Separation of Variables for the Time-Independent Schrödinger Equation for the Non-Relativistic Hydrogen-Like Atom by James Pate Williams, Jr. BA, BS, MSwE, PhD

From a previous blog entry of May 8, 2018, we have the time-independent Schrödinger equation for the non-relativistic hydrogen-like atom of atomic number Z as:

$$-\frac{h^2}{8\pi^2\mu}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)-\frac{Ze^2}{r}\psi=E\psi$$

This equation can be rewritten as illustrated below:

$$\nabla^2\psi+\frac{8\pi^2\mu Ze^2}{h^2r}\psi+\frac{8\pi^2\mu E}{h^2}\psi=0$$

Where

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

$$r=\sqrt{x^2+y^2+z^2}$$

$$\frac{1}{\mu}=\frac{1}{m_n}+\frac{1}{m_e}=\frac{m_n+m_e}{m_nm_e}$$

$$\mu=\frac{m_nm_e}{m_n+m_e}$$

It is easily discerned that the Laplacian operator is not separable in Cartesian coordinates. We will now try spherical coordinates:

$$x=r\cos\vartheta\cos\varphi$$

$$y=r\sin\vartheta\sin\varphi$$

$$z=r\cos\vartheta$$

An easy calculation shows that the following equation holds:

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

Therefore, we again find that:

$$r=\sqrt{x^2+y^2+z^2}$$

Solving for the other two variables is just as facile:

$$\vartheta = \cos^{-1}\left(\frac{z}{r}\right)$$

$$\varphi = \tan^{-1}\left(\frac{y}{x}\right)$$

In performing the transformation of the Laplacian operator, we need the following partial derivatives:

$$\frac{\partial r}{\partial x} = \frac{x}{r}$$

$$\frac{\partial^2 r}{\partial x^2} = \frac{1}{r} - \frac{x^2}{r^3}$$

$$\frac{\partial r}{\partial y} = \frac{y}{r}$$

$$\frac{\partial^2 r}{\partial y^2} = \frac{1}{r} - \frac{y^2}{r^3}$$

$$\frac{\partial r}{\partial z} = \frac{z}{r}$$

$$\frac{\partial^2 r}{\partial z^2} = \frac{1}{r} - \frac{z^2}{r^3}$$

$$\frac{\partial \vartheta}{\partial x} = -\frac{\partial}{\partial x}\left(\frac{z}{r}\right)\left(1 - \frac{z^2}{r^2}\right)^{-1/2} = \frac{xz}{r^3}\left(1 - \frac{z^2}{r^2}\right)^{-1/2}$$

$$\frac{\partial^2 \vartheta}{\partial x^2} = \left(\frac{z}{r^3} - \frac{3x^2 z}{r^5}\right)\left(1 - \frac{z^2}{r^2}\right)^{-1/2} + \frac{x^2 z^2}{r^5}\left(1 - \frac{z^2}{r^2}\right)^{-3/2}$$

$$\frac{\partial \vartheta}{\partial y} = -\frac{\partial}{\partial y}\left(\frac{z}{r}\right)\left(1 - \frac{z^2}{r^2}\right)^{-1/2} = \frac{yz}{r^3}\left(1 - \frac{z^2}{r^2}\right)^{-1/2}$$

$$\frac{\partial^2 \vartheta}{\partial y^2} = \left(\frac{z}{r^3} - \frac{3y^2 z}{r^5}\right)\left(1 - \frac{z^2}{r^2}\right)^{-1/2} + \frac{y^2 z^2}{r^5}\left(1 - \frac{z^2}{r^2}\right)^{-3/2}$$

$$\frac{\partial \vartheta}{\partial z} = -\frac{\partial}{\partial z}\left(\frac{z}{r}\right)\left(1 - \frac{z^2}{r^2}\right)^{-1/2} = \left(-\frac{1}{r} - \frac{z^2}{r^3}\right)\left(1 - \frac{z^2}{r^2}\right)^{-1/2}$$

$$\frac{\partial^2 \vartheta}{\partial z^2} = \left(\frac{z}{r^3} + \frac{2z}{r^3} - \frac{3z^3}{r^5}\right)\left(1 - \frac{z^2}{r^2}\right)^{-1/2} - \frac{1}{2}\left(-\frac{1}{r} - \frac{z^2}{r^3}\right)^2\left(1 - \frac{z^2}{r^2}\right)^{-3/2}$$

