Intro to Quantum Mechanics

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Grade Update

From the syllabus:

- **A**: $\geq 90\%$ course average.
- **B**: $\geq 80\%$ course average.
- **C**: $\geq 70\%$ course average.
- **D**: $\geq 50\%$ course average.
- **F**: $< 50\%$ course average.

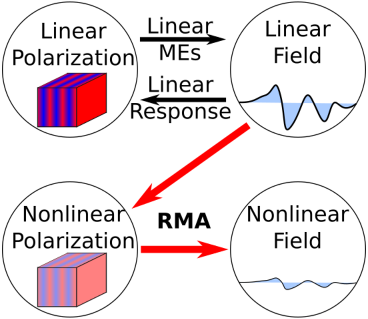
- Exercises/homework (50%)
- A mid-term exam (25%)
- A final project (25%)
- Extra credit exercises (additional 10%)

Projected averages are posted on Blackboard.

If you want a better grade grade: Act now!

- **Office hours:** Monday 3:30 - 4:30
- **Individual meetings:** On request
- Study together – compare answers!

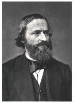
We've developed a **macroscopic theory** for molecular spectroscopy:



Today and henceforth: The *Microscopic* description of spectroscopic response – with *quantum mechanics*.

A Brief History of Quantum Mechanics

A Brief History of Quantum Mechanics – Phase I



"Everything emits like a harmonic oscillator." – Kirchoff

"Harmonic oscillators only emit right if energy is quantized. Weird." – Planck

"If you quantize the oscillators, better quantize the field too." – Einstein

"If waves act like quantized matter, couldn't matter act like waves?" – De Broglie

"Hey, the H atom only emits right if you quantize the *action* instead of the energy." – Bohr

$\Rightarrow$ **The Old Quantum Theory**

A Brief History of Quantum Mechanics – Phase II

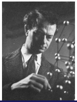
"Hey, that's cool and everything, but it doesn't work for Helium." – Pauli

"What if $xp \neq px$?" – Heisenberg

"That sounds a lot like matrices. Let's call it matrix mechanics." – Born

"I made a wave equation!" – Schrödinger

"And it's equivalent to matrix mechanics!" – Schrödinger



"Yeah, we're good. This solves all the problems." – Pauling

The Aftermath – Phase III

"None of this makes any sense." – Einstein

"Shut up." – Bohr

"Hey guys, I took a quantum picture of my cat, and it was really messed up." – Schrödinger

"You shut up too." – Bohr

"Guys, this theory is totally weird." – Einstein, Podolsky, & Rosen

"@#!$*#$" – Bohr

"The weirdness is testable." – Bell

"Yup. The universe *is* weird." – Clauser

Where does this leave us?

John Bell: "Ordinary quantum mechanics is just fine for all practical purposes." **BUT**...

To this moderate point of view I would only add the observation that contemporary physicists come in two varieties. Type 1 physicists are bothered by EPR and Bell's theorem. Type 2 (the majority) are not, but one has to distinguish two subvarieties. Type 2a physicists explain why they are not bothered. Their explanations tend either to miss the point entirely (like Born's to Einstein) or to contain physical assertions that can be shown to be false. Type 2b are not bothered and refuse to explain why. Their position is unassailable. (There is a variant of type 2b who say that Bohr straightened out[14] the whole business, but refuse to explain how.)

Bell 1990 *Phys. World* 3 (8) 33 Merman, *Physics Today* 38, 4, 38 (1985)

Quantum Mechanics For Practical Purposes

The Postulates: A Summary

- **Postulate 1**: Every quantum system is described by a *state vector* or *wavefunction* in *Hilbert space*
- **Postulate 2**: Every physical observable corresponds to a *Hermitian operator* on Hilbert space
- **Postulate 3**: The *measured value* of any observable must be one of the *eigenvalues* of the corresponding Hermitian operator.
- **Postulate 4**: The *probability* of measuring a given value is the *vector projection* of the state vector onto the corresponding *eigenvector*.
- **Postulate 5**: During measurement, the system state vector is *projected* onto the eigenvector subspace for the measured value.
- **Postulate 6**: An undisturbed quantum state evolves in time according to

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi$$

where $\hat{H}$ is the Hermitian operator corresponding to energy.

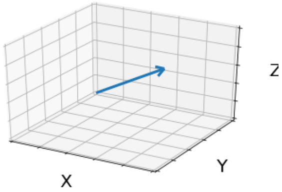
The First Postulate: State Vectors

For every physical system, there exists a state vector ψ of unit norm, an element of an infinite-dimensional Hilbert space $\mathcal{H}$, which defines statistically all physical properties of the system.

NB: In quantum mechanics, the state vector (or wavefunction) **replaces** coordinates like x and p as the fundamental quantity that defines the system state!

What is Hilbert space? Hilbert space is an infinite-dimensional analog to three-dimensional Cartesian space. It has

- An inner product (dot product) $\langle\phi|\,\psi\rangle$
- Vector projections and norms
- Orthonormal basis sets (infinite!)



Representations of Hilbert Space

There are **infinitely many** different representations of Hilbert space – All are fundamentally the same!

