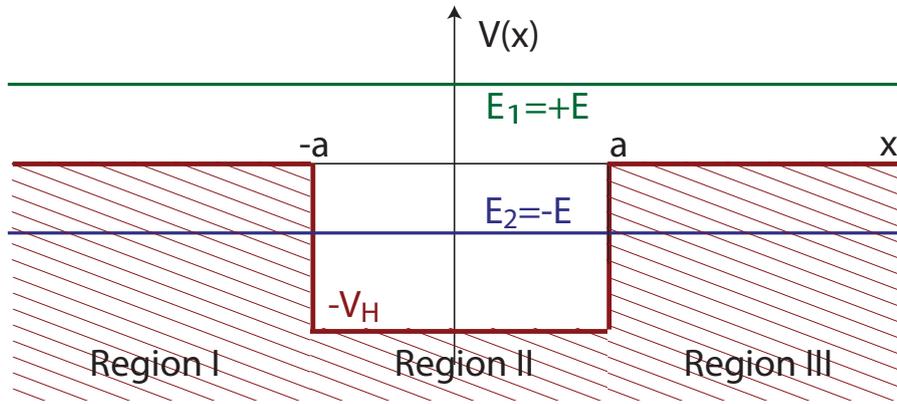


Fig. 22: Potential of a finite well. The potential is non-zero and equal to $-V_H$ in the region $-a \leq x \leq a$.

For a quantum mechanical particle we want instead to solve the Schrödinger equation. We consider two cases. In the first case, the kinetic energy is always positive:

$$\mathcal{H}\psi(x) = -\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \rightarrow \begin{cases} -\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} = E\psi(x) & \text{in Region I} \\ -\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} = (E + V_H)\psi(x) & \text{in Region II} \\ -\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} = E\psi(x) & \text{in Region III} \end{cases}$$

so we expect to find a solution in terms of traveling waves. This is not so interesting, we only note that this describes the case of an unbound particle. The solutions will be similar to scattering solutions (see mathematica demonstration). In the second case, the kinetic energy is greater than zero for $|x| \leq a$ and negative otherwise (since the total energy is negative). Notice that I set E to be a positive quantity, and the system's energy is $-E$. We also assume that $E < V_H$. The equations are thus rewritten as:

$$\mathcal{H}\psi(x) = -\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \rightarrow \begin{cases} -\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} = -E\psi(x) & \text{in Region I} \\ -\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} = (V_H - E)\psi(x) & \text{in Region II} \\ -\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} = -E\psi(x) & \text{in Region III} \end{cases}$$

Then we expect waves inside the well and an imaginary momentum (yielding exponentially decaying probability of finding the particle) in the outside regions. More precisely, in the 3 regions we find:

Region I	Region II	Region III
$k' = i\kappa,$	$k = \sqrt{\frac{2m(V_H + E_2)}{\hbar^2}}$	$k' = i\kappa,$
$\kappa = \sqrt{\frac{-2mE_2}{\hbar^2}} = \sqrt{\frac{2mE}{\hbar^2}}$	$= \sqrt{\frac{2m(V_H - E)}{\hbar^2}}$	$\kappa = \sqrt{\frac{2mE}{\hbar^2}}$

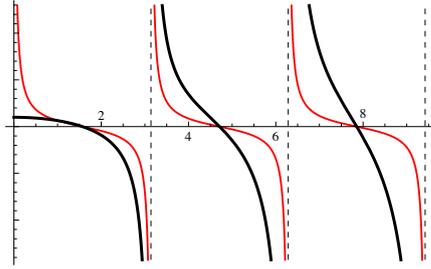


Fig. 23: $\cot z$ (Red) and $z \cot z$ (Black)

And the wavefunction is

Region I	Region II	Region III
$C'e^{-\kappa x }$	$A'e^{ikx} + B'e^{-ikx}$	$D'e^{-\kappa x}$

(Notice that in the first region I can write either $C'e^{-\kappa|x|}$ or $C'e^{\kappa x}$. The first notation makes it clear that we have an exponential decay). We now want to match the boundary conditions in order to find the coefficients. Also, we remember from the infinite well that the boundary conditions gave us not the coefficient A, B but a condition on the allowed values of the energy. We expect something similar here, since the infinite case is just a limit of the present case.

First we note that the potential is an even function of x . The differential operator is also an even function of x . Then the solution has to either be odd or even for the equation to hold. This means that A and B have to be chosen so that $\psi(x) = A'e^{ikx} + B'e^{-ikx}$ is either even or odd. This is arranged by setting $\psi(x) = A \cos(kx)$ [even solution] or $\psi(x) = A \sin(kx)$ [odd solution]. Here I choose the odd solution, $\psi(-x) = -\psi(x)$. That also sets $C' = -D'$ and we rewrite this constant as $-C' = D' = C$.

We then have:

Region I	Region II	Region III
$\psi(x) = -C'e^{\kappa x}$	$\psi(x) = A \sin(kx)$	$\psi(x) = Ce^{-\kappa x}$
$\psi'(x) = -\kappa C'e^{\kappa x}$	$\psi'(x) = kA \cos(kx)$	$\psi'(x) = -\kappa C'e^{-\kappa x}$

Since we know that $\psi(-x) = -\psi(x)$ (odd solution) we can consider the boundary matching condition only at $x = a$. The two equations are:

$$\begin{cases} A \sin(ka) = Ce^{-\kappa a} \\ Ak \cos(ka) = -\kappa C e^{-\kappa a} \end{cases}$$

Substituting the first equation into the second we find: $Ak \cos(ka) = -\kappa A \sin(ka)$. Then we obtain an equation not for the coefficient A (as it was the case for the infinite well) but a constraint on the eigenvalues k and κ :

$$\kappa = -k \cot(ka)$$

This is a condition on the eigenvalues that allows only a subset of solutions. This equation cannot be solved analytically, we thus search for a solution graphically (it could be done of course numerically!).

To do so, we first make a change of variable, multiplying both sides by a and setting $ka = z$, $\kappa a = z_1$. Notice that $z_1^2 = \frac{2mE}{\hbar^2} a^2$ and $z^2 = \frac{2m(V_H - E)}{\hbar^2} a^2$. Setting $z_0^2 = \frac{2mV_H a^2}{\hbar^2}$, we have $z_1^2 = z_0^2 - z^2$ or $\kappa a = \sqrt{z_0^2 - z^2}$. Then we can

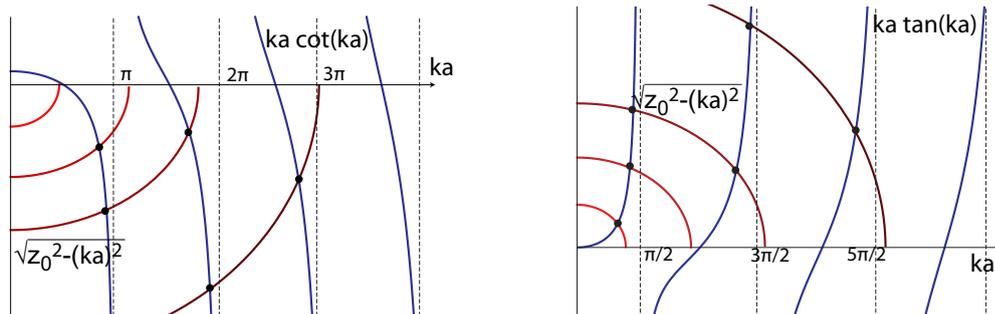


Fig. 24: Graphic solution of the eigenvalue equation. Left: **odd** solutions; Right: **even** solutions. The red curves of different tone are the function $-\sqrt{z_0^2 - z^2}$ (left) or $\sqrt{z_0^2 - z^2}$ (right) for different (increasing) values of z_0 . Crossings (solutions) are marked by a black dot.

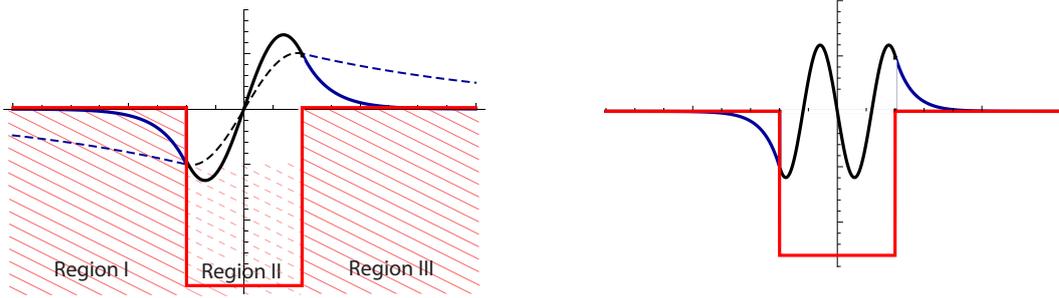


Fig. 25: Left: Odd solution for the finite barrier potential, for two potential depth. Ground state of the wavefunction. The wavefunction is a sinusoidal in Region II (Black) and an exponential decay in regions I and III (Blue). Notice that for the shallower potential (dashed lines) the wavefunction just barely “fit” inside the well. Right: Odd solution, for larger k vector (higher quantum number), allowing two oscillations.

rewrite the equation $\kappa a = -ka \cot(ka) \rightarrow z_1 = -z \cot(z)$ as $\sqrt{z_0^2 - z^2} = -z \cot(z)$, or:

$$\sqrt{z_0^2 - z^2} = -z \cot(z)$$

This is a transcendental equation for z (and hence E) as a function of z_0 , which gives the depth of the well (via V_H). To find solutions we plot both sides of the equation and look for crossings. That is, we plot $y_1(z) = -\sqrt{z_0^2 - z^2}$, which represent a quarter circle (as z is positive) of radius $z_0 = \sqrt{\frac{2mV_H a^2}{\hbar^2}}$ and $y_2(z) = z \cot(z)$.

