

7.9: Solution of Schrödinger's Time-independent Equation for the Hydrogen Atom

The Schrödinger equation is best written and solved for atoms in spherical coordinates. The expression for ∇^2 in spherical coordinates is lengthy and can be found in mathematical and many physics or chemistry texts. I am not going to reproduce it here. The expression for the potential energy of a hydrogen-like atom to be substituted for V in Schrödinger's equation is

$$V = -\frac{Ze^2}{4\pi\epsilon_0 r}. \quad (7.9.1)$$

The full solution of the equation, written out in all its glory, is impressive to behold, and it can be seen in several texts - but I am not going to write it out just yet. This is not because it is not important, nor to discourage those who would like actually to work through the algebra and the calculus in detail to arrive at the result. Indeed I would encourage those who are interested to do so. Rather, however, I want to make some points about the solution that could be overlooked if one gets too heavily bogged down in the details of the algebra. The solution is, unsurprisingly, quite similar to the solution for a vibrating solid discussed in Section 7.6, to which you will probably want to refer from time to time.

Since the spherical coordinates r , θ , ϕ are independent variables, physically meaningful solutions are those in which $\psi(r, \theta, \phi)$ is a product of separate functions of r , θ and ϕ . Upon integration of the equation, constants of integration appear, and, as in the solution for the vibrations of a sphere, these constants are restricted to integral values and for the same reasons described in section 7.6. Thus the wavefunctions can be written as

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) \cdot \Theta_{lm}(\theta) \cdot \Phi_m(\phi). \quad (7.9.2)$$

The quantum numbers are subject to the same restrictions as in section 7.6. That is, n is a positive integer; l is a nonnegative integer that can have any of the n integral values from 0 to $n-1$; m is an integer that can have any of the $2l+1$ integral values from $-l$ to $+l$. For a given n there are n^2 possible combinations of l and m , a result that you found shortly before you reached equation 7.6.4.

The only function that I shall write out explicitly is the function $\Phi_m(\phi)$. It is periodic with an integral number of antinodes between 0 and 2π and is usually written as a complex number:

$$\Phi = e^{im\phi}. \quad (7.9.3)$$

(You will recall that $e^{ix} = \cos x + i \sin x$, and the ease with which this relation allows us to deal with trigonometric functions.) Because Φ is usually written as a complex number, ψ is also necessarily complex.

Now in section 7.5 we discussed waves in a stretched string, and in that section the function $\Psi(x, t)$ was merely the transverse displacement of the string. It will be convenient to recall that, for a given frequency, the energy of the wave is proportional to the *square* of its amplitude. In section 7.6 we discussed the vibrations of a sphere, and in that case $\Psi(x, y, z; t)$ is the density, and how it varies in space and time. For a standing wave, $\psi(x, y, z)$ is the time-averaged mean density and how it varies with position. What meaning can be given to Ψ or to ψ when we are discussing the wave mechanics of a particle, or, in particular, the wavefunction that describes an electron in orbit around a proton? The interpretation that was given by Max Born is as follows. We'll start with the time-independent stationary solution ψ and we'll recall that we are writing it as a complex number. Born gives no immediate physical interpretation of ψ ; rather, he suggests the following physical interpretation of the real quantity $\psi\psi^*$, where the asterisk denotes the complex conjugate. Let $d\tau$ denote an element of volume. (In rectangular coordinates, $d\tau$ would be merely $dx dy dz$; in spherical coordinates, which we are using in our description of the hydrogen atom, $d\tau = r^2 \sin\theta dr d\theta d\phi$.) Then $\psi\psi^* d\tau$ is the probability that the electron is in that volume element $d\tau$. Thus $\psi\psi^*$ is the *probability density* function that describes the position of the electron, and ψ itself is the *probability amplitude*. Likewise, in a time-varying situation, $\psi\psi^* d\tau dt$ is the probability that, in a time interval dt , the electron is in the volume element $d\tau$.

Since $\psi\psi^* d\tau$ is a *probability* - i.e. a dimensionless number - it follows that ψ is a dimensioned quantity, having dimensions $L^{-3/2}$, and therefore when its numerical value is to be given it is essential that the units (in SI, $m^{-3/2}$) be explicitly stated. Likewise the dimensions of Ψ are $L^{-3/2}T^{-1/2}$ and the SI units are $m^{-3/2}s^{-1/2}$.

