Advanced Quantum Physics
Week 3

Michel Ferrero
Thomas Schäfer

Fall 2019

Quantum mechanics in more than one dimension

In the previous lectures, we have often considered quantum mechanics in one dimension. All the concepts the were introduced apply to higher dimensions, but for a completely general two or three-dimensional potential, finding solutions of the Schrödinger equation often becomes inaccessible. It is then usually necessary to use some approximation scheme. There is however an exception for systems with a high degree of symmetry. Indeed, exploiting symmetries, one can sometimes reduce the problem to a simpler, essentially one-dimensional, problem. In the following we will focus on the rotational symmetry which is very often encountered in quantum mechanics.

Rotation operator

Before discussing the implications of symmetry, let us discuss rotations in general. Just like for translations, there is an operator $\hat{R}_{\vec{\alpha}}$ that rotates a state around the axis given by the direction $\vec{\alpha}$ by an angle equal to the norm of the vector $\|\vec{\alpha}\|$. The operator $\hat{R}_{\vec{\alpha}}$ is unitary $\hat{R}^\dagger_{\vec{\alpha}}\hat{R}_{\vec{\alpha}} = \hat{R}_{\vec{\alpha}}\hat{R}^\dagger_{\vec{\alpha}} = \mathbb{1}$. We then clearly have that $\hat{R}_{-\vec{\alpha}} = \hat{R}^\dagger_{\vec{\alpha}}$. Unlike translations however, rotations do not commute in general. Only two rotations about the same axis commute.

Previously, we have seen that we can define momentum as the infinitesimal generator of translations. Similarly, we define the *angular momentum* $\hat{\vec{J}}$ to be the infinitesimal generator of rotations

$$\hat{R}_{\delta\vec{\alpha}} = \mathbb{1} - \frac{i}{\hbar}\hat{J}_x\delta\alpha_x - \frac{i}{\hbar}\hat{J}_y\delta\alpha_y - \frac{i}{\hbar}\hat{J}_z\delta\alpha_z = \mathbb{1} - \frac{i}{\hbar}\hat{\vec{J}}\delta\vec{\alpha}$$

The unitarity of the rotation operator implies that the operator $\hat{\vec{J}}$ is Hermitian. Following the same steps as earlier, we can show that any rotation can be written as

$$\hat{R}_{\vec{\alpha}} = \exp\left(-\frac{i}{\hbar}\hat{\vec{J}}\cdot\vec{\alpha}\right)$$

Commutation relations of the angular momentum operators

Two rotations do not commute if they are not along the same axis. As a result the operators $\hat{J}_x$, $\hat{J}_y$, $\hat{J}_z$ do not commute. We can find their commutation relations by considering a rotation of angle α about an axis $\vec{u} = (\cos\phi, \sin\phi, 0)$ in the xy plane. This rotation can be seen as the composition of a rotation about the z axis by an angle $-\phi$, followed by a rotation by an angle α about the x axis, followed by a final rotation by an angle $+\phi$ about the z axis:

$$\hat{R}_{\vec{u},\alpha} = \hat{R}_{\vec{z},\phi}\hat{R}_{\vec{x},\alpha}\hat{R}_{\vec{z},-\phi}$$

Using the angular momentum operators this reads

$$\exp\left(-\frac{i}{\hbar}\alpha\hat{\vec{J}}\cdot\vec{u}\right) = \exp\left(-\frac{i}{\hbar}\phi\hat{J}_z\right)\exp\left(-\frac{i}{\hbar}\alpha\hat{J}_x\right)\exp\left(\frac{i}{\hbar}\phi\hat{J}_z\right)$$

Let us now take the limit of $\alpha \to 0$ and Taylor expand

$$\mathbb{1} - \frac{i}{\hbar}\alpha\hat{\vec{J}}\cdot\vec{u} = \exp\left(-\frac{i}{\hbar}\phi\hat{J}_z\right)\left(\mathbb{1} - \frac{i}{\hbar}\alpha\hat{J}_x\right)\exp\left(\frac{i}{\hbar}\phi\hat{J}_z\right)$$

From which we find

$$\hat{\vec{J}}\cdot\vec{u} = \exp\left(-\frac{i}{\hbar}\phi\hat{J}_z\right)\hat{J}_x\exp\left(\frac{i}{\hbar}\phi\hat{J}_z\right)$$

