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# The Gronwall form of the Schrodinger Equation for Helium

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# The Gronwall Form of the Schrodinger Equation for Helium

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## I. SYNOPSIS

A strangely different form of the Schrödinger Equation for the two electron (Helium atom) problem is presented. To my knowledge, it has never been used for any purpose in the Physics literature other than what is cited here.

## II. INTRODUCTION

In 1937, Bartlett [1] published a piece of work by T. H. Gronwall (then deceased) called "The Helium Wave Equation" in which a new and special form of the Schrödinger equation for the 2-electron atom/ion problem was investigated. In that paper, Gronwall refers to a previous paper [2] in which he actually carries out a (for me) complicated derivation of his form of the Helium Schrödinger equation. Parenthetically, in this latter paper, his reference 7 refers to a paper which does not exist to my knowledge. Would that we had the "direct and very short calculation" which resulted in the desired

equation.

In this paper, a derivation proceeding directly from Hyllerass' [3–5] formulation is presented.

## III. DEFINITIONS

We start with Gronwall's definitions for  $x_1$ ,  $x_2$  and  $x_3$ :

$$4x_1 = r_1^2 + r_2^2 - r_{12}^2 = 2r_1 r_2 \cos \vartheta \quad (1)$$

from which we obtain

$$x_1 = \frac{1}{2} r_1 r_2 \cos \vartheta \quad (2)$$

and

$$4x_2 = r_1^2 - r_2^2 \quad (3)$$

and

$$4x_3 = \sqrt{(r_1 + r_2 + r_{12})(r_1 + r_2 - r_{12})(r_2 + r_{12} - r_1)(r_{12} + r_1 - r_2)} = 2r_1 r_2 \sin \vartheta \quad (4)$$

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This is such a strange definition that we note that the term:

$$16x_3^2 = (r_1 + r_2 + r_{12})(r_1 + r_2 - r_{12})(r_2 + r_{12} - r_1)(r_{12} + r_1 - r_2)$$

expands to

$$16x_3^2 = -r_1^4 + 2r_1^2 r_2^2 + 2r_1^2 r_{12}^2 - r_2^4 + 2r_2^2 r_{12}^2 - r_{12}^4 = 4r_1^2 r_2^2 \sin^2 \vartheta$$

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while

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$$16x_1^2 = (r_1^2 + r_2^2 - r_{12}^2)^2 = +r_1^4 + r_2^4 + r_{12}^4 + 2r_1^2 r_2^2 - 2r_1^2 r_{12}^2 - 2r_2^2 r_{12}^2 = 4r_1^2 r_2^2 \cos^2 \vartheta$$

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so, adding these two obtains

$$16(x_1^2 + x_3^2) = 4r_1^2 r_2^2 (\sin^2 \vartheta + \cos^2 \vartheta) \quad (5)$$

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Amazing. It turns out that this is Heron's formula, a piece of trigonometry which appears to have fallen out of common knowledge.

From Equation 4 we obtain

$$x_3^2 = \frac{1}{4}r_1^2 r_2^2 \sin^2 \vartheta$$

and define a hyper-radius as

$$4r = r_1^2 + r_2^2$$

We knew from Equation 5 that

$$x_1^2 + x_3^2 = \frac{1}{4}r_1^2 r_2^2$$

and

$$x_2^2 = \frac{r_1^4 - 2r_1^2 r_2^2 + r_2^4}{16}$$

so

$$x_1^2 + x_3^2 + x_2^2 = \frac{r_1^4}{16} + \frac{r_2^4}{16} - 2\frac{r_1^2 r_2^2}{16} + \frac{1}{4}r_1^2 r_2^2 = \frac{r_1^4}{16} + \frac{r_2^4}{16} + 2\frac{r_1^2 r_2^2}{16} \quad (6)$$

i.e.,

$$r^2 = x_1^2 + x_3^2 + x_2^2 = \frac{(r_1^2 + r_2^2)^2}{16} = \frac{r_1^4 + r_2^4 + 2r_1^2 r_2^2}{16}$$

We have

$$r_{12}^2 = r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta$$

i.e., the law of cosines, so

$$r_{12}^2 = 4r - 4x_1 = 4(r - x_1)$$

we obtain

$$r_{12} = 2\sqrt{r - x_1}$$

$$r_1 = \sqrt{2 \left( \sqrt{x_1^2 + x_2^2 + x_3^2} + x_2 \right)} = \sqrt{2(r + x_2)}$$

and

$$r_2 = \sqrt{2 \left( \sqrt{x_1^2 + x_2^2 + x_3^2} - x_2 \right)} = \sqrt{2(r - x_2)}$$

We seek the differential equation (Gronwall/Bartlett's equation 1)

$$\frac{\partial^2 \psi}{\partial x_1^2} + \frac{\partial^2 \psi}{\partial x_2^2} + \frac{\partial^2 \psi}{\partial x_3^2} + \frac{1}{x_3} \frac{\partial \psi}{\partial x_3} + \frac{1}{r} \left( \frac{E}{4} + \frac{1}{\sqrt{2(r + x_2)}} + \frac{1}{\sqrt{2(r - x_2)}} + \frac{1}{2Z\sqrt{(r - x_1)}} \right) \psi = 0 \quad (7)$$

which we obtain from the  $\{r_1, r_2, r_{12}\}$  form due to Hyller-aas.