$$\frac{\partial \varphi}{\partial x} = \frac{\partial}{\partial x}\left(\frac{y}{x}\right)\left(1 + \frac{y^2}{x^2}\right)^{-1} = -\frac{y}{x^2}\left(1 + \frac{y^2}{x^2}\right)^{-1}$$

$$\frac{\partial^2\varphi}{\partial x^2} = \frac{2y}{x^3}\left(1+\frac{y^2}{x^2}\right)^{-1} + \frac{y^3}{x^4}\left(1+\frac{y^2}{x^2}\right)^{-2}$$

$$\frac{\partial\varphi}{\partial y} = \frac{\partial}{\partial y}\left(\frac{y}{x}\right)\left(1+\frac{y^2}{x^2}\right)^{-1} = \frac{1}{x}\left(1+\frac{y^2}{x^2}\right)^{-1}$$

$$\frac{\partial^2\varphi}{\partial y^2} = -\frac{2y}{x^3}\left(1+\frac{y^2}{x^2}\right)^{-2}$$

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial\vartheta}{\partial x}\frac{\partial}{\partial\vartheta} + \frac{\partial\varphi}{\partial x}\frac{\partial}{\partial\varphi}$$

$$\frac{\partial}{\partial y} = \frac{\partial r}{\partial y}\frac{\partial}{\partial r} + \frac{\partial\vartheta}{\partial y}\frac{\partial}{\partial\vartheta} + \frac{\partial\varphi}{\partial y}\frac{\partial}{\partial\varphi}$$

$$\frac{\partial}{\partial z} = \frac{\partial r}{\partial z}\frac{\partial}{\partial r} + \frac{\partial\vartheta}{\partial z}\frac{\partial}{\partial\vartheta} + \frac{\partial\varphi}{\partial z}\frac{\partial}{\partial\varphi}$$

$$\frac{\partial}{\partial x} = \frac{x}{r}\frac{\partial}{\partial r} + \frac{xz}{r^3}\left(1-\frac{z^2}{r^2}\right)^{-1/2}\frac{\partial}{\partial\vartheta} - \frac{y}{x^2}\left(1+\frac{y^2}{x^2}\right)^{-1}\frac{\partial}{\partial\varphi}$$

$$\frac{\partial}{\partial y} = \frac{y}{r}\frac{\partial}{\partial r} + \frac{yz}{r^3}\left(1-\frac{z^2}{r^2}\right)^{-1/2}\frac{\partial}{\partial\vartheta} + \frac{1}{x}\left(1+\frac{y^2}{x^2}\right)^{-1}\frac{\partial}{\partial\varphi}$$

$$\frac{\partial}{\partial z} = \frac{z}{r}\frac{\partial}{\partial r} + \left(-\frac{1}{r}-\frac{z^2}{r^3}\right)\left(1-\frac{z^2}{r^2}\right)^{-1/2}\frac{\partial}{\partial\vartheta}$$

$$\frac{\partial^2}{\partial x^2} = \frac{\partial^2 r}{\partial x^2}\frac{\partial}{\partial r} + \frac{\partial^2\vartheta}{\partial x^2}\frac{\partial}{\partial\vartheta} + \frac{\partial^2\varphi}{\partial x^2}\frac{\partial}{\partial\varphi} + \frac{\partial r}{\partial x}\frac{\partial}{\partial x}\frac{\partial}{\partial r} + \frac{\partial\vartheta}{\partial x}\frac{\partial}{\partial x}\frac{\partial}{\partial\vartheta} + \frac{\partial\varphi}{\partial x}\frac{\partial}{\partial x}\frac{\partial}{\partial\varphi}$$

$$\frac{\partial^2}{\partial y^2} = \frac{\partial^2 r}{\partial y^2}\frac{\partial}{\partial r} + \frac{\partial^2\vartheta}{\partial y^2}\frac{\partial}{\partial\vartheta} + \frac{\partial^2\varphi}{\partial y^2}\frac{\partial}{\partial\varphi} + \frac{\partial r}{\partial y}\frac{\partial}{\partial y}\frac{\partial}{\partial r} + \frac{\partial\vartheta}{\partial y}\frac{\partial}{\partial y}\frac{\partial}{\partial\vartheta} + \frac{\partial\varphi}{\partial y}\frac{\partial}{\partial y}\frac{\partial}{\partial\varphi}$$

