

# PHY140Y

## 26 The Schrödinger Model for the Hydrogen Atom

### 26.1 Overview

- Spherical Polar Coordinates
- Schrödinger's Equation in Three Dimensions
- The Hydrogen Atom

### 26.2 Spherical Polar Coordinates

The Cartesian or rectangular coordinate system is one that we are comfortable working with because of its simplicity. It reflects the 3-dimensional nature of space, and it allows us to consider each dimension separately. However, it is not always the most natural coordinate system to work with. In particular, for problems that have spatial symmetries that are cylindrical or spherical, different coordinate systems may end up giving a more understandable result.

The simplest example is to consider how we talk about gravity or electrostatics. We never invoked the Cartesian coordinate system in those discussions. Instead, we typically talked about the radius  $r$  as the useful coordinate. With suitable extensions, we can develop a coordinate system that takes advantage of the spherical symmetry associated with such problems. Fig. 1 shows the usual definition of the spherical-polar coordinate system, where we now describe a point in space using the distance from the origin  $r$ , and two angles. The first angle is the polar angle  $\theta$ , and the second angle is the azimuthal angle  $\phi$ . These are shown in Fig. 1, and can be related to the Cartesian coordinates  $x, y, z$  by

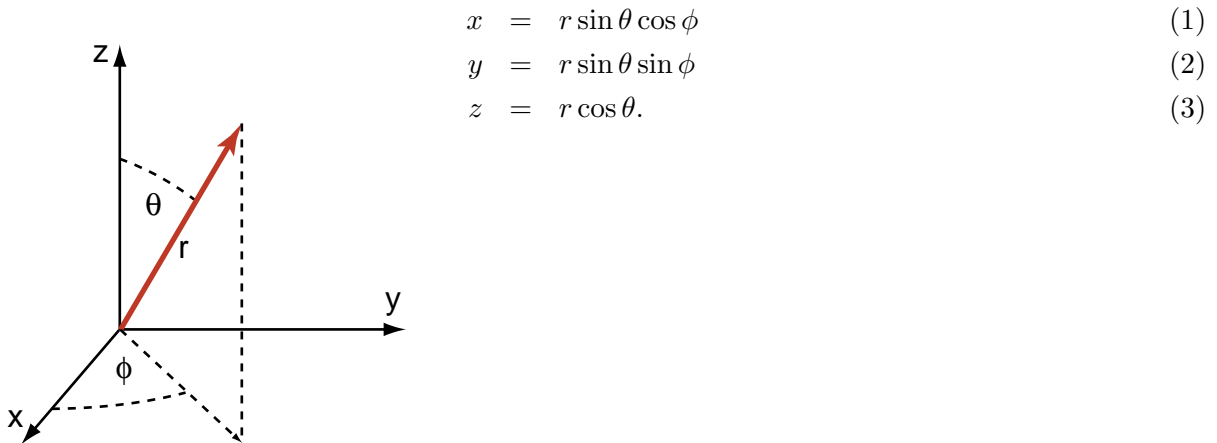


Figure 1: The relationship between the spherical-polar coordinates  $r, \theta, \phi$  and the Cartesian coordinates  $x, y, z$ .

With this definition, we will have to also develop a little more sophistication with how we deal with derivatives and integrals. In particular, since we will be working in three dimensions, we will have to introduce a new type of derivative, known as a “partial derivative” and denoted as

$$\frac{\partial f}{\partial x}. \tag{4}$$

As its name suggests, this is a derivative operator similar to the usual 1-dimensional operator you are probably familiar with, but it can act on functions of up to 3 coordinates. The rule is that when you take the partial derivative of a function with respect to one coordinate, you treat the other coordinates as being constants that have no dependence on that coordinate. In that sense, these partial derivative operators are not really different than our traditional 1-dimensional version.

A concrete example may help. Suppose

$$f(x, y, z) = 3x^2y + 4y^2 + z. \tag{5}$$

Then the following are some of the possible partial derivatives of  $f$ :

$$\frac{\partial f}{\partial x} = \frac{\partial}{\partial x} (3x^2y + 4y^2 + z) = 6xy \tag{6}$$

$$\frac{\partial f}{\partial y} = \frac{\partial}{\partial y} (3x^2y + 4y^2 + z) = 3x^2 + 8y \tag{7}$$

$$\frac{\partial f}{\partial z} = \frac{\partial}{\partial z} (3x^2y + 4y^2 + z) = 1 \tag{8}$$

$$\frac{\partial^2 f}{\partial x^2} = \frac{\partial^2}{\partial x^2} (3x^2y + 4y^2 + z) = 6y \tag{9}$$

$$\frac{\partial^2 f}{\partial y^2} = \frac{\partial^2}{\partial y^2} (3x^2y + 4y^2 + z) = 8 \tag{10}$$

$$\frac{\partial^2 f}{\partial z^2} = \frac{\partial^2}{\partial z^2} (3x^2y + 4y^2 + z) = 0 \tag{11}$$

We see that we just treat the partial derivative just like a one-dimensional derivative operator.

