

QUANTIZATION OF ANGULAR MOMENTUM

[ϕ 11.2, H 8.1-8.2, G 4.3]

Angular momentum operators

Our starting point is that we define an angular momentum operator \vec{J} by requiring that the cartesian components J_x, J_y and J_z are Hermitian operators satisfying the commutation relations

$$\begin{aligned} [J_x, J_y] &= i\hbar J_z \\ [J_y, J_z] &= i\hbar J_x \\ [J_z, J_x] &= i\hbar J_y \end{aligned} \quad \left. \right\} [J_i, J_j] = \epsilon_{ijk} J_k,$$

with ϵ_{ijk} the completely antisymmetric Levi-Cevita symbol, with $\epsilon_{xyz} = 1$.

This might seem strange. Why can't/don't the operators commute? This is related to the fact that in 3D, rotations do not commute: if you rotate something first around the x-axis, and then around the y-axis, this gives a different result compared to first rotating around the y-axis and then around the x-axis!

[The angular momentum operators are the generators of rotation, and must therefore also not commute]

For the operator for the orbital angular momentum, $\vec{L} = \vec{r} \times \vec{p}$, the commutation relations can be shown explicitly.

We can also define the operator $\vec{j}^2 = j_x^2 + j_y^2 + j_z^2$, which commutes with each of the components of \vec{j} :

$$[\vec{j}^2, j_k] = 0, \quad k = x, y, z.$$

Proof:

$$\begin{aligned} [\vec{j}^2, j_j] &= \sum_i [\vec{j}_i^2, j_j] = \sum_i [j_i, j_j] j_i + j_i [j_i, j_j] \\ &= \sum_{i,k} \epsilon_{ijk} (j_k j_i + j_i j_k) \end{aligned}$$

Since we sum over both k and i , we

can relabel $k \leftrightarrow i$ in the last term:

$$[\vec{j}^2, j_j] = \sum_{i,k} \epsilon_{ikj} (\epsilon_{ijk} + \epsilon_{ikj}) j_k j_i = 0,$$

since $\epsilon_{ijk} = -\epsilon_{ikj}$.

Since \vec{j}^2 commutes with the components, we can choose one of the components, e.g. j_z , and find simultaneous eigenvectors of \vec{j}^2 and j_z . We will write these as $|a, b\rangle$, with the property

$$\vec{j}^2 |a, b\rangle = a |a, b\rangle$$

$$j_z |a, b\rangle = b |a, b\rangle,$$

where a and b are the eigenvalues of the (?)

eigenvalues of the two operators.
So far we know nothing about what they actually are.

Eigenvalues

To find the eigenvalues, we will use operators methods similar to what we used for the harmonic oscillator. We define ladder operators

$$J_+ = J_x + iJ_y$$

$$\underline{J_- = J_x - iJ_y}$$

where $J_+^\dagger = J_-$, meaning they are not Hermitian. We will need the commutators with the other operators:

$$[\hat{J}^2, J_\pm] = 0,$$

since both J_x and J_y commute with \hat{J}^2 .

$$\begin{aligned} [J_z, J_\pm] &= [J_z, J_x] \pm i[J_z, J_y] \\ &= i\hbar J_y \pm i(-i\hbar J_x) = \pm \hbar J_\pm. \end{aligned}$$

We now follow a similar procedure as for the Harmonic oscillator, and take a closer look at the vectors $J_{\pm}|a,b\rangle$:

$$\tilde{J}^2 J_{\pm}|a,b\rangle = J_{\pm}\tilde{J}^2|a,b\rangle = J_{\pm}a|a,b\rangle = aJ_{\pm}|a,b\rangle$$

Hence $J_{\pm}|a,b\rangle$ are eigenvectors of \tilde{J}^2 with the same eigenvalue as $|a,b\rangle$.

Similarly, we calculate:

$$\begin{aligned} J_z J_{\pm}|a,b\rangle &= (J_{\pm}J_z \pm \hbar J_{\pm})|a,b\rangle \\ &= J_{\pm}(J_z \pm \hbar)|a,b\rangle = (b \pm \hbar)J_{\pm}|a,b\rangle. \end{aligned}$$

$J_{\pm}|a,b\rangle$ are eigenvectors of J_z with eigenvalues $b \pm \hbar$, granted that $J_{\pm}|a,b\rangle \neq 0$. Since J_+ increases the eigenvalue by \hbar , and J_- decreases the eigenvalue by \hbar , they are called raising and lowering operators, respectively.

