

# Solution of the Schrödinger Equation for the Hydrogen Atom in Rectangular Coordinates

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Citation: American Journal of Physics 30, 308 (1962); doi: 10.1119/1.1941997

View online: http://dx.doi.org/10.1119/1.1941997

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be requested to step up and set the audio oscillator, by "ear," first to one and then to the other of the two limit frequencies, the class being the judge of the approximation. Thus the Doppler frequency shift can be measured directly on the audio oscillator, provided its frequency dial is good enough for the purpose. An interesting observation is that a small speaker may abruptly cease to produce an output at some frequency in the 4000- to 7000-cps interval, although it may produce an appreciable output at an adjacent frequency. Thus a student may find that he cannot simulate the tone he just heard by resetting the frequency dial; the audio generating system is not capable of generating the frequency THAT THE ENTIRE CLASS HEARD JUST A FEW MOMENTS EARLIER! This result always seems to fascinate the students.

The physical constants of the pendulum using a speaker "bob" frequently are such as to allow a 1-sec swing in each direction, meaning that the Doppler-shifted frequency will be with the class for about a second. This desirable condition requires, however, that the class includes a six-footer, patient enough to hold the pendulum double-conductor string high up in the air for the time required. The reward is then a swinging arc that exceeds 6 ft in length, with very distinct frequency deviations as result.

<sup>1</sup> H. Weltin, Am. J. Phys. 29, 713 (1961).

## Solution of the Schrödinger Equation for the Hydrogen Atom in Rectangular Coordinates

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In the conventional textbook treatment of the Schrödinger equation for the one-electron atom, spherical coordinates are nearly always employed. The student is often given to believe that spherical coordinates are the only ones that can be used in central-field problems. It is the purpose of this note to point out a method of solving Schrödinger's equation for the one-electron atom in rectangular coordinates. The angular momentum eigenfunctions are found without any reference to polar angles.

Consider the time-independent Schrödinger equation

$$\nabla^2 \psi + (2m/\hbar^2) (E - V) \psi = 0.$$
 (1)

Suppose we regard the wave function as a function of x, y, z, and r, where  $r^2 = x^2 + y^2 + z^2$ . That is, whenever the combination  $x^2 + y^2 + z^2$  occurs, it will be written  $r^2$ . It will be convenient to use the notation

$$\psi(x,y,z) = f(x,y,z,r). \tag{2}$$

Then, since  $\partial r/\partial x = x/r$ , we have

$$\frac{\partial \psi}{\partial x} = \frac{\partial f}{\partial x} + \left(\frac{\partial r}{\partial x}\right) \left(\frac{\partial f}{\partial r}\right) = \frac{\partial f}{\partial x} + \left(\frac{x}{r}\right) \left(\frac{\partial f}{\partial r}\right) \tag{3}$$

and

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{\partial}{\partial x} \left[ \frac{\partial f}{\partial x} + \left( \frac{x}{r} \right) \left( \frac{\partial f}{\partial r} \right) \right] + \left( \frac{x}{r} \right) \left( \frac{\partial}{\partial r} \right) \left[ \frac{\partial f}{\partial x} + \left( \frac{x}{r} \right) \left( \frac{\partial f}{\partial r} \right) \right] 
= \frac{\partial^2 f}{\partial x^2} + 2 \left( \frac{x}{r} \right) \left( \frac{\partial^2 f}{\partial x \partial r} \right) + \left( \frac{x^2}{r^2} \right) \left( \frac{\partial^2 f}{\partial r^2} \right) + \left[ \frac{1}{r} - \left( \frac{x^2}{r^3} \right) \right] \left( \frac{\partial f}{\partial r} \right), \quad (4)$$

with similar expressions for  $\partial^2 \psi / \partial y^2$  and  $\partial^2 \psi / \partial z^2$ . Upon adding these three expressions, we readily obtain

$$\nabla^{2}\psi = \frac{\partial^{2}\psi}{\partial x^{2}} + \frac{\partial^{2}\psi}{\partial y^{2}} + \frac{\partial^{2}\psi}{\partial z^{2}}$$

$$= \frac{\partial^{2}f}{\partial x^{2}} + \frac{\partial^{2}f}{\partial y^{2}} + \frac{\partial^{2}f}{\partial z^{2}} + \left(\frac{2}{r}\right)\left(x\frac{\partial^{2}f}{\partial x\partial r} + y\frac{\partial^{2}f}{\partial y\partial r} + z\frac{\partial^{2}f}{\partial z\partial r}\right)$$

$$+ \frac{\partial^{2}f}{\partial x^{2}} + \left(\frac{2}{r}\right)\left(\frac{\partial f}{\partial x}\right), \quad (5)$$

after collecting terms and performing the obvious cancellations. In the case of a central field, since V is a function of r alone, we shall assume that the r-dependent part of f can be separated, that is

$$f(x,y,z,r) = F(x,y,z)R(r).$$
(6)