Obs. 1 The coefficient A (and thus C and D) can be found (once the eigenfunctions have been found numerically or graphically) by imposing that the eigenfunction is normalized.

Obs. 2 Notice that the first red curve never crosses the blue curves. That means that there are no solutions. If $z_0 < \pi/2$ there are no solutions (That is, if the well is too shallow there are no bound solutions, the particle can escape). Only if $V_H > \frac{\hbar^2}{ma^2} \frac{\pi^2}{8}$ there’s a bound solution.

Obs. 3 There’s a finite number of solutions, given a value of $z_0 > \pi/2$. For example, for $\pi/2 \leq z_0 \leq 3\pi/2$ there’s only one solution, 2 for $3\pi/2 \leq z_0 \leq 5\pi/2$, etc.

Remember however that we only considered the *odd* solutions. A bound solution is always possible if we consider the even solutions., since the equation to be solved is

$$\kappa a = ka \tan(ka) = \sqrt{z_0^2 - z^2}.$$

Importantly, we found that for the odd solution there is a minimum size of the potential well (width and depth) that supports bound states. How can we estimate this size? A bound state requires a negative total energy, or a kinetic energy smaller than the potential: $E_{kin} = \frac{\hbar^2 k^2}{2m} < V_H$. This poses a constraint on the wavenumber k and thus the wavelength, $\lambda = \frac{2\pi}{k}$:

$$\lambda \geq \frac{2\pi\hbar}{\sqrt{2mV_H}}$$

However, in order to satisfy the boundary conditions (that connect the oscillating wavefunction to the exponentially decay one) we need to *fit* at least half of a wavelength inside the $2a$ width of the potential., $\frac{1}{2}\lambda \leq 2a$. Then we obtain

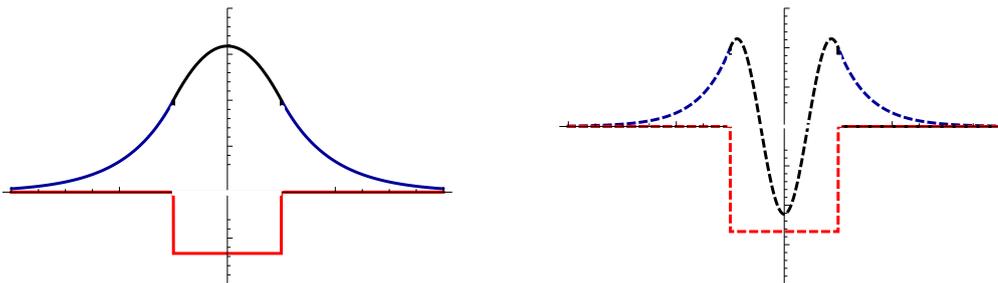


Fig. 26: Even solution for the finite barrier potential. The wavefunction is $\propto \cos(kx)$ in Region II (Black) and an exponential decay in regions I and III (Blue). Left: any wavefunction can “fit” in the well and satisfy the boundary condition (there’s no minimum well depth and width). Right, wavefunction with a higher quantum number, showing two oscillations

a relationship between the minimum potential depth and width

$$\frac{2\pi\hbar}{\sqrt{2mV_H}} \leq \lambda \leq 4a \quad \rightarrow \quad V_H \geq \frac{\hbar^2 \pi^2}{ma^2} \frac{1}{8}$$

Although we solved a 1D problem, the square well represents a 3D problem as well. Consider for example a spherical well in 3D: The potential is zero inside a region of radius a and is V_H for $r > a$. Then we can rewrite the time-independent Schrödinger equation in 3D for this potential in spherical coordinates and use separation of variables ($\{r, \vartheta, \varphi\}$). Because of symmetry, the wavefunction is a constant in ϑ and φ , thus we will have to solve just a single differential equation for the radial variable, very similar to what found here. We must then choose the odd-parity solution in order to obtain a finite wavefunction at $r = 0$. Thus in 3D, only the odd solutions are possible and we need a minimum potential well depth in order to find a bound state.

4.2 Quantum Mechanics in 3D: Angular momentum

4.2.1 Schrödinger equation in spherical coordinates

We now go back to the time-independent Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(x, y, z)\right)\psi(x) = E\psi(x)$$

We have already studied some solutions to this equations – for specific potentials in *one dimension*. Now we want to solve QM problems in 3D. Specifically, we look at 3D problems where the potential $V(\vec{x})$ is isotropic, that is, it only depends on the distance from the origin. Then, instead of using cartesian coordinates $\vec{x} = \{x, y, z\}$, it is convenient to use spherical coordinates $\vec{x} = \{r, \vartheta, \varphi\}$:

$$\begin{cases} x = r \sin \vartheta \cos \varphi \\ y = r \sin \vartheta \sin \varphi \\ z = r \cos \vartheta \end{cases} \leftrightarrow \begin{cases} r = \sqrt{x^2 + y^2 + z^2} \\ \vartheta = \arctan\left(\frac{z}{\sqrt{x^2 + y^2}}\right) \\ \varphi = \arctan(y/x) \end{cases}$$

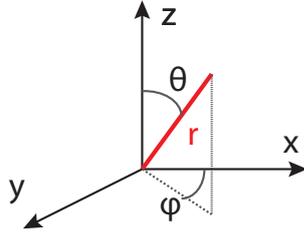


Fig. 27: Spherical Coordinates

First, we express the Laplacian ∇^2 in spherical coordinates:

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial}{\partial \vartheta} \right) + \frac{1}{r^2 \sin^2 \vartheta} \frac{\partial^2}{\partial \varphi^2}$$

To look for solutions, we use again the separation of variable methods, writing $\psi(\vec{x}) = \psi(r, \vartheta, \varphi) = R(r)Y(\vartheta, \varphi)$:

$$-\frac{\hbar^2}{2m} \left[\frac{Y}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{R}{r^2 \sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial Y}{\partial \vartheta} \right) + \frac{R}{r^2 \sin^2 \vartheta} \frac{\partial^2 Y}{\partial \varphi^2} \right] + V(r)RY = ERY$$

We then divide by RY/r^2 and rearrange the terms as

$$-\frac{\hbar^2}{2m} \left[\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) \right] + r^2(V - E) = \frac{\hbar^2}{2mY} \left[\frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial Y}{\partial \vartheta} \right) + \frac{1}{\sin^2 \vartheta} \frac{\partial^2 Y}{\partial \varphi^2} \right]$$

Each side is a function of r only and ϑ, φ , so they must be independently equal to a constant C that we set (for reasons to be seen later) equal to $C = -\frac{\hbar^2}{2m}l(l+1)$. We obtain two equations:

$$\boxed{\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2m r^2}{\hbar^2} (V - E) = l(l+1)}$$

and

$$\boxed{\frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial Y}{\partial \vartheta} \right) + \frac{1}{\sin^2 \vartheta} \frac{\partial^2 Y}{\partial \varphi^2} = -l(l+1)Y}$$

This last equation is the angular equation. Notice that it can be considered an eigenvalue equation for an operator $\frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial}{\partial \vartheta} \right) + \frac{1}{\sin^2 \vartheta} \frac{\partial^2}{\partial \varphi^2}$. What is the meaning of this operator?

4.2.2 Angular momentum operator

We take one step back and look at the angular momentum operator. From its classical form $\vec{L} = \vec{r} \times \vec{p}$ we can define the QM operator:

$$\hat{L} = \hat{r} \times \hat{p} = -i \hat{r} \times \hat{\nabla}$$

In cartesian coordinates this reads

$$\begin{aligned}\hat{L}_x &= \hat{y}\hat{p}_z - \hat{p}_y\hat{z} = -i\hbar \left(y \frac{\partial}{\partial z} - \frac{\partial}{\partial y} z \right) \\ \hat{L}_y &= \hat{z}\hat{p}_x - \hat{p}_z\hat{x} = -i\hbar \left(z \frac{\partial}{\partial x} - \frac{\partial}{\partial z} x \right) \\ \hat{L}_z &= \hat{x}\hat{p}_y - \hat{p}_x\hat{y} = -i\hbar \left(z \frac{\partial}{\partial y} - \frac{\partial}{\partial x} y \right)\end{aligned}$$

Some very important properties of this vector operator regard its commutator. Consider for example $[\hat{L}_x, \hat{L}_y]$:

$$[\hat{L}_x, \hat{L}_y] = [\hat{y}\hat{p}_z - \hat{p}_y\hat{z}, \hat{z}\hat{p}_x - \hat{p}_z\hat{x}] = [\hat{y}\hat{p}_z, \hat{z}\hat{p}_x] - [\hat{p}_y\hat{z}, \hat{z}\hat{p}_x] - [\hat{y}\hat{p}_z, \hat{p}_z\hat{x}] + [\hat{p}_y\hat{z}, \hat{p}_z\hat{x}]$$

Now remember that $[x_i, x_j] = [p_i, p_j] = 0$ and $[x_i, p_j] = i \delta_{ij}$. Also $[AB, C] = A[B, C] + [A, C]B$. This simplifies matters a lot

$$[\hat{L}_x, \hat{L}_y] = \hat{y}[\hat{p}_z, \hat{z}]\hat{p}_x - [\hat{p}_y\hat{z}, \hat{z}\hat{p}_x] - [\hat{y}\hat{p}_z, \hat{p}_z\hat{x}] + \hat{p}_y[\hat{z}, \hat{p}_z]\hat{x} = i\hbar(\hat{x}\hat{p}_y - \hat{y}\hat{p}_x) = i\hbar\hat{L}_z$$

By performing a cyclic permutation of the indexes, we can show that this holds in general:

$$[\hat{L}_a, \hat{L}_b] = i\hbar\hat{L}_c$$

Obs. Since the different components of the angular momentum do not commute, they do not possess common eigenvalues and there is an uncertainty relation for them. If for example I know with absolute precision the angular momentum along the z direction, I cannot have any knowledge of the components along x and y .