$$\begin{aligned} & \nabla_1^2 + \nabla_2^2 = \\ & \frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1} \frac{\partial}{\partial r_1} + 2\hat{r}_1 \cdot \hat{r}_{12} \frac{\partial^2}{\partial r_1 \partial r_{12}} \\ & + \frac{\partial^2}{\partial r_2^2} + \frac{2}{r_2} \frac{\partial}{\partial r_2} + 2\hat{r}_2 \cdot \hat{r}_{12} \frac{\partial^2}{\partial r_2 \partial r_{12}} \\ & + \frac{4}{r_{12}} \frac{\partial}{\partial r_{12}} + 2 \frac{\partial^2}{\partial r_{12}^2} \end{aligned} \quad (8)$$

or the alternative form in terms of  $r_1$ ,  $r_2$ , and  $y = \cos \vartheta$ :

$$\begin{aligned} & \nabla_1^2 + \nabla_2^2 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2} = \\ & \frac{1}{r_1^2} \frac{\partial}{\partial r_1} \left( r_1^2 \frac{\partial}{\partial r_1} \right) + \frac{1}{r_2^2} \frac{\partial}{\partial r_2} \left( r_2^2 \frac{\partial}{\partial r_2} \right) + \left( \frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \frac{\partial}{\partial y} \left( (1 - y^2) \frac{\partial}{\partial y} \right) \end{aligned} \quad (9)$$

in one of its many manifestations:

$$\begin{aligned} \nabla_1^2 + \nabla_2^2 &= \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2} = \\ \frac{1}{r_1^2} \frac{\partial}{\partial r_1} \left( r_1^2 \frac{\partial}{\partial r_1} \right) + \frac{1}{r_2^2} \frac{\partial}{\partial r_2} \left( r_2^2 \frac{\partial}{\partial r_2} \right) + \left( \frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \left( \frac{1}{\sin \vartheta} \right) \frac{\partial}{\partial \vartheta} \end{aligned} \quad (10)$$


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#### IV. BEGINNING

$$\left( \frac{\partial x_2}{\partial r_2} \right)_{r_2, \vartheta} = -\frac{1}{2} r_2$$

We need (for example)

$$\frac{\partial}{\partial r_1} = \left( \frac{\partial x_1}{\partial r_1} \right)_{r_2, \vartheta} \frac{\partial}{\partial x_1} + \left( \frac{\partial x_2}{\partial r_1} \right)_{r_2, \vartheta} \frac{\partial}{\partial x_2} + \left( \frac{\partial x_3}{\partial r_1} \right)_{r_2, \vartheta} \frac{\partial}{\partial x_3}$$

and

$$\left( \frac{\partial x_3}{\partial r_2} \right)_{r_2, \vartheta} = \frac{1}{2} r_1 \sin \vartheta$$

Since

$$x_1 = \frac{1}{2} r_1 r_2 \cos \vartheta$$

Therefore, we have

$$x_2 = \frac{1}{4} (r_1^2 - r_2^2)$$

$$\frac{\partial}{\partial r_1} = \frac{1}{2} r_2 \cos \vartheta \frac{\partial}{\partial x_1} + \frac{1}{2} r_1 \frac{\partial}{\partial x_2} + \frac{1}{2} r_2 \sin \vartheta \frac{\partial}{\partial x_3}$$

and

$$x_3 = \frac{1}{2} r_1 r_2 \sin \vartheta$$

Next, we need  $\frac{\partial}{\partial r_2}$ .

we have

$$\left( \frac{\partial x_1}{\partial r_2} \right)_{r_2, \vartheta} = \frac{1}{2} r_2 \cos \vartheta$$

$$\frac{\partial}{\partial r_2} = \left( \frac{\partial x_1}{\partial r_2} \right)_{r_1, \vartheta} \frac{\partial}{\partial x_1} + \left( \frac{\partial x_2}{\partial r_2} \right)_{r_1, \vartheta} \frac{\partial}{\partial x_2} + \left( \frac{\partial x_3}{\partial r_2} \right)_{r_1, \vartheta} \frac{\partial}{\partial x_3} \quad (11)$$

which is

$$\frac{\partial}{\partial r_2} = \frac{1}{2} r_1 \cos \vartheta \frac{\partial}{\partial x_1} - \frac{1}{2} r_2 \frac{\partial}{\partial x_2} + \frac{1}{2} r_1 \sin \vartheta \frac{\partial}{\partial x_3} \quad (12)$$

and

$$\left( \frac{\partial x_2}{\partial r_1} \right)_{r_2, \vartheta} = \frac{1}{2} r_1$$

Finally, we need  $\frac{\partial}{\partial \vartheta}$  which is

$$\frac{\partial}{\partial \vartheta} = \frac{\partial x_1}{\partial \vartheta} \frac{\partial}{\partial x_1} + \frac{\partial x_2}{\partial \vartheta} \frac{\partial}{\partial x_2} + \frac{\partial x_3}{\partial \vartheta} \frac{\partial}{\partial x_3}$$

and

$$\left( \frac{\partial x_3}{\partial r_1} \right)_{r_2, \vartheta} = \frac{1}{2} r_2 \sin \vartheta$$

which is

$$\frac{\partial}{\partial \vartheta} = -\frac{1}{2} r_1 r_2 \sin \vartheta \frac{\partial}{\partial x_1} + \frac{1}{2} r_1 r_2 \cos \vartheta \frac{\partial}{\partial x_3} \quad (13)$$

$$\left( \frac{\partial x_2}{\partial \vartheta} \right)_{r_2, r_1} = 0$$

#### V. CONTINUING FROM PRELIMINARIES, THE $r_1$ TERM

and

$$\left( \frac{\partial x_3}{\partial \vartheta} \right)_{r_2, r_1} = \frac{1}{2} r_1 r_2 \cos \vartheta$$

