Week 3

Mathematical Formulation of Quantum Mechanics

3.1 Vibrational Motion and the Harmonic Oscillator

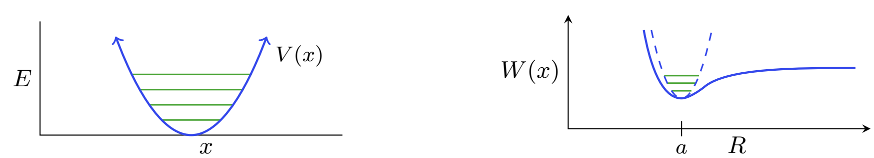
10/11:
- Suppose we have an attractive force F proportional to the displacement x from the center of a system

$$F = -kx$$

  - Then we also have an associated potential energy

$$V(x) = \frac{1}{2}kx^2$$

  - Recall that $F = -\,\partial V/\partial x$.
- Thus, we have a harmonic (or parabolic) potential well.



(a) Harmonic (parabolic) well. (b) Approximating a potential well.

Figure 3.1: Parabolic potential wells.

  - However, because this is a quantum system, the attainable energy levels will be quantized (see Figure 3.1a).
  - We can use a parabolic well to approximate the minimum of the potential well (see Figure 3.1b).
- **Reduced mass**: For two objects of mass m_A, m_B, the quantity

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

  - We can map the two body problem of two atoms being drawn together and pulled apart onto the one body problem of a single harmonic oscillator of reduced mass μ at the center of mass of the diatomic system.

- The Taylor series expansion of the Moiré Potential about $x = a$ where a is the minimum potential:

$$\begin{aligned}W(x) &= W(a) + (x-a)W'(a) + \frac{1}{2!}(x-a)^2 W''(a) + \cdots \\ &= W(a) + \frac{1}{2}(x-a)^2 W''(a) \\ &= \frac{1}{2}kx^2\end{aligned}$$

  - We reduce by noting that $W'(a) = 0$ at the minimum of the potential well, we can let $W(a) = 0$, and we can set $a = 0$ to be the origin of our coordinate system.

- The Schrödinger equation describing this system is

$$-\frac{\hbar}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi(x) + \frac{1}{2}m\omega^2 x^2 \psi(x) = E\psi(x)$$

  - Note that since $\omega = \sqrt{k/m}$, we substituted $k = m\omega^2$.

- If we let $x = y\sqrt{\hbar/m\omega}$ and $E = \omega\hbar\epsilon/2$, then we can simplify the above to the form

$$\frac{\mathrm{d}^2}{\mathrm{d}y^2}\psi(y) + (\epsilon - y^2)\psi(y) = 0$$

- Asymptotic solution: In the limit of large y, the finite value of ϵ becomes negligible, that is

$$\frac{\mathrm{d}^2}{\mathrm{d}y^2}\psi(y) - y^2\psi(y) = 0$$

- General form solution:

$$\psi(y) = y^p \mathrm{e}^{-y^2/2}$$

  - This is the Gaussian exponential.
  - p is any integer.

- Because the sign of the exponential must be negative for the wave function to be bounded, we have the form

$$\psi(y) = \mathrm{e}^{-y^2/2}H(y)$$

  where $H(y)$ are polynomials.

- Hermite equation:

$$\frac{\mathrm{d}^2}{\mathrm{d}y^2}H(y) - 2y\frac{\mathrm{d}}{\mathrm{d}y}H(y) - (\epsilon - 1)H(y) = 0$$

  - Whenever $H(y)$ solves this equation, it yields a full solution.

- What are the correct polynomials?
  - The polynomials that are even about the origin will give us the even solutions, and vice versa for the odd ones.
  - Even solution: Because the potential has a definite parity (even-ness or odd-ness), we know that the solution to the polynomials must be even or odd.
  - Expanding in an infinite power series:

$$H(y) = \sum_{j=0}^{\infty} c_j y^{2j}$$

- This is the power series solution to differential equations. We have to plug into the differential equation and get a recursion relation.
  - Upon substitution,
$$\sum_{j=0}^{\infty}\left(2j(2j-1)c_jy^{2j-2}+(\epsilon-1-4j)c_jy^{2j}\right)=0$$
  - The indices are arbitrary, so
$$\sum_{j=0}^{\infty}(2(j+1)(2j+1)c_{j+1}+(\epsilon-1-4j))y^{2j}=0$$
  - Recursion relation: The whole coefficient above must equal 0 for all j, but that gives us a relationship between c_j and c_{j+1}! Explicitly,
$$c_{j+1}=\frac{4j+1-\epsilon}{2(j+1)(2j+1)}c_j$$
- How do we know when to stop?
  - If the recursion never stops, then the ratio is approximately equal to
$$\frac{c_{j+1}}{c_j}=\frac{1}{j}$$
  - But this means that asymptotically, the boundary conditions will be violated because it will keep expanding. The probability of finding the particle will actually diverge (infinite probability at infinite distances). Thus, the expansion procedure *must* terminate.
  - The truncation of this expansion requires us to pick a particular energy ϵ (in particular, one such that $\epsilon=4j+1$).
- Test on Friday:
  - 5 questions. Each question is approximately 20 points.
  - There will be a formula page in the back with formulas and constants.
  - There will be a periodic table provided.
  - Topics: Everything in problem sets 1-2. BB radiation, Photoelectric effect, SG experiment, particle-wave duality, Heisenberg uncertainty relations, Gaussian wave packets and their role in the Heisenberg uncertainty, de Broglie formula, free particles, particle in a box, potential step, and a bit of the harmonic oscillator.
  - Study for it by going back to the problem sets and seeing which ones might be doable in a 50 minute test.
  - Go back to your notes and review some of the key highlights of each of the topics in the topic list.
  - You're allowed to use a calculator. The test won't be too calculator-heavy though.
  - Deriving vs. understanding and applying: Emphasis on applying and getting answers.

3.2 Harmonic Oscillator (cont.)

10/13:

- Assume that the $(n+1)^{\text{th}}$ coefficient vanishes by the recurrence relation; this causes the energy to be quantized.
  - Therefore, $\epsilon=4n+1$.

- For each value of n, there is an even Hermite polynomial[1].
  - Thus, our even solutions include $H_0(y) = 1$, $H_2(y) = 4y^2 - 2$, $H_4(y) = 16y^4 - 48y^2 - 2$, for example.
- Odd solutions:
  - Let
$$H(y) = \sum_{j=0}^{\infty} d_j y^{2j+1}$$
  - Our recurrence relation works out to be
$$d_{j+1} = \frac{4j+3-\epsilon}{2(j+1)(2j+3)} d_j$$
  - Again, if it does not terminate, $d_{j+1}/d_j \approx 1/j$, so the solutions will blow up at the edges due to the high powers of y. Therefore, the series must truncate.
  - If the coefficient at n exists but the next one will vanish, it must be true that $4n + 3 = \epsilon$.
  - Example odd solutions: $H_1(y) = 2y$, $H_3(y) = 8y^3 - 12y$, $H_5(y) = 32y^5 - 160y^3 + 120y$.
    - Note that you can make the coefficients pretty much of any scale because they will be normalized later as part of the wave function.
- Energies and wave functions:
  - The energy levels are $\epsilon_n = 2n + 1$ for $n = 0, 1, 2, \ldots$ or $E_n = (n + \frac{1}{2})\hbar\omega$ for $n = 0, 1, 2, \ldots$.
  - It follows that if $\psi(y) = N_y \mathrm{e}^{-y^2/2} H_n(y)$, where
$$N_y = \frac{1}{\sqrt{2^n n! \sqrt{\pi}}}$$
  - In terms of x, we get
$$N_x = \sqrt[4]{\frac{\omega m}{\hbar}} N_y$$
  - Observations:
    1. The energy levels are quantized (discrete).
    2. The energy levels are equally spaced apart where $\Delta E = \hbar\nu$.
    3. The energy levels are non-degenerate.
    4. The zero-point energy is equal to $\hbar\omega/2$. (Recall that the finite energy is there due to the Uncertainty Relation.)
    5. Similar to the levels discovered by Max Planck.
- Classical harmonic oscillator:
  - Position: $x = x_0 \sin(\omega t)$.
  - Velocity: $v = \cos x_0 \sin(\omega t)$.
  - Energy: $E = m\omega^2 x_0^2/2$.
  - Turning point: $x_0 = \sqrt{2E/m\omega^2}$.
  - Probability of the oscillator being at x:
$$P(x)\,\mathrm{d}x = \frac{\frac{2\mathrm{d}x}{v}}{T} = \frac{\mathrm{d}x}{\pi\sqrt{x_0^2 - x^2}}$$

[1] So named because they were studied by the mathematician Charles Hermite before they were utilized in Quantum Mechanics.

- Thus, classically, the oscillator spends most of its time at the turning points (this makes intuitive sense because a pendulum slows down at the turning points, spending more time there).
- In quantum mechanics, we don't have a hard turning point the way we do classically.
- Classical limit of quantum theory: In higher and higher order Hermite polynomials, the probability gets pushed to the edges.