CHEM 26100 Notes

5/10:

- A preview of where the complex analysis comes in.
  - This is an ordinary differential equation that physicists care about:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + V(x)\cdot\psi(x) = E\psi(x)$$

  - What do they do with it?
    - They take a potential energy function $V:\mathbb{R}\to\mathbb{R}$ of interest and use this equation to solve for a corresponding $\psi:\mathbb{R}\to\mathbb{R}$.
    - Some potential energy functions V give rise to special differential equations, such as the **Hermite equation** and **Legendre equation**.
  - Why do we care?
    - We can use complex analysis and the hypergeometric function introduced on Problem Set 2 to solve these equations.
- Quantum mechanics background.
  - In the name of being concise in my background, I'm going to intentionally skip some details. You're free to ask me about these things, but I have done my best to present a cohesive, standalone introduction.
  - Quantum mechanics is better *done* than *understood* at first. Understanding typically develops with experience in doing the computations, which is a strange but fairly valid pedagogical approach. However, since I don't have the time to walk you through a bunch of computations, I will do my best to offer a handwavey verbal explanation.
    - Quote my physics textbook here??
  - Classical physics: Matter is composed of particles whose motion is governed by Newton's laws, most famously, the second-order differential equation

$$-\frac{\mathrm{d}V}{\mathrm{d}x} = F = ma = m\frac{\mathrm{d}^2x}{\mathrm{d}t^2}$$

    - Analyze larger objects as collections of particles each evolving under Newton's laws.
    - Matter has a fundamentally *particle-like* nature.
  - New results challenge this postulate.
    - Einstein (1905): The photoelectric effect equation and the mass-energy equation.

$$E = h\nu = \frac{hc}{\lambda} \qquad\qquad E = mc^2$$

    - Combining these, we find that light has mass!

$$\begin{aligned} mc^2 &= \frac{hc}{\lambda} \\ m &= \frac{h}{\lambda c} \end{aligned}$$

    - Louis de Broglie (1924): Turns in a 4-page PhD thesis and says:

$$\lambda = \frac{h}{mc}$$

    - Paris committee will fail him, but they write to Einstein who recognizes the importance of this work (Labalme, 2023, p. 7).

    - Takeaway: de Broglie has just postulated that fundamental particles of matter (e.g., electrons) have a wavelike nature.
    - Davisson-Germer experiment: Update to Thomas Young's double-slit experiment. They use electrons and *still* observe a diffraction pattern. Confirms de Broglie's hypothesis.
- So what is matter?
    - Modern physicists and chemists will say it has a **dual wave-particle nature**.
    - What does this mean? I mean, I can picture a wave, I can picture a particle, and they don't look the same! How should I picture it?
    - Remember, all we can do as scientists is provide a model to summarize our experimental results.
    - Occam's razor: Simpler models are better.
    - There are some experimental results in which light behaves like a particle and some in which it behaves like a wave. We will use each model when appropriate and leave the true nature of matter unsettled until we have more data.
- For the remainder of this discussion, let us confine ourselves to one-dimensional space.
- So if matter is a wave, then it is spread out over all space in some sense; it does not exist locally at some point x, but rather at each point $x \in \mathbb{R}$, it has some intensity $\psi(x)$ given by a wave function $\psi : \mathbb{R} \to \mathbb{R}$.
- What constraints can we put on ψ?
- Schrödinger (1925):
$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + V(x)\cdot\psi(x) = E\psi(x)$$
    - In the Swiss Alps with his mistress.
        - Wasn't just Oppenheimer.
    - Richard Feynman: "Where did we get that [equation] from? Nowhere. It is not possible to derive it from anything you know. It came from the mind of Schrödinger."
    - Feynman, true to character, was being mildly facetious, but the core of what he says is true: It was a pretty out-of-left-field result.
- So say we're given some potential $V(x)$ and get a $\psi(x)$ that solves the TISE. What does $\psi(x)$ tell us?
    - Nothing directly.
    - Born (1926): $|\psi(x)|^2$ gives the probability that the wave/particle is at x.
    - Examples likening densities to orbitals from Gen Chem I final review session..
- The universe can still be quantized even if we can't see it.
    - The Earth can still be round even if we can't see it.
    - The pixels in a screen can still be quantized even if we can't see them.
- Now, where is all of this going? Why am I talking about quantum mechanics in my complex analysis final project?
    - While you or I might care about the solutions to these questions in the abstract and just for funsies, the people who will pay you to do your research might not. As such, it is important to be able to explain to a non-mathematician where your problem comes from and how a solution will benefit the average Joe.
- This brings us to microwaves.
    - Personally, I like microwaves. They heat up food far more quickly than a traditional oven, they're energy efficient, and they go ding when they're done.
    - Microwaves work because of quantum mechanics.