We form

$$r_1^2 \frac{\partial}{\partial r_1} = r_1^2 \left( \frac{1}{2} r_2 \cos \vartheta \frac{\partial}{\partial x_1} + \frac{1}{2} r_1 \frac{\partial}{\partial x_2} + \frac{1}{2} r_2 \sin \vartheta \frac{\partial}{\partial x_3} \right) \quad (14)$$

we have

$$\left( \frac{\partial x_1}{\partial r_2} \right)_{r_2, \vartheta} = \frac{1}{2} r_1 \cos \vartheta$$

and ask, what is  $\frac{\partial(r_1^2 \frac{\partial}{\partial r_1})}{\partial r_1}$  i.e.,

$$\begin{aligned} \frac{\partial \left( r_1^2 \frac{\partial}{\partial r_1} \right)}{\partial r_1} &= 2r_1 \left( \frac{1}{2} r_2 \cos \vartheta \frac{\partial}{\partial x_1} + \frac{1}{2} r_1 \frac{\partial}{\partial x_2} + \frac{1}{2} r_2 \sin \vartheta \frac{\partial}{\partial x_3} \right) \\ &+ r_1^2 \left( \frac{1}{2} r_2 \cos \vartheta \frac{\partial \frac{\partial}{\partial x_1}}{\partial r_1} + \frac{1}{2} \frac{\partial}{\partial x_2} + \frac{1}{2} r_1 \frac{\partial \frac{\partial}{\partial x_2}}{\partial r_1} + \frac{1}{2} r_2 \sin \vartheta \frac{\partial \frac{\partial}{\partial x_3}}{\partial r_1} \right) \end{aligned} \quad (15)$$

or,

$$\begin{aligned} \frac{\partial \left( r_1^2 \frac{\partial}{\partial r_1} \right)}{\partial r_1} &= 2r_1 \left( \frac{1}{2} r_2 \cos \vartheta \frac{\partial}{\partial x_1} + \frac{1}{2} r_1 \frac{\partial}{\partial x_2} + \frac{1}{2} r_2 \sin \vartheta \frac{\partial}{\partial x_3} \right) \\ &+ r_1^2 \left[ \left( \frac{1}{2} r_2 \cos \vartheta \left\{ \frac{1}{2} r_2 \cos \vartheta \frac{\partial \frac{\partial}{\partial x_1}}{\partial x_1} + \frac{1}{2} r_1 \frac{\partial \frac{\partial}{\partial x_1}}{\partial x_2} + \frac{1}{2} r_2 \sin \vartheta \frac{\partial \frac{\partial}{\partial x_1}}{\partial x_3} \right\} \right) + \right. \\ &\quad \frac{1}{2} \frac{\partial}{\partial x_2} + \\ &\quad \frac{1}{2} r_1 \left\{ \frac{1}{2} r_2 \cos \vartheta \frac{\partial \frac{\partial}{\partial x_2}}{\partial x_1} + \frac{1}{2} r_1 \frac{\partial \frac{\partial}{\partial x_2}}{\partial x_2} + \frac{1}{2} r_2 \sin \vartheta \frac{\partial \frac{\partial}{\partial x_2}}{\partial x_3} \right\} + \\ &\quad \left. \frac{1}{2} r_2 \sin \vartheta \left\{ \frac{1}{2} r_2 \cos \vartheta \frac{\partial \frac{\partial}{\partial x_3}}{\partial x_1} + \frac{1}{2} r_1 \frac{\partial \frac{\partial}{\partial x_3}}{\partial x_2} + \frac{1}{2} r_2 \sin \vartheta \frac{\partial \frac{\partial}{\partial x_3}}{\partial x_3} \right\} \right] \end{aligned} \quad (16)$$

or

$$\begin{aligned} \frac{1}{r_1^2} \frac{\partial \left( r_1^2 \frac{\partial}{\partial r_1} \right)}{\partial r_1} &= \frac{2}{r_1} \left( \frac{1}{2} r_2 \cos \vartheta \frac{\partial}{\partial x_1} + \frac{1}{2} r_1 \frac{\partial}{\partial x_2} + \frac{1}{2} r_2 \sin \vartheta \frac{\partial}{\partial x_3} \right) \\ &+ \frac{1}{4} r_2^2 \cos^2 \vartheta \frac{\partial^2}{\partial x_1^2} + \frac{1}{4} r_2 r_1 \cos \vartheta \frac{\partial^2}{\partial x_1 \partial x_2} + \frac{1}{4} r_2^2 \cos \vartheta \sin \vartheta \frac{\partial^2}{\partial x_1 \partial x_3} + \\ &\quad \frac{1}{2} \frac{\partial}{\partial x_2} + \\ &\quad \frac{1}{4} r_1 r_2 \cos \vartheta \frac{\partial^2}{\partial x_2 \partial x_1} + \frac{1}{4} r_1^2 \frac{\partial^2}{\partial x_2^2} + \frac{1}{4} r_1 r_2 \sin \vartheta \frac{\partial^2}{\partial x_2 \partial x_3} + \\ &\quad \frac{1}{4} r_2^2 \sin \vartheta \cos \vartheta \frac{\partial^2}{\partial x_3 \partial x_1} + \frac{1}{4} r_2 r_1 \sin \vartheta \frac{\partial^2}{\partial x_3 \partial x_2} + \frac{1}{4} r_2^2 \sin^2 \vartheta \frac{\partial^2}{\partial x_3^2} \end{aligned} \quad (17)$$

