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Lecture 2 – Mechanics and Phase Space

I. Classical Mechanics

A. Newtonian Mechanics

We have talked about the statistics part of statistical mechanics, now we need a quick review of the mechanics part.

Aside: Why the multiple names: Statistical mechanics or statistical thermodynamics? They are equivalent. The former emphasizes the connection to physics.

The mechanics that you learned in introductory physics is Newtonian mechanics. For a set of N particles, Newton's Second Law is:

$$m_i \frac{d^2 \underline{r}_i}{dt^2} = \underline{F}_i$$

$\underline{r}_i$: position vector of particle i

$\underline{F}_i$: force on particle i

m_i : mass of particle i

Often, the force on a particle can be described by a potential, U. They are related by

$$\underline{F}_i = -\frac{\partial U}{\partial \underline{r}_i} = -\underline{\nabla}_i U \qquad U = U(\underline{r}_1, \underline{r}_2, \ldots, \underline{r}_N)$$

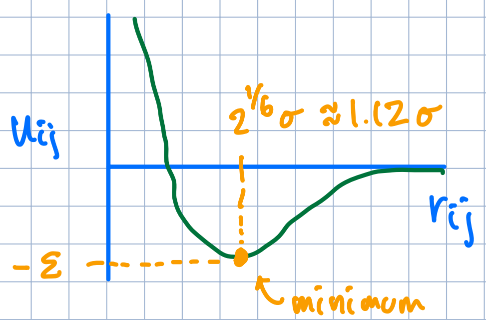
If there are no external forces, and only interactions between particles, then the total potential U can be simplified to a sum of pairwise potentials between the particles.

$$U = \sum_{i<j} u_{ij}(|\underline{r}_i - \underline{r}_j|)$$

$u_{ij}(r_{ij})$: pairwise potential

$r_{ij} = |\underline{r}_i - \underline{r}_j|$

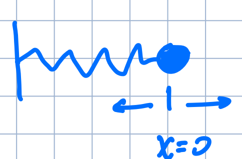
Example: Lennard Jones Potential



$$u_{ij}(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

We are going to need to compare Newtonian mechanics to two other types of mechanics (Lagrangian and Hamiltonian), so I want to do a simple example. We will also want a solved problem to discuss the concept of phase space.

Example: Harmonic Oscillator



Spring potential : $U = \frac{1}{2}kx^2$

particle mass : m

initial conditions: $x(0) = x_0$, $v(0) = v_0$

Newton's equation of motion:

$$m\frac{d^2x}{dt^2} = F \qquad F = -\frac{\partial U}{\partial x} = -\frac{\partial}{\partial x}\left(\frac{1}{2}kx^2\right) = -kx$$

$$m\frac{d^2x}{dt^2} = -kx \Rightarrow \frac{d^2x}{dt^2} + \frac{k}{m}x = 0 \qquad \text{let } \omega = \sqrt{\frac{k}{m}}$$

$$[=]\sqrt{\frac{kg}{s^2}\cdot\frac{1}{kg}}$$

$$\frac{d^2x}{dt^2} + \omega^2 x = 0 \qquad \omega \text{ is a frequency}$$

$$[=]\sqrt{1/s^2} = 1/s$$

This is a second order, homogeneous ODE. ω^2 is always positive, so solutions are given by:

$$x(t) = A\sin(\omega t) + B\cos(\omega t) \quad , A \,\&\, B \text{ are constants}$$

Solving for A and B from the initial condition,

$$x(0) = A\sin(0) + B\cos(0) = B = x_0$$

$$v(t) = \frac{dx}{dt} = A\omega\cos(\omega t) - B\omega\sin(\omega t)$$

$$v(0) = A\omega\cos(0) - B\omega\sin(0) = A\omega = v_0 \,,\quad A = \frac{v_0}{\omega}$$

So, the final solution is

$$\boxed{\begin{aligned} x(t) &= \frac{v_0}{\omega}\sin(\omega t) + x_0\cos(\omega t) \\ v(t) &= v_0\cos(\omega t) - x_0\omega\sin(\omega t) \end{aligned}}$$

B. Lagrangian Mechanics

Lagrange thought of mechanics differently than Newton. Rather than thinking of forces and inertia, he thought that Nature in some ways always acted optimally. So, in this way of thinking, the equations that govern dynamics minimize something. This something is called the action.

$$\underset{\text{action}}{S} = \int_{t_1}^{t_2} \underset{\text{Lagrangian}^*}{L(\underline{q}_i, \dot{\underline{q}}_i, t)}$$

$\underline{q}_i$: generalized coordinates

$\dot{\underline{q}}_i$: generalized velocities

* shorthand for: $L(\underline{q}_1, \underline{q}_2, \dots, \underline{q}_N, \dot{\underline{q}}_1, \dot{\underline{q}}_2, \dots, \dot{\underline{q}}_N, t)$ N particles

The generalized coordinates can be x, y, z, or they can be a coordinate transformation like r, θ, ϕ in spherical coordinates. The generalized velocities are time derivatives of the generalized coordinates. Mathematically, this is represented as

$$
\begin{aligned}
\underline{r}_1 &= \underline{r}_1(\underline{q}_1, \underline{q}_2, \dots, \underline{q}_N) \\
\underline{r}_2 &= \underline{r}_2(\underline{q}_1, \underline{q}_2, \dots, \underline{q}_N) \\
&\vdots \\
\underline{r}_N &= \underline{r}_N(\underline{q}_1, \underline{q}_2, \dots, \underline{q}_N)
\end{aligned}
\quad \text{or} \quad
\begin{aligned}
\underline{q}_1 &= \underline{q}_1(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N) \\
\underline{q}_2 &= \underline{q}_2(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N) \\
&\vdots \\
\underline{q}_N &= \underline{q}_N(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N)
\end{aligned}
$$

The Lagranginan is like a "cost" that the particles pay. The action is a sum of the cost, and minimizing the action gives us the path or trajectory with the least cost.

Minimizing the action functional gives the Euler-Lagrange equations for the i^{th} particle

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\underline{q}}_i}\right) - \frac{\partial L}{\partial \underline{q}_i} = 0. \qquad i = 1, 2, \dots, N$$

The Lagrangian is given by

$$L = K(\dot{\underline{q}}_i) - U(\underline{q}_i)$$

K: kinetic energy

U: potential energy

So, the system "wants" to chart a path that balances kinetic energy and potential energy.

Let's show that the Euler-Lagrange equations give us the same thing as Newton's 2nd Law.

Equivalence of Lagrangian and Newtonian Mechanics:

Euler-Lagrange equation:

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}}\right) - \frac{\partial L}{\partial q} = 0$$

1 particle, constant m

$q = x$

$\dot{q} = \dot{x} = v$

Lagrangian:

$$L = K - U$$

$$K = \frac{1}{2}mv^2$$

Put together:

$$\frac{d}{dt}\left[\frac{\partial}{\partial v}\left(\frac{1}{2}mv^2\right)\right] - \frac{\partial}{\partial x}\left(\frac{1}{2}mv^2 - U\right) = 0$$

doesn't depend on x

$$\frac{d}{dt}\left[mv\right] + \frac{\partial U}{\partial x} = 0$$

$$m\frac{dv}{dt} = -\frac{\partial U}{\partial x} \Rightarrow \boxed{ma = F}$$

So, the Lagrangian way of doing mechanics is equivalent.

Why learn it?

- It can solve some problems much more easily.
  - problems with constraints
  - problems in different coordinates (no messy coordinate transforms)

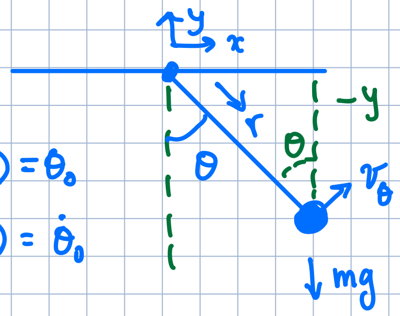
  The Euler-Lagrange Eq. is invariant to coordinate transforms (proof in book). This is the reason for "generalized coordinates!"
- It comes up in stat thermo. "Story of your Life", Ted Chiang
- Additional physical principle / way of understanding the world.
- Connection to Hamiltonian mechanics (next)

To conclude, lets solve an example problem with it.

Example: Pendulum with a Lagrangian

$\theta(0) = \theta_0$

$\dot{\theta}(0) = \dot{\theta}_0$



What is our generalized coordinate?

r, θ? x, y? could be any.

θ is the easiest.

