

QM 4

The Quantum description of the Hydrogen Atom

In general, we can't say *exactly* where an electron is, we have to consider it as a probability distribution that's a function of the radius

$$\Psi(r) = \frac{e^{-\frac{r}{r_0}}}{\sqrt{\pi r_0^3}}$$

Where r_0 is a constant.

Potential energy for the hydrogen atom

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

The *time independent* schrodinger equation is then

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi - \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2} \Psi = E\Psi$$

One electron Atoms

Imagine the following system, in a normal Hydrogen Atom (1_1H), there is a single electron of mass m_e orbiting around a much more massive proton of mass m_p .

In reality, the center of mass is to the right of the proton, and so both particles orbit the center of mass. It's much more convenient for us to treat the proton itself as the center of mass and give the electron the *reduced mass* μ .

$$\mu = \frac{Mm}{m + M}$$

Where M is the true mass of the nucleus, and m is the true mass of the electron. We can apply this model to any single electron atoms. The electron of reduced mass μ under the influence of the coulomb potential, is represented as follows.

$$V(x, y, z) = \frac{-Ze^2}{4\pi\epsilon_0\sqrt{x^2 + y^2 + z^2}}$$

Where $x, y, \text{ and } z$ are rectangular coordinates of an electron relative to the nucleus centered at the origin. The square root in the denominator is just the electron-nucleus separation distance r . The nuclear charge is $+Ze$ ($Z = 1$ for neutral hydrogen, $Z = 2$ for singly ionized helium, etc.)

Let's develop the Schrodinger equation by first finding the total energy for the system.

$$E = \frac{1}{2\mu}(p_x^2 + p_y^2 + p_z^2) + V(x, y, z)$$

The quantities p_x, p_y, p_z are the x, y, z components of the linear momentum of the electron. Thus the first term on the left is the kinetic energy of the system, while the second term is its potential energy. Now we replace the dynamical quantities $p_x^2 + p_y^2$, and p_z^2 and E by their associated *differential* operators, using an obvious three-dimensional scheme. This gives us the *operator equation*.

$$-\frac{\hbar}{2\mu} \cdot \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(x, y, z) = i\hbar \frac{\partial}{\partial t}$$

With some simplifying this becomes

$$-\frac{\hbar}{2\mu} = \nabla^2 \Psi + V\Psi = E\Psi$$

note: $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$. Often called the *Laplacian operator*.

There are time independent solutions for this function, due to the fact that V does not depend on time! However this function seems difficult to manage. We could solve it using separation of variables to split the partial differential equation into a set of three ordinary differential equations, each involving only one coordinate and solve them independently. However the trouble comes when dealing with V . We get around this by switching to *spherical polar coordinates*. These are r, θ and φ .

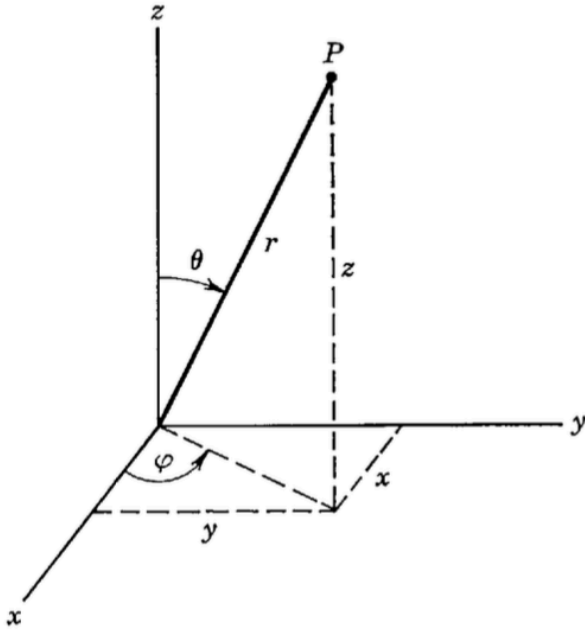


Figure 7-2 The spherical coordinates r, θ, φ of a point P , and its rectangular coordinates x, y, z .