Can we raise or lower the eigenvalue indefinitely? Intuitively we should expect that the eigenvalue $|b|$ should be smaller than \sqrt{a} , since J_z is a component of \tilde{J} .

To show this, we can again use the requirement that the norm of a vector should be positive. We calculate the norm of $J_{\pm}|a,b\rangle$:

$$\langle a, b | (J_{\pm})^+ J_{\pm} | a, b \rangle = \langle a, b | J_{\mp} J_{\pm} | a, b \rangle \geq 0.$$

We need an expression for $J_{\mp} J_{\pm}$:

$$\begin{aligned} J_{\mp} J_{\pm} &= (J_x \mp i J_y)(J_x \pm i J_y) \\ &= J_x^2 + J_y^2 \pm i \underbrace{(J_x J_y - J_y J_x)}_{i \hbar J_z} + J_z^2 - J_z^2 \\ &= J_x^2 - J_z^2 \mp \hbar J_z. \end{aligned}$$

Inserted into the expression for the norm, we get

$$\begin{aligned} &\langle a, b | J_x^2 - J_z^2 \mp \hbar J_z | a, b \rangle \\ &= \langle a, b | a - b^2 \mp \hbar b | a, b \rangle \\ &= a - b^2 + \hbar b = a - b(b \mp \hbar) \geq 0, \end{aligned}$$

can be violated for both positive and negative b !

We therefore require that there exists a , b_{\max} and b_{\min} such that

$$J_+ |a, b_{\max}\rangle = 0$$

$$J_- |a, b_{\min}\rangle = 0,$$

where b_{\max} and b_{\min} must satisfy

$$a = b_{\max}(b_{\max} + \hbar),$$

$$a = b_{\min}(b_{\min} - \hbar),$$

meaning that $b_{\max} = b_{\min} - \hbar$ or $b_{\max} = -b_{\min}$. The first option would mean that $b_{\max} < b_{\min}$, which by assumption is not true. Hence, we conclude that $b_{\min} = -b_{\max}$.

We have also seen that we can change the eigenvalue b of \hat{J}_z in steps of \hbar , and we should be able to move between the state with b_{\max} and the state with b_{\min} by applying ladder operators n times, meaning:

$$b_{\max} = b_{\min} + n\hbar, \quad n = 0, 1, 2, 3, \dots$$

$$\Rightarrow b_{\max} = \frac{n\hbar}{2}.$$

Inserted back into the equation relating a and b_{\max} , we get

$$a = \frac{\hbar^2 n(n+2)}{4},$$

the eigenvalue of \hat{J}^2 .

Notice that

$$a = \frac{\hbar^2 n(n+2)}{4} > b_{\min}^2 = \frac{\hbar^2 n^2}{4},$$

the eigenvalue of \hat{J}_z^2 is always smaller than that of \hat{J}^2 , meaning that the length of \hat{J}_z is always smaller than the total length of \hat{J} .

This is related to the fact that since $\hat{J}_x, \hat{J}_y, \hat{J}_z$ don't commute, we cannot know all simultaneously. (96)

To switch to the standard notation, we define $j = \frac{n}{2}$, and $m = \frac{b}{\hbar}$, resulting in the eigenvalue equations

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

$$J_z |j, m\rangle = \hbar m |j, m\rangle$$

with

$$m = -j, -j+1, \dots, j-2, j-1, j$$

and

$$j = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots$$

We can move to a state with eigenvalue $m \pm 1$ using the ladder operators:

$$J_{\pm} |j, m\rangle = \hbar \sqrt{j(j+1) - m(m \pm 1)} |j, m \pm 1\rangle.$$

This is very similar to the solutions we would find for the orbital angular momentum operator $\hat{L} = \hat{r} \times \hat{p}$. However, in that case, j could only take the values $0, 1, 2, \dots$, i.e. non-negative integers.

The half-integer values of j can not be explained by \hat{L} , and means that such states cannot be described by the position representation of QM.