? Question : what is the uncertainty relation for the x and y components?

$$\Delta L_x \Delta L_y \geq \frac{\hbar}{2} |\langle L_z \rangle|$$

? Question: Assume we know with certainty the angular momentum along the z direction. What is the uncertainty in the angular momentum in the x and y directions?

From the uncertainty relations, $\Delta L_x \Delta L_z \geq \frac{\hbar}{2} |\langle L_y \rangle|$ and $\Delta L_y \Delta L_z \geq \frac{\hbar}{2} |\langle L_x \rangle|$, we have that if $\Delta L_z = 0$ (perfect knowledge) then we have a complete uncertainty in L_x and L_y .

Obs. Consider the squared length of the angular momentum vector $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$. We can show that $[\hat{L}_a, \hat{L}^2] = 0$ (for $a = \{x, y, z\}$). Thus we can always know the length of the angular momentum plus one of its components.

For example, choosing the z -component, we can represent the angular momentum as a cone, of length $\langle L \rangle$, projection on the z -axis $\langle L_z \rangle$ and with complete uncertainty of its projection along x and y .

We now express the angular momentum using spherical coordinates. This simplifies particularly how the azimuthal angular momentum \hat{L}_z is expressed:

$$\begin{aligned}\hat{L}_x &= i\hbar \left(\sin \varphi \frac{\partial}{\partial \vartheta} + \cot \vartheta \cos \varphi \frac{\partial}{\partial \varphi} \right), \\ \hat{L}_y &= -i\hbar \left(\cos \varphi \frac{\partial}{\partial \vartheta} - \cot \vartheta \sin \varphi \frac{\partial}{\partial \varphi} \right), \\ \hat{L}_z &= -i\hbar \frac{\partial}{\partial \varphi}\end{aligned}$$

The form of \hat{L}^2 should be familiar:

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial}{\partial \vartheta} \right) + \frac{1}{\sin^2 \vartheta} \frac{\partial^2}{\partial \varphi^2} \right]$$

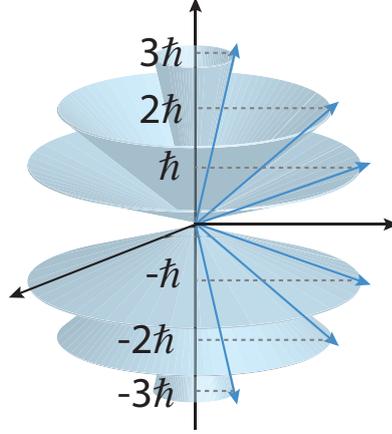


Fig. 28: Graphical representation of the angular momentum, with fixed L_z and L^2 , but complete uncertainty in L_x and L_y .

as you should recognize the angular part of the 3D Schrödinger equation. We can then write the eigenvalue equations for these two operators:

$$\hat{L}^2\Phi(\vartheta, \varphi) = \hbar^2 l(l+1)\Phi(\vartheta, \varphi)$$

and

$$\hat{L}_z\Phi(\vartheta, \varphi) = \hbar m_z\Phi(\vartheta, \varphi)$$

where we already used the fact that they share common eigenfunctions (then, we can label these eigenfunctions by l and m_z : $\Phi_{l,m_z}(\vartheta, \varphi)$).

The allowed values for l and m_z are integers such that $l = 0, 1, 2, \dots$ and $m_z = -l, \dots, l-1, l$. This result can be inferred from the commutation relationship. For interested students, the derivation is below.

Derivation of the eigenvalues. Assume that the eigenvalues of L^2 and L_z are unknown, and call them λ and μ . We introduce two new operators, the raising and lowering operators $L_+ = L_x + iL_y$ and $L_- = L_x - iL_y$. The commutator with L_z is $[L_z, L_{\pm}] = \pm\hbar L_{\pm}$ (while they of course commute with L^2). Now consider the function $f_{\pm} = L_{\pm}f$, where f is an eigenfunction of L^2 and L_z :

$$L^2 f_{\pm} = L_{\pm}L^2 f = L_{\pm}\lambda f = \lambda f_{\pm}$$

and

$$L_z f_{\pm} = [L_z, L_{\pm}]f + L_{\pm}L_z f = \pm\hbar L_{\pm}f + L_{\pm}\mu f = (\mu \pm \hbar)f_{\pm}$$

Then $f_{\pm} = L_{\pm}f$ is also an eigenfunction of L^2 and L_z . Furthermore, we can keep finding eigenfunctions of L_z with higher and higher eigenvalues $\mu' = \mu + \hbar + \hbar + \dots$, by applying the L_+ operator (or lower and lower with L_-), while the L^2 eigenvalue is fixed. Of course there is a limit, since we want $\mu' \leq \lambda$. Then there is a maximum eigenfunction such that $L_+f_M = 0$ and we set the corresponding eigenvalue to $\hbar l_M$. Now notice that we can write L^2 instead of by using $L_{x,y}$ by using L_{\pm} :

$$L^2 = L_-L_+ + L_z^2 + \hbar L_z$$

Using this relationship on f_M we find:

$$L^2 f_M = \lambda f_M \quad \rightarrow \quad (L_-L_+ + L_z^2 + \hbar L_z)f_M = [0 + \hbar^2 l_M^2 + \hbar(\hbar l_M)]f_M \quad \rightarrow \quad \lambda = \hbar^2 l_M(l_M + 1)$$

In the same way, there is also a minimum eigenvalue l_m and eigenfunction s.t. $L_-f_m = 0$ and we can find $\lambda = \hbar^2 l_m(l_m - 1)$. Since λ is always the same, we also have $l_m(l_m - 1) = l_M(l_M + 1)$, with solution $l_m = -l_M$ (the other solution would have $l_m > l_M$). Finally we have found that the eigenvalues of L_z are between $+\hbar l$ and $-\hbar l$ with integer increases, so that $l = -l + N$ giving $l = N/2$: that is, l is either an integer or a half-integer. We thus set $\lambda = \hbar^2 l(l+1)$ and $\mu = \hbar m$, $m = -l, -l+1, \dots, l$. \square

We can gather some intuition about the eigenvalues if we solve first the second equation, finding

$$-i\hbar \frac{\partial \Phi_{l,m}}{\partial \varphi} = \hbar m_z \Phi(\vartheta, \varphi), \quad \Phi_{l,m}(\vartheta, \varphi) = \Theta_l(\vartheta) e^{im_z \varphi}$$

where, because of the periodicity in φ , m_z can only take on integer values (positive and negative) so that $\Phi_{l,m}(\vartheta, \varphi + 2\pi) = \Phi_{l,m}(\vartheta, \varphi)$.

If we solve the first equation, we would find for each eigenvalue l there are many eigenfunctions. What is the degeneracy of the eigenvalue l ? We know that given l , m_z can take many values (between $-l$ and l), in particular $2l + 1$ values. This is the degeneracy of l .

? Question: What are the possible values of \hat{L}_x if $l = 7$ and $m_z = 5$?

We know that we can define quantum numbers $m_{x(y)}$ such that they take integer numbers $m_{x(y)} = -l, \dots, l - 1, l$. Also, we have the relation among the expectation values:

$$\langle \hat{L}^2 \rangle = \langle \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \rangle \rightarrow l(l+1) = m_z^2 + \langle \hat{L}_x^2 + \hat{L}_y^2 \rangle / \hbar^2$$

so in general

$$\langle \hat{L}_x^2 \rangle \leq \hbar^2 [l(l+1) - m_z^2]$$

Then here we have

$$\langle \hat{L}_x^2 \rangle \leq \hbar^2 (56 - 25) = 31\hbar^2$$

If \hat{L}_x could only take its maximum value (with probability one) we would have $\langle \hat{L}_x^2 \rangle = \sum P_i L_{x,i}^2 = L_{x,max}^2$ thus we have $L_{x,max} \leq 5\hbar$ (with 5 the closest integer to $\sqrt{31}$). Often, because of symmetry, we have $\langle \hat{L}_x^2 \rangle = \langle \hat{L}_y^2 \rangle$ and,

$$\langle \hat{L}_x^2 \rangle = \hbar^2 [l(l+1) - m_z^2] / 2$$

thus restricting even further the maximum value of L_x .