If ψ is a solution of Schrödinger's time-independent equation, that any constant multiple of ψ is also a solution. However, in view of the interpretation of $\psi\psi^*$ as a probability, the constant multiplier that is chosen, the so-called *normalization constant*, is chosen such as to satisfy

$$\int_0^{2\pi} \int_0^\pi \int_0^\infty \psi \psi^* r^2 \sin \theta dr d\theta d\phi = 1. \quad (7.9.4)$$

This just means that the probability that the electron is *somewhere* is unity. The function ψ is a complicated function of the coordinates and the quantum numbers, and the normalization constant is also a complicated function of the quantum numbers. For many purposes it is not necessary to know the exact form of the function, and I am tempted not to show the function at all. I shall now, however, write out in full the normalized wavefunction for hydrogen, though I do so for just two reasons. One is to give myself some practice with the equation editor of the computer program that I am using to prepare this document. The other is just to reassure the reader that there does indeed exist an actual mathematical expression for the function, even if we shall rarely, if ever in this chapter, have occasion to use it. The function, then, is

$$\psi_{lmn}(r, \theta, \phi) = \frac{e^{im\phi}}{\sqrt{2\pi}} \sqrt{\frac{(2l+1)(l-|m|)!}{2(l+|m|)!}} \cdot \sin^{|m|} \theta \cdot P_l^{|m|}(\cos \theta) \cdot \sqrt{\frac{4(n-l-1)!Z^3}{[(n+1)!]^3 n^4 a_0^3}} \cdot \left(\frac{2Zr}{na_0}\right)^l \cdot e^{-\frac{Zr}{na_0}} \quad (7.9.5)$$

$$\cdot L_{n+1}^{2l+1}\left(\frac{2Zr}{na_0}\right).$$

Here P and L are the associated Legendre and Laguerre polynomials respectively, and a_0 is given by equation 7.4.3 with $n = 1$, $Z = 1$ and $\mu = m$; that is, 0.0529 nm. You might at least like to check that the dimensions of ψ are correct. Obviously I have not shown how to *derive* this solution of the Schrödinger equation; mathematicians are paid good money to do things like that. I just wanted to show that a solution really does exist, and what it means.

The specific equations for $\Phi_m(\phi)$, $\Theta_{lm}(\theta)$, $R_{nl}(r)$ and their squares, and graphical drawings of them, for particular values of the quantum numbers, are given in many books. I do not do so here. I do make some remarks concerning them. For example some of the drawings of the function $[\Theta(\theta)]^2$ have various pleasing shapes, such as, for example, something that resembles a figure 8. It must not be thought, however, that such a figure represents the orbit that the electron pursues around the nucleus. Nor must it be thought that the drawing represents a volume of space within which an electron is confined. It represents a polar diagram showing the angular dependence of the probability density. Thus the probability that the electron is within angular distances θ and $\theta + d\theta$ of the z -axis is equal to $[\Theta(\theta)]^2$ times the solid angle subtended (at the nucleus) by the zone between θ and $\theta + d\theta$, which is $2\pi \sin \theta d\theta$. Likewise the probability that the distance of the electron from the nucleus is between r and $r + dr$ is $[R(r)]^2$ times the volume of the shell of radii r and $r + dr$, which is $4\pi r^2 dr$. It might be noted that the radial function for $n = 1$ goes through a maximum at a distance from the nucleus of $r = a_0$, the radius of the first Bohr orbit.

Although I have not reproduced the individual radial, meridional and azimuthal functions for particular values of the quantum numbers, this is not because they are not important, and those who have books that list those functions and show graphs of them will probably like to pore over them - but I hope they will do so with a greater understanding and appreciation of them following my brief remarks above.

? Exercise 7.9.1

Exercise: What are the dimensions and SI units of the functions R , Θ , and Φ ?

The wavefunction 7.9.5 is a complicated one. However, it is found by experience that many of the mathematical operations that are performed on it during the course of quantum mechanical calculations result in a very similar function, of the same form but with perhaps different values of the quantum numbers. Sometimes all that results is the very same function, with the same quantum numbers, except that the operation results merely in multiplying the function by a constant. In the latter case, the wavefunction is called an *eigenfunction* of the operator concerned, and the multiplier is the corresponding *eigenvalue*. We shall meet some examples of each. Because of this circumstance, it is often convenient, instead of writing out equation 7.9.5 in full every time, merely to list the quantum numbers of the function inside a "ket". Thus the right hand side of equation 7.9.5 may be written instead merely as $|lmn\rangle$. With practice (and usually with only a little practice) it becomes possible to manipulate these kets very quickly indeed. (It might be remarked that, if the practice is allowed to lapse, the skills also lapse!)

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