

## 5 The Central Force Problem in Quantum Mechanics

### 5.1 Three-Dimensional Schrödinger Equation

5/12:

- The hydrogen atom will now be solved using the methods developed previously.
- The quantum mechanics, summarized in Labalme (2023, pp. 56–58).
  - Starting with the 3D TISE.
  - Introduction of polar coordinates and a spherically symmetric potential.
  - The Laplacian in spherical coordinates.
  - Separation of variables into a radial and angular equation, with the separation constant being denoted  $\lambda$  so that, in particular,

$$\lambda = -\frac{1}{Y} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] Y$$

- The angular momentum operator.
- Separation of the angular variables into the polar and azimuthal equations, and solution to the azimuthal equation.
- This all gets us to one substitution — namely,  $x = \cos \theta$  — away from a precursor to the general Legendre equation.

### 5.2 Legendre's Equation

- We have arrived at the following differential equation.

$$(1-x^2) \frac{d^2}{dx^2} f(x) - 2x \frac{d}{dx} f(x) + \left( \lambda - \frac{m^2}{1-x^2} \right) f(x) = 0$$

- This ODE has three regular singular points (at  $x = \infty$  and  $x = \pm 1$ ), so we will look to transform it into the typical hypergeometric equation.
- We now begin the changes of variable.
  - Begin with the (unmotivated) substitution

$$f(x) = v(x)w(x)$$

- Using this substitution and rewriting the resulting differential equation in terms of  $w$  yields

$$\begin{aligned} 0 &= (1-x^2) \frac{d^2}{dx^2} [vw] - 2x \frac{d}{dx} [vw] + \left( \lambda - \frac{m^2}{1-x^2} \right) vw \\ &= (1-x^2) \frac{d}{dx} [v'w + vw'] - 2x(v'w + vw') + \left( \lambda - \frac{m^2}{1-x^2} \right) vw \\ &= (1-x^2)[(v''w + v'w') + (v'w' + vw'')] - 2x(v'w + vw') + \left( \lambda - \frac{m^2}{1-x^2} \right) vw \\ &= (1-x^2)vw''(x) + [2(1-x^2)v' - 2xv]w'(x) + \left[ (1-x^2)v'' - 2xv' + \left( \lambda - \frac{m^2}{1-x^2} \right) v \right] w(x) \end{aligned}$$

- For our next (unmotivated) substitution, we will let

$$v(x) = (1-x^2)^a$$

- To pin down the exact value of  $a$ , first observe that it would be nice if we could just divide the  $v$  out of the second-order term, leaving only an expression of the independent variable behind as in the hypergeometric equation's second term.
- However, doing this would also necessitate dividing  $v$  out of the rest of the equation. In particular, we would need the coefficient of the zero-order term to be constant following this division, i.e., we need the zero-order term as written to be proportional to  $v$ .<sup>[1]</sup>
- Let  $c$  be the constant of proportionality.
- If  $v = (1 - x^2)^a$ , then

$$\begin{aligned} v'(x) &= a(1 - x^2)^{a-1} \cdot (-2x) \\ &= -2ax(1 - x^2)^{a-1} \end{aligned}$$

and

$$\begin{aligned} v''(x) &= -2a(1 - x^2)^{a-1} - 2ax(a-1)(1 - x^2)^{a-2} \cdot (-2x) \\ &= -2a(1 - x^2)^{a-1} + 4x^2(a^2 - a)(1 - x^2)^{a-2} \end{aligned}$$

- Substituting into the zero-order term's coefficient, we obtain

$$\begin{aligned} cv &= (1 - x^2) [-2a(1 - x^2)^{a-1} + 4x^2(a^2 - a)(1 - x^2)^{a-2}] \\ &\quad - 2x \cdot -2ax(1 - x^2)^{a-1} + \left( \lambda - \frac{m^2}{1 - x^2} \right) (1 - x^2)^a \\ c(1 - x^2)^a &= -2a(1 - x^2)^a + 4a^2x^2(1 - x^2)^{a-1} - 4ax^2(1 - x^2)^{a-1} \\ &\quad + 4ax^2(1 - x^2)^{a-1} + \lambda(1 - x^2)^a - m^2(1 - x^2)^{a-1} \\ c &= (\lambda - 2a) + (4a^2x^2 - m^2)(1 - x^2)^{-1} \end{aligned}$$