4.2.3 Spin angular momentum

The quantization of angular momentum gave the result that the angular momentum quantum number was defined by integer values. There is another quantum operator that has the same commutation relationship as the angular momentum but has no classical counterpart and can assume half-integer values. It is called the intrinsic spin angular momentum \hat{S} (or for short, spin). Because it is not a classical properties, we cannot write spin in terms of position and momentum operator. The spin is defined in an abstract spin space (not the usual phase space).

Every elementary particle has a specific and immutable value of the intrinsic spin quantum number s (with s determining the eigenvalues of \hat{S}^2 , $\hbar^2 s(s+1)$), which we call the spin of that particular species: pi mesons have spin 0; electrons have spin 1/2; photons have spin 1; gravitons have spin 2; and so on. By contrast, the orbital angular momentum quantum number l of a particle can a priori take on any (integer) value, and l will change when the system is perturbed.

The eigenvectors of the spin operators are not spherical harmonics. Actually, since the spin is not defined in terms of position and momentum, they are not a function of position and are not defined on the usual phase space. The eigenstates are instead described by linear vectors, for example, two-dimensional vectors for the spin-1/2. Thus the operators will be as well represented by matrices.

We already saw the operators describing the spin-1/2 operators and we even calculated their eigenvalues and eigenvectors (see section 2.2)

We can then also define the total angular momentum, which is the sum of the usual angular momentum (called the *orbital* angular momentum) and the spin:

$$\hat{J} = \hat{L} + \hat{S}$$

What is the meaning of the sum of two angular momentum operators and what are the eigenvalues and eigenfunctions of the resulting operators?

4.2.4 Addition of angular momentum

We have seen above that any elementary particle posses an intrinsic spin. Then, we can always define the total angular momentum as the sum of the orbital angular momentum and the intrinsic spin. This is an example of addition of angular momentum. Then of course we could also consider two distinct particles and ask what is the total orbital angular momentum of the two particles (or of more particles). There are thus many cases of addition of angular momentum, for example:

1. $\hat{J} = \hat{L} + \hat{S}$

2. $\hat{L} = \hat{L}_1 + \hat{L}_2$
3. $\hat{J} = \hat{J}_1 + \hat{J}_2 = \hat{L}_1 + \hat{S}_1 + \hat{L}_2 + \hat{S}_2$
4. $\hat{S} = \hat{S}_1 + \hat{S}_2 + \hat{S}_3$
5. ...

Consider for example the second case. A possible state of the two particles can be described by the eigenvalues/eigenfunctions of each particle angular momentum. For example we could specify l_1 and m_z^1 as well as l_2 and m_z^2 (I will from now on just write m_1 for m_z^1 etc.). Then a state could be for example written in Dirac's notation as $|l_1, m_1, l_2, m_2\rangle$. This however does not tell us anything about the total system and its angular momentum. Sometime this quantity is more interesting (for example if the two particles are interacting, their total angular momentum is bound to determine their energy, and not the state of each particle alone).

A. Coupled and uncoupled representations

The sum of angular momentum satisfy the general commutation rules, $[L^2, L_z] = 0$, $[L_x, L_y] = i L_z$ etc. We can then also define the eigenvalues (and eigenfunctions) of the total angular momentum \hat{L} , for example l (for L^2) and m (for L_z). However, since we only have 2 quantum numbers, we expect the eigenfunctions to be degenerate and we still need to find two more quantum numbers. Equivalently, what we need to do is to find a complete set of commuting observables, such that an eigenfunction (common to all these observables) is well defined –no ambiguity in it– by the set of eigenvalues (or quantum numbers) of the observables.

The first question we can ask is : are these eigenfunctions going to be in common with the single particle operators? To determine this, we need to look at the commutation of the operators.

Now we know that $[L_1^2, L_{z,1}] = 0$, but what about $[L^2, L_{z,1}]$?

We first express L^2 explicitly: $L^2 = |\hat{L}_1 + \hat{L}_2|^2 = L_1^2 + L_2^2 + 2\hat{L}_1 \cdot \hat{L}_2$. Then the commutator is:

$$\begin{aligned} [L^2, L_{z,1}] &= [L_1^2 + L_2^2 + 2(L_{x,1}L_{x,2} + L_{y,1}L_{y,2} + L_z^1L_z^2), L_{z,1}] \\ &= [2(L_{x,1}L_{x,2} + L_{y,1}L_{y,2}), L_{z,1}] = 2i ((L_{y,1}L_{x,2} - L_{x,1}L_{y,2}) \neq 0 \end{aligned}$$

Thus the two operators do not commute and do not share common eigenfunctions. What about L_1^2 ?

$$[L^2, L_1^2] = [L_1^2 + L_2^2 + 2(L_{x,1}L_{x,2} + L_{y,1}L_{y,2} + L_z^1L_z^2), L_1^2] = 0$$

since $[L_1^2, L_{a,1}] = 0$. This means that there are common eigenfunctions of L_1^2 , L_2^2 , L^2 and L_z . These operators are a complete set of commuting observables. An eigenfunction is thus well defined by the set of eigenvalues l, m, l_1 and l_2 and we can write the eigenstates as ψ_{l,m,l_1,l_2} or $|l, m, l_1, l_2\rangle$.

There are then two possible representations of the combined system (two possible basis to represent a general state):

Representation	Eigenstates	Complete set of commuting observables
Uncoupled	$ l_1, m_1, l_2, m_2\rangle$,	$L_1^2, L_2^2, L_{1,z}$ and $L_{2,z}$
Coupled	$ l, m, l_1, l_2\rangle$,	L_1^2, L_2^2, L^2 and L_z .

How do we go from one basis to the other? As usual this is done by expressing each vector in one basis as a linear combination of vectors in the other basis:

$$|l, m, l_1, l_2\rangle = \sum_{m_1, m_2} c_{m_1, m_2}^l |l_1, m_1, l_2, m_2\rangle$$

Notice that since the total angular momentum in the z direction must be m , we limit the sum to terms s.t. $m_1 + m_2 = m$.

What are the coefficients c_{m_1, m_2}^l ?

Since the two representations are two orthogonal basis, we have that $\langle l_1', m_1', l_2', m_2' | l_1, m_1, l_2, m_2 \rangle = 0$ unless all the indexes are equal. Then the coefficient can be calculated (as usual!) from the inner product of $|l_1, m_1, l_2, m_2\rangle$ and $|l, m, l_1, l_2\rangle$:

$$c_{m_1, m_2}^l = \langle l_1, m_1, l_2, m_2 | l, m, l_1, l_2 \rangle$$

These coefficients are called the **Clebsch-Gordon** coefficients.

B. Addition rules: Two particles

In describing the energy levels of atoms and nuclei it is very convenient to be able to find the allowed values of (l, m) given the values of (l_1, l_2) for two given particles (e.g. electrons, protons or neutrons). Indeed, we saw that the operator \hat{L}^2 appears in the Hamiltonian of the system. Thus its eigenvalue $\hbar^2 l(l+1)$ will be important in determining the system energy.

Even if we cannot fix the value of l if we only know l_1, m_1, l_2 and m_2 we can at least restrict the possible values of l . In order to do so, one has to analyze the possible maximum length of the total angular momentum and the degeneracy of the eigenvalues.

1) Maximum l : For two particles with quantum numbers l_1 and l_2 we know that in the coupled representation we cannot fix the values of m_1 and m_2 . However, we know that given l_1 and l_2 only some values of m_1 and m_2 are allowed (e.g. $m_1 = -l_1, -l_1 + 1, \dots, l_1$). Then the maximum values of m_1 and m_2 are $m_1 = l_1$ and $m_2 = l_2$. This also determines the maximum value of m : $m_{max} = l_1 + l_2$. But m itself can only take values $m = -l, \dots, l-1, l$. Then the maximum value of l is $m_{max} = l_{max}$. Thus, what we just proved is that $l \leq l_1 + l_2$.

2) Minimum l : To find the minimum l value we need to look at the degeneracy of the state $|l, m, l_1, l_2\rangle$. Since this state could be also written (in the uncoupled representation) as $\sum_{m_1+m_2=m} c_{m_1, m_2}^l |l_1, m_1, l_2, m_2\rangle$, the degeneracy of the state must be the same. What are the two degeneracies?

We know that for a given angular momentum operator \hat{L} with total angular momentum quantum number l , there are $2l + 1$ states with the same angular momentum $\hbar^2 l(l+1)$.

Then, considering the uncoupled representation we have $\mathcal{D} = (2l_1 + 1)(2l_2 + 1)$ possible states with l_1 and l_2 .

In the coupled representation instead we have to consider all the states that have an allowed l : $\mathcal{D} = \sum_{l=l_{min}}^{l_1+l_2} (2l+1)$.

We want these two quantities to be equal. Now remember that $\sum_{k=1}^K k = \frac{K(K+1)}{2}$. Then $\sum_{l=l_{min}}^{l_1+l_2} (2l+1) = (1+l_1+l_2)^2 - l_{min}^2$, so that $l_{min}^2 = (1+l_1+l_2)^2 - (2l_1+1)(2l_2+1) = (l_1-l_2)^2$.

Using the degeneracy condition we thus proved that $l \geq |l_1 - l_2|$.