Now taking the limit of $\phi \to 0$, we obtain

$$\hat{\vec{J}}\cdot\vec{u} = \hat{J}_x\cos\phi + \hat{J}_y\sin\phi = \hat{J}_x + \hat{J}_y\phi = \left(\mathbb{1} - \frac{i}{\hbar}\phi\hat{J}_z\right)\hat{J}_x\left(\mathbb{1} + \frac{i}{\hbar}\phi\hat{J}_z\right)$$

Comparing the terms linear in ϕ, we see that

$$\hat{J}_y = \frac{i}{\hbar}\hat{J}_x\hat{J}_z - \frac{i}{\hbar}\hat{J}_z\hat{J}_x \quad \to \quad i\hbar\hat{J}_y = \left[\hat{J}_z, \hat{J}_x\right]$$

The same argument taking the vector $\vec{u}$ in the yz and zx plane leads to the following commutation relations

$$[\hat{J}_x, \hat{J}_y] = i\hbar\hat{J}_z \qquad [\hat{J}_y, \hat{J}_z] = i\hbar\hat{J}_x \qquad [\hat{J}_z, \hat{J}_x] = i\hbar\hat{J}_y$$

This can also be written as

$$\hat{\vec{J}}\times\hat{\vec{J}} = i\hbar\hat{\vec{J}}$$

These commutation relations were obtained purely from geometrical arguments. They encode the structure of the rotation group and define the *Lie algebra* of the angular momentum operators. Starting from these relations we can find many properties that will help us to characterize the eigenstates of rotationally-invariant systems. It turns out that there are other operators in quantum mechanics that obey those same commutation relations. So all the results that we will derive here, will be valid for these other operators as well.

The operator $\hat{J}^2$

It is useful in the theory of Lie algebras to identify operators that commute with all the infinitesimal generators (they are called Casimir invariants of the Lie algebra). For the angular momentum operators, we can check that the operator $\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2$ commutes with all the infinitesimal generators

$$[\hat{J}_x, \hat{J}^2] = 0 \qquad [\hat{J}_y, \hat{J}^2] = 0 \qquad [\hat{J}_z, \hat{J}^2] = 0$$

It is therefore possible to measure simultaneously the norm of the angular momentum and one of its Cartesian components.

Systems with rotational symmetry

We have seen that if a system has a symmetry, its Hamiltonian commutes with the symmetry operator. For rotations this means that $[\hat{\mathcal{H}}, \hat{R}_{\vec{\alpha}}] = 0$. This can be shown by considering the evolution operator or by observing that $\langle\phi|\hat{R}^\dagger\hat{\mathcal{H}}\hat{R}|\Psi\rangle = \langle\phi|\hat{\mathcal{H}}|\Psi\rangle$, which implies that $\hat{R}^\dagger\hat{\mathcal{H}}\hat{R} = \hat{\mathcal{H}}$ and therefore $\hat{\mathcal{H}}\hat{R} = \hat{R}\hat{\mathcal{H}}$.

The Hamiltonian also commutes with the infinitesimal generators of the symmetry $[\hat{\mathcal{H}}, \hat{J}_u] = 0$ for $u = x, y, z$. It is then clear the Hamiltonian also commutes with $\hat{J}^2$. This means that we can find a common eigenbasis of $\{\hat{\mathcal{H}}, \hat{J}^2, \hat{J}_z\}$. Here the choice of $\hat{J}_z$ is arbitrary, we could also have chosen $\hat{J}_x$ or $\hat{J}_y$. However, it is not possible to find a basis that would diagonalize $\{\hat{\mathcal{H}}, \hat{J}^2, \hat{J}_z\}$ and also e.g. $\hat{J}_y$ because the latter operator does not commute with $\hat{J}_z$.

From this discussion, we see that even without an explicit expression for the Hamiltonian, it can be very useful to find the general form of common eigenstates of $\{\hat{J}^2, \hat{J}_z\}$. This is the topic of the next section.

Angular momentum observables

We will derive general properties for observables that have the following commutation relations

$$[\hat{J}_x, \hat{J}_y] = i\hbar\hat{J}_z \qquad [\hat{J}_y, \hat{J}_z] = i\hbar\hat{J}_x \qquad [\hat{J}_z, \hat{J}_x] = i\hbar\hat{J}_y$$

Again, the results obtained here will apply for the angular momentum and any observables that obey these relations.