## VI. THE $r_2$ TERM

We form

$$r_2^2 \frac{\partial}{\partial r_2} = r_2^2 \left( \frac{1}{2} r_1 \cos \vartheta \frac{\partial}{\partial x_1} - \frac{1}{2} r_2 \frac{\partial}{\partial x_2} + \frac{1}{2} r_1 \sin \vartheta \frac{\partial}{\partial x_3} \right) \quad (18)$$

What is  $\frac{\partial(r_2^2 \frac{\partial}{\partial r_2})}{\partial r_2}$  i.e.,

$$\begin{aligned} \frac{\partial(r_2^2 \frac{\partial}{\partial r_2})}{\partial r_2} &= 2r_2 \left( \frac{1}{2}r_1 \cos \vartheta \frac{\partial}{\partial x_1} - \frac{1}{2}r_2 \frac{\partial}{\partial x_2} + \frac{1}{2}r_1 \sin \vartheta \frac{\partial}{\partial x_3} \right) \\ &+ r_2^2 \left[ \left( \frac{1}{2}r_1 \cos \vartheta \left\{ \frac{1}{2}r_1 \cos \vartheta \frac{\partial \frac{\partial}{\partial x_1}}{\partial x_1} - \frac{1}{2}r_2 \frac{\partial \frac{\partial}{\partial x_1}}{\partial x_2} + \frac{1}{2}r_1 \sin \vartheta \frac{\partial \frac{\partial}{\partial x_1}}{\partial x_3} \right\} \right) \right. \\ &\quad \left. - \frac{1}{2} \frac{\partial}{\partial x_2} + \right. \\ &\quad \left. - \frac{1}{2}r_2 \left\{ \frac{1}{2}r_1 \cos \vartheta \frac{\partial \frac{\partial}{\partial x_2}}{\partial x_1} - \frac{1}{2}r_2 \frac{\partial \frac{\partial}{\partial x_2}}{\partial x_2} + \frac{1}{2}r_1 \sin \vartheta \frac{\partial \frac{\partial}{\partial x_2}}{\partial x_3} \right\} + \right. \\ &\quad \left. \frac{1}{2}r_1 \sin \vartheta \left\{ \frac{1}{2}r_1 \cos \vartheta \frac{\partial \frac{\partial}{\partial x_3}}{\partial x_1} - \frac{1}{2}r_2 \frac{\partial \frac{\partial}{\partial x_3}}{\partial x_2} + \frac{1}{2}r_1 \sin \vartheta \frac{\partial \frac{\partial}{\partial x_3}}{\partial x_3} \right\} \right] \end{aligned} \quad (19)$$

which becomes

$$\begin{aligned} \frac{1}{r_2^2} \frac{\left( \partial r_2^2 \frac{\partial}{\partial r_2} \right)}{\partial r_2} &= \frac{2}{r_2} \left( \frac{1}{2}r_1 \cos \vartheta \frac{\partial}{\partial x_1} - \frac{1}{2}r_2 \frac{\partial}{\partial x_2} + \frac{1}{2}r_1 \sin \vartheta \frac{\partial}{\partial x_3} \right) \\ &+ \left( \frac{1}{4}r_1^2 \cos^2 \vartheta \frac{\partial^2}{\partial x_1^2} - \frac{1}{4}r_2 r_1 \cos \vartheta \frac{\partial^2}{\partial x_2 x_1} + \frac{1}{4}r_1^2 \sin \vartheta \cos \vartheta \frac{\partial^2}{\partial x_1 x_3} \right. \\ &\quad \left. - \frac{1}{2} \frac{\partial}{\partial x_2} \right. \\ &\quad \left. - \frac{1}{4}r_1 r_2 \cos \vartheta \frac{\partial^2}{\partial x_2 x_1} + \frac{1}{4}r_2^2 \frac{\partial^2}{\partial x_2^2} - \frac{1}{4}r_1 r_2 \sin \vartheta \frac{\partial^2}{\partial x_2 x_3} \right. \\ &\quad \left. + \frac{1}{4}r_1^2 \sin \vartheta \cos \vartheta \frac{\partial^2}{\partial x_1 x_3} - \frac{1}{4}r_2 r_1 \sin \vartheta \frac{\partial^2}{\partial x_2 x_3} + \frac{1}{4}r_1^2 \sin^2 \vartheta \frac{\partial^2}{\partial x_3^2} \right) \end{aligned} \quad (20)$$


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## VII. THE $\vartheta$ TERM

which becomes

Finally, we had

$$\frac{\partial}{\partial \vartheta} = -\frac{1}{2}r_1 r_2 \sin \vartheta \frac{\partial}{\partial x_1} + \frac{1}{2}r_1 r_2 \cos \vartheta \frac{\partial}{\partial x_3} \quad (21)$$

which means that

$$\frac{\partial \sin \vartheta \frac{\partial}{\partial \vartheta}}{\partial \vartheta} = \frac{\partial \sin \vartheta \left( -\frac{1}{2}r_1 r_2 \sin \vartheta \frac{\partial}{\partial x_1} + \frac{1}{2}r_1 r_2 \cos \vartheta \frac{\partial}{\partial x_3} \right)}{\partial \vartheta} \quad (22)$$

or

$$\frac{\partial \sin \vartheta \frac{\partial}{\partial \vartheta}}{\partial \vartheta} = \frac{\partial \left( -\frac{1}{2}r_1 r_2 \sin^2 \vartheta \frac{\partial}{\partial x_1} + \frac{1}{2}r_1 r_2 \sin \vartheta \cos \vartheta \frac{\partial}{\partial x_3} \right)}{\partial \vartheta} \quad \text{i.e.,}$$