One very important example of such a state is the spin of the electron, which has $j = \frac{1}{2}$. (q7)

ORBITAL ANGULAR MOMENTUM

The classical expression for the orbital angular momentum is $\vec{L} = \vec{r} \times \vec{p}$, and the quantum mechanical operators are given by the same expression

$$\begin{aligned}\hat{L}_x &= \hat{y}\hat{p}_z - \hat{z}\hat{p}_y \\ \hat{L}_y &= \hat{z}\hat{p}_x - \hat{x}\hat{p}_z \\ \hat{L}_z &= \hat{x}\hat{p}_y - \hat{y}\hat{p}_x\end{aligned}$$

These satisfy the commutation relations for angular momentum,

$$[\hat{L}_i, \hat{L}_j] = i\hbar \sum_u \epsilon_{ijk} L_u.$$

For instance:

$$\begin{aligned}[\hat{L}_x, \hat{L}_y] &= [y\hat{p}_z - z\hat{p}_y, z\hat{p}_x - x\hat{p}_z] \\ &= [\hat{y}\hat{p}_z, \hat{z}\hat{p}_x] - [\hat{y}\hat{p}_z, \hat{x}\hat{p}_z] \\ &\quad - [\hat{z}\hat{p}_x, \hat{z}\hat{p}_x] + [\hat{z}\hat{p}_x, \hat{x}\hat{p}_z] \\ &= y[\hat{p}_z, \hat{z}]_{\hat{p}_x} + x[\hat{z}, \hat{p}_z]\hat{p}_y \\ &= i\hbar(x\hat{p}_y - y\hat{p}_x) = i\hbar \hat{L}_z \quad \text{OK.}\end{aligned}$$

Spherical coordinates

If we use spherical coordinates r, θ, ϕ , related to x, y, z by

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

we can define position basis vectors $|r\rangle \equiv |r(\theta, \phi)\rangle$. (6)

In this case we have

$$\nabla = \hat{r} \frac{\partial}{\partial r} + \hat{\theta} \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{\phi} \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi},$$

leading to the orbital angular momentum operators ($\hat{p} = \frac{\hbar}{i} \nabla$)

$$L_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}$$

$$\hat{L}^2 = -\hbar^2 \left(\frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right),$$

where $[\hat{L}^2, L_z] = 0$. Hence, there exist eigenvectors $|l, m\rangle$ (notice that we use l for the orbital angular momentum) such that

$$\hat{L}^2 |l, m\rangle = \hbar^2 l(l+1) |l, m\rangle$$

$$L_z |l, m\rangle = \hbar m |l, m\rangle, \quad (*)$$

which follows from our earlier discussion.

Position representation

We want to find the wavefunction,

$$Y_{lm}(r, \theta, \phi) \equiv \langle r, \theta, \phi | l, m \rangle,$$

which is an eigenfunction of L_z and \hat{L}^2 .

We proceed by multiplying (*) by $L(r, \theta, \phi)$ from the left:

$$\langle r, \theta, \phi | L_z | l, m \rangle = \hbar m \langle r, \theta, \phi | l, m \rangle.$$

$$\begin{aligned} &= \langle l, m | L_z | r, \theta, \phi \rangle^* = \langle l, m | \frac{\hbar}{i} \frac{\partial}{\partial \phi} | r, \theta, \phi \rangle^* \\ &= \frac{\hbar}{i} \frac{\partial}{\partial \phi} \langle l, m | r, \theta, \phi \rangle^* = \frac{\hbar}{i} \frac{\partial}{\partial \phi} \langle r, \theta, \phi | l, m \rangle. \end{aligned}$$

Hence, we have the eigenvalue equation

$$\frac{\hbar}{i} \frac{\partial}{\partial \phi} Y_{lm}(r, \theta, \phi) = \hbar m Y_{lm}(r, \theta, \phi)$$

Similarly, for \hat{L}^2 , we get

$$-\hbar^2 \left(\frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin \theta} \frac{\partial^2}{\partial \phi^2} \right) Y_{lm} = \hbar^2 l(l+1) Y_{lm}$$

Since neither of these equations depend on r , we can separate the solution,

$$Y_{lm}(r, \theta, \phi) = R(r) Y_{lm}(\theta, \phi),$$

where $Y_{lm}(\theta, \phi)$ are angular functions

which satisfy the same equations as Y_{lm} ,

$$Y_{lm}(\theta, \phi) = \langle \theta, \phi | l, m \rangle.$$

The solutions $Y_{lm}(\theta, \phi)$ are the spherical harmonics, which can be written on the form

$$Y_{lm}(\theta, \phi) = G_{lm}(\theta) e^{im\phi}.$$

They form a orthonormalized, complete set.