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\theta}}\right) - \frac{\partial L}{\partial \theta} = 0 \qquad L = K - U$$

What is the kinetic energy?

$$K = \frac{1}{2} m v^2$$

$$v = r \cdot \dot{\theta} \Rightarrow K = \frac{1}{2} m r^2 \dot{\theta}^2$$

What is the potential energy? Assume $U = 0$ at $y = -r$, the bottom of the pendulum.

$$U = mg(y + r)$$

$$y = -r\cos\theta \Rightarrow U = mg(r - r\cos\theta)$$

Combine to get L:

$$L = K - U = \frac{1}{2} m r^2 \dot{\theta}^2 - mgr(1 - \cos\theta)$$

$$\frac{\partial L}{\partial \dot{\theta}} = m r^2 \dot{\theta}$$

$$\frac{\partial L}{\partial \theta} = -mgr\sin\theta$$

Plug into Euler-Lagrange Eq:

$$\frac{d}{dt}\left(m r^2 \dot{\theta}\right) + mgr\sin\theta = 0 \qquad m, g, r \text{ are constants}$$

$$m r^2 \ddot{\theta} + mgr\sin\theta = 0 \Rightarrow \frac{d^2\theta}{dt^2} + \frac{g}{r}\sin\theta = 0$$

This is a nonlinear 2^{nd} order ODE. We can solve it numerically or in the case where $\theta \ll 1$. In the latter case:

$$\sin\theta \simeq \theta + \frac{1}{2}\theta^2 + \dots$$ keep to 1^{st} order only.

$$\frac{d^2\theta}{dt^2} + \frac{g}{r}\theta = 0 \qquad \theta(0) = \theta_0, \quad \dot{\theta}(0) = \dot{\theta}_0$$

same equation as harmonic motion, but $\omega^2 = g/r$.

$$\theta(t) = \frac{\dot{\theta}_0}{\omega}\sin(\omega t) + \theta_0\cos(\omega t)$$

$$\dot{\theta}(t) = \dot{\theta}_0\cos(\omega t) + \theta_0 \omega \sin(\omega t)$$

$$\omega = \sqrt{g/r}$$

check units:

θ = rad, $\dot{\theta}$ = rad/s

$$\omega = \sqrt{\frac{cm/s^2}{cm}} = \sqrt{\frac{1}{s^2}} = \frac{1}{s} \checkmark$$

For the numerical solution:

$$\frac{d^2\theta}{dt^2} + \omega^2\sin\theta = 0, \quad \omega^2 = g/r \Rightarrow \frac{d\dot{\theta}}{dt} = -\omega^2\sin\theta, \quad \dot{\theta}(0) = \dot{\theta}_0$$

$$\frac{d\theta}{dt} = \dot{\theta}, \quad \theta(0) = \theta_0$$

C. Hamiltonian Mechanics and Phase Space

Lagrangian mechanics have some advantages over Newtonian mechanics such as easier coordinate transforms and the ability to more easily incorporate constraints. However, statistical mechanics is usually expressed in terms of Hamiltonian mechanics. I will first explain the equations and then provide some perspective on why it is used and what it has to do with phase space.

In Hamiltonian mechanics, we work with generalized coordinates again. However, a key difference is that we use a generalized momentum p_i, rather than a generalized velocity. The generalized momentum is defined in terms of the Lagrangian:

$$p_i = \frac{\partial L}{\partial \dot{q}_i} \quad i = 1, 2, \ldots, 3N$$

Note the change in indexing from Lagrangian Mechanics. We are "flattening" the 2D array to 1D.

What is the generalized momentum? Just like we have the gen. coordinate and gen. velocity, this provides a definition of a momentum that is invariant to coordinate transformations. It makes our life easier with different coordinate systems.

With this new coordinate (that replaces $\dot{q}_i$), we can define a new quantity called the Hamiltonian by a Legendre transform of the Lagrangian:

$$H(q_i, p_i, t) = \sum_i \dot{q}_i p_i - L(q_i, \dot{q}_i, t) \qquad (1)$$

What is the Hamiltonian and what does it mean? It is usually the total energy (except in rare circumstances).

When is the Hamiltonian equal to the Energy?
(1) the coordinate transform is time independent
(2) the potential is velocity independent

Demonstration that H is the total energy

$$L = K(\dot{q}) - U(q)$$ Assume cartesian, 1D

$$L = \frac{1}{2}mv^2 - U \qquad p = \frac{\partial L}{\partial \dot{q}} = \frac{\partial L}{\partial v} = mv$$

conventional definition of momentum

$$H = \dot{q}p - L$$
$$= vp - L = v \cdot mv - \frac{1}{2}mv^2 + U$$
$$= \frac{1}{2}mv^2 + U$$

$$\boxed{H = K + U}$$

Using the total derivative dH, the derivative of equation (1), and the Euler Lagrange equation gives Hamilton's equations,

$$\boxed{\frac{dq_i}{dt} = \frac{\partial H}{\partial p_i} \quad , \quad \frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i}}$$

Two 1st order ODEs instead of one 2nd order ODE.

It is often the case in stat mech that we have quantities that are functions of the p_i and q_i (e.g. pressure). We can use Hamilton's equations to describe the dynamics of these quantities too.

Consider a quantity f that is a function of the p_i, q_i and time,

$$f = f(q_i, p_i, t) \qquad i = 1, 2, \ldots, 3N$$

The total derivative of f is given by

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \sum_{i=1}^{3N} \left(\frac{\partial f}{\partial q_i}\frac{dq_i}{dt} + \frac{\partial f}{\partial p_i}\frac{dp_i}{dt} \right)$$

$\frac{df}{dt}$: total change as f moves through phase space

$\frac{\partial f}{\partial t}$: change of f at one point in phase space.

Now, using Hamilton's equations

$$\frac{dq_i}{dt} = \frac{\partial H}{\partial p_i} \;, \quad \frac{\partial p_i}{\partial t} = -\frac{\partial H}{\partial q_i}$$

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \sum_{i=1}^{3N} \left(\frac{\partial f}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial f}{\partial p_i}\frac{\partial H}{\partial q_i} \right)$$

analogous to the material derivative. How does f change as if is convected through phase space?

There is a compact way of writing the sum on the right-hand side. It is called a Poisson bracket

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \{f, H\}$$

← equation of motion of f.

$$\{A, B\} = \sum_{i=1}^{3N} \left(\frac{\partial A}{\partial q_i}\frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i}\frac{\partial B}{\partial q_i} \right).$$

Why use Hamilton's E.O.M rather than Newton or Lagrange?

(1) Like Lagrange, better coordinate transforms than Newton's E.O.M.

(2) Two 1st order ODEs can sometimes make life easier especially when numerically integrating.

The real value of Hamiltonian mechanics is conceptual, rather than practical.

Key Concept 1: Geometry

Let us call the 6N-dimensional space (where N is the number of particles) defined by the Lagrangian variables q_i and $\dot{q}_i$ state space. In addition, let us call the 6N-dimensional space defined by the Hamiltonian canonical variables q and p phase space.

Phase space has an important property that state space is not guaranteed to have. Phase space has a symplectic geometry. A symplectic geometry means that the volume of phase space doesn't change with time. The space is incompressible.

A perhaps simplistic way to think about this is that

$$\int dq_1 \, dq_2 \cdots dq_{3N} \, dp_1 \, dp_2 \cdots dp_{3N} = \text{const}$$

← guaranteed for p_i but not for $\dot{q}_i$.

This is a critical mathematical property, because it allows us to define a probability density. If phase space changed volume, then we could not normalize probabilities.

Another way to think about this is that p_i are the "proper" variables. They are the correct "conjugate" variable to q.

Show Python Example with symplectic and non-symplectic system.

There is an important theorem for statistical thermodynamics that results from this property. Suppose that $\rho = \rho(q_i, p_i, t)$ is the probability density of a given instance of a set of molecules having the positions q_i and momenta p_i. The symplectic property of phase space implies that phase space is like an incompressible fluid, i.e. that the density is constant. Mathematically, this is expressed as

Poisson Bracket

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \{\rho, H\} = 0$$

$$\boxed{\begin{aligned} \frac{\partial \rho}{\partial t} &= -\{\rho, H\} \\ \frac{\partial \rho}{\partial t} &= -\sum_{i=1}^{3N}\left(\frac{\partial \rho}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i}\frac{\partial H}{\partial q_i}\right) \end{aligned}}$$

Liouville's Theorem
or
Liouville's Equation

change in prob density at a given point in phase space = − change in prob density as system moves in phase space.

This is a foundational equation for non-equilibrium stat mech. We will come back to it later. For now, just note that phase space has this important property.

Finally, note that Liouville's equation also applies at equilibrium. Here,

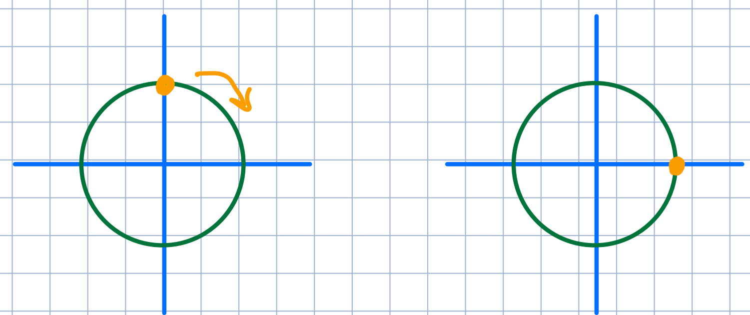
$$\frac{\partial \rho}{\partial t} = 0 \Rightarrow \{\rho, H\} = 0 \text{ and } \rho = \rho_{eq}$$

Key concept 2: Symmetry

Above, we saw that dynamics can be thought of as motion in phase space. What does symmetry of this motion imply?

First, what do we mean by symmetry? We mean that when we do some kind of transformation, something doesnt change.

Example:



Rotation of a circle leaves the shape unchanged.

So, it is rotationally invariant or rotationally symmetric.

Invariance of the equations of motion to transformation are kinds of symmetries as well.

Noether's theorem says that if the system's dynamics have a symmetry, then this implies there is a conserved quantity that corresponds to that symmetry.

Example: time invariance.