The addition rule states thus that

$$\text{The total angular momentum quantum number is bounded by } |l_1 - l_2| \leq l \leq l_1 + l_2$$

Example: Consider two spins-1/2 particles (for example two electrons with zero orbital angular momentum). Since we choose spin- $\frac{1}{2}$ we have only 1 possible value $s = \frac{1}{2}$ and two values for m_z : $m_z = \pm \frac{1}{2}$. We can omit writing explicitly the s quantum number (since it's always $\frac{1}{2}$, and we write $|+\frac{1}{2}, +\frac{1}{2}\rangle = |+\frac{1}{2}\rangle$ and $|+\frac{1}{2}, -\frac{1}{2}\rangle = |-\frac{1}{2}\rangle$). A basis for the uncoupled representation is then given by:

$$|s_1, m_1, s_2, m_2\rangle = \begin{cases} |+\frac{1}{2}, +\frac{1}{2}, +\frac{1}{2}, +\frac{1}{2}\rangle = |+\frac{1}{2}, +\frac{1}{2}\rangle \\ |+\frac{1}{2}, +\frac{1}{2}, +\frac{1}{2}, -\frac{1}{2}\rangle = |+\frac{1}{2}, -\frac{1}{2}\rangle \\ |+\frac{1}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{1}{2}\rangle = |-\frac{1}{2}, +\frac{1}{2}\rangle \\ |+\frac{1}{2}, -\frac{1}{2}, +\frac{1}{2}, -\frac{1}{2}\rangle = |-\frac{1}{2}, -\frac{1}{2}\rangle \end{cases}$$

Consider now the coupled representation. The possible values for s are 1 or 0. In the first case, we have 3 possible values for $m = -1, 0, 1$. While the second only has $m = 0$. Again, since the values of s_1 and s_2 are fixed we do not write them:

$$|s, m, s_1, s_2\rangle = \begin{cases} |0, 0, \frac{1}{2}, \frac{1}{2}\rangle = |0, 0\rangle \\ |1, -1, \frac{1}{2}, \frac{1}{2}\rangle = |1, -1\rangle \\ |1, 0, \frac{1}{2}, \frac{1}{2}\rangle = |1, 0\rangle \\ |1, 1, \frac{1}{2}, \frac{1}{2}\rangle = |1, 1\rangle \end{cases}$$

In this particular example it is easy to calculate the Clebsch-Gordon coefficients and we find the relations between the two representations:

$$\begin{aligned} |0, 0\rangle &= \frac{|+\frac{1}{2}, -\frac{1}{2}\rangle - |-\frac{1}{2}, +\frac{1}{2}\rangle}{\sqrt{2}} \\ |1, -1\rangle &= |-\frac{1}{2}, -\frac{1}{2}\rangle \\ |1, 0\rangle &= \frac{|+\frac{1}{2}, -\frac{1}{2}\rangle + |-\frac{1}{2}, +\frac{1}{2}\rangle}{\sqrt{2}} \\ |1, 1\rangle &= |+\frac{1}{2}, +\frac{1}{2}\rangle \end{aligned}$$

C. Addition rules: many particles

The addition rules can be generalized to many particles, by just repetitively applying the two-particle rules. We then find for N particles:

- $l_{max} = \sum_{k=1}^N l_k$

- $l_{min} = \max\{0, 2l_N - l_{max}\}$

where l_N is the largest of the $\{l_k\}$.

4.3 Solutions to the Schrödinger equation in 3D

We now go back to the Schrödinger equation in spherical coordinates and we consider the angular and radial equation separately to find the energy eigenvalues and eigenfunctions.

D. Angular Equation

The angular equation was found to be:

$$\frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial Y_l^m(\vartheta, \varphi)}{\partial \vartheta} \right) + \frac{1}{\sin^2 \vartheta} \frac{\partial^2 Y_l^m(\vartheta, \varphi)}{\partial \varphi^2} = -l(l+1)Y_l^m(\vartheta, \varphi)$$

Notice that this equation does not depend at all on the potential, thus it will be common to all problems with an isotropic potential.

We can solve the equation by using again separation of variables: $Y(\vartheta, \varphi) = \Theta(\vartheta)\Phi(\varphi)$. By multiplying both sides of the equation by $\sin^2(\vartheta)/Y(\vartheta, \varphi)$ we obtain:

$$\frac{1}{\Theta(\vartheta)} \left[\sin \vartheta \frac{d}{d\vartheta} \left(\sin \vartheta \frac{d\Theta}{d\vartheta} \right) \right] + l(l+1) \sin^2 \vartheta = -\frac{1}{\Phi(\varphi)} \frac{d^2\Phi}{d\varphi^2}$$

As usual we separate the two equations in the different variables and introduce a constant $C = m^2$:

$$\frac{d^2\Phi}{d\varphi^2} = -m^2\Phi(\varphi)$$

$$\sin \vartheta \frac{d}{d\vartheta} \left(\sin \vartheta \frac{d\Theta}{d\vartheta} \right) = [m^2 - l(l+1) \sin^2 \vartheta] \Theta(\vartheta)$$

The first equation is easily solved to give $\Phi(\varphi) = e^{im\varphi}$ with $m = 0, \pm 1, \pm 2, \dots$ since we need to impose the periodicity of Φ , such that $\Phi(\varphi + 2\pi) = \Phi(\varphi)$.

The solutions to the second equations are associated Legendre Polynomials: $\Theta(\vartheta) = AP_l^m(\cos \vartheta)$, the first few of which are in table 1. Notice that, as previously found when solving for the eigenvalues of the angular momentum, we have that $m = -l, -l+1, \dots, l$, with $l = 0, 1, \dots$

$l \setminus m$	0	1	2	3
0	$P_0^0 = 1$			
1	$P_1^0 = \cos \vartheta$	$P_1^1 = \sin \vartheta$		
2	$P_2^0 = \frac{1}{2}(3 \cos^2 \vartheta - 1)$	$P_2^1 = 3 \cos \vartheta \sin \vartheta$	$P_2^2 = 3 \sin^2 \vartheta$	
3	$P_3^0 = \frac{1}{2}(5 \cos^3 \vartheta - 3 \cos \vartheta)$	$P_3^1 = \frac{3}{2}(5 \cos^2 \vartheta - 1) \sin \vartheta$	$P_3^2 = 15 \cos \vartheta \sin^2 \vartheta$	$P_3^3 = 15 \sin^3 \vartheta$

Table 1: Legendre Polynomials

The normalized angular eigenfunctions are then Spherical Harmonic functions, given by the normalized Legendre polynomial times the solution to the equation in φ , (see also Table 2)

$$Y_l^m(\vartheta, \varphi) = \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} P_l^m(\cos \vartheta) e^{im\varphi}$$

As we expect from eigenfunctions, the Spherical Harmonics are orthogonal:

$$\int_{4\pi} d\Omega Y_l^m(\vartheta, \varphi) Y_{l'}^{m'}(\vartheta, \varphi) = \delta_{l,l'} \delta_{m,m'}$$

E. The radial equation

We now turn to the radial equation:

$$\frac{d}{dr} \left(r^2 \frac{dR(r)}{dr} \right) - \frac{2m r^2}{\hbar^2} (V - E) = l(l+1)R(r)$$

$$\begin{aligned}
Y_0^0(\vartheta, \phi) &= \sqrt{\frac{1}{4\pi}} & Y_2^{-2}(\vartheta, \phi) &= \frac{1}{4} \sqrt{\frac{15}{2\pi}} \sin^2 \vartheta e^{-2i\phi} \\
Y_1^{-1}(\vartheta, \phi) &= \sqrt{\frac{3}{8\pi}} \sin \vartheta e^{-i\phi} & Y_2^{-1}(\vartheta, \phi) &= \frac{1}{2} \sqrt{\frac{15}{2\pi}} \sin \vartheta \cos \vartheta e^{-i\phi} \\
Y_1^0(\vartheta, \phi) &= \sqrt{\frac{3}{4\pi}} \cos \vartheta & Y_2^0(\vartheta, \phi) &= \frac{1}{4} \sqrt{\frac{5}{\pi}} (3 \cos^2 \vartheta - 1) \\
Y_1^1(\vartheta, \phi) &= -\sqrt{\frac{3}{8\pi}} \sin \vartheta e^{i\phi} & Y_2^1(\vartheta, \phi) &= \frac{-1}{2} \sqrt{\frac{15}{2\pi}} \sin \vartheta \cos \vartheta e^{i\phi} \\
&& Y_2^2(\vartheta, \phi) &= \frac{1}{4} \sqrt{\frac{15}{2\pi}} \sin^2 \vartheta e^{2i\phi}
\end{aligned}$$

Table 2: Spherical Harmonics

To simplify the solution, we introduce a different function $u(r) = rR(r)$. Then the equation reduces to:

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[V + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] u(r) = Eu(r)$$

This equation is very similar to the Schrödinger equation in 1D if we define an *effective potential* $V'(r) = V(r) + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2}$. The second term in this effective potential is called the **centrifugal** term.

Solutions can be found for some forms of the potential $V(r)$, by first calculating the equation solutions $u_{n,l}(r)$, then finding $R_{n,l}(r) = u_{n,l}(r)/r$ and finally the wavefunction

$$\Psi_{n,l,m}(r, \vartheta, \varphi) = R_{n,l}(r) Y_l^m(\vartheta, \varphi).$$

Notice that we need 3 quantum numbers (n, l, m) to define the eigenfunctions of the Hamiltonian in 3D.