General considerations

We want to find common eigenvectors of $\{\hat{J}^2, \hat{J}_z\}$. By convention, the eigenvalue associated to $\hat{J}^2$ is written $j(j+1)\hbar^2$ and that associated to $\hat{J}_z$ is written $m\hbar$, so that we can use j and m to label the eigenstates

$$\hat{J}^2 |j,m\rangle = j(j+1)\hbar^2 |j,m\rangle$$
$$\hat{J}_z |j,m\rangle = m\hbar |j,m\rangle$$

The reason for this convention will become more obvious below. The eigenvectors associated to the eigenvalues j, m belong to the eigensubspace $\mathcal{E}_{j,m}$. This eigensubspace could be of dimension larger than one so we should in principle write the eigenvectors with an extra label $|j,m,r\rangle$. For clarity we will however omit this extra label in the following. Note that for now $j, m \in \mathbb{R}$ but we will show that in fact j and m cannot take any values. The construction of the argument will be very similar to that of the harmonic oscillator.

The eigenvalues of $\hat{J}^2$ are positive

Let us start by showing that the eigenvalues of $\hat{J}^2$ are positive. Indeed, if λ is the eigenvalue, then

$$\langle j,m|\hat{J}^2|j,m\rangle = \lambda\langle j,m|j,m\rangle = \lambda = \left\| \hat{J}_x|j,m\rangle \right\|^2 + \left\| \hat{J}_y|j,m\rangle \right\|^2 + \left\| \hat{J}_z|j,m\rangle \right\|^2 \geq 0$$

This shows that $\lambda \geq 0$ and justifies that we can write this eigenvalue as $j(j+1)\hbar^2$ with $j \geq 0$.

The ladder operators $\hat{J}_\pm$

We introduce the two ladder operators $\hat{J}_\pm$ defined by

$$\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y$$

They are conjugate to each other $\hat{J}_+ = \hat{J}_-^\dagger$. It is easy to show that they satisfy the following commutation relations

$$\left[\hat{J}^2, \hat{J}_\pm\right] = 0 \qquad \left[\hat{J}_z, \hat{J}_\pm\right] = \pm\hbar\hat{J}_\pm \qquad \left[\hat{J}_+, \hat{J}_-\right] = 2\hbar\hat{J}_z$$

Also the product of the two ladder operators is Hermitian and is given by

$$\hat{J}_{\mp}\hat{J}_{\pm} = \hat{J}^2 - \hat{J}_z\left(\hat{J}_z \pm \hbar\mathbb{1}\right)$$

We now consider a state $|j,m\rangle \in \mathcal{E}_{j,m}$ and act on it with $\hat{J}_{\pm}$. We see that

$$\hat{J}^2\hat{J}_{\pm}|j,m\rangle = \hat{J}_{\pm}\hat{J}^2|j,m\rangle = j(j+1)\hbar^2\hat{J}_{\pm}|j,m\rangle$$

Also

$$\hat{J}_z\hat{J}_{\pm}|j,m\rangle = \left(\hat{J}_{\pm}\hat{J}_z \pm \hbar\hat{J}_{\pm}\right)|j,m\rangle = (m\pm 1)\hbar\hat{J}_{\pm}|j,m\rangle$$

These results show that $\hat{J}_{\pm}|j,m\rangle$ is either the null vector or a new eigenstate of $\{\hat{J}^2, \hat{J}_z\}$ with eigenvalues $j(j+1)\hbar^2$ and $(m\pm 1)\hbar$. The square norm of $\hat{J}_{\pm}|j,m\rangle$ is

$$\begin{aligned}\left\|\hat{J}_{\pm}|j,m\rangle\right\|^2 &= \langle j,m|\hat{J}_{\mp}\hat{J}_{\pm}|j,m\rangle = \langle j,m|\hat{J}^2 - \hat{J}_z\left(\hat{J}_z \pm \hbar\mathbb{1}\right)|j,m\rangle \\ &= j(j+1)\hbar^2 - m\,(m\pm 1)\,\hbar^2 \geq 0\end{aligned}$$

This condition both implies that $-(j+1) \leq m \leq j$ and that $-j \leq m \leq (j+1)$, which means that

$$-j \leq m \leq j$$

We also see that the null vector is obtained in two situations

$$\hat{J}_{+}|j,m=j\rangle = 0 \qquad \hat{J}_{-}|j,m=-j\rangle = 0$$

To summarize, we have shown that $\hat{J}_{\pm}|j,m\rangle \in \mathcal{E}_{j,m\pm 1}$ unless $m = \pm j$ where $\hat{J}_{\pm}|j,\pm j\rangle = 0$.

