Intro to Quantum Mechanics

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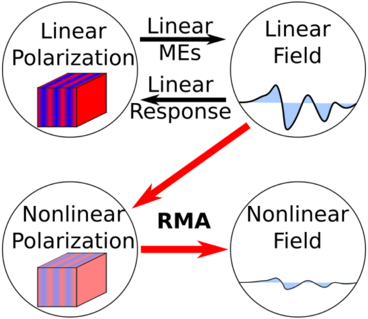
Previously on CHM676...

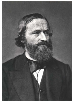
We've developed a **macroscopic theory** for molecular spectroscopy:



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



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– Kirchoff

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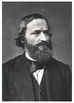

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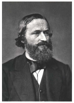

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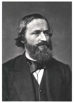

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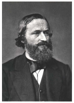

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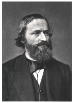

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$\Rightarrow$ **The Old Quantum Theory**

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

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"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

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- **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

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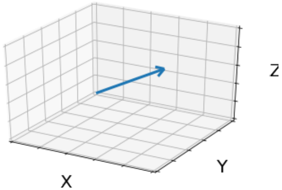
What is Hilbert space? Hilbert space is an infinite-dimensional analog to three-dimensional Cartesian space. It has

- 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: $\|\psi(x)\|^2 = \int_{-\infty}^{\infty} dx \|\psi(x)\|^2$.

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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:

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- $\left\langle \phi \middle| \hat{A} \middle| \psi \right\rangle$ corresponds to the *scalar* quantity

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

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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

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

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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

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

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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.

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

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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.