- Choosing  $a$  such that  $4a^2 = m^2$  ensures that  $c$  is constant, since then

$$\begin{aligned} c &= \lambda - 2a + 4a^2(x^2 - 1)(1 - x^2)^{-1} \\ &= \lambda - 2a - 4a^2 \end{aligned}$$

- But if  $4a^2 = m^2$ , then  $a = \pm|m|/2$  and hence

$$v(x) = (1 - x^2)^{\pm|m|/2}$$

- At this point, we have solved for the second-order coefficient  $(1 - x^2)$  and the zero-order coefficient  $(\lambda - 2a - 4a^2)$  of our transformed differential equation in terms of  $a$ . Let's look at the first-order coefficient now in terms of  $a$ .

- Using the above substitutions, this coefficient should be

$$\begin{aligned} \frac{1}{v} \cdot 2(1 - x^2)v' - 2xv &= \frac{2(1 - x^2) \cdot -2ax(1 - x^2)^{a-1} - 2x(1 - x^2)^a}{(1 - x^2)^a} \\ &= -2(1 + 2a)x \end{aligned}$$

- Now, let's put everything together for this second substitution.

- In terms of  $a$ , we get

$$(1 - x^2)w''(x) - 2(1 + 2a)xw'(x) - (4a^2 + 2a - \lambda)w(x) = 0$$

- Substituting  $a = \pm|m|/2$ , we get

$$(1 - x^2)w''(x) - 2(1 \pm |m|)xw'(x) - (m^2 \pm |m| - \lambda)w(x) = 0$$

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<sup>1</sup>More thoughts on justifying this and the last claim?? See the comment on the zero-order factor being "proportional to  $v$ " on Seaborn (1991, pp. 72–73).

– Finally, we embark on our last substitution.

- The zero-order term is set at this point, so we just need to change the independent variable.
- In particular, looking at the second-order term, we would like to transform  $1 - x^2$  into  $z(1 - z)$ . To facilitate this, let

$$1 - x^2 = \alpha z(1 - z)$$

where  $\alpha$  is an undetermined constant.

- We can determine  $\alpha$  using the following constraint.

$$\begin{aligned} z(1 - z) \frac{d^2 w}{dz^2} &= (1 - x^2) \frac{d^2 w}{dx^2} \\ &= \alpha z(1 - z) \left[ \frac{d^2 w}{dz^2} \cdot \left( \frac{dz}{dx} \right)^2 + \frac{dw}{dz} \frac{d^2 z}{dx^2} \right] \\ \frac{1}{\alpha} \cdot \frac{d^2 w}{dz^2} + 0 \cdot \frac{dw}{dz} &= \left( \frac{dz}{dx} \right)^2 \cdot \frac{d^2 w}{dz^2} + \frac{d^2 z}{dx^2} \cdot \frac{dw}{dz} \end{aligned}$$

- Comparing like terms, the above constraint splits into the two constraints

$$\frac{1}{\alpha} = \left( \frac{dz}{dx} \right)^2 \qquad 0 = \frac{d^2 z}{dx^2}$$

- Using the right constraint above, we learn that there exist  $a, b \in \mathbb{C}$  such that

$$z = ax + b$$

- Applying the left constraint above to this result tells us that

$$\alpha = \frac{1}{a^2}$$

- Thus, returning to the original equation,

$$\begin{aligned} 1 - x^2 &= \frac{1}{a^2} (ax + b) [1 - (ax + b)] \\ &= \frac{1}{a^2} (ax + b - a^2 x^2 - abx - abx - b^2) \\ 1 + 0x - x^2 &= \frac{1}{a^2} (b - b^2 + (a - 2ab)x - a^2 x^2) \\ 1 + 0x &= \frac{b - b^2}{a^2} + \frac{1 - 2b}{a} x \end{aligned}$$

- Comparing like terms, we obtain the two-variable two-equation system

$$1 = \frac{b - b^2}{a^2} \qquad 0 = \frac{1 - 2b}{a}$$

- Solving the right equation above, we learn that

$$b = \frac{1}{2}$$

- Using this to solve the left equation above, we learn that

$$\begin{aligned} 1 &= \frac{\frac{1}{2} - \frac{1}{4}}{a^2} \\ a &= \pm \frac{1}{2} \end{aligned}$$