Suppose that $H = H(q_i, p_i)$, not a function of time.

$$\frac{dH}{dt} = \frac{\partial H}{\partial t} + \{H, H\} \qquad \frac{\partial H}{\partial t} = 0 \text{ is implied from above}$$

$$\frac{dH}{dt} = \{H, H\} = \sum_{i=1}^{3N}\left(\frac{\partial H}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial H}{\partial p_i}\frac{\partial H}{\partial q_i}\right) = 0$$

Time invariance implies that H doesn't change.

$\left(\frac{\partial H}{\partial t} = 0\right)$ $\left(\frac{dH}{dt} = 0\right)$

In other words, energy is conserved if the equations of motion don't depend on time!

Other examples that I won't prove are that translational symmetry in phase space means that linear momentum is conserved and rotational symmetry in phase space means that angular momentum is conserved.

If the Hamiltonian doesn't explicitly depend on time, conserved quantities can be identified using the Poisson bracket

$$\frac{df}{dt} = \overbrace{\cancel{\frac{\partial f}{\partial t}}}^{0 \text{ if } f \neq f(t)} + \{f, H\}$$

therefore if $\{f, H\} = 0$ $\quad \frac{df}{dt} = 0$. f is a constant of motion or f is "conserved."

Example : Linear momentum is conserved

$$\{p_j, H\} = \sum_{i=1}^{3N}\left[\frac{\partial p_j}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial p_j}{\partial p_i}\frac{\partial H}{\partial q_i}\right] = -\frac{\partial H}{\partial q_j} = -\frac{\partial V}{\partial q_j}$$

zero b/c p & q. are independent variables

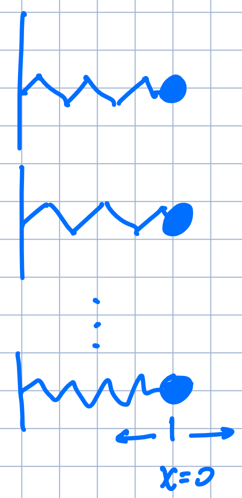
$\delta_{ij} = 0$ for all $i \neq j$. 1 for $i = j$

$H = T(p) + V(q)$

if $V \neq V(q_j)$ then $\frac{\partial V}{\partial q_j} = 0$

translational invariance in q_j

Example: N-component harmonic oscillator



spring potential: $U = \sum_i \frac{1}{2} k x_i^2$ ← spring constant

kinetic energy: $K = \sum_i \frac{1}{2} m v_i^2$ ← particle mass

initial conditions:

$$x_i(0) = x_{i,0} \quad v_i(0) = v_{i,0}$$

Compare and contrast with Lagrangian formalism.

$$L = K - U \qquad q_i = x_i \quad \dot{q}_i = v_i$$

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) - \frac{\partial L}{\partial q_i} = 0 \Rightarrow \frac{d}{dt}\left(\frac{\partial L}{\partial v_i}\right) - \frac{\partial L}{\partial x_i} = 0$$

$$L = \sum_i \left[\frac{1}{2} m v_i^2 - \frac{1}{2} k x_i^2\right] \qquad \frac{\partial L}{\partial v_i} = m v_i \quad \frac{\partial L}{\partial x_i} = k x_i$$

$$\frac{d}{dt}\left(m v_i\right) - k x_i = 0 \Rightarrow m \frac{dv_i}{dt} - k x_i = 0$$

$$\frac{dv_i}{dt} - \frac{k}{m} x_i = 0$$

$$\boxed{\begin{array}{l} \dfrac{dv_i}{dt} - \omega^2 x_i = 0 \ , \quad \omega^2 = k/m \\ v_i(0) = v_{i,0} \quad x_i(0) = x_{i,0} \end{array}}$$

Hamiltonian formalism

$$H = K + U \qquad q_i = x_i \qquad p_i = \frac{\partial L}{\partial \dot{q}_i} = \frac{\partial L}{\partial v_i} = m v_i \Rightarrow v_i = p_i/m$$

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \qquad \dot{p}_i = -\frac{\partial H}{\partial q_i}$$ Hamilton's equations

$$\frac{dx_i}{dt} = \frac{\partial H}{\partial p_i} \qquad \frac{dp_i}{dt} = -\frac{\partial H}{\partial x_i}$$

$$H = \sum_i \left[\frac{1}{2} m v_i^2 + \frac{1}{2} k x_i^2\right] = \sum_i \left[\frac{p_i^2}{2m} + \frac{1}{2} k x_i^2\right]$$

$$\frac{\partial H}{\partial p_i} = \frac{p_i}{m} \qquad \frac{\partial H}{\partial x_i} = k x_i$$

$$\boxed{\begin{array}{ll} \dfrac{dx_i}{dt} = \dfrac{p_i}{m} & \dfrac{dp_i}{dt} = -k x_i \\ x_i(0) = x_{i,0} & p_i(0) = m v_i(0) \end{array}}$$

What about if we add friction (a damped oscillator)? We don't get Hamilton's equations, because the system is not conservative. The equations of motion are:

$$\frac{dx_i}{dt} = \frac{p_i}{m}, \quad \frac{dp_i}{dt} = -k x_i - \gamma p_i$$

$$x_i(0) = x_{i,0}, \quad p_i(0) = m v_i(0)$$

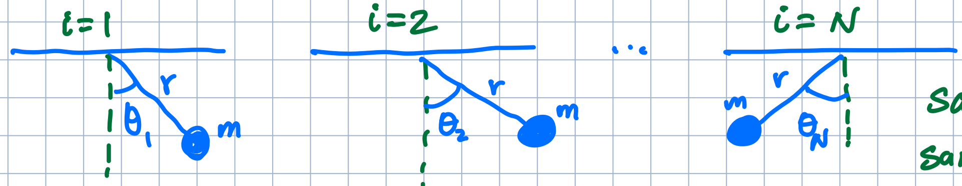
friction proportional to p_i with friction coefficient γ.

γ has units of $\frac{1}{\text{time}}$.

D. Some Extra Examples

Example: N-component pendulum using Hamiltonian mechanics

Compare and contrast with the Lagrangian framework above.



Same mass, m
same length, r

$$K = \sum_i \frac{1}{2} m r^2 \dot{\theta}_i^2$$

$$U = \sum_i \frac{1}{2} mg(r - r\cos\theta_i)$$

$$H = K + U = \sum_i \left[\frac{1}{2} m r^2 \dot{\theta}_i^2 + \frac{1}{2} mg(r - r\cos\theta_i)\right]$$

Need to write in terms of generalized momenta

$$p_i = \frac{\partial L}{\partial \dot{q}_i} = \frac{\partial L}{\partial \dot{\theta}_i} = \frac{\partial K}{\partial \dot{\theta}_i} = mr^2 \dot{\theta}_i \Rightarrow \dot{\theta}_i = \frac{p_i}{mr^2}$$

$$H = \sum_i \left[\frac{1}{2} \frac{p_i^2}{mr^2} + \frac{1}{2} mg(r - r\cos\theta_i) \right]$$ find H in terms of p_i

Now get the equations of motion

$$\frac{dq_i}{dt} = \frac{\partial H}{\partial p_i}, \quad \frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i} \Rightarrow \frac{d\theta_i}{dt} = \frac{\partial H}{\partial p_i} \quad \frac{dp_i}{dt} = -\frac{\partial H}{\partial \theta_i}$$

convert to θ_i, p_i

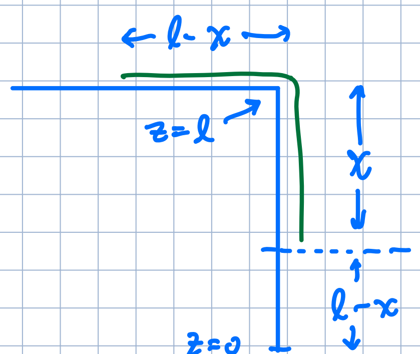
we need these derivatives

$$\frac{\partial H}{\partial p_i} = \frac{p_i}{mr^2} \qquad \frac{\partial H}{\partial \theta_i} = \frac{1}{2} mgr\sin\theta$$

now substitute back into Hamilton's Eq's.

$$\boxed{\begin{array}{ll} \dfrac{d\theta_i}{dt} = \dfrac{p_i}{mr^2} & \dfrac{dp_i}{dt} = -\dfrac{1}{2} mgr\sin\theta \\ \theta_i(0) = \theta_{i,0} & p_i(0) = mr^2 \dot{\theta}_{i,0} \end{array}}$$

Example: Chain sliding off a table



chain length: l } mass density

chain mass: m } $\lambda = \frac{m}{l}$

kinetic energy: $K = \frac{1}{2} \lambda l v^2$

$= \frac{1}{2} m v^2$

Potential energy: $U = \int F \, dz$

$= \int mg \, dz$

more potential energy:

- need a function for $m(z)$:

$$\left.\begin{aligned} m=0 &\quad \text{when} \quad z=\ell-x \\ m=\lambda x &\quad \text{when} \quad z=\ell \end{aligned}\right\}$$

slope $=\lambda$

$m=\lambda z+\text{const}$ ← solve for const

$0=\lambda(\ell-x)+\text{const}$

$\text{const}=\lambda(x-\ell)$

$m(z)=\lambda(z+x-\ell)$

- Now integrate to find U:

$$U=\int_{\ell-x}^{\ell} m(z)\,g\,dz$$

$$=\int_{\ell-x}^{\ell}\lambda g(z+x-\ell)\,dz=\int_{\ell-x}^{\ell}\lambda g z\,dz+\int_{\ell-x}^{\ell}\lambda g(x-\ell)\,dz$$

$$=\left[\frac{\lambda g z^2}{2}+\lambda g(x-\ell)z\right]_{\ell-x}^{\ell}=\frac{1}{2}\lambda g\ell^2+\lambda g(x-\ell)\ell-\frac{1}{2}\lambda g(\ell-x)^2+\lambda g(\ell-x)^2$$

$$=-\frac{1}{2}\lambda g\ell^2+\lambda g\ell x+\frac{1}{2}\lambda g(\ell-x)^2$$

$$=-\tfrac{1}{2}\cancel{\lambda g\ell^2}+\lambda g\cancel{\ell}x+\frac{1}{2}\lambda g(\cancel{\ell^2}-\cancel{2\ell x}+x^2)$$

$$=\frac{1}{2}\lambda g x^2$$

so, $K=\frac{1}{2}\lambda\ell v^2$ & $U=\frac{1}{2}\lambda g x^2$

$L=K-U$, $\quad \frac{\partial L}{\partial v}=\frac{\partial K}{\partial v}=\lambda\ell v$, $\quad \frac{\partial L}{\partial x}=\frac{\partial U}{\partial x}=\lambda g x$

$$\frac{d}{dt}\left(\frac{\partial L}{\partial v}\right)-\frac{\partial L}{\partial x}=0 \quad\Rightarrow\quad \frac{d}{dt}(\lambda\ell v)-\lambda g x=0$$

$$\frac{dv}{dt}=\frac{g}{\ell}x$$

$$\boxed{\frac{d^2x}{dt^2}=\frac{g}{\ell}x}$$

II. Quantum Mechanics

Classical mechanics is great for many, many situations. However, if particles are small enough, their quantum nature needs to be accounted for. We will quantify what "small enough" means in a few minutes.

One quick note: I am not a quantum mechanics guy, so please forgive some of my ignorance in this area.

A. Mathematics of waves

It really helps in Q.M. to be familiar with waves.
Let's quickly review.

Classical wave equation in 1D:

$$\frac{\partial^2 u}{\partial t^2} = c^2 \frac{\partial^2 u}{\partial x^2}$$

u: thing propagating
t: time
c: wave propagation speed
x: space

Solution for a traveling wave:

$$u = A e^{-i(kx-\omega t)} + B e^{i(kx-\omega t)}$$

k: wave number $\left(\frac{rad}{cm}\right)$
ω: angular frequency $\left(\frac{rad}{s}\right)$
A, B: constants determined by ICs, BCs

$\omega = 2\pi f$ (f: frequency) $k = 2\pi/\lambda$ (λ: wavelength; k: continuous wavenumber) $\omega = kc$

Recall (Euler's formula):

$e^{i\theta} = \cos\theta + i\sin\theta$

$\sin\theta = (e^{i\theta} - e^{-i\theta})/2i$

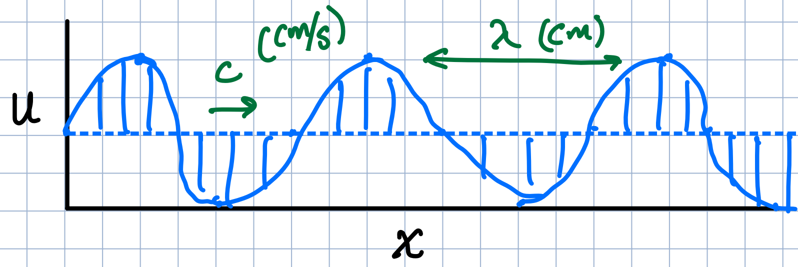
$\cos\theta = (e^{i\theta} + e^{-i\theta})/2$

Solution for a standing wave (single mode):

$$u = (a e^{-i\omega_n t} + b e^{i\omega_n t})(c e^{-ik_n x} + d e^{ik_n x})$$

discrete wavenumber

Note for future lectures: Work these two examples out more carefully.



$f = c/\lambda = \frac{\#\text{ waves}}{\text{time}}$ $\left(\frac{\text{cycles}}{s}\right)$

(i) Work out the solution for the traveling wave

$$\frac{\partial^2 \hat{u}}{\partial t^2} = c^2(-k^2\hat{u}) = -k^2c^2\hat{u}$$

$$\frac{\partial^2 \hat{u}}{\partial t^2} + k^2c^2\hat{u} = 0 \qquad kc = \omega$$

2nd order, linear, homogeneous.

constant coefficient

Fourier transform

$$\hat{u} = \int e^{-ikx} u(x,t)\,dx$$

$$u = \frac{1}{2\pi}\int e^{ikx}\hat{u}(k,t)\,dx$$

$$\omega^2 > 0 \rightarrow \text{sines } \& \text{ cosines}$$

$$\hat{u} = A(k)e^{ikct} + B(k)e^{-ikct} = A(k)e^{i\omega t} + B(k)e^{-i\omega t}$$

Boundary conditions for a traveling wave with a single wavelength, λ_0: $k_0 = 2\pi/\lambda_0$, $\omega_0 = ck_0$

$$\lim_{x\to-\infty} u(x,t) = \lim_{x\to\infty} u(x,t) = a e^{i(k_0x - \omega_0 t)}$$ Definition of the B.C.

$$\hat{u}(-\infty,t) = \hat{u}(\infty,t) = 2\pi a e^{-i\omega_0 t}\delta(k-k_0)$$ Take F.T. of B.C.

Matching with our solution gives:

$$\hat{u}(k,t) = 2\pi a\, e^{-i\omega t}\delta(k-k_0) = A(k)e^{i\omega t} + B(k)e^{-i\omega t}$$

$$A(k) = 0 \qquad B(k) = 2\pi a\,\delta(k-k_0)$$

Now take the inverse Fourier transform

$$\boxed{u(x,t) = a\, e^{i(k_0 x - \omega_0 t)}}$$

← the single mode traveling wave we proscribed at the boundaries.

(ii) Work out a solution for a standing wave

Solve by separation of variables

$$\frac{\partial^2 u}{\partial t^2} = c^2 \frac{\partial^2 u}{\partial x^2} \qquad \text{let } u = f(t)\, g(x)$$

$$\frac{\partial^2 (fg)}{\partial t^2} = c^2 \frac{\partial^2 (fg)}{\partial x^2} \Rightarrow g \frac{\partial^2 f}{\partial t^2} = c^2 f \frac{\partial^2 g}{\partial x^2}$$

$$\frac{1}{c^2}\frac{1}{f}\frac{\partial^2 f}{\partial t^2} = \frac{1}{g}\frac{\partial^2 g}{\partial x^2} = -\gamma^2$$

← must equal a constant because LHS = fn of t and RHS = fn of x.

must be negative because exponential growth won't satisfy physical B.C.s

Solve time ODE for f(t):

$$\frac{d^2 f}{dt^2} = -\gamma^2 c^2 f \Rightarrow \frac{d^2 f}{dt^2} + \gamma^2 c^2 f = 0$$

← 2nd order, linear, constant coefficient gives sines & cosines.

$$f(t) = a\, e^{-i\gamma c t} + b\, e^{i\gamma c t}$$

← a or b depends on ICs.

Solve space ODE for g(x):

$$\frac{d^2 g}{dx^2} = -g\gamma^2 \Rightarrow \frac{d^2 g}{dx^2} + g\gamma^2 = 0$$

← Again, 2nd order, linear constant coefficient. Gives sines & cosines.

$$g(x) = c\, e^{-i\gamma x} + d\, e^{i\gamma x}$$

When stationary, only fixed values of γ are allowed.

Example: $g(0) = 0$, $g(2\pi) = 0$ (string w/ fixed ends)

$$g(0) = c e^0 + d e^0 = c + d = 0 \quad \Rightarrow c = -d$$

$$g(2\pi) = c e^{-i\gamma(2\pi)} + d e^{i\gamma(2\pi)}$$

$$= d\left(e^{2\pi i \gamma} - e^{-2\pi i \gamma}\right)$$

$$= 2 i d \sin(2\pi\gamma) = 0$$

we can identify γ as $1/\lambda$ now.

either $d = 0$ or $\gamma_n = 0, 1/2, 1, 3/2, \dots$ for $n = 0, 1, 2, \dots$

$$g(x) = c e^{-ik_n x} + d e^{ik_n x} \qquad k_n = \pi n, \; n = 0, 1, \dots$$

Putting it all together gives:

$$u(x,t) = g(t) f(x)$$

$$= \left(a e^{-i\gamma_n c t} + b e^{i\gamma_n c t}\right)\left(c e^{-ik_n x} + d e^{ik_n x}\right)$$

shift bc $e^{2\pi}$ $\quad 2\pi\gamma_n c = \omega_n$

$$\boxed{u(x,t) = \left(a e^{-i\omega_n t} + b e^{i\omega_n t}\right)\left(c e^{-ik_n x} + d e^{ik_n x}\right)}$$

This is for a single mode only. For all modes the solution is

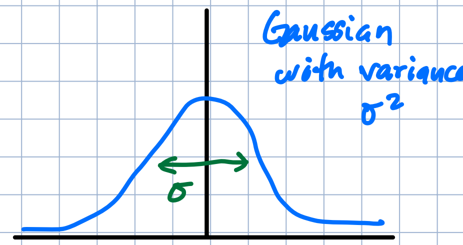
$$u(x,t) = \sum_{n=0}^{\infty} \left(a e^{-i\omega_n t} + b e^{i\omega_n t}\right)\left(c e^{-ik_n x} + d e^{ik_n x}\right)$$

(iii) uncertainty principle of waves

The above illustrates an "uncertainty principle" between x and k. I know k exactly. The delta function sets $k = k_0$. Because of this, I have a plane wave spread out over all x.