The two we use most often are:

Matrix Mechanics:

- States ψ correspond to sequences $(a_1, a_2, a_3, ...)$.
- Inner product: $(a_1, a_2, ...)^\dagger \cdot (b_1, b2, ...) = a_1^* b_1 + a_2^* b_2 + ...$
- Vector norm: $\|(a_1, a_2, ...)\|^2 = |a_1|^2 + |a_2|^2 + ...$

Wave Mechanics:

- States ψ correspond to functions $\psi(x)$.
- Inner product: $(\phi(x), \psi(x)) = \int_{-\infty}^{\infty} dx \phi^*(x) \psi(x)$
- Vector norm: $\|\psi(x)\|^2 = \int_{-\infty}^{\infty} dx \|\psi(x)\|^2$.

The Second Postulate: Hermitian Operators

To every measurable physical quantity A characterizing the state of a system, there corresponds a Hermitian operator $\hat{A}$ operating in $\mathcal{H}$.

An **operator** maps vectors to other vectors ($\hat{A} : \psi \to \phi = \hat{A}\psi$), just like a function maps numbers to other numbers ($f : x \to y = f(x)$).

In vector spaces, **Linear operators** can be represented as *matrices*. **Hermitian operators** correspond to *Hermitian symmetric* matrices:

$$A_{mn} = A^*_{nm}$$

$$\hat{A}$$

$$\Downarrow$$

$$\sum_{mn} |m\rangle A_{mn} \langle n|$$

$$\Downarrow$$

$$\begin{bmatrix} A_{11} & A_{12} & \dots \\ A_{21} & A_{22} & \dots \\ \vdots & \vdots & \ddots \end{bmatrix}$$

Side Note: Bra-Ket Notation

Dirac introduced a concise notation for vector operations:

- $|\psi\rangle$ corresponds to a *column vector* $\psi = \begin{bmatrix} a_1 \\ a_2 \\ \vdots \end{bmatrix}$
- $\langle\phi|$ corresponds to the *conjugate transpose row vector* $\phi^\dagger = \begin{bmatrix} b_1^* & b_2^* \ldots \end{bmatrix}$ of the ket $|\phi\rangle$.
- $\langle\phi|\,\psi\rangle$ represents the *inner product* $(\phi, \psi) = \begin{bmatrix} b_1^* & b_2^* \ldots \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ \vdots \end{bmatrix}$.
- $\left\langle \phi \middle| \hat{A} \middle| \psi \right\rangle$ corresponds to the *scalar* quantity

$$(\phi, \hat{A}\psi) = \begin{bmatrix} b_1^* & b_2^* \ldots \end{bmatrix} \begin{bmatrix} A_{11} & A_{12} & \ldots \\ A_{21} & A_{22} & \ldots \\ \vdots & \vdots & \ddots \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ \vdots \end{bmatrix}$$

The Third Postulate

For any physical observable, the only values which are possible to obtain in a measurement are those in the eigenvalue spectrum of the corresponding Hermitian operator.

In quantum mechanics, *only certain values* are possible for measured quantities. The list of possibilities is often discrete $\Rightarrow$ “quantized” or “quantum” mechanics.

An **eigenvalue** of the operator $\hat{A}$ is a complex number λ for which

$$\hat{A}\psi = \lambda\psi$$

$$\begin{bmatrix} \lambda_1 & 0 & \dots \\ 0 & \lambda_2 & \dots \\ \vdots & \vdots & \ddots \end{bmatrix}$$

for some vector ψ. Eigenvalues of Hermitian operators are real numbers!

The Fourth Postulate

In any experimental measurement of an observable a corresponding to Hermitian operator $\hat{A}$ with a purely discrete spectrum, the probability of obtaining the value λ is given by

$$P(a == \lambda) = |\langle \phi_\lambda | \, \psi \rangle|^2$$

where ϕ_λ is the eigenvector corresponding to λ.

$$\begin{aligned}
\langle a \rangle &= \sum_n \lambda_n P(a == \lambda_n) \\
&= \sum_n \langle \psi | \, \phi_n \rangle \, \lambda_n \, \langle \phi_n | \, \psi \rangle \\
&= \left\langle \psi \middle| \hat{A} \middle| \psi \right\rangle .
\end{aligned}$$

NB: The eigenvectors of a Hermitian (more precisely, self-adjoint) operator *always* form a complete basis!

The Fifth Postulate

During experimental measurements, the state of the system "collapses" to the eigenvectur ϕ_n corresponding to the experimentally-measured value of the measured observable.

Quantum-mechanical measurements *always disturb the system state* in a manner that *cannot be predicted* ahead of time.

"If we are going to stick to this damned quantum-jumping, then I regret that I ever had anything to do with quantum theory." – Schrödinger

The Sixth Postulate

In the absence of outside perturbation, the wave vector of the system evolves according to the differential equation

$$i\hbar \frac{d}{dt}\psi(t) = \hat{H}\psi(t),$$

where $\hat{H}$ *is the Hamiltonian operator for the system, corresponding to the total energy observable.*

In *between* measurements, quantum states change *smoothly and deterministically* in time.

If $\hat{H}$ is time-independent, then:

$$\psi(t) = \sum_n e^{-\frac{i}{\hbar}\varepsilon_n t}\phi_n(\phi_n, \psi(0))$$

where ε_n are the eigenvalues of $\hat{H}$ – i.e. the system energies.

Addendum to the Postulates

Note that the postulates do **not** tell you how to find the appropriate operators!

This is established empirically. But, most of the time, you can just make the replacements

$$x \to \hat{x}$$

$$p \to -i\hbar \frac{\partial}{\partial x}$$

to get the coordinate-basis "wave mechanics" relationships – then transform as desired.