Accordingly, Eq. (5) becomes

$$\nabla^2 \psi = R \nabla^2 F + \left(\frac{2}{r}R'\right) \left(x \frac{\partial F}{\partial x} + y \frac{\partial F}{\partial y} + z \frac{\partial F}{\partial z}\right) + FR'' + \frac{2}{r}FR',$$

and the Schrödinger equation may be written

$$\frac{R}{F} \nabla^2 F + \left(\frac{2R'}{rF}\right) \left(x\frac{\partial F}{\partial x} + y\frac{\partial F}{\partial y} + z\frac{\partial F}{\partial z}\right) + R'' + \frac{2}{r}R' + \left(\frac{2m}{k^2}\right)(E - V)R = 0 \quad (7)$$

after division by F.

Let us seek solutions such that F satisfies Laplace's equation  $\nabla^2 F = 0$ . It is readily verified, by differentiating, that the function

$$F_l = (ax + by + cz)^l \tag{8}$$

is a solution, provided

$$a^2 + b^2 + c^2 = 0. (9)$$

Thus at least one of the three constants a, b, and c must be complex. Furthermore, if  $F_l$  is to be single-valued, then l must be an integer. Now, by direct substitution, we find that

$$x\frac{\partial F_l}{\partial x} + y\frac{\partial F_l}{\partial y} + z\frac{\partial F_l}{\partial z} = lF_l. \tag{10}$$

Consequently, Eq. (7) reduces to the radial equation

$$R'' + [2(l+1)/r]R' + (2m/\hbar^2)(E-V)R = 0.$$
 (11)

For a one-electron atom of nuclear charge Ze, we have  $V = -Ze^2/r$ . Upon introducing the dimensionless variable  $\rho = \alpha r$  and the eigenvalue parameter  $\lambda = (-2E)^{-\frac{1}{2}}Ze^2m^{\frac{1}{2}}\hbar^{-1}$ , where  $\alpha = 2mZe^2\hbar^{-2}\lambda^{-1}$ , and letting  $R(\rho) = e^{-\rho/2}L(\rho)$ , Eq. (11) transforms into

$$\rho L'' + [2(l+1) - \rho]L' + (\lambda - l - 1)L = 0.$$
 (12)

Well-behaved solutions of the above equation are the associated Laguerre polynomials  $L_{n+1}^{2l+1}(\rho)$ , where  $\lambda=n$  (an integer). Thus the eigenvalues of E are given by the well-known formula  $E_n=-mZ^2e^4\hbar^{-2}2^{-1}n^{-2}$ . Our corresponding eigenfunctions can be written explicitly as follows:

$$\psi_{n, l} = F_l R_{n, l} = (ax + by + cz)^l \exp\left[-\alpha/2 (x^2 + y^2 + z^2)^{\frac{1}{2}}\right]$$

$$L_{n+l}^{2l+1} \left[\alpha (x^2 + y^2 + z^2)^{\frac{1}{2}}\right]$$
 (13)

Consider now the angular momentum M. We have

$$M_z \psi = -i\hbar \left[ x \left( \frac{\partial}{\partial y} \right) - y \left( \frac{\partial}{\partial x} \right) \right] \psi \tag{14}$$

with similar expressions for  $M_x$  and  $M_y$ . Letting  $\psi = FR$ , as above, we find that we can write

$$M_z F = -i\hbar [x(\partial/\partial y) - y(\partial/\partial x)] F, \qquad (15)$$

where we have made use of Eq. (3). In other words, the r-dependent factor R commutes with the angular momentum operator and can be cancelled out. Similarly, we find that R commutes with the operator  $M^2$ , and we can write

$$M^{2}F = -\hbar^{2} \left[ \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)^{2} + \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)^{2} + \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right)^{2} \right] F. \quad (16)$$

Upon letting  $F = F_l$ , subject to condition (9), we find that the above equation directly gives

$$M^{2}F_{l} = \hbar^{2}l(l+1)F_{l}. \tag{17}$$

Thus the eigenvalues of  $M^2$  are  $\hbar^2 l(l+1)$ . Notice that we have not designated any particular axis as preferred.