Our new solution to the Schrodinger equation is the following form.

$$\Psi(r, \theta, \varphi) = R(r)\Theta(\theta)\Phi(\varphi)$$

Solutions in multiple dimensions.

$$\Phi(\varphi) = e^{im_l\varphi}$$

$$e^{im_l2\pi} = e^{im_l0}$$

This can only be true if the values of m_l are the following.

$$|m_l| = 0, 1, 2, 3, \dots$$

In other words, m_l can be only a positive or negative integer. Thus the set of functions which are *acceptable* solutions to are defined below. The *quantum number* m_l is used as a subscript to identify the specific form of an acceptable solution.

$$\Phi_{m_l}(\varphi) = e^{im_l\varphi}$$

In solving (7-16) for the functions $\Theta(\theta)$, the procedure is similar to that used in Appendix I to obtain analytical solutions of the time independent Schrodinger equation for the simple harmonic oscillator potential. Here we shall only quote the results. It is found that solutions to which are acceptable (remain finite) are obtained only if the constant 1 is equal to one of the integers.

$$l = |m_l|, |m_l| + 1, |m_l| + 2, |m_l| + 3, \dots$$

$$\Theta_{lm_l}(\theta) = \sin^{|m_l|}(\theta) F_{|m_l|}(\cos(\theta))$$

and eventually,

$$R_{nl}(r) = e^{\frac{-Zr}{na_0}} \left(\frac{Zr}{a_0} \right)^l G_{nl} \left(\frac{Zr}{a_0} \right)^l$$

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2}$$

Because of its role in specifying the total energy of the atom, n is sometimes called the *principal* quantum number.

Because the azimuthal, or orbital, angular momentum of the atom depends on l , its called the *azimuthal* quantum number.

If the atom is in an external magnetic field there is a dependence of its energy on m_l . Consequently, m_l sometimes called the *magnetic* quantum number.

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

$$l = |m_l|, |m_l| + 1, |m_l| + 2, |m_l| + 3, \dots$$

$$n = 1 + 1, 1 + 2, 1 + 3, \dots$$

rather, $n = 1, 2, 3, \dots$ and $l = n - 1$ and m_l can range from l to $-l$.

These conditions show that for a given value of n there are several different possible values of l and m_l . Since the form of the eigen-functions depends on all three quantum numbers, there are situations in which two or more completely different eigenfunctions correspond to exactly the same eigenvalue E .

Since the energy eigenfunctions describe the behavior of the atom, it has states with **different** behavior that nevertheless have the same *total* energy. In physics the word used to characterize this phenomenon is *degeneracy*, and eigenfunctions corresponding to the same eigenvalue are said to be *degenerate*.

Inspection of these properties shows that:

- For each value of n , there are n possible values of l .
- For each value of l , there are $(2l + 1)$ possible values of m_l .
- For each value of n , there are a total of n^2 degenerate eigenfunctions.

Eigenfunctions of a one electron atom

So the question becomes the following. We've done a lot of work to develop a means of making predictions that we already had before in the form of the Bohr model of the atom. So the question becomes, is this *worth*

the extra work? **YES**

Eigenfunctions give us so much more information than the Bohr model. They are formed by taking the following product.

$$\Psi = R_{nl}(r)\Theta_{lm_l}(\theta)\Phi_{m_l}(\varphi)$$

We also know the forms of each of these functions.

$$\Theta_{lm_l}(\theta) = \sin^{|m_l|}(\theta)(\text{polynomial in } \cos(\theta))$$

$$\Phi(\varphi) = e^{im_l\varphi}$$

$$R(r) = e^{-r/n}r^l$$

Example 7-2: Verify that the eigenfunction ψ_{211} , and the associated eigenvalue E_2 , satisfy the time-independent Schrodinger equation for the one-electron atom with $Z = 1$.

Answer: Since the differential equation is linear in ψ , for the purposes of this verification we can ignore completely the multiplicative constant $1/8\pi^{1/2}a_0^{5/2}$, and write the eigenfunction as $\psi = re^{-r/2a_0} \sin(\theta)e^{i\varphi}$

$$\psi = g(\theta, \varphi)re^{-r/2a_0}$$

We go back to our original schrodinger equation,

$$E\psi = -\frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2(\theta)} \left(\frac{\partial \psi}{\partial \varphi} \right)^2 \right] + V\psi$$

Refer to the table on the last page for better information / pattern matching.

Probability Densities

We begin to extract information from the one-electron atom eigenfunctions by studying the forms of the corresponding probability density functions.

$$\Psi^*\Psi = \psi_{nlm_l}^* e^{iE_n t/\hbar} \psi_{nlm_l} e^{-iE_n t/\hbar} = \psi_{nlm_l}^* \psi_{nlm_l}$$

We define the *radial probability density* $P(r)$, defined so that $P(r)dr$ is the probability of finding the electron at any location with radial coordinate between r and $r + dr$. By integrating the probability density P^*h which is a probability unit volume, over the volume enclosed between spheres of radii r and $r + dr$ easy to show $P(r) = 4\pi r^2 |\psi|^2$.

Sources

<http://www.nat.vu.nl/~wimu/EDUC/MNW-lect-2.pdf>

<https://www.physics.rutgers.edu/ugrad/323/QM4.html>