- It follows that

$$\alpha = a^{-2} = 4$$

- The last remaining question is which sign we should choose for  $a$ . In fact, it doesn't matter, so WLOG we will choose the minus sign because it will simplify things later down the road.<sup>[2]</sup>
- Therefore,

$$z = \frac{1}{2}(1 - x)$$

- Using this substitution, we obtain

$$\begin{aligned} 0 &= [1 - (1 - 2z)^2] \frac{d}{dz} \left( \frac{dw}{dz} \cdot -\frac{1}{2} \right) \cdot -\frac{1}{2} - 2(1 \pm |m|)(1 - 2z) \frac{dw}{dz} \cdot -\frac{1}{2} - (m^2 \pm |m| - \lambda)w(z) \\ &= \frac{1}{4}[1 - (1 - 4z + 4z^2)] \frac{d^2w}{dz^2} + (1 \pm |m| - 2z \mp 2|m|z) \frac{dw}{dz} - (m^2 \pm |m| - \lambda)w(z) \\ &= z(1 - z)w''(z) + [1 \pm |m| - 2(1 \pm |m|)z]w'(z) - (m^2 \pm |m| - \lambda)w(z) \end{aligned}$$

- We may now invoke our prior general solution to the hypergeometric equation.

- Observe that when  $\theta = 0$ ,

$$z = \frac{1}{2}(1 - x) = \frac{1}{2}(1 - \cos \theta) = 0$$

- Since such points are physically *allowed*, we must discard the solution that is singular at  $z = 0$  by setting  $B = 0$  in the general solution.
- Therefore, the solution to the above differential equation that is fully acceptable on physical grounds is

$$w(z) = {}_2F_1(a, b; c; z)$$

where

$$a + b = 1 \pm 2|m| \qquad ab = m^2 \pm |m| - \lambda \qquad c = 1 \pm |m|$$

- Since the hypergeometric function is invariant under interchange of  $a, b$ , we may solve the left two equations above for  $a$  and  $b$  and WLOG take  $b$  to be the larger of the two. This yields

$$w(z) = {}_2F_1(\underbrace{\frac{1}{2}(1 - \sqrt{4\lambda + 1}) \pm |m|}_a, \underbrace{\frac{1}{2}(1 + \sqrt{4\lambda + 1}) \pm |m|}_b; \underbrace{1 \pm |m|}_c; z)$$

- To determine the right choice of sign, we examine the behavior of the complete solution at the physically accessible point  $z = 0$  (equivalently,  $x = 1$ ).
- Returning our substitutions, we obtain the following with  $a, b, c$  defined as above.

$$\begin{aligned} f(x) &= Av(x)w(x) \\ &= A(1 - x^2)^{\pm|m|/2} \sum_{k=0}^{\infty} \frac{(a)_k(b)_k}{k!(c)_k} [z(x)]^k \\ &= A(1 - x^2)^{\pm|m|/2} \left[ 1 + \sum_{k=1}^{\infty} \frac{(a)_k(b)_k}{k!(c)_k} \left( \frac{1}{2} - \frac{1}{2}x \right)^k \right] \end{aligned}$$

- As  $x \rightarrow 1$ , the quantity in brackets approaches 1 and  $1 - x^2 \rightarrow 0$ . Thus, to ensure that the  $v(x)$  term does not become a pole (hence  $f$  stays well behaved near 1), we choose the positive sign.
- Recalling that the original instance of “ $\pm$ ” in  $v(x)$  is what led to all other instances, this one choice resolves all other sign choices.

<sup>2</sup>This appears to be what Seaborn (1991, p. 73) suggests with “will satisfy our requirements,” but am I reading this right??