$$\frac{\partial^2}{\partial z^2} = \frac{\partial^2 r}{\partial z^2}\frac{\partial}{\partial r} + \frac{\partial^2\vartheta}{\partial z^2}\frac{\partial}{\partial\vartheta} + \frac{\partial^2\varphi}{\partial z^2}\frac{\partial}{\partial\varphi} + \frac{\partial r}{\partial z}\frac{\partial}{\partial z}\frac{\partial}{\partial r} + \frac{\partial\vartheta}{\partial z}\frac{\partial}{\partial z}\frac{\partial}{\partial\vartheta} + \frac{\partial\varphi}{\partial z}\frac{\partial}{\partial z}\frac{\partial}{\partial\varphi}$$

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

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

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

$$\frac{\partial^2}{\partial x^2} = \left(\frac{1}{r}-\frac{x^2}{r^3}\right)\frac{\partial}{\partial r} + \left(\frac{x}{r}\right)^2\frac{\partial^2}{\partial r^2} + \cdots$$

$$\frac{\partial^2}{\partial y^2} = \left(\frac{1}{r} - \frac{y^2}{r^3}\right)\frac{\partial}{\partial r} + \left(\frac{y}{r}\right)^2 \frac{\partial^2}{\partial r^2} + \cdots$$

$$\frac{\partial^2}{\partial z^2} = \left(\frac{1}{r} - \frac{z^2}{r^3}\right)\frac{\partial}{\partial r} + \left(\frac{z}{r}\right)^2 \frac{\partial^2}{\partial r^2} + \cdots$$

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \frac{\partial^2}{\partial r^2} + \left(\frac{3}{r} - \frac{r^2}{r^3}\right)\frac{\partial}{\partial r} + \cdots = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \cdots = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \cdots$$

I leave the derivation of the theta and phi terms as an exercise for the reader.

There is a much easier way to derive the Laplacian operator in any three-dimensional orthogonal curvilinear coordinate system using the equation [1]:

$$\nabla^2 = \frac{1}{h_1 h_2 h_3}\left[\frac{\partial}{\partial x_1}\left(\frac{h_2 h_3}{h_1}\frac{\partial}{\partial x_1}\right) + \frac{\partial}{\partial x_2}\left(\frac{h_1 h_3}{h_2}\frac{\partial}{\partial x_2}\right) + \frac{\partial}{\partial x_3}\left(\frac{h_1 h_2}{h_3}\frac{\partial}{\partial x_3}\right)\right]$$

The scale functions are calculated from the metric tensor elements as follows:

$$h_1 = \sqrt{g_{11}}, h_2 = \sqrt{g_{22}}, h_3 = \sqrt{g_{33}}$$

The metric tensor elements maybe calculated from the line element as shown below:

$$ds^2 = g_{mn} dx^m dx^n$$

$$dx = \sin\vartheta \cos\varphi \, dr + r\cos\vartheta \cos\varphi \, d\vartheta - r\sin\vartheta \sin\varphi \, d\varphi$$

$$dy = \sin\vartheta \sin\varphi \, dr + r\cos\vartheta \sin\varphi d\vartheta + r\sin\vartheta \cos\varphi \, d\varphi$$

$$dz = \cos\vartheta \, dr - r\sin\vartheta \, d\vartheta$$

$$\begin{aligned}(dx)^2 = {} & (\sin\vartheta)^2(\cos\varphi)^2(dr)^2 + r^2(\cos\vartheta)^2(\cos\varphi)^2(d\vartheta)^2 + r^2(\sin\vartheta)^2(\sin\varphi)^2(d\varphi)^2 \\ & + 2r\sin\vartheta\cos\vartheta(\cos\varphi)^2 dr d\vartheta - 2r(\sin\vartheta)^2\cos\varphi\sin\varphi \, dr d\varphi \\ & - 2r^2\cos\vartheta\sin\vartheta\cos\varphi\sin\varphi d\vartheta d\varphi\end{aligned}$$