For example we can have a simple spherical well: $V(r) = 0$ for $r < r_0$ and $V(r) = V_0$ otherwise. In the case of $l = 0$, this is the same equation as for the square well in 1D. Notice however that since the boundary conditions need to be such that $R(r)$ is finite for all r , we need to impose that $u(r = 0) = 0$, hence only the odd solutions are acceptable (as we had anticipated). For $l > 0$ we can find solutions in terms of Bessel functions

Two other important examples of potential are the harmonic oscillator potential $V(r) = V_0 \frac{r^2}{r_0^2} - V_0$ (which is an approximation for any potential close to its minimum) and the Coulomb potential $V(r) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$, which describes the atomic potential and in particular the Hydrogen atom.

4.3.1 The Hydrogen atom

We want to solve the radial equation for the Coulomb potential, or at least find the eigenvalues of the equation. Notice we are looking for bound states, thus the total energy is negative $E < 0$. Then we define the real quantity $\kappa = \sqrt{\frac{-2mE}{\hbar^2}}$, and the quantities⁸:

$$\text{Bohr radius: } a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2}, \quad \text{Rydberg constant: } \mathbb{R} = \frac{\hbar^2}{2ma_0^2}$$

and $\lambda^2 = \frac{\mathbb{R}}{|E|}$. The values of the two constants are $a_0 = 5.29 \times 10^{-11} \text{m}$ and $\mathbb{R} = 13.6 \text{ eV}$ (thus λ is a dimensionless parameter). The Bohr radius gives the distance at which the kinetic energy of an electron (classically) orbiting around the nucleus equals the Coulomb interaction: $\frac{1}{2} m_e v^2 = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r}$. In the semi-classical Bohr model, the angular momentum $L = m_e v r$ is quantized, with lowest value $L = \hbar$, then by inserting in the equation above, we find $r = a_0$. We will see that the Rydberg energy gives instead the minimum energy for the hydrogen.

We further apply a change of variable $\rho = 2\kappa r$, and we rewrite the radial equation as:

$$\frac{d^2 u}{d\rho^2} = \left[\frac{1}{4} - \frac{\lambda}{\rho} + \frac{l(l+1)}{\rho^2} \right] u(\rho)$$

There are two limiting cases:

For $\rho \rightarrow 0$, the equation reduces to $\frac{d^2 u}{d\rho^2} = \frac{l(l+1)}{\rho^2} u$, with solution $u(\rho) \sim \rho^{l+1}$.

For $\rho \rightarrow \infty$ we have $\frac{d^2 u}{d\rho^2} = \frac{u(\rho)}{4}$, giving $u(\rho) \sim e^{-\rho/2}$.

⁸ Note that the definition of the Bohr radius is slightly different if the Coulomb potential is not expressed in SI units but in cgs units

A general solution can then be written as $u(\rho) = e^{-\rho/2} \rho^{l+1} S(\rho)$ (with S to be determined). We then expand $S(\rho)$ in series as $S(\rho) = \sum_{j=0}^{\infty} s_j \rho^j$ and try to find the coefficients s_j . By inserting $u(\rho) = e^{-\rho/2} \rho^{l+1} \sum_{j=0}^{\infty} s_j \rho^j$ in the equation we have:

$$\left[\rho \frac{d^2}{d\rho^2} + (2l+2-\rho) \frac{d}{d\rho} - (l+1-\lambda) \right] S(\rho) = 0$$

From which we obtain:

$$\sum_j [\rho \{j(j+1)s_{j+1}\rho^{j-1}\} + (2l+2-\rho)\{(j+1)s_{j+1}\rho^j\} - (l+1-\lambda)\{s_j\rho^j\}] = 0$$

(where the terms in brackets correspond to the derivatives of $S(\rho)$). This equation defines a recursive equation for the coefficients s_j :

$$s_{j+1} = \frac{j+l+1-\lambda}{j(j+1) + (2l+2)(j+1)} s_j$$

If we want the function $u(\rho)$ to be well defined, we must impose that $u(\rho) \rightarrow 0$ for $\rho \rightarrow \infty$. This imposes a maximum value for j , j_{max} , such that all the higher coefficients $s_{j>j_{max}}$ are zero.

We thus impose that $s_{j_{max}+1} = 0$, setting the numerator of the formula above to zero.

Then we have that $j_{max} + l + 1 - \lambda = 0$. But this is an equation for λ , which in turns determines the energy eigenvalue:

$$\lambda = j_{max} + l + 1.$$

We then rename the parameter λ the principal quantum number n , since it is an integer (as j and l are integers). Then the energy is given by $E = -\frac{\mathbb{R}}{n^2}$ and the allowed energies are given by the famous **Bohr formula**:

$$E_n = -\frac{1}{n^2} \frac{m_e}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2$$

Obs.: Note that the energy is only determined by the principal quantum number. What is the degeneracy of the n quantum number? We know that the full eigenfunction is specified by knowing the angular momentum L^2 and one of its components (e.g. L_z). From the equation above, $n = j_{max} + l + 1$, we see that for each n , l can vary from $l = 0$ to $l = n - 1$. Then we also have $2l + 1$ m values for each l (and 2 spin states for each m). Finally, the degeneracy is then given by

$$\sum_{l=0}^{n-1} 2(2l+1) = 2n^2$$

4.3.2 Atomic periodic structure

We calculated the energy levels for the Hydrogen atom. This will give us spectroscopy information about the excited states that we can excite using, for example, laser light. How can we use this information to infer the structure of the atoms?

A neutral atom, of atomic number Z , consists of a heavy nucleus, with electric charge Ze , surrounded by Z electrons (mass m and charge $-e$). The Hamiltonian for this system is

$$\mathcal{H} = \sum_{j=1}^Z \left[-\frac{\hbar^2}{2m} \nabla_j^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_j} \right] + \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{j \neq k}^Z \frac{e^2}{|\vec{r}_j - \vec{r}_k|}$$

The first term is simply the kinetic energy of each electron in the atom. The second term is the potential energy of the j th electron in the electric field created by the nucleus. Finally the last sum (which runs over all values of j and k except $j = k$) is the potential energy associated with the mutual repulsion of the electrons (the factor of $1/2$ in front corrects for the fact that the summation counts each pair twice).

Given this Hamiltonian, we want to find the energy levels (and in particular the ground state, which will give us the stable atomic configuration). We then need to solve Schrödinger's equation. But what would an eigenstate of this equation now be?

Consider for example Helium, an atom with only two electrons. Neglecting for the moment spin, we can write the wavefunction as $\Psi(\vec{r}_1, \vec{r}_2, t)$ (and stationary wavefunctions, $\psi(\vec{r}_1, \vec{r}_2)$), that is, we have a function of the spatial coordinates of both electrons. The physical interpretation of the wavefunction is a simple extension of the one-particle wavefunction: $|\psi(\vec{r}_1, \vec{r}_2)|^2 d^3\vec{r}_1 d^3\vec{r}_2$ is the probability of finding contemporaneously the two electrons at the positions

\vec{r}_1 and \vec{r}_2 , respectively. The wavefunction must then be normalized as $\int |\psi(\vec{r}_1, \vec{r}_2)|^2 d^3\vec{r}_1 d^3\vec{r}_2 = 1$. The generalization to many electrons (or more generally to many particles) is then evident. To determine the ground state of an atom we will then have to solve the Schrödinger equation

$$\mathcal{H}\psi(\vec{r}_1, \dots, \vec{r}_Z) = E\psi(\vec{r}_1, \dots, \vec{r}_Z)$$

This equation has not been solved (yet) except for the case $Z=1$ of the Hydrogen atom we saw earlier. What we can do is to make a very crude approximation and ignore the Coulomb repulsion among electrons. Mathematically this simplifies tremendously the equation, since now we can simply use separation of variables to write many equations for each independent electron. Physically, this is often a good enough approximation because mutual repulsion of electron is not as strong as the attraction from all the protons. Then the Schrödinger equation becomes:

$$\sum_{j=1}^Z \left[-\frac{\hbar^2}{2m} \nabla_j^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_j} \right] \psi(\vec{r}_1, \dots, \vec{r}_Z) = E\psi(\vec{r}_1, \dots, \vec{r}_Z)$$

and we can write $\psi(\vec{r}_1, \dots, \vec{r}_Z) = \psi(\vec{r}_1)\psi(\vec{r}_2)\dots\psi(\vec{r}_Z)$

Then, we can solve for each electron separately, as we did for the Hydrogen atom equation, and find for each electron the same level structure as for the Hydrogen, except that since the potential energy is now $\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_j}$ the electron energy (Bohr's formula) is now multiplied by Z . The solutions to the time-independent Schrödinger equations are then the same eigenfunctions we found for the hydrogen atom, $\psi(\vec{r}_j) = \psi_{lmn}(r, \vartheta, \varphi)$.

Thus if we ignore the mutual repulsion among electrons, the individual electrons occupy one-particle hydrogenic states (n, l, m) , called **orbitals**, in the Coulomb potential of a nucleus with charge Ze .

There are $2n^2$ hydrogenic wave functions (all with the same energy E_n) for a given value of n . Looking at the Periodic Table we see this periodicity, with two elements in the $n = 1$ shell, 8 in the $n = 2$ shell, 18 in the third shell. Higher shells however are more influenced by the electron-electron repulsion that we ignored, thus simple considerations from this model are no longer valid.

However, we would expect instead the electrons in the atoms to occupy the state with lowest energy. The ground state would then be a situation where all the electron occupy their own ground state ($n = 0, l = 0, m = 0$). But is this correct? This is not what is observed in nature, otherwise all the atom would show the same chemical properties. So what happens?