j and m are integers or half-integers

Let us start with a state $|j,m\rangle \in \mathcal{E}_{j,m}$ and apply $\hat{J}_{+}$ several times on this state. This will generate new eigenvectors with eigenvalues $m+1, m+2, m+3, \ldots$. If m is chosen randomly this may generate eigenvalues larger than j and contradict the result we found above. The only way to avoid this is that one of the generated eigenstates is the null vector. In other words, there must be an integer N such that $m+N = j$. We can do the same reasoning by applying several times $\hat{J}_{-}$ and we conclude that there must be an integer N' such that $m - N' = -j$. By taking the difference $(m+N)-(m-N') = 2j = N - N'$ we see that $2j$ must be an integer. This brings us to the important result that j is either an integer or a half-integer and so is $m \in \{-j, -j+1, \ldots, j-1, j\}$.

The standard basis $|n,j,m\rangle$

Above we have found some properties of the numbers j and m. We however do not know the exact structure of the subspaces $\mathcal{E}_{j,m}$ (e.g. their dimension) which is problem dependent. One can nevertheless prove that all the subspaces $\mathcal{E}_{j,m}$ for $m \in \{-j, -j+$

$1, \ldots, j\}$ have the same dimension. Let us consider a basis $|n, j, m\rangle$ of $\mathcal{E}_{j,m}$. We can construct new states $|n, j, m \pm 1\rangle$ according to

$$\hat{J}_{\pm}|n, j, m\rangle = \hbar\sqrt{j(j+1) - m(m \pm 1)}|n, j, m \pm 1\rangle$$

One can prove that these states are normalized, linearly independent and that they span $\mathcal{E}_{j,m\pm1}$. This construction of a basis can be repeated for all subspaces $\mathcal{E}_{j,m}$. The resulting basis $|n, j, m\rangle$ for $m \in \{-j, -j+1, \ldots, j\}$ is often called the *standard basis*.

Summary and discussion

To summarize, we have found very general properties of observables that obey the commutation relations

$$[\hat{J}_x, \hat{J}_y] = i\hbar\hat{J}_z \qquad [\hat{J}_y, \hat{J}_z] = i\hbar\hat{J}_x \qquad [\hat{J}_z, \hat{J}_x] = i\hbar\hat{J}_y$$

In particular, one can find common eigenstates of both $\{\hat{J}^2, \hat{J}_z\}$ with the following properties

- The eigenvalues of $\hat{J}^2$ can be written $j(j+1)\hbar^2$ where j is either an integer or a half-integer.
- The eigenvalues of $\hat{J}_z$ can be written $m\hbar$ with $m \in \{-j, -j+1, \ldots, j-1, j\}$.
- The dimension of the eigensubspaces $\mathcal{E}_{j,m}$ is independent of m.
- We can construct a *standard basis* $\{|n, j, m\rangle\}$ of common eigenvectors of $\{\hat{L}^2, \hat{L}_z\}$ using
$$\hat{J}_{\pm}|n, j, m\rangle = \hbar\sqrt{j(j+1) - m(m \pm 1)}|n, j, m \pm 1\rangle$$

The orbital angular momentum

Let us now investigate rotations in three-dimensional space more carefully. These rotations form the $SO(3)$ group. In the following, we will show that the angular momentum $\hat{\vec{L}}$ is the infinitesimal generator of rotations. Then we will look for the eigenstates of $\{\hat{L}^2, \hat{L}_z\}$, the so-called *spherical harmonics*.

Infinitesimal generators of rotations

We start by considering a rotation by an angle α around the z axis

$$\begin{cases} x' = x\cos\alpha + y\sin\alpha \\ y' = -x\sin\alpha + y\cos\alpha \\ z' = z \end{cases}$$

For an infinitesimal rotation $\delta\alpha$ we find

$$\begin{cases} x' = x + \alpha y \\ y' = -\alpha x + y \\ z' = z \end{cases}$$

The action of this infinitesimal rotation on a wavefunction is therefore

$$\begin{aligned} \left(\hat{R}_{z,\delta\alpha}\Psi\right)(x,y,z) &= \Psi(x+\alpha y, -\alpha x + y, z) = \Psi(x,y,z) + \alpha y\frac{\partial\Psi}{\partial x} - \alpha x\frac{\partial\Psi}{\partial y} \\ &= \Psi(x,y,z) + \alpha y\frac{i}{\hbar}\hat{p}_x\Psi(x,y,z) - \alpha x\frac{i}{\hbar}\hat{p}_y\Psi(x,y,z) \\ &= \left(\mathbb{1} - \frac{i}{\hbar}\alpha(\hat{x}\hat{p}_y - \hat{y}\hat{p}_x)\right)\Psi(x,y,z) \\ &= \left(\mathbb{1} - \frac{i}{\hbar}\alpha\hat{L}_z\right)\Psi(x,y,z) \end{aligned}$$