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$$\begin{aligned} \frac{1}{\sin \vartheta} \frac{\partial \sin \vartheta \frac{\partial}{\partial \vartheta}}{\partial \vartheta} &= \\ &-r_1 r_2 \cos \vartheta \frac{\partial}{\partial x_1} - \frac{1}{2}r_1 r_2 \sin \vartheta \left( -\frac{1}{2}r_1 r_2 \sin \vartheta \frac{\partial^2}{\partial x_1^2} + \frac{1}{2}r_1 r_2 \cos \vartheta \frac{\partial^2}{\partial x_1 x_3} \right) \\ &+ \frac{1}{2}r_1 r_2 \left( \frac{\cos^2 \vartheta - \sin^2 \vartheta}{\sin \vartheta} \right) \frac{\partial}{\partial x_3} + \frac{1}{2}r_1 r_2 \cos \vartheta \left( -\frac{1}{2}r_1 r_2 \sin \vartheta \frac{\partial^2}{\partial x_1 x_3} + \frac{1}{2}r_1 r_2 \cos \vartheta \frac{\partial^2}{\partial x_3^2} \right) \end{aligned} \quad (23)$$

which is, expanding

$$\begin{aligned} \frac{1}{\sin \vartheta} \frac{\partial \sin \vartheta \frac{\partial}{\partial \vartheta}}{\partial \vartheta} = \\ -r_1 r_2 \cos \vartheta \frac{\partial}{\partial x_1} + \frac{1}{4} r_1^2 r_2^2 \sin^2 \vartheta \frac{\partial^2}{\partial x_1^2} - \frac{1}{4} r_1^2 r_2^2 \sin \vartheta \cos \vartheta \frac{\partial^2}{\partial x_1 \partial x_3} \\ + \frac{1}{2} r_1 r_2 \left( \frac{\cos^2 \vartheta - \sin^2 \vartheta}{\sin \vartheta} \right) \frac{\partial}{\partial x_3} - \frac{1}{4} r_1^2 r_2^2 \cos \vartheta \sin \vartheta \frac{\partial^2}{\partial x_1 \partial x_3} + \frac{1}{4} r_1^2 r_2^2 \cos^2 \vartheta \frac{\partial^2}{\partial x_3^2} \end{aligned} \quad (24)$$

### VIII. SUMMING UP

Adding the three terms, we have (marking some terms which will cancel):

$$\begin{aligned} \frac{1}{r_1^2} \frac{\partial \left( r_1^2 \frac{\partial}{\partial r_1} \right)}{\partial r_1} + \frac{1}{r_2^2} \frac{\partial \left( r_2^2 \frac{\partial}{\partial r_2} \right)}{\partial r_2} + \left( \frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \left( \frac{1}{\sin \vartheta} \frac{\partial \sin \vartheta \frac{\partial}{\partial \vartheta}}{\partial \vartheta} \right) = \\ \frac{2}{r_1} \left( \frac{1}{2} r_2 \cos \vartheta \frac{\partial}{\partial x_1} + \frac{1}{2} r_1 \frac{\partial}{\partial x_2} + \frac{1}{2} r_2 \sin \vartheta \frac{\partial}{\partial x_3} \right) + \\ \underbrace{\frac{1}{4} r_2^2 \cos^2 \vartheta \frac{\partial^2}{\partial x_1 \partial x_1}}_{+} + \underbrace{\frac{1}{4} r_2 r_1 \cos \vartheta \frac{\partial^2}{\partial x_1 \partial x_2}}_{+} + \frac{1}{2} r_2 \cos \vartheta \frac{1}{2} r_2 \sin \vartheta \frac{\partial^2}{\partial x_1 \partial x_3} + \\ \underbrace{\frac{1}{2} \frac{\partial}{\partial x_2}}_{+} \\ \underbrace{\frac{1}{4} r_1 r_2 \cos \vartheta \frac{\partial^2}{\partial x_2 \partial x_1}}_{+} + \frac{1}{4} r_1^2 \frac{\partial^2}{\partial x_2^2} + \frac{1}{4} r_1 r_2 \sin \vartheta \frac{\partial^2}{\partial x_2 \partial x_3} + \\ \underbrace{\frac{1}{4} r_2^2 \sin \vartheta \cos \vartheta \frac{\partial^2}{\partial x_3 \partial x_1}}_{+} + \underbrace{\frac{1}{4} r_2 r_1 \sin \vartheta \frac{\partial^2}{\partial x_3 \partial x_2}}_{+} + \frac{1}{4} r_2^2 \sin^2 \vartheta \frac{\partial^2}{\partial x_3^2} + \end{aligned} \quad (25)$$

$$\begin{aligned} \underbrace{\frac{2}{r_2} \left( \frac{1}{2} r_1 \cos \vartheta \frac{\partial}{\partial x_1} - \frac{1}{2} r_2 \frac{\partial}{\partial x_2} + \frac{1}{2} r_1 \sin \vartheta \frac{\partial}{\partial x_3} \right)}_{-} \\ + \left( \frac{1}{4} r_1^2 \cos^2 \vartheta \frac{\partial^2}{\partial x_1^2} - \underbrace{\frac{1}{4} r_2 r_1 \cos \vartheta \frac{\partial^2}{\partial x_2 x_1}}_{+} + \frac{1}{4} r_1^2 \sin \vartheta \cos \vartheta \frac{\partial^2}{\partial x_1 x_3} \right. \\ \left. - \underbrace{\frac{1}{2} \frac{\partial}{\partial x_2}}_{+} \right) \quad (26) \end{aligned}$$