$$\begin{aligned}(dy)^2 = {} & (\sin\vartheta)^2(\sin\varphi)^2(dr)^2 + r^2(\cos\vartheta)^2(\sin\varphi)^2(d\vartheta)^2 + r^2(\sin\vartheta)^2(\cos\varphi)^2(d\varphi)^2 \\ & + 2r\sin\vartheta\cos\vartheta(\sin\varphi)^2 dr d\vartheta + 2r(\sin\vartheta)^2\cos\varphi\sin\varphi \, dr d\varphi \\ & + 2r^2\cos\vartheta\sin\vartheta\cos\varphi\sin\varphi d\vartheta d\varphi\end{aligned}$$

$$(dz)^2 = (\cos\vartheta)^2(dr)^2 + r^2(\sin\vartheta)^2(d\vartheta)^2 - 2r\cos\vartheta\sin\vartheta \, dr d\vartheta$$

$$\begin{aligned}(ds)^2 &= (dx)^2 + (dy)^2 + (dz)^2 \\ &= (\sin\vartheta)^2[(\cos\varphi)^2 + (\sin\varphi)^2](dr)^2 + (\cos\vartheta)^2(dr)^2 \\ &+ r^2(\cos\vartheta)^2[(\cos\varphi)^2 + (\sin\varphi)^2](d\vartheta)^2 + r^2(\sin\vartheta)^2(d\vartheta)^2 \\ &+ r^2(\sin\vartheta)^2[(\sin\varphi)^2 + (\cos\varphi)^2](d\varphi)^2 = (dr)^2 + r^2(d\vartheta)^2 + r^2(\sin\vartheta)^2(d\varphi)^2\end{aligned}$$

$$h_r = 1, h_\vartheta = r, h_\varphi = r\sin\vartheta$$

$$\nabla^2 = \frac{1}{h_r h_\vartheta h_\varphi}\left[\frac{\partial}{\partial r}\left(\frac{h_\vartheta h_\varphi}{h_r}\frac{\partial}{\partial r}\right) + \frac{\partial}{\partial \vartheta}\left(\frac{h_r h_\varphi}{h_\vartheta}\frac{\partial}{\partial \vartheta}\right) + \frac{\partial}{\partial \varphi}\left(\frac{h_r h_\vartheta}{h_\varphi}\frac{\partial}{\partial \varphi}\right)\right]$$

$$= \frac{1}{r^2 \sin\vartheta}\left[\frac{\partial}{\partial r}\left(r^2 \sin\vartheta \frac{\partial}{\partial r}\right) + \frac{\partial}{\partial \vartheta}\left(\frac{r\sin\vartheta}{r}\frac{\partial}{\partial \vartheta}\right) + \frac{\partial}{\partial \varphi}\left(\frac{r}{r\sin\vartheta}\frac{\partial}{\partial \varphi}\right)\right]$$

$$= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\vartheta}\frac{\partial}{\partial \vartheta}\left(\sin\vartheta\frac{\partial}{\partial \vartheta}\right) + \frac{1}{r^2(\sin\vartheta)^2}\frac{\partial^2}{\partial \varphi^2}$$

$$\psi(r,\vartheta,\varphi) = R(r)Y(\vartheta,\varphi)$$

$$\frac{Y}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{R}{r^2\sin\vartheta}\frac{\partial}{\partial \vartheta}\left(\sin\vartheta\frac{\partial Y}{\partial \vartheta}\right) + \frac{R}{r^2(\sin\vartheta)^2}\frac{\partial^2 Y}{\partial \varphi^2} + \frac{8\pi^2\mu Z e^2}{h^2 r}RY + \frac{8\pi^2\mu E}{h^2}RY = 0$$

$$\frac{1}{Rr^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{1}{Yr^2\sin\vartheta}\frac{\partial}{\partial \vartheta}\left(\sin\vartheta\frac{\partial Y}{\partial \vartheta}\right) + \frac{1}{Yr^2(\sin\vartheta)^2}\frac{\partial^2 Y}{\partial \varphi^2} + \frac{8\pi^2\mu Z e^2}{h^2 r} + \frac{8\pi^2\mu E}{h^2} = 0$$