There is a general uncertainty principle of Fourier transform conjugate variables.

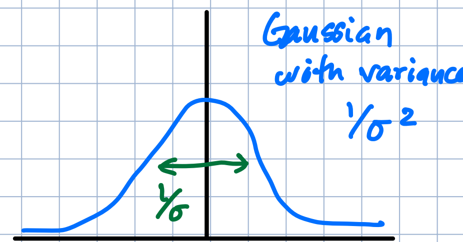
Suppose I have a Gaussian function



$$f(x) = \frac{1}{\sqrt{2\pi}\,\sigma} \exp\left(-\frac{x^2}{2\sigma^2}\right)$$

The Fourier Transform of f is

$$\hat{f}(k) = \exp\left(-\tfrac{1}{2}k^2\sigma^2\right)$$



This is also a Gaussian, but the variance is $1/\sigma^2$.

lets define $\sigma_x^2 = \sigma^2$ and σ_k^2 as follows:

$$\hat{f}(k) = \exp\left(-\frac{k^2}{2\sigma_k^2}\right) \Rightarrow \sigma_k^2 = 1/\sigma^2$$

Therefore : $\boxed{\sigma_x^2 \cdot \sigma_k^2 = 1}$

If the variance in the position goes up (down), then the variance in the wavenumber, k, goes down (up).

3Blue1Brown has a good example for giving us intuition here. If I am sitting at a stop light in the turn lane, and the blinkers seem to be in sync (frequency), the longer I wait, the more sure I am that they do have the same frequency. In other words, longer times tell me more information about frequencies. It would take infinite time to tell they were the exact same frequency (and not just off by a little bit).

Conversely, suppose there were very many frequencies of blinkers. It would only take a very short time to tell they were all different.

"When did I know" that the blinkers were the same?

- Frequencies very close → spread out over time
- Frequencies spread out → located more precisely in time.

B. Wave-Particle Duality

There is this sort of fundamental split at the heart of physics, and really, in mathematics. We have discrete things (e.g., number of apples) and continuous things (e.g., time). In physics prior to c.1900, and it should be noted in everyday experience, the world was neatly divided into these two things. Two pertinent examples are light and electrons.

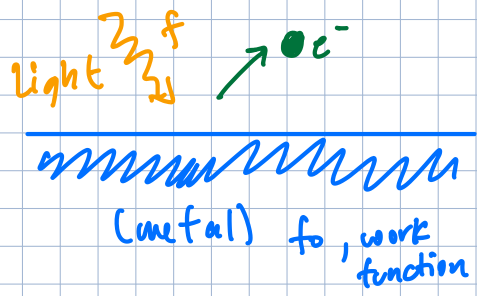
Light was seen as continuous. It obeyed Maxwell's equations. It propagates as a wave (see above).

$$\frac{\partial^2 \underline{E}}{\partial t^2} = c^2 \nabla^2 \underline{E} \qquad \frac{\partial^2 \underline{B}}{\partial t^2} = c^2 \nabla^2 \underline{B} \qquad c: \text{speed of light}$$

$\underline{E}$: electric field $\qquad$ $\underline{B}$: magnetic field.

Particles, as we have been talking about, were seen as discrete. Electrons were known to be a type of particle.

There were a series of surprising experimental discoveries.
The photoelectric effect demonstrated that light had a particle nature.



- minimum frequency of light needed to excite an electron
- higher intensity didn't matter if frequency too low.

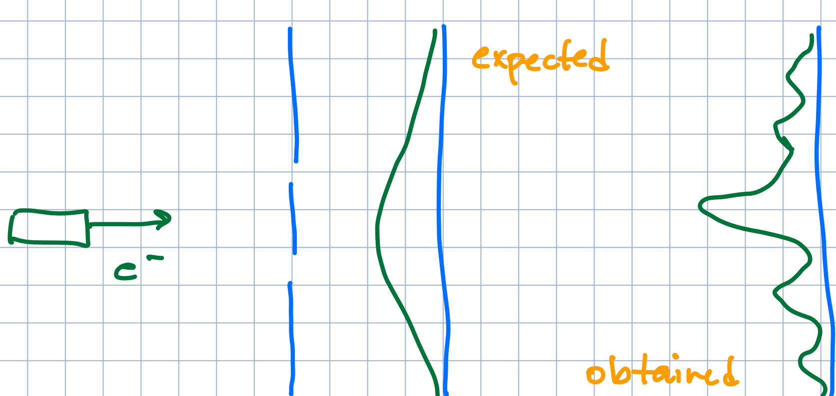
The conclusion is that light has a particle nature (photon) and the energy of the light was hypothesized to be given by:

$$E = hf \quad \text{or} \quad \boxed{E = \hbar\omega} \qquad \hbar = \frac{h}{2\pi}$$

(Planck's Formula) $\qquad h = 6.626 \times 10^{-34}$ Js

(Aside) Planck developed formula while trying to solve the blackbody radiation UV catastrophe. Einstein connected it to the photoelectric effect. Einstein given the nobel prize for this.

Subsequently, electrons (particles) were discovered to have a wave like character in the double-slit experiment.



Matter diffracted (interfered) like light. Show video from wikipedia.

Notes:

- Even one particle acts as if interfering with itself.
- Pattern is built up statistically. Particles appear in a "random" fashion.
- If you try to detect the particle before it hits, it changes its state. ← small enough you can't measure w/o interfering.

Resulting conclusion: matter particles are wavelike in some way.

$\boxed{\underline{p} = \hbar \underline{k}}$. Particle momentum $\propto$ wave number.

Equations for E & $\underline{p}$ are Planck-Einstein equations.
They are fundamental to Q.M. They are like "laws".
They are postulates based on experimental observations.

(Aside) The second P-E equation is equivalent to the de Broglie wavelength : $\lambda = \frac{h}{p} = \frac{h}{mv}$ ← very small number

λ is big when p is small.

<u>Main takeaways:</u>

- Light and matter are not particles or waves, they are "particle-waves". They are both things. This is what is meant by "wave-particle duality."
- These effects only happen for matter if momentum is small.

<u>Example</u>: Colloidal particle in water (e.g. polyethylene)

size: $R = 1\,\mu m$ speed: $v = 1\,\mu m/s$ density: $\rho \approx 1\,g/cm^3$

$$m = \rho \cdot V = \rho \cdot \frac{4}{3}\pi R^3 = \frac{1g}{cm^3} \cdot \frac{4}{\cancel{3}}\cancel{\pi}(1\mu m)^3 \approx \frac{1000\,kg}{m^3} \cdot 4 \cdot 10^{-18}\,m^3$$

$$m \approx 4 \times 10^{-15}\,kg$$

$$p = mv = 4 \times 10^{-15}\,kg \cdot 10^{-6}\,\frac{m}{s} = 4 \times 10^{-21}\,kg\,m/s$$

$$\lambda = \frac{h}{p} = \frac{6.626 \times 10^{-34}\,Js}{4 \times 10^{-21}\,\frac{kg\,m}{s}} \approx 1.5 \times 10^{-13}\,\cancel{kg}\,m^{\cancel{2}}/\cancel{s} \cdot \frac{\cancel{s}}{\cancel{kg\,m}} = 1.5 \times 10^{-13}\,m$$

$$Js = \frac{kg\,m^2}{s}$$

$$\frac{\lambda}{R} = \frac{1.5 \times 10^{-13}\,m}{10^{-6}\,m} = \boxed{1.5 \times 10^{-7}}$$ negligible!

<u>Example 2:</u> Electron accelerated at 100 V.

$$E = qV \qquad q_e = 1.602 \times 10^{-19}\,C$$

$$E = 1.6 \times 10^{-19}\,C \cdot 100\,V = 1.6 \times 10^{-17}\,J$$

$$E = \frac{p^2}{2m_e} \Rightarrow p = \sqrt{2m_e E} \qquad m_e = 9.109 \times 10^{-31}\,kg$$

$$p = \left[2 \cdot 9.1 \times 10^{-31}\,kg \cdot 1.6 \times 10^{-17}\,\frac{kg\,m^2}{s^2}\right]^{1/2}$$

$$= 5. \times 10^{-24}\,kg\,m/s$$

$$\lambda = \frac{h}{p} = \frac{6 \times 10^{-34}\,kg\,m^2/s}{5 \times 10^{-24}\,kg\,m/s} \approx 1.2 \times 10^{-10}\,m \approx 1.2\,Å$$

atomic radius of hydrogen, $r_{H_2} \approx 0.25\,Å$

$$\boxed{\frac{\lambda}{r_{H_2}} \approx 5}$$ definitely not negligible!

- Measurements always result in interactions that cannot be neglected. Again, this is a result of scale. E.g., even a single photon messes with the state of an electron.