$$\begin{aligned} - \underbrace{\frac{1}{4} r_1 r_2 \cos \vartheta \frac{\partial^2}{\partial x_2 x_1}}_{+} + \frac{1}{4} r_2^2 \frac{\partial^2}{\partial x_2^2} - \underbrace{\frac{1}{4} r_1 r_2 \sin \vartheta \frac{\partial^2}{\partial x_2 x_3}}_{+} \\ + \frac{1}{4} r_1^2 \sin \vartheta \cos \vartheta \frac{\partial^2}{\partial x_1 x_3} - \underbrace{\frac{1}{4} r_2 r_1 \sin \vartheta \frac{\partial^2}{\partial x_2 x_3}}_{+} + \frac{1}{4} r_1^2 \sin^2 \vartheta \frac{\partial^2}{\partial x_3^2} + \\ \left( \frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \left( -r_1 r_2 \cos \vartheta \frac{\partial}{\partial x_1} + \frac{1}{4} r_1^2 r_2^2 \sin^2 \vartheta \frac{\partial^2}{\partial x_1^2} - \frac{1}{4} r_1^2 r_2^2 \sin \vartheta \cos \vartheta \frac{\partial^2}{\partial x_1 x_3} \right. \\ \left. + \frac{1}{2} r_1 r_2 \left( \frac{\cos^2 \vartheta - \sin^2 \vartheta}{\sin \vartheta} \right) \frac{\partial}{\partial x_3} - \frac{1}{4} r_1^2 r_2^2 \cos \vartheta \sin \vartheta \frac{\partial^2}{\partial x_1 x_3} + \frac{1}{4} r_1^2 r_2^2 \cos^2 \vartheta \frac{\partial^2}{\partial x_3^2} \right) \end{aligned} \quad (27)$$

which becomes upon doing the cancellations,

$$\begin{aligned} \frac{1}{r_1^2} \frac{\partial}{\partial r_1} \left( r_1^2 \frac{\partial}{\partial r_1} \right) + \frac{1}{r_2^2} \frac{\partial}{\partial r_2} \left( r_2^2 \frac{\partial}{\partial r_2} \right) + \left( \frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \left( \frac{1}{\sin \vartheta} \frac{\partial \sin \vartheta}{\partial \vartheta} \frac{\partial}{\partial \vartheta} \right) = \\ \underbrace{\frac{r_2}{r_1} \cos \vartheta \frac{\partial}{\partial x_1} + \frac{\partial}{\partial x_2}}_{+ \frac{r_2}{r_1} \sin \vartheta \frac{\partial}{\partial x_3}} + \\ \underbrace{\frac{1}{4} r_2^2 \cos^2 \vartheta \frac{\partial^2}{\partial x_1^2}}_{+ \frac{1}{4} r_2^2 \cos \vartheta \sin \vartheta \frac{\partial^2}{\partial x_1 \partial x_3}} + \\ \frac{1}{4} r_1^2 \frac{\partial^2}{\partial x_2^2} + \end{aligned} \quad (28)$$

$$\begin{aligned} \underbrace{\frac{1}{4} r_2^2 \sin \vartheta \cos \vartheta \frac{\partial^2}{\partial x_3 \partial x_1}}_{+ \frac{1}{4} r_2^2 \sin^2 \vartheta \frac{\partial^2}{\partial x_3^2}} + \\ \cdots \\ \underbrace{\frac{r_1}{r_2} \cos \vartheta \frac{\partial}{\partial x_1} - \frac{\partial}{\partial x_2}}_{+ \frac{r_1}{r_2} \sin \vartheta \frac{\partial}{\partial x_3}} + \\ \underbrace{\frac{1}{4} r_1^2 \cos^2 \vartheta \frac{\partial^2}{\partial x_1^2}}_{+ \frac{1}{4} r_1^2 \sin \vartheta \cos \vartheta \frac{\partial^2}{\partial x_1 x_3}} + \\ \frac{1}{4} r_2^2 \frac{\partial^2}{\partial x_2^2} + \\ \underbrace{\frac{1}{4} r_1^2 \sin \vartheta \cos \vartheta \frac{\partial^2}{\partial x_1 x_3}}_{+ \frac{1}{4} r_1^2 \sin^2 \vartheta \frac{\partial^2}{\partial x_3^2}} \end{aligned} \quad (29)$$

$$+ \frac{1}{r_1^2} \left( -r_1 r_2 \cos \vartheta \frac{\partial}{\partial x_1} + \frac{1}{4} r_1^2 r_2^2 \sin^2 \vartheta \frac{\partial^2}{\partial x_1^2} - \underbrace{\frac{1}{4} r_1^2 r_2^2 \sin \vartheta \cos \vartheta \frac{\partial^2}{\partial x_1 \partial x_3}}_{\cdots} \right) \quad (29)$$

$$+ \frac{1}{r_2^2} \left( -r_1 r_2 \cos \vartheta \frac{\partial}{\partial x_1} + \underbrace{\frac{1}{4} r_1^2 r_2^2 \sin^2 \vartheta \frac{\partial^2}{\partial x_1^2}}_{- \frac{1}{4} r_1^2 r_2^2 \sin \vartheta \cos \vartheta \frac{\partial^2}{\partial x_1 \partial x_3}} \right) \quad (29)$$