- Therefore, the complete solution to the precursor to the general Legendre equation is

$$f(x) = A(1 - x^2)^{|m|/2} {}_2F_1\left(\frac{1}{2}(1 - \sqrt{4\lambda + 1}) + |m|, \frac{1}{2}(1 + \sqrt{4\lambda + 1}) + |m|; 1 + |m|; z\right)$$

- Finally, as with the Hermite polynomials, we can show that the series diverges at certain values of  $x$ , so we must put a termination condition on it.
- An example of a case where it currently diverges but should be physically accessible.
  - Consider the behavior of  ${}_2F_1(a, b; c; z)$  at  $z = 1$ .
  - We have

$${}_2F_1(a, b; c; 1) = \sum_{k=0}^{\infty} \frac{(a)_k (b)_k}{k! (c)_k}$$

- This series diverges if there is ever a case in which the  $(k + 1)^{\text{th}}$  term is not smaller than the  $k^{\text{th}}$  term.
  - In such a case, we would have

$$\frac{(a)_{k+1} (b)_{k+1}}{(k+1)! (c)_{k+1}} \geq \frac{(a)_k (b)_k}{k! (c)_k}$$

- This condition is equivalent to

$$\begin{aligned} (a + k)(b + k) &\geq (k + 1)(c + k) \\ ab + (a + b)k &\geq c + ck \end{aligned}$$

- Thus, in the limit of large  $k$ , this condition is fulfilled if  $a + b \geq c$ .
- Critically, in this particular case,  $a + b$  actually *is* greater than  $c$  since  $|m| \geq 0$ :

$$\begin{aligned} a + b &= \left[\frac{1}{2}(1 - \sqrt{4\lambda + 1}) + |m|\right] + \left[\frac{1}{2}(1 + \sqrt{4\lambda + 1}) + |m|\right] \\ &= 1 + 2|m| \\ &\geq 1 + |m| \\ &= c \end{aligned}$$

- To address this divergence, we must require the series to terminate.
  - In particular, either  $a$  or  $b$  must be a nonpositive integer.
  - In fact, it is sufficient for  $a$  to be a nonpositive integer.

- This is because  $b$  nonpositive implies  $a$  nonpositive. Here's why.

*Proof.* Suppose  $b$  is a nonpositive integer. By choice,  $b \geq a$ . Since  $a + b = 2|m| + 1$  is an odd natural number, we have that  $a \neq b$  and hence the strict inequality  $b > a$  holds. The  $a + b = 2|m| + 1$  condition combined with the fact that  $b \in \mathbb{Z}$  also implies that  $a \in \mathbb{Z}$ . Therefore,  $a$  is an integer strictly less than zero, as desired.  $\square$

- In particular,  $a$  being a nonpositive integer means that

$$\frac{1}{2}(1 - \sqrt{4\lambda + 1}) + |m| = a = -n \quad (n = 0, 1, 2, \dots)$$

- Note: Since  $a = -n$  and  $a + b = 2|m| + 1$ , it also follows that  $b = n + 2|m| + 1$ .

- This termination condition allows us to solve for  $\lambda$ .

$$\begin{aligned} -n &= \frac{1}{2}(1 - \sqrt{4\lambda + 1}) + |m| \\ -2(n + |m|) &= 1 - \sqrt{4\lambda + 1} \\ 4\lambda + 1 &= 1 + 4(n + |m|) + 4(n + |m|)^2 \\ \lambda &= (n + |m|)(n + |m| + 1) \end{aligned}$$

- Define  $\ell := n + |m|$ . Then the separation constant is

$$\lambda = \ell(\ell + 1) \quad (\ell = 0, 1, 2, \dots)$$

- Seaborn (1991) comments a bit on the physical interpretation of this quantization as quantized angular momentum.
- Additional consequence: Rearranging the definition of  $\ell$  to  $\ell - |m| = n \geq 0$ , we obtain the following two relations between  $\ell, m$ .

$$\ell \geq |m| \quad -\ell \leq m \leq \ell$$

- It follows that in terms of these new parameters, the solution to the precursor to the general Legendre equation is

$$f_{\ell m}(x) = A_{\ell m}(1 - x^2)^{|m|/2} {}_2F_1(-\ell + |m|, \ell + |m| + 1; |m| + 1; \frac{1}{2} - \frac{1}{2}x)$$