C. The Schrödinger Equation

So, with the idea that matter is a dual wave/particle, the founders of quantum mechanics wanted to re-write mechanics in terms of wave equations

$$\frac{\partial^2 \phi}{\partial t^2} = v^2 \frac{\partial^2 \phi}{\partial x^2}. \quad \leftarrow \text{wave equation}$$

We saw above, that the wave equation has a solution for a traveling wave (in 1D)

$$\psi(x,t) = a\, e^{i(kx - \omega t)} .$$

We will now substitute the Planck-Einstein equations into this expression

$$E = \hbar \omega$$

$$\underline{p} = \hbar \underline{k} \longrightarrow \text{1D version} \quad p = \hbar k \Bigg\} \quad \omega = E/\hbar, \quad k = p/\hbar$$

$$\psi(x,t) = a \exp\left(i \frac{px - Et}{\hbar}\right) \qquad (*)$$

This is a traveling "wave-particle" in free space! The founders arrived at this by intuition, by combining ideas of waves and particle mechanics. We would like to go backwards and find a differential equation that is consistent with this solution. Then, perhaps, we can solve more complex problems. What follows here is not really a derivation. It is more like the reasoning the founders of QM used to arrive at the Schrödinger Equation.

Let's first look at the time-dependence. To do this we will take the time derivative of (*). Taking the time derivative gives,

$$\frac{\partial \psi}{\partial t} = -\frac{iE}{\hbar} a \exp\left(i \frac{px - Et}{\hbar}\right)$$

$$(i\hbar)\frac{\partial \psi}{\partial t} = -\frac{iE}{\hbar}\psi\,(i\hbar) \Rightarrow i\hbar\frac{\partial \psi}{\partial t} = E\psi$$

We will pause there for now, and look at the spatial dependence next. Taking the derivative of (*) with respect to space twice,

$$\frac{\partial \psi}{\partial x} = \frac{ip}{\hbar} a \exp\left(i\frac{px - Et}{\hbar}\right) = \frac{ip}{\hbar}\psi$$

$$\frac{\partial^2 \psi}{\partial x^2} = \left(\frac{ip}{\hbar}\right)^2 \psi = -\frac{p^2}{\hbar^2}\psi \Rightarrow -\hbar^2 \frac{\partial^2 \psi}{\partial x^2} = p^2 \psi .$$

Recall that the energy of a freely moving particle consists of the kinetic energy only

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m} \Rightarrow p^2 = 2mE$$

So,

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} = E\psi$$

Putting both the time derivative and the spatial derivative together gives,

Hamiltonian

$$i\hbar\frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} \Rightarrow i\hbar\frac{\partial \psi}{\partial t} = \hat{H}\psi$$

For a particle in a potential, the Hamiltonian is actually

$$\hat{H} = \hat{K} + \hat{U} = \frac{p^2}{2m} + \hat{U},$$

and the differential equation can be written as

$$i\hbar \frac{\partial \psi}{\partial t} = \left[\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x) \right] \psi$$

What did we do?

- We used the Planck-Einstein equations and the solution for a plane wave to provide a wave-like differential equation in terms of the particle Hamiltonian.
- More rigorously, this equation is a postulate or a law, like Newton's 2nd law.

Of course, this equation is called Schrödinger's equation. Let's write out the general, 3D Time-dependent Schrödinger Equation

$$\boxed{i\hbar \frac{\partial}{\partial t} \psi(\underline{r}, t) = \left[-\frac{\hbar^2}{2m} \nabla^2 + U(\underline{r}, t) \right] \psi(\underline{r}, t)}$$

$|\psi\rangle$ ket vector in a Hilbert space

$$\boxed{i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H}(t) |\psi(t)\rangle}$$

$\hat{H}$: Hamiltonian operator

When the Hamiltonian doesn't depend on time, the time-dependent equation can be "formally" integrated,

$$|\psi(t)\rangle = \exp\left(-\frac{i}{\hbar} \hat{H} t\right) |\psi(\underline{r}, 0)\rangle$$

operator/matrix in an exponential

Using a spectral decomposition, this can be written as

$$\psi(\underline{r},t) = \sum_{n=0}^{\infty} c_n \exp\left(\frac{-iE_n t}{\hbar}\right) \phi_n(\underline{r})$$

More on the time-dependent solution later when we do some examples. Substituting just one of these modes (any n) into the Schrödinger Equation gives,

$$i\hbar \frac{\partial}{\partial t}\left[e^{-iE_n t/\hbar}\psi_n(r)\right] = \left[\frac{-\hbar^2}{2m}\nabla^2 + u\right]\left(e^{-iE_n t/\hbar}\psi_n(\underline{r})\right)$$

$$\cancel{i\hbar}\,\psi_n(r)\cdot \frac{\cancel{-i}E_n}{\cancel{\hbar}} \cancel{e^{-iE_n t/\hbar}} = \left[\frac{-\hbar^2}{2m}\nabla^2 + u\right]\psi(r)\, \cancel{e^{-iE_n t/\hbar}}$$ doesn't depend on x

$$E_n \psi_n(r) = \left[\frac{-\hbar^2}{2m}\nabla^2 + u\right]\psi_n(r)$$

This gives us the so-called Time-Independent Schrödinger Equation

$$\boxed{\left[\frac{-\hbar^2}{2m}\nabla^2 + u\right]\psi_n(r) = E_n\psi(r)}$$

$$\boxed{\hat{H}\,|\psi_n\rangle = E_n|\psi_n\rangle}$$

This is an eigenvalue problem. $|\psi_n\rangle$ is the eigenket vector or eigen-function. E_n, the energy, is the eigenvalue.

The Fourier transform of the Schrödinger equation gives an equation explicit in the momentum

$$i\hbar \frac{\partial \hat{\psi}}{\partial t} = \frac{p^2}{2m}\hat{\psi} + \frac{1}{(2\pi\hbar)^{3/2}}\int_{-\infty}^{\infty} \hat{u}(p-p')\,\hat{\psi}\, d\underline{p}'$$

$$F[\Psi] = \hat{\Psi}(\underline{p},t) = \hat{\Psi}$$

$$F[u] = \hat{u}$$

The Fourier transform definition

$$F[\Psi] = \frac{1}{(2\pi\hbar)^{3/2}} \int_{-\infty}^{\infty} e^{\frac{i\underline{p}\cdot\underline{r}}{\hbar}} \Psi(\underline{r})\, d\underline{p}$$

Note that the momentum is the Fourier conjugate variable to position.

- Uncertainty principle!
- Another reason why position and momentum are the canonical variables in the Hamiltonian.

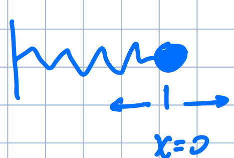
D. Examples

Example 1: Particle in Free Space

Note to self: Add this one next year

Example 2: Harmonic Oscillator

Reminder: classical Harmonic oscillator



Spring potential: $U = \frac{1}{2}kx^2 = \frac{1}{2}\omega^2 m x^2$

particle mass: m

initial conditions: $x(0) = x_0$, $v(0) = v_0$

$$m\frac{d^2x}{dt^2} = -\frac{\partial U}{\partial x}$$

$$\frac{d^2x}{dt^2} + \frac{k}{m}x = 0 \Rightarrow \frac{d^2x}{dt^2} + \omega^2 x = 0 \qquad \omega^2 = k/m,\ k = \omega^2 m$$

$$\boxed{\begin{aligned} x(t) &= \frac{v_0}{\omega}\sin(\omega t) + x_0\cos(\omega t) \\ v(t) &= v_0\cos(\omega t) - x_0\omega\sin(\omega t) \end{aligned}}$$

Back to the Quantum Harmonic Oscillator (QHO) ...

The 1D time-dependent Schrödinger Equation is

$$i\hbar \frac{\partial \psi}{\partial t} = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U\right]\psi \qquad U = \frac{1}{2}m\omega^2 x^2$$

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + \frac{1}{2}m\omega^2 x^2 \psi$$

Initial condition: $\psi(x,0) = \psi_0(x)$

Boundary Conditions: $\psi(-\infty,t) = \psi(+\infty,t) = 0$

(i) Dimensional Analysis

First, to simplify, lets make the problem dimensionless

$$\tilde{x} = x/l \qquad \tilde{t} = t/\tau \qquad \tilde{\psi} = \frac{\psi}{l^{1/2}} \qquad \left[\psi \sim L^{-1/2} \text{ because } \int |\psi^2|\, dx = 1\right]$$

Parameters? $m, \hbar, \omega$ $\qquad m \to kg \qquad \hbar \to J\cdot s \qquad \omega \to 1/s$

τ is pretty straightforward. Let $\tau = 1/\omega$

l is not as obvious. We can leave it and solve for it while we non-dimensionalize.

$$i\hbar\omega\, l^{1/2} \frac{\partial \tilde{\psi}}{\partial \tilde{t}} = -\frac{\hbar^2}{2m}\cdot\frac{l^{1/2}}{l^2}\frac{\partial^2 \tilde{\psi}}{\partial \tilde{x}^2} + \frac{1}{2}m\omega^2 l^{5/2}\tilde{x}^2\tilde{\psi}$$

- all $l^{1/2}$ cancel
- also divide by $\hbar\omega$

$$i\frac{\partial \tilde{\psi}}{\partial \tilde{t}} = -\frac{\hbar}{2m\omega}\frac{1}{l^2}\frac{\partial^2 \tilde{\psi}}{\partial \tilde{x}^2} + \frac{1}{2}\frac{m\omega}{\hbar}l^2\tilde{x}^2\tilde{\psi}$$

let $\frac{\hbar}{m\omega l^2} = 1 \Rightarrow l^2 = \frac{\hbar}{m\omega} \Rightarrow l = \left(\frac{\hbar}{m\omega}\right)^{1/2}$

$$(*) \quad \boxed{i\frac{\partial \tilde{\psi}}{\partial \tilde{t}} = -\frac{1}{2}\frac{\partial^2 \tilde{\psi}}{\partial \tilde{x}^2} + \frac{1}{2}\tilde{x}^2\tilde{\psi}} \qquad \boxed{\tilde{x} = x\left(\frac{m\omega}{\hbar}\right)^{1/2}, \quad \tilde{t} = \omega t}$$

The dimensionless equation has the natural length ($\ell = \sqrt{\hbar/m\omega}$) and time ($\tau = 1/\omega$) units for this problem.