The final innovation we need to introduce is what the second derivative operator looks like in three dimensions. In Cartesian coordinates, the operator

$$\frac{d^2 f}{dx^2} \Rightarrow \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2}. \tag{12}$$

This is known as the Laplacian operator,  $\nabla^2$ , and looks even scarier in spherical-polar coordinates:

$$\nabla^2 f = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial f}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial f}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial f}{\partial \phi}, \tag{13}$$

where now one has to keep track of a real mess. We will only work with that part that depends on  $r$ , so in practice this won't be so scary.

### 26.3 Schrödinger's Equation in Three Dimensions

We can now extend Schrödinger's equation to 3-dimensional applications. We note that the potential function  $U$  now will be a function of all three spatial coordinates,  $U(r, \theta, \phi)$ , as will the wave function  $\psi(r, \theta, \phi)$ . The second derivative operator in 1-dimension will be replaced by the Laplacian operator. Thus, the Schrödinger equation becomes

$$-\frac{\hbar^2}{2m}\nabla^2\psi + U\psi = E\psi. \quad (14)$$

As before, solutions to this equation have to obey the boundary conditions for the given problem.

We can now turn to the hydrogen atom again as it serves on the one hand as perhaps the simplest realistic physical system that is governed by quantum mechanics, and on the other hand is a system for which we can find exact solutions to Schrödinger's equation.

### 26.4 The Hydrogen Atom

For the hydrogen atom, we have a potential energy function

$$U(r, \theta, \phi) = -\frac{ke^2}{r}, \quad (15)$$

so with this Schrödinger's equation becomes

$$-\frac{\hbar^2}{2m}\nabla^2\psi - \frac{ke^2}{r}\psi = E\psi. \quad (16)$$

If we first look for solutions that only have an  $r$ -dependence, then this becomes

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)\psi - \frac{ke^2}{r}\psi = E\psi. \quad (17)$$

Solving this differential equation is a non-trivial exercise, though the appropriate course in applied mathematics will give you the appropriate tools. At this point, I will just note that the simplest solution to this differential equation is

$$\psi(r) = Ae^{-r/a_0}, \quad (18)$$

which can be verified by direct substitution:

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)\psi - \frac{ke^2}{r}\psi = E\psi \quad (19)$$

$$\Rightarrow -\frac{\hbar^2}{2ma_0r^2}\left(2re^{-r/a_0} - \frac{r^2}{a_0}e^{-r/a_0}\right) - \frac{ke^2}{r}e^{-r/a_0} = Ee^{-r/a_0} \quad (20)$$

$$\Rightarrow -\frac{\hbar^2}{ma_0r} - \frac{\hbar^2}{2ma_0^2} - \frac{ke^2}{r} = E, \quad (21)$$

which can only hold true for all  $r$  if and only if the terms with different powers of  $r$  are equal on both sides of the equation. This means that

$$-\frac{\hbar^2}{2ma_0^2} = E \quad \text{and} \quad -\frac{\hbar^2}{ma_0} - ke^2 = 0 \quad (22)$$

$$\Rightarrow E = -\frac{\hbar^2}{2ma_0^2} = -13.6 \text{ eV} \quad (23)$$

$$a_0 = \frac{\hbar^2}{ke^2m} = 5.3 \times 10^{-11} \text{ m}. \quad (24)$$

Thus, we find that that the wave function in Eq. 18 has an energy of  $-13.6$  eV, which is identical to the ground state in the Bohr model.

If we look for other solutions to this form of Schrödinger's equation, one quickly finds that they exist and all have higher energies than this. In fact, one can label the different excited states with the principal quantum number  $n = 2, 3, 4, \dots$ , each with energy

$$E_n = -\frac{\hbar^2}{2ma_0^2} \frac{1}{n^2}. \quad (25)$$

These energies are identical to the predictions of the Bohr model, but reveal an entirely different interpretation.