The situation concerning a particular component of M is a little more involved. From Eq. (15) we find that

$$M_z F_l = -i\hbar l \left( \frac{bx - ay}{ax + by + cz} \right) F_l.$$

Thus  $F_l$  does not yield a definite value for  $M_z$ . But let us examine the condition that  $F_l$  be a solution of Laplace's equation, namely  $a^2+b^2+c^2=0$ . This condition can be satisfied by defining a, b, and c in terms of two arbitrary complex numbers u and v as follows:

$$a = u^2 - v^2$$
  $b = -i(u^2 + v^2)$   $c = -2uv$ . (18)

Then

$$F_{l} = [(u^{2} - v^{2})x - i(u^{2} + v^{2})y - 2uvz]^{l}$$
  
=  $[u^{2}(x - iy) - 2uvz - v^{2}(x + iy)]^{l}$ . (19)

Expressed in this way,  $F_l$  is a homogeneous polynomial of degree 2l in u and v, and therefore  $F_l$  contains 2l+1 terms, the coefficients of which are polynomials of degree l in x, y, and z, viz.,

$$F_{l} = \sum_{m=-l}^{l} u^{l-m} v^{l+m} Q_{l}^{m}(x, y, z).$$
 (20)

For example, if l=2 (d states), we have

$$\begin{split} F_2 &= \left\lceil u^2(x-iy) - 2uvz - v^2(x+iy) \right\rceil^2 \\ &= u^4(x-iy)^2 + 4u^3v(x-iy)z + 2u^2v^2(2z^2-x^2-y^2) \\ &\qquad \qquad -4uv^3(x+iy)z + v^4(x+iy)^2. \end{split}$$

$$\begin{split} Q_2^{-2} &= (x-iy)^2, \quad Q_2^{-1} = (x-iy)z, \quad Q_2^0 = 2z^2 - x^2 - y^2, \\ Q_2^1 &= (x+iy)z, \quad Q_2^2 = (x+iy)^2. \end{split}$$

Owing to the fact that u and v are arbitrary, the Q's are each solutions of Laplace's equation. They are therefore suitable eigenfunctions for our central field problem.1 Furthermore, it is easily verified for the above Q's (l=2), and it can be shown to be true in general2 that

$$-i[x(\partial/\partial y) - y(\partial/\partial x)]Q_{l}^{m} = mQ_{l}^{m}, \tag{21}$$

where m can have any of the values -l, -l+1, ... l. Thus, from Eqs. (15) and (21), it follows that in the Q representation the z component of the angular momentum has the eigenvalues mh. The corresponding eigenfunctions

$$\psi_{n, l, m} = Q_{l}^{m}(x, y, z)R_{n, l}(x^{2} + y^{2} + z^{2})^{\frac{1}{2}},$$
 (22)

where  $R_{n,l}$  is the same as that appearing in Eq. (13).

<sup>1</sup> There are just 2l+1 linearly independent polynomials of degree l in x, y, and z that satisfy Laplace's equation. There is any number of ways of choosing a set of these polynomials, and Eqs. (19) and (20) indicate one way of constructing such a set. See, for example, E. W. Hobson, Spherical and Ellipsoidal Harmonics (Cambridge University Press, New York, 1931).

<sup>2</sup> This can be done directly or by transforming to spherical coordinates. See, for example, H. A. Kramers, Quantum Mechanics (Interscience Publishers, Inc., New York, 1957).

AMERICAN JOURNAL OF PHYSICS

VOLUME 30, NUMBER 4

APRIL, 1962

### LETTERS TO THE EDITOR

#### Electromotive Force Again

In discussing "Conservative fields in dc networks" [Am. J. Phys. 29, 484 (1961)], Emerson M. Pugh has sought to clarify the confusion which often surrounds the concept of electromotive force. In this he has been only partially successful. It is true that in a dc network powered by a thermocouple, a chemical cell, or a Van de Graaf generator there are forces per unit charge in addition to those represented by E in Maxwell's equations. (In these devices the emf is the line integral of these forces per unit charge around a complete circuit.) But this is not the case for electromagnetic generators of any kind, which are fully understood in terms of Faraday's law of induction, with appreciation of the role of frames of reference in relative motion.

Let us consider two dc electromagnetic induction devices. The motion of conductors in constant uniform magnetic fields produces no emf in any single frame of reference, which is equivalent to stating the obvious fact that there is no emf in a rigid coil at rest in a constant magnetic field. Thus a linear conductor moving uniformly in a uniform magnetic field cannot properly be said to have an emf produced "across it," since the existence of an emf depends on how the circuit is completed. An emf does exist in the loop formed by a conductor cutting lines of B and flexible or sliding contacts to a stationary galvanometer, for example. The "homopolar generator" seems more complicated, but the essential physical situation becomes apparent if the magnet is not made a part of the conducting circuit, and if the usual metal Faraday disk is replaced by an