

Physics 8D Lecture Notes
Atomic Quantum Mechanics

We have already discussed the example of a particle in a box and how that relates to the energy quantization conditions. For the hydrogen atom, we replace the box potential with a spherical potential, $U(r)$, that depends only on distance from the origin (the nucleus). In such a potential it turns out that energy and angular momentum are quantized (as Bohr already postulated).

We can determine the quantized values for the angular momentum by using the method of operators to determine the wave function for the angular momentum (probable amplitude) and requiring it to be single-valued ($\phi + 2\pi = \phi$, $\theta + 2\pi = \theta$).

$$L_z = xp_y - yp_x$$

$$[L_z]\Phi = \frac{\hbar}{i} \left(x \frac{d}{dy} - y \frac{d}{dx} \right) \Phi = L_z \Phi$$

Where L_z is the eigenvalue of the operator $[L_z]$ and similar relations hold for L_y and L_x .

To use the quantization conditions, we can express $[L_z]$ in polar coordinates by using the chain rule:

$$\frac{d\Phi}{dz} = \left(\frac{d\Phi}{dr} \right) \frac{dr}{dz} + \left(\frac{d\Phi}{d\theta} \right) \frac{d\theta}{dz} + \left(\frac{d\Phi}{d\phi} \right) \frac{d\phi}{dz}$$

$$\frac{d\Phi}{dx} = \left(\frac{d\Phi}{dr} \right) \frac{dr}{dx} + \left(\frac{d\Phi}{d\theta} \right) \frac{d\theta}{dx} + \left(\frac{d\Phi}{d\phi} \right) \frac{d\phi}{dx}$$

$$\frac{d\Phi}{dy} = \left(\frac{d\Phi}{dr} \right) \frac{dr}{dy} + \left(\frac{d\Phi}{d\theta} \right) \frac{d\theta}{dy} + \left(\frac{d\Phi}{d\phi} \right) \frac{d\phi}{dy}$$

where

$$z = r \cos \theta$$

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

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

$$r^2 = x^2 + y^2 + z^2$$

The result for L_z is that $[L_z] = -i\hbar \frac{d}{d\phi} \Phi$, or,

$$-i\hbar \frac{d}{d\phi} \Phi = L_z \Phi .$$

The solution to this equation is:

$$\Phi = A e^{iL_z \phi / \hbar}$$

where A is still an arbitrary constant, and,

$$e^{iL_z / \hbar \phi} = e^{iL_z / \hbar (\phi + 2\pi)} .$$

This is satisfied iff

$$L_z = m_l \hbar$$

where $m_l = \pm 1, 2, 3, \dots$

You would expect, then, that L_x , L_y , and L_z could each be measured and the total angular momentum could be determined. There is a problem with measuring any two components of the angular momentum simultaneously, since knowledge of, say, L_z and L_y would allow one to know in theory what the position and momentum of our particle were at a certain time, in violation of the uncertainty principle. i.e.

$$L_z = xp_y - yp_x \qquad L_y = zp_x - xp_z$$

If, say, $L_y = L_z = 0$, then we would know that the particle was definitely orbiting in the yz plane, so that $p_x = 0$. If p_x is zero then the L_z relation shows that either p_y is zero for all times (which it isn't), or that $x = 0$ which would sound reasonable except that we would then know both p_x and x exactly, in violation of the uncertainty principle $\Delta x \Delta p \geq \hbar$

Why are these observables quantized? The answer comes from the conservation law governing energy, momentum, and angular momentum, and the uncertainty principle for energy, momentum, and position.

To know the angular momentum for a particle means to know its magnitude and direction. This in turn means that each component can be specified exactly. But there is no way to do this, so we must instead measure the magnitude of the angular momentum:

$$L = \sqrt{L_x^2 + L_y^2 + L_z^2}$$

or we can measure

$$L^2 = (L_x^2 + L_y^2 + L_z^2).$$

We can determine the eigenvalues for the L^2 operator by using the definition of each component of L and the chain rule. The result is that

$$[L^2]\Theta = -\hbar^2 \left(\frac{d^2\Theta}{d\theta^2} + \cot\theta \frac{d\Theta}{d\theta} \right) - \csc^2\theta (\hbar^2 m_l^2) \Theta.$$

But we're really interested in the eigenvalues, L^2 , of $[L^2]$, aren't we? Yes we are! But to find them we need to find a function $\Theta(\theta)$ that satisfies this equation. There exists a whole class of functions that satisfy this eigenvalue relation called Legendre polynomials of order l , depending on the value of m_l above, so they are written P_l^m . The mathematical basis that underlies Legendre polynomials derives from the planet Mathematica where Schrödinger, Von Newman, Einstein, Dirac, and presumably Legendre came from, so we won't try to derive them from elementary logic just yet.

Anyway, the composite function $\Theta(\theta, \phi)$ that satisfies the eigenvalue equation is then:

$$\begin{aligned} \Theta(\theta, \phi) &= P_l^m e^{im_l\phi} \\ &= Y_l^m(\theta, \phi) \quad (\text{spherical harmonics}) \end{aligned}$$

No sweat you say? Good! The first ten spherical harmonics are given in your text book.

It is a fact of life on the planet Mathematica that the eigenvalues of the spherical harmonics are given by

$$[L^2]Y_l^m = \hbar^2 l(l+1)Y_l^m$$

$$\text{and } [L_z]Y_l^m = \hbar m_l Y_l^m$$

To put it another way, the measurable values of L and L_z are given by:

$$L_z = m_l \hbar$$

$$|L| = \hbar \sqrt{l(l+1)}$$

l is known as the orbital quantum number, while m is the magnetic quantum number. It is also well known on Mathematica that

$$l = 0, 1, 2, 3, \dots$$

$$m_l = 0, \pm 1, \pm 2, \pm 3, \dots \pm l$$

This relationship between l and m leads to (or is derived from?) space quantization.

Notice that nothing we've done so far has any features special to atoms. To make it special, we only have to add in the potential energy

$$U(r) = -\frac{Ze^2}{4\pi\epsilon r}$$

We also note that the Schrödinger equation $H\Psi = E\Psi$ becomes

$$\left(\frac{p_r^2}{2m} + \frac{L^2}{2mr^2} + U(r) \right) \Psi = E\Psi$$

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

if we let Ψ be equal to $R(r)Y_l^m(\theta, \phi)$.

Note that the first term on the left is really the kinetic energy operator operating $R(r)$ in polar coordinates, and the second term is like an effective potential energy

$$U_{\text{eff}} = U(r) + \frac{\hbar^2 l(l+1)}{2mr^2}.$$

Note that the energy eigenvalues then can have no dependence on m_l and thus there are $2l + 1$ different quantum states that have the same energy.

The solution to $R(r)$, the radial wave equation, is called the radial wave function and it is written R_{n_l} . Note that by substituting R_{n_l} into the SEQ, the energies are

$$E_n = -\frac{k_e^2 Z^2}{2a_0 n^2}$$

as predicted by Bohr. Also note that while n can have any value, l is restricted to $l = 0, 1, 2, \dots, n-1$.

The probability that a particle will be in a particular region of space between r and $r + dr$ is found by integrating over θ and ϕ for a spherical shell of thickness dr . It turns out that

$$P(r)dr = r^2 |R(r)|^2 dr.$$