Here we see why m , and therefore also l , must be an integer in the case of orbital angular momentum: If m is half-integer:

$$Y_{lm}(\theta, \phi + 2\pi) = - Y_{lm}(\theta, \phi),$$

which does not give a continuous wavefunction! Hence only integer l, m are allowed.

See slides for some examples of $Y_{lm}(\theta, \phi)$.

HYDROGEN ATOM

We'll recapitulate the main results for the hydrogen atom, as these results will be used and referred to later in the course.

Spherically symmetric potential

In the case of a spherically symmetric potential, $V(\vec{r}) = V(|\vec{r}|) = V(r)$, it is convenient to use spherical coordinates (r, θ, ϕ) . In this case, the Schrödinger equation reads

$$\begin{aligned} \hat{H}\psi &= \left[-\frac{\hbar^2}{2m} \nabla^2 + V(r) \right] \psi = E\psi \\ &= \left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + V(r) + \frac{\vec{L}^2}{2mr^2} \right] \psi = E\psi. \end{aligned}$$

The Hamiltonian commutes both with \vec{L}^2 and the components of \vec{L} , since all angular dependence is contained in the \vec{L} -term.
Hence:

- \vec{L}^2, L_x, L_y, L_z are constants of motion
- = There exists simultaneous eigenstates of \hat{H}, \vec{L}^2 and e.g. L_z .

Using as ansatz $\psi(r, \theta, \phi) = R(r) Y_m(\theta, \phi)$, we can insert $\vec{L}^2 Y_m(\theta, \phi) = \hbar^2 l(l+1) Y_m(\theta, \phi)$, resulting in a radial equation

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

Coulomb potential

For the hydrogen atom, the potential reads

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

and we get the radial equation for
 $u(r) = r R(r)$

$$\frac{\hbar^2}{2m} \frac{d^2u}{dr^2} + \left[\frac{e^2}{4\pi\epsilon_0} \frac{1}{r} - \frac{\ell(\ell+1)\hbar^2}{2mr^2} + E \right] u = 0.$$

We'll not solve this equation in detail, but look at how the solutions should behave for large and small r :

$r \rightarrow \infty$:

The equation simplifies to

$$\frac{d^2u}{dr^2} = -\frac{2mE}{\hbar^2} u,$$

meaning that for bound states ($E < 0$)

$$u(r) \propto e^{-Kr}, \quad K = \sqrt{-\frac{2mE}{\hbar^2}}.$$

$r \rightarrow 0$

In this case, we get

$$\frac{d^2u}{dr^2} \approx \frac{\ell(\ell+1)}{r^2} u$$

which has solutions

$$u(r) \propto r^{\ell+1} \quad \text{and} \quad u(r) \propto r^{-\ell}.$$

In order to have a non-singular solution, we must choose the first, $R(r) \propto r^\ell$.

Based on these two limits, one can use as ansatz

$$u(r) = e^{-kr} v(r),$$

where $v(r)$ is a polynomial with r^{l+1} as lowest order term. Based on the fact that $u(r) \propto e^{-kr}$ for large r , one finds certain requirements for the coefficients of $v(r)$, leading to the quantized energies

$$E_n = -\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{1}{n} = \frac{E_1}{n^2}, \quad n=1,2,3,\dots$$

with $E_1 = -13.6 \text{ eV}$, and the radial functions

$$R_{nl}(r) \propto -\rho^l e^{-\frac{1}{2}\rho} L_{n+l}^{2l+1}(\rho),$$

where $\rho = \frac{2r}{na}$, with Bohr radius a , and associated Laguerre polynomials $L_{n+l}^{2l+1}(\rho)$, see plots in slides. R_{nl} is a polynomial of degree $n-l$, times the exponential factor. The full wavefunction $Y_{lm} \propto R_{nl} Y_{lm}$.

Later, when we start looking at perturbation methods, we will calculate corrections to the spectrum E_n .