$$+ \frac{1}{r_1^2} \left( \frac{1}{2} r_1 r_2 \left( \frac{\cos^2 \vartheta - \sin^2 \vartheta}{\sin \vartheta} \right) \frac{\partial}{\partial x_3} - \underbrace{\frac{1}{4} r_1^2 r_2^2 \cos \vartheta \sin \vartheta \frac{\partial^2}{\partial x_1 x_3}}_{+ \frac{1}{4} r_1^2 r_2^2 \cos^2 \vartheta \frac{\partial^2}{\partial x_3^2}} \right) \quad (30)$$

$$+ \frac{1}{r_2^2} \left( \frac{1}{2} r_1 r_2 \left( \frac{\cos^2 \vartheta - \sin^2 \vartheta}{\sin \vartheta} \right) \frac{\partial}{\partial x_3} - \frac{1}{4} r_1^2 r_2^2 \cos \vartheta \sin \vartheta \frac{\partial^2}{\partial x_1 x_3} + \frac{1}{4} r_1^2 r_2^2 \cos^2 \vartheta \frac{\partial^2}{\partial x_3^2} \right) \quad (31)$$

and continuing the ecstasy of cancelling, we have

$$\begin{aligned} \frac{1}{r_1^2} \frac{\partial (r_1^2 \frac{\partial}{\partial r_1})}{\partial r_1} + \frac{1}{r_2^2} \frac{\partial (r_2^2 \frac{\partial}{\partial r_2})}{\partial r_2} + \left( \frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \left( \frac{1}{\sin \vartheta} \frac{\partial \sin \vartheta \frac{\partial}{\partial \vartheta}}{\partial \vartheta} \right) = \\ \frac{1}{4} (r_1^2 + r_2^2) \left( \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_1^3} + \frac{\partial^2}{\partial x_2^2} \right) \\ + \frac{r_2}{r_1} \cos \vartheta \frac{\partial}{\partial x_1} + \frac{r_2}{r_1} \sin \vartheta \frac{\partial}{\partial x_3} \\ + \overbrace{\frac{1}{2} (r_1^2 + r_2^2) \cos \vartheta \sin \vartheta \frac{\partial^2}{\partial x_1 \partial x_3}}^{(32)} \end{aligned}$$

$$+ \frac{r_1}{r_2} \cos \vartheta \frac{\partial}{\partial x_1} + \frac{r_1}{r_2} \sin \vartheta \frac{\partial}{\partial x_3}$$

$$- \frac{r_1 r_2}{r_1^2} \cos \vartheta \frac{\partial}{\partial x_1} - \overbrace{\frac{1}{4} \frac{r_1^2 r_2^2}{r_1^2} \sin \vartheta \cos \vartheta \frac{\partial^2}{\partial x_1 \partial x_3}}^{(33)}$$

$$- \frac{r_1 r_2}{r_2^2} \cos \vartheta \frac{\partial}{\partial x_1} - \overbrace{\frac{1}{4} \frac{r_1^2 r_2^2}{r_2^2} \sin \vartheta \cos \vartheta \frac{\partial^2}{\partial x_1 \partial x_3}}^{(33)}$$

$$+ \frac{1}{2} \frac{r_1 r_2}{r_1^2} \left( \frac{\cos^2 \vartheta - \sin^2 \vartheta}{\sin \vartheta} \right) \frac{\partial}{\partial x_3} - \overbrace{\frac{1}{4} \frac{r_1^2 r_2^2}{r_1^2} \cos \vartheta \sin \vartheta \frac{\partial^2}{\partial x_1 x_3}}^{(34)}$$

$$+ \frac{1}{2} \frac{r_1 r_2}{r_2^2} \left( \frac{\cos^2 \vartheta - \sin^2 \vartheta}{\sin \vartheta} \right) \frac{\partial}{\partial x_3} - \overbrace{\frac{1}{4} \frac{r_1^2 r_2^2}{r_2^2} \cos \vartheta \sin \vartheta \frac{\partial^2}{\partial x_1 x_3}}^{(35)}$$

and continuing the orgy, we have

$$\begin{aligned} \frac{1}{r_1^2} \frac{\partial (r_1^2 \frac{\partial}{\partial r_1})}{\partial r_1} + \frac{1}{r_2^2} \frac{\partial (r_2^2 \frac{\partial}{\partial r_2})}{\partial r_2} + \left( \frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \left( \frac{1}{\sin \vartheta} \frac{\partial \sin \vartheta \frac{\partial}{\partial \vartheta}}{\partial \vartheta} \right) = \\ \frac{1}{4} (r_1^2 + r_2^2) \left( \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2} \right) \\ + \overbrace{\frac{r_2}{r_1} \cos \vartheta \frac{\partial}{\partial x_1} + \frac{r_2}{r_1} \sin \vartheta \frac{\partial}{\partial x_3}}^{(36)} \end{aligned}$$

$$+ \overbrace{\frac{r_1}{r_2} \cos \vartheta \frac{\partial}{\partial x_1} + \frac{r_1}{r_2} \sin \vartheta \frac{\partial}{\partial x_3}}^{(37)}$$

$$- \overbrace{\frac{r_2}{r_1} \cos \vartheta \frac{\partial}{\partial x_1}}^{(37)} \\ - \overbrace{\frac{r_1}{r_2} \cos \vartheta \frac{\partial}{\partial x_1}}^{(38)}$$