Repeating this argument for rotations about x and y, we see that the angular momentum

$$\hat{\vec{L}} = \hat{\vec{r}} \times \hat{\vec{p}} = \begin{pmatrix} \hat{y}\hat{p}_z - \hat{z}\hat{p}_y \\ \hat{z}\hat{p}_x - \hat{x}\hat{p}_z \\ \hat{x}\hat{p}_y - \hat{y}\hat{p}_x \end{pmatrix}$$

is indeed the infinitesimal generator of rotations. As such, any rotation can be written as

$$\hat{R}_{\vec{\alpha}} = \exp\left(-\frac{i}{\hbar}\hat{\vec{L}}\cdot\vec{\alpha}\right)$$

We have already shown above (without explicitly writing $\hat{\vec{L}}$) that the infinitesimal generators of rotations have the following commutation relations

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z \qquad [\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x \qquad [\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y$$

Now that we have an expression for $\hat{\vec{L}}$ we can check whether this is indeed true. For example,

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

This leads to

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

We obtain the expected result. One can do the same exercise for the other commutators.

Spherical coordinates

Because we will be interested in systems that are rotationally invariant, it is natural to work in spherical coordinates (r, θ, φ). The angle θ is the polar angle, φ the azimuthal angle and r the radial distance. The wavefunction $\Psi(r, \theta, \varphi)$ becomes a function of these variables. One can then ask how this wavefunction is modified by infinitesimal rotations about x, y and z and find the expression of the angular momentum $\hat{\vec{L}}$ in spherical coordinates. Those can then be used to find expressions for $\hat{L}^2$ and $\hat{L}_\pm$. We skip the details here and only show the result

$$\hat{L}_z\Psi(r, \theta, \varphi) = \frac{\hbar}{i}\frac{\partial}{\partial\varphi}\Psi(r, \theta, \varphi)$$
$$\hat{L}^2\Psi(r, \theta, \varphi) = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)\Psi(r, \theta, \varphi)$$

and also

$$\hat{L}_x\Psi(r, \theta, \varphi) = i\hbar\left(\sin\varphi\frac{\partial}{\partial\theta} + \frac{\cos\varphi}{\tan\theta}\frac{\partial}{\partial\varphi}\right)\Psi(r, \theta, \varphi)$$
$$\hat{L}_y\Psi(r, \theta, \varphi) = i\hbar\left(-\cos\varphi\frac{\partial}{\partial\theta} + \frac{\sin\varphi}{\tan\theta}\frac{\partial}{\partial\varphi}\right)\Psi(r, \theta, \varphi)$$
$$\hat{L}_\pm\Psi(r, \theta, \varphi) = \hbar e^{\pm i\varphi}\left(\pm\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\varphi}\right)\Psi(r, \theta, \varphi)$$

Note that these expressions never involve r. This is clear as rotations do not act on the radial distance. The eigenvalue equations that we want to solve read

$$\hat{L}^2\Psi(r, \theta, \varphi) = \ell(\ell+1)\hbar^2\Psi(r, \theta, \varphi)$$
$$\hat{L}_z\Psi(r, \theta, \varphi) = m\hbar\Psi(r, \theta, \varphi)$$

or using the previous expressions

$$-\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)\Psi(r, \theta, \varphi) = \ell(\ell+1)\Psi(r, \theta, \varphi)$$
$$-i\frac{\partial}{\partial\varphi}\Psi(r, \theta, \varphi) = m\Psi(r, \theta, \varphi)$$

Because these equations do not involve the radial part, we can look for eigenvectors in the form $\Psi(r,\theta,\varphi) = R(r)Y_{\ell,m}(\theta,\varphi)$. The normalization imposes that

$$\langle\Psi|\Psi\rangle = \underbrace{\int_0^\infty |R(r)|^2 r^2 dr}_{=1} \underbrace{\int_0^\pi \int_0^{2\pi} |Y_{\ell,m}|^2 \sin\theta d\theta d\varphi}_{=1} = 1$$