    - Essentially, they shoot light of just the right frequency at your food so that molecules in it — which are already vibrating harmonically — vibrate faster. Faster vibrations means warmer food.
    - But how do we analyze such a vibrating molecule to know what frequency of light to shoot at it? Well, a vibrating molecule can be modeled as a quantum harmonic oscillator, that is, a quantum particle with
$$V(x) = \frac{1}{2}kx^2$$
    - Sparing you the gory details, if we plug this into the Schrödinger equation and do some rearranging, we end up having to solve the **Hermite equation**:
$$\frac{\mathrm{d}^2 H}{\mathrm{d}y^2} - 2y\frac{\mathrm{d}H}{\mathrm{d}y} + (\epsilon - 1)H(y) = 0$$
    - To solve the Hermite equation, we need complex analysis and the hypergeometric function.
  - Alright, where else can we use such techniques?
    - What if we care about chemistry, at all?
    - Once atoms and molecules were discovered, chemistry developed as the discipline that uses atoms and molecules to do stuff, be it synthesizing a new medicine, mass-producing the ammonia fertilizer that feeds the planet, or literally anything else.
    - "Doing stuff" with atoms and molecules, however, is greatly facilitated by a good understanding of how atoms and molecules interact, and hence how they're structured.
    - Once again, quantum mechanics provides the answers we need.
    - A classic example is the electronic structure of the hydrogen atom, which consists of a single electron (a quantum particle) existing in the potential
$$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$$
      - FYI, that is not Euler's number in the numerator but rather the charge of an electron.
    - Sparing you the gory details once again, if we plug this into the Schrödinger equation and do some rearranging, we end up having to solve the **Legendre equation**:
$$(1 - x^2)\frac{\mathrm{d}^2 P}{\mathrm{d}x^2} - 2x\frac{\mathrm{d}P}{\mathrm{d}x} + \left[\ell(\ell + 1) - \frac{m^2}{1 - x^2}\right] P(x) = 0$$
      - Actually, we start off with the not-quite-Legendre's equation and have to derive Legendre's equation as we're solving it! We'll get there.

- Labalme (2023, pp. 28–31): Hermite polynomials derivation.
  - Address the quantum harmonic oscillator.
  - Apply the 1D TISE.
  - Change coordinates.
  - Take an asymptotic solution.
  - Discover that the general solutions are of the form $H(y)\mathrm{e}^{-y^2/2}$.
  - Substituting back into the TISE, we obtain the Hermite equation.
  - Solve via a series expansion and recursion relation.
  - Truncate the polynomial expansion to quantize.
- Labalme (2023, pp. 56–65): Legendre polynomials and associated Legendre functions derivation.
  - Address the hydrogen atom.

- Starting from the 3D TISE in spherical coordinates, use separation of variables to isolate a one-variable portion of the angular equation. When rearranged, this ODE becomes **Legendre's equation**.
- Solving Legendre's equation when $m = 0$ gives the Legendre polynomials $P_\ell(x)$.
- Solving Legendre's equation when $m \neq 0$ gives the associated Legendre functions

$$P_\ell^{|m|}(x) = (1 - x^2)^{|m|/2} \frac{\mathrm{d}^{|m|}}{\mathrm{d}x^{|m|}} [P_\ell(x)]$$