$$+ \frac{1}{2} \frac{r_2}{r_1} \left( \frac{\cos^2 \vartheta - \sin^2 \vartheta}{\sin \vartheta} \right) \frac{\partial}{\partial x_3} \quad (39)$$

$$+ \frac{1}{2} \frac{r_1}{r_2} \left( \frac{\cos^2 \vartheta - \sin^2 \vartheta}{\sin \vartheta} \right) \frac{\partial}{\partial x_3} \quad (40)$$

which penultimately results in

$$\frac{1}{r_1^2} \frac{\partial (r_1^2 \frac{\partial}{\partial r_1})}{\partial r_1} + \frac{1}{r_2^2} \frac{\partial (r_2^2 \frac{\partial}{\partial r_2})}{\partial r_2} + \left( \frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \left( \frac{1}{\sin \vartheta} \frac{\partial \sin \vartheta \frac{\partial}{\partial \vartheta}}{\partial \vartheta} \right) = \\ - - - - - \frac{1}{4} (r_1^2 + r_2^2) \left( \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2} \right) + \left( \frac{r_2}{r_1} + \frac{r_1}{r_2} \right) \sin \vartheta \frac{\partial}{\partial x_3} \quad (41)$$

$$+ \frac{1}{2} \frac{r_2}{r_1} \left( \frac{\cos^2 \vartheta - \sin^2 \vartheta}{\sin \vartheta} \right) \frac{\partial}{\partial x_3} \quad (42)$$

$$+ \frac{1}{2} \frac{r_1}{r_2} \left( \frac{\cos^2 \vartheta - \sin^2 \vartheta}{\sin \vartheta} \right) \frac{\partial}{\partial x_3} \quad (43)$$

or, collecting terms,

$$\frac{1}{r_1^2} \frac{\partial (r_1^2 \frac{\partial}{\partial r_1})}{\partial r_1} + \frac{1}{r_2^2} \frac{\partial (r_2^2 \frac{\partial}{\partial r_2})}{\partial r_2} + \left( \frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \left( \frac{1}{\sin \vartheta} \frac{\partial \sin \vartheta \frac{\partial}{\partial \vartheta}}{\partial \vartheta} \right) = \\ - - - - - \frac{1}{4} (r_1^2 + r_2^2) \left( \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_1^3} + \frac{\partial^2}{\partial x_2^2} \right) \\ + \frac{(r_1^2 + r_2^2)}{r_1 r_2} \sin \vartheta \frac{\partial}{\partial x_3} + \frac{1}{2} \frac{r_1^2 + r_2^2}{r_1 r_2} \left( \frac{\cos^2 \vartheta - \sin^2 \vartheta}{\sin \vartheta} \right) \frac{\partial}{\partial x_3} \quad (44)$$

The coefficient of  $\frac{\partial}{\partial x_3}$  in Equation 44 can be simplified; we ultimately arrive at

$$\frac{(r_1^2 + r_2^2)}{r_1 r_2} \sin \vartheta + \frac{1}{2} \frac{r_1^2 + r_2^2}{r_1 r_2} \left( \frac{\cos^2 \vartheta - \sin^2 \vartheta}{\sin \vartheta} \right) = \frac{(r_1^2 + r_2^2)}{r_1 r_2} \sin \vartheta + \frac{1}{2} \frac{r_1^2 + r_2^2}{r_1 r_2 \sin \vartheta} \\ - \frac{2}{2} \frac{r_1^2 + r_2^2}{r_1 r_2} \left( \frac{\sin^2 \vartheta}{\sin \vartheta} \right)$$

which yields

$$\frac{r_1^2 + r_2^2}{r_1 r_2} \sin \vartheta - \frac{r_1^2 + r_2^2}{r_1 r_2} \sin \vartheta + \frac{1}{2} \frac{r_1^2 + r_2^2}{r_1 r_2 \sin \vartheta}$$

which leads to

$$\frac{1}{r_1^2} \frac{\partial (r_1^2 \frac{\partial}{\partial r_1})}{\partial r_1} + \frac{1}{r_2^2} \frac{\partial (r_2^2 \frac{\partial}{\partial r_2})}{\partial r_2} + \left( \frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \left( \frac{1}{\sin \vartheta} \frac{\partial \sin \vartheta \frac{\partial}{\partial \vartheta}}{\partial \vartheta} \right) = \\ \frac{1}{4} (r_1^2 + r_2^2) \left\{ \left( \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_1^3} + \frac{\partial^2}{\partial x_2^2} \right) + \frac{1}{x_3} \frac{\partial}{\partial x_3} \right\}$$

which leads to

$$\left\{ \left( \frac{\partial^2 \psi}{\partial x_1^2} + \frac{\partial^2 \psi}{\partial x_1^3} + \frac{\partial^2 \psi}{\partial x_2^2} \right) + \frac{1}{x_3} \frac{\partial \psi}{\partial x_3} \right\} \\ + \frac{1}{r} \left( \frac{E}{4} + \frac{1}{\sqrt{2(r+x_2)}} + \frac{1}{(\sqrt{2(r-x_2)})} - \frac{1}{2Z \sqrt{(r-x_1)}} \right) \psi = 0$$

which is Equation 7.

[1] T. H. Gronwall, Phys. Rev. **51**, 655 (1937).

[2] T. H. Gronwall, Annals of mathematics **33**, 279 (1932).

- [3] E. A. Hylleraas, Zeits. f. Physik **54**, 347 (1929).
- [4] E. A. Hylleraas, Zeits. f. Physik **48**, 469 (1928).
- [5] E. A. Hylleraas, Zeits. f. Physik **65**, 209 (1930).