Quick units check: $\frac{\hbar}{m\omega} = \frac{J\cdot s}{kg\ 1/s} = \frac{kg\, m^2/s^2 \cdot s}{kg/s} = m^2$ ✓

$$\frac{1}{\omega} = \frac{1}{1/s} = s \checkmark$$

Now we can focus on the math and add the units/parameters back later when we want them.

(ii) Separation of variables

The equation (*) is a linear PDE. It is 1^{st} order in time and second order in space. It is complex. There are various methods of solution. We will use the method of separation of variables.

$$i\frac{\partial \psi}{\partial t} = -\frac{1}{2}\frac{\partial^2\psi}{\partial x^2} + \frac{1}{2}x^2\psi$$

- Drop the tildes.
- Sort of like a diffusion equation with a spatially dependent reaction (but complex time).

Assume the form of a product solution:

$$\psi = f(t)\,g(x)$$

$$i\frac{\partial(fg)}{\partial t} = -\frac{1}{2}\frac{\partial^2(fg)}{\partial x^2} + \frac{1}{2}x^2 fg$$

$$ig\frac{\partial f}{\partial t} = -\frac{1}{2}f\frac{\partial^2 g}{\partial x^2} + \frac{1}{2}x^2 fg$$ Divide by fg

$$\underbrace{\frac{i}{f}\frac{\partial f}{\partial t}}_{\text{only depends on } t} = \underbrace{-\frac{1}{2}\frac{1}{g}\frac{\partial^2 g}{\partial x^2} + \frac{1}{2}x^2}_{\text{only depends on } x} = \lambda$$ Must equal a constant.

We've divided our PDE into two ODEs. One is an ODE-IVP in time. The other is an ODE-BVP in space

① $$\frac{i}{f}\frac{df}{dt} = \lambda \Rightarrow \frac{df}{dt} = -i\lambda f$$

② $$-\frac{1}{2}\frac{1}{g}\frac{d^2g}{dx^2} + \frac{1}{2}x^2 = \lambda \Rightarrow -\frac{1}{2}\frac{d^2g}{dx^2} + \frac{1}{2}x^2 g = \lambda g$$

This is an eigenvalue problem

$$\mathcal{L}g = \lambda g \quad , \quad \mathcal{L} = -\frac{1}{2}\frac{d^2}{dx^2} + \frac{x^2}{2}$$

eigenvalue

differential operator
Has eigenfunction solutions.

(iii) Solve ODE #1

$$\frac{df}{dt} = -i\lambda f \Rightarrow \frac{1}{f}df = -i\lambda\, dt \Rightarrow \ln f = -i\lambda t + \text{const}$$

$$\boxed{f(t) = \text{const}\,\exp(-i\lambda t)}$$

(iv) Solve ODE #2 (time independent Schrödinger equation)

$$-\frac{1}{2}\frac{d^2g}{dx^2} + \frac{1}{2}x^2 g = \lambda g \Rightarrow \frac{d^2g}{dx^2} - x^2 g = -2\lambda g$$

$$\frac{d^2g}{dx^2} + (2\lambda - x^2)g = 0$$

This is a 2nd order, non-constant coefficient ODE. Non-constant coefficient ODEs are special cases. (Remember Bessel functions, spherical Bessel functions, etc.)

It turns out this ODE is more well-known in a different form. We need to change variables to be able to look it up and use numerical packages.

let $g(x) = \exp(-x^2/2)\, h(x)$

[Aside] Work out the transformation:

$$\frac{dg}{dx} = -x e^{-x^2/2} h(x) + e^{-x^2/2} \frac{dh}{dx}$$

$$\frac{d^2g}{dx^2} = -e^{-x^2/2} h(x) + x^2 e^{-x^2/2} h(x) - x e^{-x^2/2} \frac{dh}{dx} - x e^{-x^2/2} \frac{dh}{dx} + e^{-x^2/2} \frac{d^2h}{dx^2}$$

$$= (x^2-1) e^{-x^2/2} h - 2x e^{-x^2/2} \frac{dh}{dx} + e^{-x^2/2} \frac{d^2h}{dx^2}$$

Substitute into the original ODE:

$$\left[(x^2-1)h - 2x\frac{dh}{dx} + \frac{d^2h}{dx^2}\right] \cancel{e^{-x^2/2}} + (2\lambda - x^2)\cancel{e^{-x^2/2}}\, h = 0$$

$$\frac{d^2h}{dx^2} - 2x\frac{dh}{dx} + (x^2 - 1 + 2\lambda - x^2)h = 0$$

$$\boxed{\frac{d^2h}{dx^2} - 2x\frac{dh}{dx} + (2\lambda - 1)h = 0}$$

This equation is called Hermite's differential equation.

This is a singular Sturm-Liouville eigenvalue problem.

$$\mathcal{L}h = \gamma h, \quad \mathcal{L} = \frac{d^2}{dx^2} - 2x\frac{d}{dx}, \quad \gamma = 2\lambda - 1$$

Solutions to Hermites DE are given by a sum of linearly independent eigenfunctions

$$h(x) = c_1 H_n(x) + c_2 Y_n(x) \quad \text{where} \quad \gamma = 2n \quad n=0,1,2,\ldots$$

Hermite polynomials (of the 1st kind)

Hermite functions of the 2nd kind

eigenvalues

$$2\lambda - 1 = 2n$$

$$\lambda = n + 1/2$$

[Aside] How do we calculate $H_n(x)$ and $Y_n(x)$?

The $H_n(x)$ can be obtained by the expression

$$H_n(x) = (-1)^n e^{x/2} \frac{d^n}{dx^n}\left(e^{-x^2}\right)$$

$$H_0(x) = 1$$

$$H_1(x) = (-1)\, e^{x^2} \frac{d}{dx}\left(e^{-x^2}\right) = -e^{x^2}\left(-2x e^{-x^2}\right) = 2x$$

$$H_2(x) = (-1)^2 e^{x^2} \frac{d^2}{dx^2}\left(e^{-x^2}\right) = e^{x^2}\left(-2e^{-x^2} + 4x^2 e^{-x^2}\right)$$

$$= 4x^2 - 2$$

$$H_3(x) = 8x^3 - 12x, \quad H_4(x) = 16x^4 - 48x^2 + 12$$

from wikipedia

Let's check to make sure these are actually solutions.

$$\frac{d^2 H_n}{dx^2} - 2x\frac{dH_n}{dx} + 2n H_n(x) = 0$$

$$n=0: \; H_0 = 1 \quad \frac{dH_0}{dx} = 0 \;\Rightarrow\; 0 - 2x\cdot 0 + 2\cdot 0\cdot 1 \stackrel{?}{=} 0 \; ✓$$

$$n=1: \; H_1 = 2x \quad \frac{dH_1}{dx} = 2 \quad \frac{d^2H_1}{dx^2} = 0 \;\Rightarrow\; 0 - 2x\cdot 2 + 2\cdot 1\cdot 2x \stackrel{?}{=} 0 \; ✓$$

$$n=2: \; H_2 = 4x^2 - 2 \quad \frac{dH_2}{dx} = 8x \quad \frac{d^2H_2}{dx^2} = 8 \;\Rightarrow\; 8 - 2x(8x) + 2\cdot 2\cdot(4x^2-2) \stackrel{?}{=} 0 \; ✓$$

The problem is finding what is tabulated. Kummer's DE is given by

$$z\frac{d^2w}{dz^2} + (b-z)\frac{dw}{dz} - aw = 0$$

It has solutions $M(a,b,z)$ and $U(a,b,z)$ which are called confluent hypergeometric functions of the first (M) and second (U) kind. These also come up in the Graetz problem in forced convection.

Alternate notation for M is:

$$M(a,b,z) = {}_1F_1(a,b,z)$$ ← notation for generalized hypergeometric series

"hyp1f1" is the name of the Python function

One can write Hermite polynomials and functions using confluent hypergeometric functions.

$$H_n(x) = 2^n U\left(-\frac{n}{2}, \frac{1}{2}, x^2\right)$$ ← hyperu is the Python function.

$$Y_n(x) = M\left(-\frac{n}{2}, \frac{1}{2}, x^2\right)$$

M is also known as Kummer's confluent hypergeometric function.

U is also known as Tricomi's confluent hypergeometric function.

The $Y_n(x)$ cannot be physical solutions. They diverge to infinity at points in the domain, so $|\psi|^2 \not< \infty$. So, these cannot be wave functions. ($Y_n(x)$ are not compatible with B.C.'s).

