Chemistry 271 – Quantum Mechanics

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Material on CourseWork

Grades
Problem sets 40%
Final 60%

Full details about class on coursework web site and material sent to you.
Lecture slides posted on web site.
Basic Concepts

Absolute Size

The Superposition Principle

Size

Classical Mechanics
Relative

Quantum Mechanics
Absolute

What does relative vs. absolute size mean?

Why does it matter?
Classical Mechanics

Excellent for: bridges
airplanes
the motion of baseballs

Size is relative.

Tell whether something is big or small by comparing it to something else.

Rocks come in all sizes.

Comparison determines if a rock is big or small.
Why does the definition of size matter?

To observe something, must interact with it.
Always true - in classical mechanics
in quantum mechanics

Light hits flower, "bounces off."
Detect (observe) with eye, camera, etc.
Definition of Big and Small
(Same for classical mechanics and quantum mechanics.)

Disturbance caused by observation (measurement)
- negligible → object big
- non-negligible → object small

Classical Mechanics
Assume: when making an observation can always find a way to make a negligible disturbance. Can always make object big.

- Do wrong experiment → object small.
- Do right experiment → object big.

- Observe wall with light → big.
- Observe wall with billiard balls → small.

Implies – Size is relative. Size depends on the object and your experimental technique.
Nothing inherent.
Classical, systems evolve with causality.

Free particle
a rock
\( t = 0 \)

\( x \) - position
\( p \) - momentum

\( t = t' \)
observe

Following non-negligible disturbance – don't know outcome.

Make observation of trajectory. Predict future location.

\( a \) rock
\( t = 0 \)

\( x \) – position
\( p \) – momentum
predict

\( t = t' \)
observe

\( x \) – position
\( p \) – momentum
bird

bird – rock scattering event

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Quantum Mechanics
Size is absolute.

Quantum Mechanics is fundamentally different from classical mechanics in the way it treats size.

Absolute Meaning of Size

Assume: "There is a limit to the fineness of our powers of observation and the smallness of the accompanying disturbance, a limit which is inherent in the nature of things and can never be surpassed by improved technique or increased skill on the part of the observer."

Dirac
Quantum Mechanics – Absolute Definition of Size

Big object – unavoidable limiting disturbance is negligible.

Small object – unavoidable limiting disturbance is not negligible. 
Object is small in an absolute sense. 
No improvement in experimental technique will make the disturbance negligible.

Classical mechanics not set up to describe objects that are small in an absolute sense.
Q. M. – Observation of an Absolutely small system.

\[ t = 0 \]

\[ \text{an electron} \rightarrow \text{observe} \rightarrow t = t' \]

\[ \text{photon} \rightarrow \text{predict} \]

Photon – Electron scattering. **Non-negligible disturbance.**

Can’t predict trajectory after observation.

Causality is assumed to apply to undisturbed systems.

Act of observation of a small Q. M. system causes a non-negligible disturbance.

Therefore, the results of one observation will not allow a causal prediction of the results of a subsequent observation.

Not surprising from the definition of a small Q. M. system.

Indeterminacy comes in calculation of observables.

Act of observation destroys causality.

Theory gives probability of obtaining a particular result.
The Superposition Principle

Fundamental Law of Q. M. Inherently different from classical mechanics. Pervades quantum theory.

Two examples to illustrate idea before formulating Superposition Principle.
  - Polarization of photons
  - Interference of photons

Polarization of light (direction of $E$-field)

Light polarized along one axis goes through polarizer. $I_{||}$
Light polarized along other axis does not go through. Perpendicular axis, $I_{\perp}$.

Classical electromagnetic theory tells what happens.

Light is a wave.

Light polarized parallel goes through.
Light polarized perpendicular is reflected or diverted.
What happens when light is polarized at an angle, $\alpha$?

The projection of the electric field, $E$, on the parallel axis is

$E = \cos \alpha$.

Intensity is proportional to $|E|^2$.

$I \propto |E|^2$

A fraction, $\cos^2 \alpha$ of the light goes through the polarizer.
Photo-electric Effect – Classical Theory – Light is a wave.

**Experimental results**

Shine light of one color on metal – electrons come out with a certain speed.

Increase light intensity

get more electrons out with **identical speed**.

Tune frequency far enough to red

no electrons come out.

**Low Intensity - Small Wave**

Light wave “hits” electron gently.

Electrons come out – low speed.

**High Intensity - Big Wave**

Light wave “hits” electron hard.