The spherical harmonics

Let us look for the eigenvalues ℓ, m and corresponding eigenfunctions $Y_{\ell,m}(\theta,\varphi)$ of the operators $\{\hat{L}^2, \hat{L}_z\}$. From the general considerations above, we know that ℓ and m must be either integer and half-integer. The functions $Y_{\ell,m}(\theta,\varphi)$ satisfy

$$\hat{L}_z Y_{\ell,m}(\theta,\varphi) = m\hbar Y_{\ell,m}(\theta,\varphi) \quad \rightarrow \quad \frac{\partial Y_{\ell,m}(\theta,\varphi)}{\partial\varphi} = imY_{\ell,m}(\theta,\varphi)$$

This has the general solution

$$Y_{\ell,m}(\theta,\varphi) = F_{\ell,m}(\theta)e^{im\varphi}$$

But because $Y_{\ell,m}(\theta,\varphi+2\pi) = Y_{\ell,m}(\theta,\varphi)$, we see that m must be an integer. Then also ℓ must be an integer. So we have $\ell \in \mathbb{N}$ and $m \in \{-\ell, -\ell+1, \ldots, \ell\}$.

In order to find the expression for $F_{\ell,m}(\theta)$ we can use the following strategy. We start by finding $F_{\ell,-\ell}(\theta)$ by remembering that $\hat{L}_-$ acting on $Y_{\ell,-\ell}$ must give zero

$$\hat{L}_-\left(F_{\ell,-\ell}(\theta)e^{-i\ell\varphi}\right) = \hbar e^{-i\varphi}\left(-\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\varphi}\right)\left(F_{\ell,-\ell}(\theta)e^{-i\ell\varphi}\right) = 0$$

Simplifying we see that $F_{\ell,-\ell}(\theta)$ must be the solution of

$$\frac{\partial F_{\ell,-\ell}}{\partial\theta} = \ell\,\frac{\cos\theta}{\sin\theta}\,F_{\ell,-\ell}(\theta)$$

This equation is first order and has a unique solution $F(\theta)_{\ell,-\ell} = c_\ell \sin^\ell\theta$. We have obtained a first spherical harmonic

$$Y_{\ell,-\ell} = c_\ell \sin^\ell\theta e^{-i\ell\varphi}$$

From there, the other spherical harmonics $Y_{\ell,m}$ are obtained by repeated actions of $\hat{L}_+$. For example, here are a few spherical harmonics

$$Y_{0,0}(\theta,\varphi) = \frac{1}{\sqrt{4\pi}} \quad Y_{1,0}(\theta,\varphi) = \sqrt{\frac{3}{4\pi}}\cos\theta \quad Y_{1,\pm1}(\theta,\varphi) = \mp\sqrt{\frac{3}{8\pi}}e^{\pm i\varphi}\sin\theta$$

Here are some properties of spherical harmonics

- $\hat{L}^2 Y_{\ell,m}(\theta,\varphi) = \ell(\ell+1)\hbar^2 Y_{\ell,m}(\theta,\varphi)$, where $\ell \in \mathbb{N}$.

- $\hat{L}_z Y_{\ell,m}(\theta,\varphi) = m\hbar Y_{\ell,m}(\theta,\varphi)$, where $m \in \{-\ell, -\ell+1, \ldots, \ell\}$.
- $Y_{\ell,m}(\theta,\varphi) = F_{\ell,m}(\theta)e^{im\varphi}$, where $F_{\ell,m}(\theta)$ is a real function with $\ell - |m|$ zeros in the interval $]0,\pi]$.
- $Y^*_{\ell,m}(\theta,\varphi) = (-1)^m Y_{\ell,-m}(\theta,\varphi)$
- $Y_{\ell,m}(\pi-\theta,\varphi+\pi) = (-1)^\ell Y_{\ell,m}(\theta,\varphi)$
- The spherical harmonics are a basis of the space of complex functions of (θ,φ). Therefore any function $Y(\theta,\varphi)$ can be expressed as

$$Y(\theta,\varphi) = \sum_{\ell,m} c_{\ell,m} Y_{\ell,m}(\theta,\varphi),$$

where

$$c_{\ell,m} = \int\int Y^*_{\ell,m}(\theta,\varphi) Y(\theta,\varphi) \sin\theta d\theta d\varphi$$

The figure below illustrates some spherical harmonics.