To understand, we need to analyze the statistical properties of identical particles. But before that, we will introduce the solution for another central potential, the harmonic oscillator potential $V(r) = V_0 \frac{r^2}{r_0^2} - V_0$ (which is an approximation for any potential close to its minimum).

4.3.3 The Harmonic Oscillator Potential

The quantum h.o. is a model that describes systems with a characteristic energy spectrum, given by a ladder of evenly spaced energy levels. The energy difference between two consecutive levels is ΔE . The number of levels is infinite, but there must exist a minimum energy, since the energy must always be positive. Given this spectrum, we expect the Hamiltonian will have the form

$$\mathcal{H} |n\rangle = \left(n + \frac{1}{2} \right) \omega |n\rangle,$$

where each level in the ladder is identified by a number n . The name of the model is due to the analogy with characteristics of classical h.o., which we will review first.

A. Classical harmonic oscillator and h.o. model

A classical h.o. is described by a potential energy $V = \frac{1}{2}kx^2$ (the radial potential considered above, $V(r) = V_0 \frac{r^2}{r_0^2} - V_0$, has this form). If the system has a finite energy E , the motion is bound by two values $\pm x_0$, such that $V(x_0) = E$. The equation of motion is given by

$$\begin{cases} \frac{dx}{dt} = \frac{p(t)}{m}, \\ \frac{dp}{dt} = -kx \end{cases} \quad \rightarrow \quad m \frac{d^2x}{dt^2} = -kx,$$

and the kinetic energy is of course

$$T = \frac{1}{2}m\dot{x}^2 = \frac{p^2}{2m}.$$

The energy is constant since it is a conservative system, with no dissipation. Most of the time the particle is in the position x_0 since there the velocity is zero, while at $x = 0$ the velocity is maximum.

The h.o. oscillator in QM is an important model that describes many different physical situations. It describes e.g. the electromagnetic field, vibrations of solid-state crystals and (a simplified model of) the nuclear potential. This is because any potential with a local minimum can be locally described by an h.o.. Provided that the energy is low enough (or x close to x_0), any potential can in fact be expanded in series, giving: $V(x) \approx V(x_0) + b(x - x_0)^2 + \dots$ where $b = \frac{d^2V}{dx^2}|_{x_0}$.

It is easy to solve the equation of motion. Instead of just solving the usual equation, we follow a slightly different route. We define dimensionless variables,

$$P = \frac{p}{\sqrt{m\omega}}, \quad X = x\sqrt{m\omega},$$

where we defined a parameter with units of frequency: $\omega = \sqrt{k/m}$ and we introduce a complex classical variable (following Roy J. Glauber -[Phys. Rev. 131](#), 2766-2788 (1963))

$$\alpha = \frac{1}{\sqrt{2}}(X + iP).$$

The classical equations of motion for x and p define the evolution of the variable α :

$$\begin{cases} \frac{dx}{dt} = \frac{p(t)}{m}, \\ \frac{dp}{dt} = -kx \end{cases} \quad \rightarrow \quad \frac{d\alpha}{dt} = -i\omega\alpha(t)$$

The evolution of α is therefore just a rotation in its phase space: $\alpha(t) = \alpha(0)e^{-i\omega t}$.

Since $X = \sqrt{2}Re(\alpha)$ and $P = \sqrt{2}Im(\alpha)$, X and P oscillate, as usual in the classical case:

$$\begin{aligned} X &= \frac{1}{\sqrt{2}}(\alpha_0 e^{-i\omega t} + \alpha_0^* e^{i\omega t}) \\ P &= \frac{-i}{\sqrt{2}}(\alpha_0 e^{-i\omega t} - \alpha_0^* e^{i\omega t}) \end{aligned}$$

The classical energy, given by $\omega/2(X^2 + P^2) = \omega\alpha_0^2$, is constant at all time.

B. Oscillator Hamiltonian: Position and momentum operators

Using the operators associated with position and momentum, the Hamiltonian of the quantum h.o. is written as:

$$\mathcal{H} = \frac{p^2}{2m} + \frac{kx^2}{2} = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2.$$

In terms of the dimensionless variables, P and X , the Hamiltonian is $\mathcal{H} = \frac{\omega}{2}(X^2 + P^2)$.

In analogy with the classical variable $a(t)$ [and its complex conjugate $a^*(t)$], which simplified the equation of motion, we introduce two operators, a , a^\dagger , hoping to simplify the eigenvalue equation (time-independent Schrödinger equation):

$$\begin{aligned} a &= \frac{1}{\sqrt{2\hbar}}(X + iP) = \frac{1}{\sqrt{2\hbar}}(\sqrt{m\omega}x + \frac{i}{\sqrt{m\omega}}p) \\ a^\dagger &= \frac{1}{\sqrt{2\hbar}}(X - iP) = \frac{1}{\sqrt{2\hbar}}(\sqrt{m\omega}x - \frac{i}{\sqrt{m\omega}}p), \end{aligned}$$

Also, we define the number operator as $N = a^\dagger a$, with eigenvalues n and eigenfunctions $|n\rangle$. The Hamiltonian can be written in terms of these operators. We substitute a , a^\dagger at the place of X and P , yielding $\mathcal{H} = \hbar\omega(a^\dagger a + \frac{1}{2}) = \hbar\omega(N + \frac{1}{2})$ and the minimum energy $\omega/2$ is called the zero point energy.

The commutation properties are: $[a, a^\dagger] = 1$ and $[N, a] = -a$, $[N, a^\dagger] = a^\dagger$. Also we have:

$$\begin{aligned} x &= \sqrt{\frac{\hbar}{2m\omega}}(a^\dagger + a) \\ p &= i\sqrt{\frac{m\omega\hbar}{2}}(a^\dagger - a) \end{aligned}$$

□ Prove the commutation relationships of the raising and lowering operators.

$$[a, a^\dagger] = \frac{1}{2}[X + iP, X - iP] = \frac{1}{2}([X, -iP] + [iP, X]) = -\frac{i}{\hbar}[X, P] = -\frac{i}{\hbar}[x, p] = 1$$

So we also have $aa^\dagger = [a, a^\dagger] + a^\dagger a = 1 + a^\dagger a = 1 + N$.

$$[N, a] = [a^\dagger a, a] = [a^\dagger, a]a = -a \quad \text{and} \quad [N, a^\dagger] = [a^\dagger a, a^\dagger] = a^\dagger[a, a^\dagger] = a^\dagger$$

□

From the commutation relationships we have:

$$a|n\rangle = [a, N]|n\rangle = an|n\rangle - Na|n\rangle \rightarrow N(a|n\rangle) = (n-1)(a|n\rangle),$$

that is, $a|n\rangle$ is also an eigenvector of the N operator, with eigenvalue $(n-1)$. Thus we confirm that this is the lowering operator: $a|n\rangle = c_n|n-1\rangle$. Similarly, $a^\dagger|n\rangle$ is an eigenvector of N with eigenvalue $n+1$:

$$a^\dagger|n\rangle = [N, a^\dagger]|n\rangle = Na^\dagger|n\rangle - a^\dagger n|n\rangle \rightarrow N(a^\dagger|n\rangle) = (n+1)(a^\dagger|n\rangle).$$

We thus have $a|n\rangle = c_n|n-1\rangle$ and $a^\dagger|n\rangle = d_n|n+1\rangle$. What are the coefficients c_n , d_n ? Since

$$\langle n|N|n\rangle = \langle n|a^\dagger a|n\rangle = n$$

and

$$\langle n|a^\dagger a|n\rangle = (\langle an|)(a|n\rangle) = \langle n-1|n-1\rangle c_n^2,$$

we must have $c_n = \sqrt{n}$. Analogously, since $aa^\dagger = N+1$, as seen from the commutation relationship:

$$d_n^2 \langle n+1|n+1\rangle = \langle a^\dagger n|a^\dagger n\rangle = \langle n|aa^\dagger|n\rangle \langle n|(N+1)|n\rangle = n+1$$

So in the end we have :

$$a|n\rangle = \sqrt{n}|n-1\rangle; \quad a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle.$$

All the n eigenvalues of N have to be non-negative since $n = \langle n|N|n\rangle = \langle \psi_{n_1}|\psi_{n_1}\rangle \geq 0$ (this follows from the properties of the inner product and the fact that $|\psi_{n_1}\rangle = a|n\rangle$ is just a regular state vector). However, if we apply over and over the a (lowering) operator, we could arrive at negative numbers n : we therefore require that $a|0\rangle = 0$ to truncate this process. The action of the raising operator a^\dagger can then produce any eigenstate, starting from the 0 eigenstate:

$$|n\rangle = \frac{(a^\dagger)^n}{\sqrt{n!}}|0\rangle.$$

The matrix representation of these operator in the $|n\rangle$ basis (with infinite-dimensional matrices) is particularly simple, since $\langle n|a|n'\rangle = \delta_{n',n-1}\sqrt{n}$ and $\langle n|a^\dagger|n'\rangle = \delta_{n',n+1}\sqrt{n+1}$:

$$a = \begin{bmatrix} 0 & \sqrt{1} & 0 & \dots \\ 0 & 0 & \sqrt{2} & \dots \\ 0 & 0 & 0 & \dots \end{bmatrix} \quad a^\dagger = \begin{bmatrix} 0 & 0 & 0 & \dots \\ \sqrt{1} & 0 & 0 & \dots \\ 0 & \sqrt{2} & 0 & \dots \end{bmatrix}$$