- **Legendre's equation:** The linear, second-order, homogeneous differential equation (with rational coefficients) given as follows, which is the special case of the precursor to the general Legendre equation obtained when  $m = 0$  and  $\lambda = \ell(\ell + 1)$ . *Given by*

$$(1 - x^2)f''(x) - 2xf'(x) + \ell(\ell + 1)f(x) = 0$$

### 5.3 Legendre Polynomials and Associated Legendre Functions

- **Legendre polynomial** (of order  $\ell$ ): A solution to Legendre's equation. *Denoted by  $P_\ell(x)$ . Given by*

$$P_\ell(x) := {}_2F_1(-\ell, \ell + 1; 1; \frac{1}{2} - \frac{1}{2}x)$$

- **General Legendre equation:** The generalization of Legendre's equation that we originally solved above. *Given by*

$$(1 - x^2)\frac{d^2}{dx^2}P_\ell^m(x) - 2x\frac{d}{dx}P_\ell^m(x) + \left[\ell(\ell + 1) - \frac{m^2}{1 - x^2}\right]P_\ell^m(x) = 0$$

- We now derive the **associated Legendre functions**.

- Differentiate  $p$  times the Legendre polynomial of order  $\ell$ :

$$\frac{d^p}{dx^p}P_\ell(x) = (-1)^p \sum_{k=p}^{\infty} \frac{(-\ell)_k(\ell + 1)_k}{2^k k! (1)_k} (k - p + 1)_p (1 - x)^{k-p}$$

- Reindex  $k - p$  to  $k$ :

$$\frac{d^p}{dx^p}P_\ell(x) = (-1)^p \sum_{k=0}^{\infty} \frac{(-\ell)_{k+p}(\ell + 1)_{k+p}}{2^{k+p} (k + p)! (1)_{k+p}} (k + 1)_p (1 - x)^k$$

- Iteratively apply Pochhammer symbol identity 6 from Section 2.2:

$$\begin{aligned} \frac{d^p}{dx^p}P_\ell(x) &= (-1)^p \sum_{k=0}^{\infty} \frac{(-\ell)_p(-\ell + p)_k(\ell + 1)_p(\ell + 1 + p)_k}{2^k 2^p (k + p)! (1)_p (1 + p)_k} (k + 1)_p (1 - x)^k \\ &= (-1)^p \frac{(-\ell)_p(\ell + 1)_p}{2^p (1)_p} \sum_{k=0}^{\infty} \frac{(-\ell + p)_k(k + 1)_p(\ell + 1 + p)_k}{2^k (k + p)! (1 + p)_k} (1 - x)^k \\ &= (-1)^p \frac{(-\ell)_p(\ell + 1)_p}{2^p p!} \sum_{k=0}^{\infty} \frac{(-\ell + p)_k(k + 1)_p(\ell + p + 1)_k}{2^k k! (k + 1)_p (p + 1)_k} (1 - x)^k \\ &= (-1)^p \frac{(-\ell)_p(\ell + 1)_p}{2^p p!} \sum_{k=0}^{\infty} \frac{(-\ell + p)_k(\ell + p + 1)_k}{2^k k! (p + 1)_k} (1 - x)^k \end{aligned}$$

- Use the hypergeometric function to simplify the notation above.

$$\frac{d^p}{dx^p} P_\ell(x) = (-1)^p \frac{(-\ell)_p (\ell+1)_p}{2^p p!} {}_2F_1(-\ell+p, \ell+p+1; p+1; \tfrac{1}{2} - \tfrac{1}{2}x)$$

- By relating  $p \sim |m|$  and comparing the above to  $f_{\ell m}(x)$ , we can see that the functions defined as follows will be solutions to the general Legendre equation. Note that the big constant above takes the role of  $A_{\ell m}$ .

- **Associated Legendre functions:** The canonical solutions to the general Legendre equation. Also known as **associated Legendre polynomials**. Denoted by  $P_\ell^m(x)$ . Given by

$$P_\ell^m(x) := (1-x^2)^{|m|/2} \frac{d^{|m|}}{dx^{|m|}} P_\ell(x)$$

- Let's take an additional moment to relate the above definition to the preceding derivation.
  - Via the Pochhammer symbol identities from Section 2.2, we may obtain the identities

$$(-1)^{|m|} (-\ell)_{|m|} = (\ell - |m| + 1)_{|m|} \quad \text{Identity 2}$$

$$= \frac{\ell!}{(\ell - |m|)!} \quad \text{Identity 2}$$

and

$$(\ell + 1)_{|m|} = \frac{(\ell + |m|)!}{\ell!} \quad \text{Identity 3}$$

■ Note that  $\ell - |m|$  is nonnegative and hence a valid argument for the factorial because  $\ell \geq |m|$ .