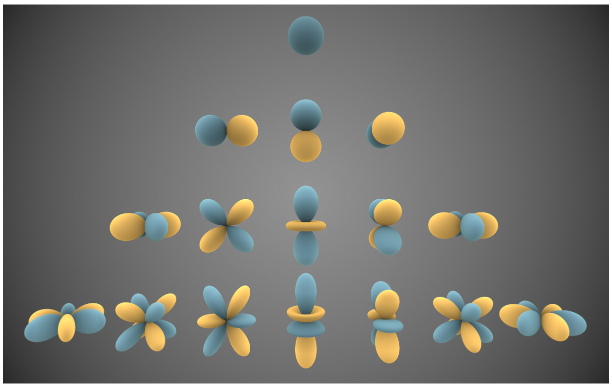

Figure 1: Illustration of the first spherical harmonics. The lines correspond to increasing values of ℓ.

Example: the rigid rotor

As a simple illustration of a system with spherical symmetry, we can consider the rotations of a diatomic molecule. The molecule is modeled by two masses m_1 and m_2 that are kept at a fixed distance R_0. The Hamiltonian of this system can be written as

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_{\text{cm}} + \hat{\mathcal{H}}_{\text{rot}} = \frac{\hat{P}^2}{2M} + \frac{\hat{L}^2}{2I},$$

where $\hat{\vec{P}}$ is the momentum of the center of mass, $M = m_1 + m_2$ is the total mass, $\hat{L}$ is the angular momentum of the masses with moment of inertia $I = \mu R^2$ and reduced mass $\mu = m_1 m_2/(m_1+m_2)$. We will ignore the motion of the center of mass and only focus on the rotational degrees of freedom described by $\hat{\mathcal{H}}_{\text{rot}}$.

It is clear that the spherical harmonics are eigenfunctions of this Hamiltonian

$$\frac{\hat{L}^2}{2I} Y_{\ell,m}(\theta,\varphi) = E_\ell Y_{\ell,m}(\theta,\varphi) \quad \rightarrow \quad E_\ell = \ell(\ell+1)\hbar^2$$

The eigenvalue E_ℓ is $2\ell+1$ times degenerate because it does not depend on m. The eigenvalue spectrum is discrete, unlike what would be expected from the classical counterpart of this system. This quantification is a consequence of the quantification of the angular momentum. The resulting energy spectrum is a fingerprint of the molecule and can be investigated with rotational spectroscopy. Indeed, if the molecule is put in a magnetic field, the latter will be absorbed only for energies that correspond to a transition between two eigenenergies. For example, for two neighboring energies the absorption would happen for frequencies that satisfy

$$\omega = \frac{E_{\ell+1} - E_\ell}{\hbar} = \frac{\hbar}{I}(\ell+1).$$

Rotational spectroscopy is also used with radiotelescopes to investigate the composition of distant stellar objects, as in the figure below.

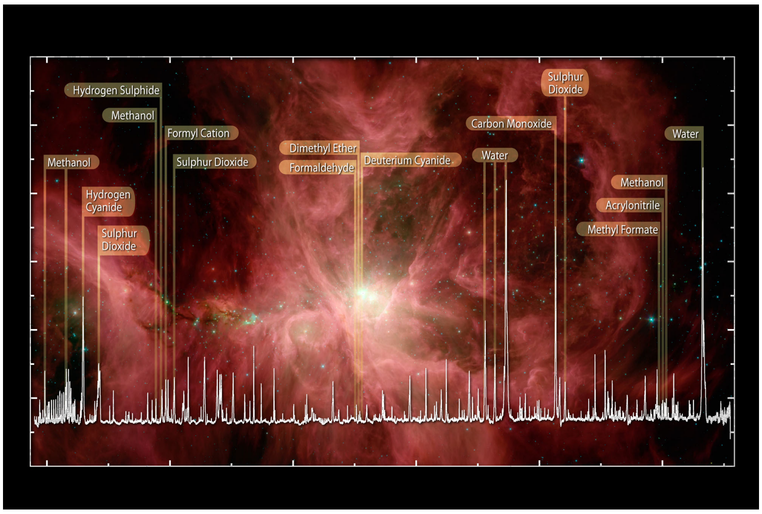

Figure 2: Measurement of the far-infrared spectrum of the Orion Nebula, breaking down the far-infrared light into a wide range of wavelengths. This reveals a series of spikes, or emission lines, caused by radiation which is emitted at particular wavelengths by particular elements and molecules.