We now have the solution for $g(x)$

$$g(x) = c \cdot e^{-x^2/2} \cdot H_n(x)$$

[Aside] The g(x) need to be normalized so that

$$\langle g_n(x) | g_n(x) \rangle = 1$$

complex conjugate

$$\int_{-\infty}^{\infty} g_n(x)\, g_n^*(x)\, dx = 1$$

use this to solve for c

This will give us a proper probability density. I found these values and verified using Mathematica.

$$c_n = \left(2^n n! \sqrt{\pi}\right)^{-1/2}$$

The integrals for Y_n only converge for $n \in$ even. This is why they are not physical. But for the even ones, the normalization constant is

$$c_n = \left(2^n \frac{(n/2)!^2}{n!} \sqrt{\pi}\right)^{-1/2}$$

Wow! ChatGPT recognized this sequence as the central binomial coefficients. Super cool!

After normalizing, we have our complete set of orthonormal basis functions, and the solution to the problem in the x-direction.

$$g_n(x) = c_n e^{-x^2/2} H_n(x)$$

$$c_n = \left(2^n n! \sqrt{\pi}\right)^{-1/2}$$

$$\lambda_n = n + 1/2, \quad n = 0, 1, \ldots, \infty$$

Where the orthonormal property of $g_n(x)$ says that

$$\langle g_n | g_m \rangle = \delta_{nm} = \begin{cases} 0, & n \neq m \\ 1, & n = m \end{cases}$$

$$\int_{-\infty}^{\infty} g_n(x)\, g_m(x)\, dx = \delta_{nm}$$

(v) Product solution

Now we can put our two solutions together,

$$\psi(x,t) = f(t)\, g(x) = A_n \exp(-i\lambda_n t)\, c_n \exp(-x^2/2)\, H_n(x).$$

← coefficient for I.C.

By superposition, a sum of solutions is also a solution, so the general solution is

$$\boxed{\psi(x,t) = \sum_{n=0}^{\infty} A_n c_n \exp\left(-i\lambda_n t - x^2/2\right) H_n(x) \qquad \lambda_n = n + 1/2 \qquad c_n = \left(2^n n! \sqrt{\pi}\right)^{-1/2}}$$

(vi) Initial condition

The last thing we need to do is use the initial condition to determine the A_n.

Let the initial state be $\psi_0(x)$. For example, it could be

$$\psi_0(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(\frac{-(x-x_0)^2}{2\sigma^2}\right)$$

A Gaussian wave packet.

The coefficients are given by

$$A_n = \langle \psi_0 | g_n \rangle$$

$$A_n = \int_{-\infty}^{\infty} \psi_0(x)\, g_n(x)\, dx = \int_{-\infty}^{\infty} \psi_0(x)\, c_n e^{-x^2/2} H_n(x)\, dx$$

We need to evaluate this integral for each n. We can do this numerically. Hopefully $A_n \to 0$ as $n \to \infty$ quickly, so our infinite sum converges and we don't have to do too many integrals.

[Aside] Proof of formula for A_n

$$\langle \psi_0 | g_n \rangle = \int_{-\infty}^{\infty} \psi_0(x)\, g_n(x)\, dx$$

$$= \int_{-\infty}^{\infty} \underbrace{\left[\sum_{m=0}^{\infty} A_m \exp(0) \cdot g_m(x) \right]}_{\text{spectral representation of } \psi_0(x)} g_n(x)\, dx$$

$$= \sum_{m=0}^{\infty} A_m \int_{-\infty}^{\infty} g_n(x)\, g_m(x)\, dx$$

$$= \sum_{m=0}^{\infty} A_m \delta_{mn} = A_n \checkmark$$

(vii) Closing comments

- The eigenvalue λ_n is the dimensionless energy.

$$\lambda_n = \frac{E_n}{\hbar\omega} \quad , \quad E_n = \hbar\omega(n + 1/2) \quad , n = 0, 1, 2, \ldots$$

units: $\hbar\omega = J \cdot s \cdot \frac{1}{s}$ ✓

We can see this because the eigenvalue problem for $g(x)$ is the time-independent Schrödinger equation.

In the classical problem, the energy is continuous. Any value is allowed. In the quantum problem this is not so.

- One may also want to look at the momentum. What is the dimensionless momentum?

$$p = \hbar k \qquad \tilde{k} = \ell k \qquad \ell = \sqrt{\frac{\hbar}{m\omega}}$$

$$= \frac{\hbar}{\ell}\tilde{k}$$

$$\tilde{p} = \frac{p\ell}{\hbar} = \tilde{k}$$

$$p = \tilde{p}\frac{\hbar}{\ell} = \hbar\sqrt{\frac{m\omega}{\hbar}}\,\tilde{k} = \sqrt{m\omega\hbar}\,\tilde{k}$$

$$\tilde{p} = \tilde{k} = \frac{p}{(\hbar m\omega)^{1/2}}$$

check units: $\hbar m\omega = J\cdot s\cdot kg\cdot 1/s$

$$= \frac{kg\,m^2}{s^2}\cdot kg = kg^2 m^2/s^2$$

$$(\hbar m\omega)^{1/2} = kg\,m/s \checkmark$$

(momentum)

(viii). Review Numerical Solution

- Go over numerical solution
- Talk about in context with the postulates (below).

(Add more details here)

E. Postulates of Quantum Mechanics

What is a succinct summary of the minimum set of rules we need to describe quantum mechanics? This will help us understand what quantum mechanics really is, what it means, and how to mathematically compute what we need.

(i). Classical Mechanics

1. The state of the system at time t_0 is described by specifying $3N$ generalized coordinates $q_i(t_0)$ and their conjugate momenta $p_i(t_0)$.

2. The value of any function of the q_i and p_i, $f(q_i, p_i, t)$, is determined for any time t when the initial state is specified at t_0.

3. The time evolution of the state of the system is given by Hamilton's equations,

$$\frac{dq_i}{dt} = \frac{\partial H}{\partial p_i} \qquad H = \frac{p_i^2}{2m} + U(q_i, t)$$

$$\frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i}.$$

(ii.) Quantum Mechanics

1. The state of the system is defined by specifying a ket vector $|\psi(t_0)\rangle$ at time t_0.
   - This is equivalent to specifying a wavefunction $\psi(x, t_0)$ or $\hat{\psi}(p, t_0)$.

2. Every measurable physical quantity A is described by an operator $\hat{A}$ in the Hilbert space. This operator is an "observable".

• Example: The Hamiltonian operator

$$\hat{H} = \underbrace{-\frac{\hbar}{2m}\nabla^2}_{\text{Kinetic Energy operator}} + \underbrace{\hat{U}(r,t)}_{\text{Potential Energy operator}}$$

• Example: Position

$$\hat{R} = \underline{r}$$

• Example: Momentum

$$\hat{\underline{P}} = i\hbar \underline{\nabla}$$

3. The only possible measurement of a physical quantity A is one of the eigenvalues of the observable $\hat{A}$.

$$\hat{A}|\psi\rangle = A|\psi\rangle$$

• Example: Energy

$$\hat{H}|\psi\rangle = E|\psi\rangle$$ Energy is the eigenvalue.

4. The probability of measuring an eigenvalue a_n corresponding to the physical quantity A from a system in state $|\psi\rangle$ is given by

$$P(a_n) = |\langle u_n|\psi\rangle|^2 = \left|\int_{-\infty}^{\infty} u_n(x,t)\,\psi_n(x,t)\,dx\right|^2$$

where $|u_n\rangle$ are eigenvectors corresponding to the eigenvalues a_n,

$$\hat{A}|u_n\rangle = a_n|u_n\rangle \Rightarrow \hat{A}u_n(x,t) = a_n u_n(x,t).$$

operator. This is usually a D.E.

[Aside] There is an easier way to get $P(a_n)$ using the spectral (eigenvalue) decomposition.

$$|\psi\rangle = \sum_n c_n |u_n\rangle \quad \text{(spectral decomposition)}$$

Using this expression gives

$$|\langle u_n|\psi\rangle|^2 = |\langle u_n|c_n|u_n\rangle| = |c_n|^2$$

so,

$$P(a_n) = |c_n|^2$$

We get the c_n by using the orthonormality of the eigen-kets

$$\langle u_m|\psi\rangle = \sum_n \langle u_m|c_n|u_n\rangle$$

$$= \sum_n c_n \underbrace{\langle u_m|u_n\rangle}_{\delta_{mn} = \begin{cases} 1 & \text{if } m=n \\ 0 & \text{if } m\neq n \end{cases}} = c_m$$

$$c_m = \langle u_m|\psi\rangle = \int_{-\infty}^{\infty} u_m(x)\,\psi(x,t)\,dx$$

5. If the measurement of the quantity A gives the value a_n, then the system immediately after becomes the eigen-ket associated with that value, $|u_n\rangle$.

$$|\psi\rangle \overset{a_n}{\Longrightarrow} \frac{c_n}{|c_n|}|u_n\rangle$$

It renormalizes. c_n could be complex, so there could be a phase shift.

6. The time evolution of the state vector $|\psi(t)\rangle$ is governed by the Schrödinger equation:

$$i\hbar \frac{d}{dt}|\psi(t)\rangle = H(t)|\psi(t)\rangle$$

where $H(t)$ is the observable associated with the total energy.

Some Comments:

- Postulates 3, 4, and 5 are kind of weird. Why does the wave-function "collapse" to an eigenfunction? This is what different interpretations of QM try to explain. The rest is sort of straightforward from the math.
- The uncertainty principle is a consequence of the postulates, not a postulate itself. It is a natural result of the wave mechanics.

F. The classical Limit

(Future years) Show how averages of the observables can be used to give Hamilton's equations. Maybe also show how the commutator leads to the Poisson bracket.

Other ideas:

- Born-Oppenheimer approximation
- Hydrogen atom