- Therefore,

$$\begin{aligned} P_\ell^m(x) &= (1-x^2)^{|m|/2} \frac{(-1)^{|m|} (-\ell)_{|m|} \cdot (\ell+1)_{|m|}}{2^{|m|} |m|!} {}_2F_1(-\ell+|m|, \ell+|m|+1; |m|+1; \tfrac{1}{2} - \tfrac{1}{2}x) \\ &= (1-x^2)^{|m|/2} \frac{\ell! \cdot (\ell+|m|)!}{2^{|m|} |m|! (\ell-|m|)! \cdot \ell!} {}_2F_1(-\ell+|m|, \ell+|m|+1; |m|+1; \tfrac{1}{2} - \tfrac{1}{2}x) \\ &= \frac{(\ell+|m|)! (1-x^2)^{|m|/2}}{2^{|m|} |m|! (\ell-|m|)!} {}_2F_1(-\ell+|m|, \ell+|m|+1; |m|+1; \tfrac{1}{2} - \tfrac{1}{2}x) \end{aligned}$$

- We now define an inner product on the Legendre polynomials to discuss their **orthogonality**.
  - Orthogonality will be covered more in Chapter 12 (including for associated Legendre functions!), but for now we will just say that by “ $P_\ell(x)$  is orthogonal to  $P_{\ell'}(x)$  for  $\ell \neq \ell'$ ,” we mean that

$$\int_{-1}^1 P_\ell(x) P_{\ell'}(x) dx = 0 \quad (\ell \neq \ell')$$

- We now prove this orthogonality relation.

*Proof.* Let  $\ell \neq \ell'$ . Since  $P_\ell(x), P_{\ell'}(x)$  are both Legendre polynomials, they satisfy Legendre's equation. Mathematically, we have that

$$(1-x^2)P_\ell''(x) - 2xP_\ell'(x) + \ell(\ell+1)P_\ell(x) = 0$$

and

$$(1-x^2)P_{\ell'}''(x) - 2xP_{\ell'}'(x) + \ell'(\ell'+1)P_{\ell'}(x) = 0$$

Multiply the top equation above by  $P_{\ell'}(x)$ , the bottom by  $P_\ell(x)$ , and subtract the first from the second to obtain

$$(1-x^2)[P_\ell P_{\ell'}'' - P_{\ell'} P_\ell''] - 2x[P_\ell P_{\ell'}' - P_{\ell'} P_\ell'] + [\ell'(\ell'+1) - \ell(\ell+1)]P_\ell P_{\ell'} = 0$$

Using a bit of calculus, the left two terms above can be combined. Additionally, the rightmost term can be moved over to the right side of the equation. This yields

$$\frac{d}{dx}\{(1-x^2)[P_\ell P'_{\ell'} - P'_\ell P_{\ell'}]\} = [\ell(\ell+1) - \ell'(\ell'+1)]P_\ell P_{\ell'}$$

Integrating both sides from  $-1$  to  $1$  yields

$$\begin{aligned} \int_{-1}^1 d(1-x^2)[P_\ell P'_{\ell'} - P'_\ell P_{\ell'}] &= \int_{-1}^1 [\ell(\ell+1) - \ell'(\ell'+1)]P_\ell P_{\ell'} dx \\ (1-x^2)[P_\ell(x)P'_{\ell'}(x) - P'_\ell(x)P_{\ell'}(x)] \Big|_{-1}^1 &= [\ell(\ell+1) - \ell'(\ell'+1)] \int_{-1}^1 P_\ell(x)P_{\ell'}(x) dx \end{aligned}$$

Since  $1-x^2$  goes to 0 at both 1 and  $-1$ , the left side of the above equation is zero. Thus, we can divide out the constant term in front of the integral on the right side of the above equation, leaving us with

$$0 = \int_{-1}^1 P_\ell(x)P_{\ell'}(x) dx$$

as desired. □