Symmetries and degeneracies

When a system has a given symmetry, the observable associated to the infinitesimal generator of the symmetry commutes with the Hamiltonian $[\hat{A}, \hat{\mathcal{H}}] = 0$. This implies that there is a common eigenbasis for $\hat{A}$ and $\hat{\mathcal{H}}$. Phrased slightly differently, this means that if I consider an eigenstate of the Hamiltonian $|\Psi\rangle$, then $\hat{A}|\Psi\rangle$ is also an eigenstate of the Hamiltonian with the same energy. Two situations can arise

- $|\Psi\rangle$ is itself an eigenstate of $\hat{A}$. This is what happens if we consider translations. Indeed, the eigensubspaces are of dimension 1, meaning that an eigenstate of $\hat{T}_a$ is also an eigenstate of $\hat{\mathcal{H}}$. This turned out to be a powerful tool to find the eigenstates of the Hamiltonian.
- $|\Psi\rangle$ is not an eigenstate of $\hat{A}$. In this case $\hat{A}|\Psi\rangle$ is a new eigenstate of the Hamiltonian with the same energy. By acting several times with $\hat{A}$ we span a degenerate eigensubspace of the Hamiltonian.

When the system is rotationally invariant, we are facing the second situation. Imagine we find common eigenstates $|n, \ell, m\rangle$ of $\{\hat{\mathcal{H}}, \hat{L}^2, \hat{L}_z\}$. If we start from one of these eigenstates and act with $\hat{L}_x$ on that state, we will produce a new state because $\hat{L}_x$ and $\hat{L}_z$ do not commute. However, rotations about x are a symmetry of the Hamiltonian, therefore this new state will still have the same energy. Repeating this operation will eventually span the eigensubspace associated to the energy E_n for some value of ℓ. This eigensubspace will in general be of dimension larger than 1. For example, when we considered the diatomic molecule, every energy was $2\ell+1$ times degenerate. This is the main message of this section: in general symmetries will lead to degeneracies in the eigenvalue spectrum. Conversely, if there are degeneracies in the eigenvalue spectrum, there is in general some symmetry associated with it.

The hydrogen atom is another example. The three $2p$ states are degenerate, the $3d$ states are five times degenerate, etc. This is illustrated in the figure below.

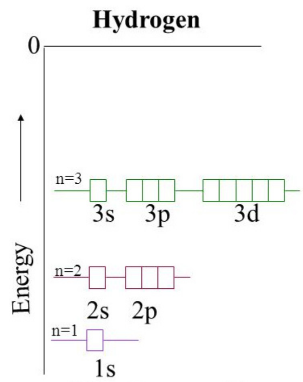

Figure 3: Energy levels of the hydrogen atom.

The degeneracy of the $2p$ or $3d$ states naturally stems from the rotational symmetry of the hydrogen atom. It is however much more surprising that the $2s$ and $2p$ states are also degenerate. It turns out that there is indeed an additional hidden symmetry, specific to $1/r$ potentials, that explains this degeneracy!

What happens when one introduces a small perturbation that breaks the symmetry of a system? In general, one will then observe that the degeneracy is lifted. An example is the C_{60} molecule shown below. This molecule is roughly spherical, but does not have full rotational symmetry. As a result, the degeneracies in its eigenvalue spectrum will be slightly lifted. But one can still recognize the original structure of a fully rotationally-symmetric system, as shown in the figure below.

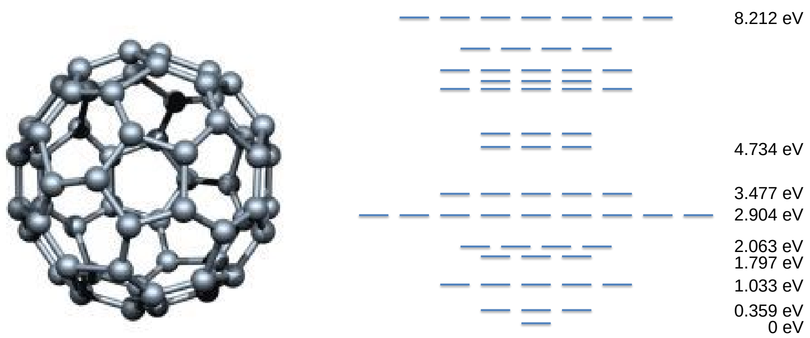

Figure 4: Energy levels in the C_{60} as obtained from a tight-binding calculation. The first three energy levels still have the degeneracy of a fully rotationally-symmetric potential. The forth energy level has been split into $3 + 4$ states.