C. Position representation

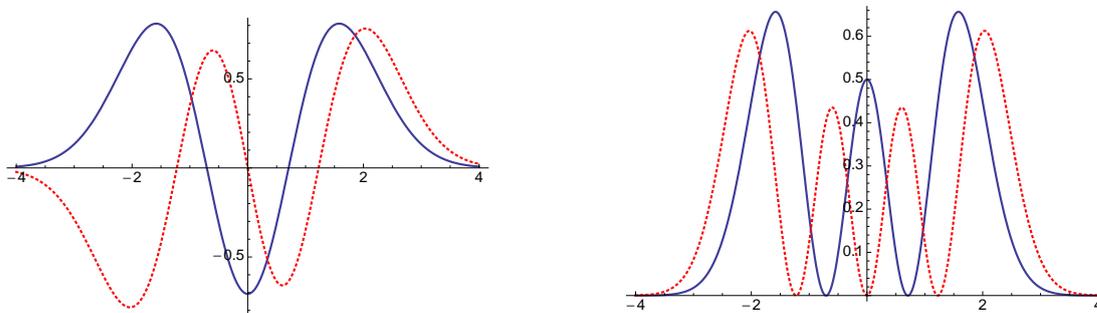


Fig. 29: Left: Harmonic oscillator wavefunction. Right: corresponding probability distribution function for $n=2$ (blue) and $n=3$ (Red, dotted).

We have now started from a (physical) description of the h.o. Hamiltonian and made a change of basis in order to arrive at a simple diagonal form of it. Now that we know its eigenkets, we would like to go back to a more intuitive picture of position and momentum. We thus want to express the eigenkets $|n\rangle$ in terms of the position representation.

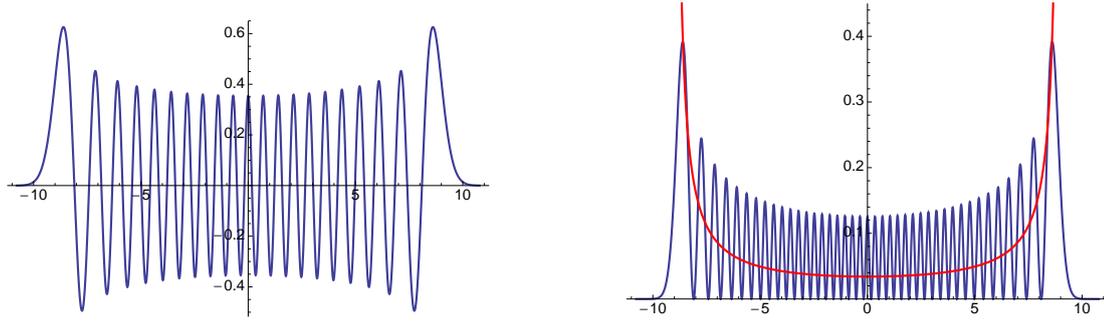


Fig. 30: Left: Harmonic oscillator wavefunction. Right: corresponding probability distribution function for $n = 40$. In Red, the classical probability.

The position representation corresponds to expressing a state vector $|\psi\rangle$ in the position basis: $|\psi\rangle = \int dx \langle x|\psi\rangle |x\rangle = \int dx \psi(x) |x\rangle$ (where $|x\rangle$ is the eigenstate of the position operator that is a continuous variable, hence the integral). This defines the wavefunction $\psi(x) = \langle x|\psi\rangle$.

The wave function description in the x representation of the quantum h.o. can be found by starting with the ground state wavefunction. Since $a|0\rangle = 0$ we have $\frac{1}{\sqrt{2\hbar}}(X + iP)|0\rangle = \frac{1}{\sqrt{2\hbar}}(\sqrt{m\omega}x + \frac{ip}{\sqrt{m\omega}})|0\rangle = 0$. In the x representation, given $\psi_0(x) = \langle x|0\rangle$

$$\frac{1}{\sqrt{2\hbar}} \langle x|(\sqrt{m\omega}x + \frac{ip}{\sqrt{m\omega}})|0\rangle = 0 \quad \rightarrow \quad (m\omega x + \frac{d}{dx})\psi_0(x) = 0 \quad \rightarrow \quad \psi_0(x) \propto e^{-m\omega x^2/2}$$

The other eigenstates are built using Hermite Polynomials $H_n(x)$, using the formula⁹ $|n\rangle = \frac{(a^\dagger)^n}{\sqrt{n!}}|0\rangle$ to derive differential equations:

$$\psi_n(x) = \langle x|n\rangle = \frac{1}{\sqrt{n!2^n}} \left[\sqrt{m\omega}x - \frac{1}{\sqrt{m\omega}} \frac{d}{dx} \right]^n \psi_0(x)$$

with solutions $\psi_n(x) = \langle x|n\rangle = \frac{1}{\sqrt{2^n n!}} H_n(x) \psi_0(x)$. The $n = 2$ and $n = 3$ wavefunctions are plotted in the following figure, while the second figure displays the probability distribution function. Notice the different parity for even and odd number and the number of zeros of these functions. Classically, the probability that the oscillating particle is at a given value of x is simply the fraction of time that it spends there, which is inversely proportional to its velocity $v(x) = x_0\omega\sqrt{1 - \frac{x^2}{x_0^2}}$ at that position. For large n , the probability distribution becomes close to the classical one (see Fig. ??).

⁹ For more details on Hermite Polynomials and their generator function, look on Cohen-Tannoudji. Online information from: Eric W. Weisstein. [Hermite Polynomial](#). From MathWorld—A Wolfram Web Resource.

4.4 Identical particles

We start first with the simplest case of a two-particle system. The wavefunction is then: $\psi(\vec{r}_1, \vec{r}_2)$ and if we assume that there is no interaction between the two particles, we will be able to describe the states using separation of variables:

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_a(\vec{r}_1)\psi_b(\vec{r}_2)$$

where a and b label two different single-particle states. Implicit in this expression is the assumption that I can distinguish the two particles by some mean, and link particle one to the position 1 and the state a . However, if we consider two identical particles (2 electrons, two photons, two neutrons) there is no physical mean to distinguish them. Even if we try to measure them in order to keep track of which one is which, we know that in the process we destroy the state (by the wavefunction collapse) so not even this is a possibility.

4.4.1 Bosons, fermions

In quantum mechanics identical particles are fundamentally indistinguishable. Then the expression above does not correctly describe the state anymore. In order to faithfully describe a state in which we cannot know if particle a or b is at r_1 or r_2 , we can take a linear combination of these two possibilities: $\psi(\vec{r}_1, \vec{r}_2) = A_1\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) + A_2\psi_b(\vec{r}_1)\psi_a(\vec{r}_2)$. Now, since the two possibilities have the same probability, we have $|A_1| = |A_2| = \frac{1}{\sqrt{2}}$. Then there are two possible combinations:

$$\psi(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} [\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \pm \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)]$$

These two combinations describe two types of particles. The combination with the plus sign describes **bosons**, particles that are invariant under exchange of a particle pair. The combination with the minus sign describes **fermions**:

- all particles with integer spin are **bosons**
- all particles with half-integer spin are **fermions**

(This can be proved in relativistic QM).

4.4.2 Exchange operator

We can define an operator \hat{P} that interchanges the two particles:

$$\hat{P}[\psi(\vec{r}_1, \vec{r}_2)] = \psi(\vec{r}_2, \vec{r}_1)$$

Since of course $\hat{P}[\hat{P}[\psi(\vec{r}_1, \vec{r}_2)]] = \psi(\vec{r}_1, \vec{r}_2)$, we have that $\hat{P}^2 = 1$. Then the eigenvalues of \hat{P} must be ± 1 . [If φ_n is an eigenfunction of \hat{P} with eigenvalue p_n , we have $\hat{P}^2\varphi_n = p_n^2\varphi_n = \varphi_n$, from which $p_n^2 = 1$.] If two particles are identical, then the Hamiltonian is invariant with respect to their exchange and $[\mathcal{H}, \hat{P}] = 0$. Then we can find energy eigenfunctions that are common eigenfunctions of the exchange operator, or $\psi(\vec{r}_1, \vec{r}_2) = \pm\psi(\vec{r}_2, \vec{r}_1)$. Then if the system is initially in such a state, it will be always be in a state with the same exchange symmetry. For the considerations above, however, we have seen that the wavefunction is not only allowed, but it must be in a state with a definite symmetry:

$$\psi(\vec{r}_1, \vec{r}_2) = \begin{cases} \psi(\vec{r}_2, \vec{r}_1) & \text{bosons} \\ -\psi(\vec{r}_2, \vec{r}_1) & \text{fermions} \end{cases}$$

4.4.3 Pauli exclusion principle

From the form of the allowed wavefunction for fermions, it follows that two fermions cannot occupy the same state. Assume that $\psi_a(\vec{r}) = \psi_b(\vec{r})$, then we always have that

$$\psi_f(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} [\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) - \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)] = 0.$$

This is the well-known Pauli exclusion principle. Notice that of course it applies to any fermions. For example, it applies to electrons, and this is the reason why electrons do not pile up in the lowest energy level of the atomic structure, but form a shell model. We will see that the same applies as well to protons and neutrons, giving rise to the shell model for nuclei.

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