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{1}{Y\sin\vartheta}\frac{\partial}{\partial \vartheta}\left(\sin\vartheta\frac{\partial Y}{\partial \vartheta}\right) + \frac{1}{Y(\sin\vartheta)^2}\frac{\partial^2 Y}{\partial \varphi^2} + \frac{8\pi^2\mu Z e^2}{h^2}r + \frac{8\pi^2\mu E}{h^2}r^2 = 0$$

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{8\pi^2\mu Z e^2}{h^2}r + \frac{8\pi^2\mu E}{h^2}r^2 = -\frac{1}{Y\sin\vartheta}\frac{\partial}{\partial \vartheta}\left(\sin\vartheta\frac{\partial Y}{\partial \vartheta}\right) - \frac{1}{Y(\sin\vartheta)^2}\frac{\partial^2 Y}{\partial \varphi^2} = \lambda^2$$

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{8\pi^2\mu Z e^2}{h^2}r + \frac{8\pi^2\mu E}{h^2}r^2 - \lambda^2 = 0$$

$$-\frac{1}{Y\sin\vartheta}\frac{\partial}{\partial \vartheta}\left(\sin\vartheta\frac{\partial Y}{\partial \vartheta}\right) - \frac{1}{Y(\sin\vartheta)^2}\frac{\partial^2 Y}{\partial \varphi^2} - \lambda^2 = 0$$

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{8\pi^2\mu Z e^2}{h^2}rR + \frac{8\pi^2\mu E}{h^2}r^2 R - \lambda^2 R = 0$$

$$-\frac{1}{\sin\vartheta}\frac{\partial}{\partial \vartheta}\left(\sin\vartheta\frac{\partial Y}{\partial \vartheta}\right) - \frac{1}{(\sin\vartheta)^2}\frac{\partial^2 Y}{\partial \varphi^2} - \lambda^2 Y = 0$$

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \left(\lambda^2 - \frac{8\pi^2\mu Z e^2}{h^2}r - \frac{\mu E}{h^2}r^2\right)R = 0$$

$$Y(\vartheta,\varphi) = \Theta(\vartheta)\Phi(\varphi)$$

$$-\frac{\Phi}{\sin\vartheta}\frac{\partial}{\partial \vartheta}\left(\sin\vartheta\frac{\partial \Theta}{\partial \vartheta}\right) - \frac{\Theta}{(\sin\vartheta)^2}\frac{\partial^2 \Phi}{\partial \varphi^2} - \lambda^2\Theta\Phi = 0$$

$$-\frac{1}{\Theta\sin\vartheta}\frac{\partial}{\partial \vartheta}\left(\sin\vartheta\frac{\partial \Theta}{\partial \vartheta}\right) - \frac{1}{\Phi(\sin\vartheta)^2}\frac{\partial^2 \Phi}{\partial \varphi^2} - \lambda^2 = 0$$

$$-\frac{\sin\vartheta}{\Theta}\frac{\partial}{\partial \vartheta}\left(\sin\vartheta\frac{\partial \Theta}{\partial \vartheta}\right) - \frac{1}{\Phi}\frac{\partial^2 \Phi}{\partial \varphi^2} - \lambda^2(\sin\vartheta)^2 = 0$$

$$-\frac{\sin\vartheta}{\Theta}\frac{\partial}{\partial \vartheta}\left(\sin\vartheta\frac{\partial \Theta}{\partial \vartheta}\right) - \lambda^2(\sin\vartheta)^2 = -\frac{1}{\Phi}\frac{\partial^2 \Phi}{\partial \varphi^2} = \nu^2$$

$$\sin\vartheta \frac{d}{d\vartheta}\left(\sin\vartheta \frac{\mathrm{d}\Theta}{d\vartheta}\right) + \lambda^2(\sin\vartheta)^2\Theta - \nu^2\Theta = 0$$

$$\frac{d^2\Phi}{d\varphi^2} + \nu^2\Phi = 0$$

$$m = \nu$$

$$\Phi(\varphi) = Ae^{im\varphi} + Be^{-im\varphi}, m \neq 0$$

$$\Phi(\varphi) = A + B\varphi, m = 0$$

$$\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi}$$

References

[1] H. F. Davis and A. D. Snider, "5.2 Orthogonal Curvilinear Coordinates," in *Introduction to Vector Analysis 4th Edition*, Boston, Allyn and Bacon, Inc., 1979, pp. 237-246.