Electrons come out – high speed.
Einstein explains the photoelectric effect (1905)

Light is composed of small particles – photons.

One photon hits one electron.

Increase intensity – more photons, more electrons hit – more come out.

Each photon hits an electron with same impact whether there are many or few.

Therefore, electrons come out with same speed independent of the intensity.

Tune to red, energy to low to overcome binding energy.

Light not a wave – light is composed of photons

Beam of light composed of polarized photons.

No problem if light $\parallel$ or $\perp$.

$\parallel$ photon goes right through the polarizer

$\perp$ photon does not go through (reflected)

What happens if a photon is polarized at some angle, $\alpha$?
Photons polarized at angle, $\alpha$ - need an experiment.

Q. M. describes observables. Can only ask questions about observables. Need experiment.

Experiment – single photons incident on polarizer one at a time.

Q. M. predicts results
- Some times get “whole” photon at back side of polarizer. Photon has same energy as incident photon.
- Sometimes get nothing.
- When “find” photon, it is always polarized parallel.
- Do this for many photons – observed $\cos^2 \alpha$ of them at back.
Act of “observation” of polarization by polarizer causes a non-negligible disturbance of photon.

Photon with polarization $\alpha$ “jumps” to either polarization $\parallel$ or $\perp$.

Superposition of photon polarization states

Photon of polarization $\alpha \rightarrow P_\alpha$

$P_\alpha$ is some type of “superposition” of polarization states, $\parallel$ and $\perp$.

$P_\alpha = a \ P_\parallel + b \ P_\perp$

Any state of polarization can be resolved into or expressed as a superposition of two mutually perpendicular states of polarization.
\[ P_\alpha = a \, P_\parallel + b \, P_\perp \]

Coefficients \( a \) and \( b \) tell how much of each of the “special” states, \( P_\parallel \) and \( P_\perp \) comprise the state \( P_\alpha \).

When the photon meets the polarizer, we are observing whether it is polarized \( \parallel \) or \( \perp \).

Observation of the system forces the system from the state \( P_\alpha \) into one of the states, \( P_\parallel \) and \( P_\perp \).

The special states are called “eigenstates.”

Observation causes non-negligible disturbance that changes the system from being in the state \( P_\alpha \) into one of the states \( P_\parallel \) or \( P_\perp \).

System makes sudden jump from being part in each state to being in only one state.

Probability laws determine which is the final state.
Interference of light – described classically by Maxwell’s Equations in terms of light waves.

Classical description – Maxwell’s Equations: wave functions

A light wave enters the interferometer.
Light wave is split into two waves by 50% beam splitter.
Each wave reflects from end mirror, returns, and crosses at small angle.
In region of overlap, light waves constructively and destructively interfere to give interference pattern.
Einstein taught us that light is not a wave but particles, photons.

Initial idea:

Classical E&M wave function described **number of photons in a region of space.** Otherwise, everything the same.

Photons enter interferometer. At beam splitter, half go into one leg, half go into the other leg.
They come together and interfere.

Many problems with this description.
Example: interference pattern unchanged when light intensity approaches zero.
Photon in superposition state $T$. It should be thought of as being in both legs of apparatus. Can’t say which one it is in. Each photon interferes with itself. No problem at low light intensity.

The “translation state” $T$ of a photon can be written as a superposition

$$T = T_1 + T_2$$

Photon in superposition state $T$. It should be thought of as being in both legs of apparatus. Can’t say which one it is in.

Each photon interferes with itself. No problem at low light intensity.

Wave function ➔ probability of finding a single photon (particle) in each leg of the apparatus (region of space). Not number in each leg.
State

Collection of bodies with various properties

mass
moment of inertia

Bodies interact according to specific laws of force.

Certain motions consistent with bodies and laws.

Each such motion is a state of the system.

Definition: The state of a system is an undisturbed motion that is restricted by as many conditions as are theoretically possible without contradiction.

Example – s, p, d states of H atom

State can be at a single time or time dependent.
Superposition Principle

Assume: Whenever a system is in one state it can always be considered to be partly in each of two or more states.

Original state – can be regarded as a superposition of two or more states.
Conversely – two or more states can be superimposed to give a new state.

Non-classical superposition.
In mathematics can always form superpositions.
Sometimes physically useful, sometimes not.

In Q. M., superposition of states is central to the theoretical description of nature.
Observables in Q. M.

Consider system with two states – A and B. [Correct notation will be introduced shortly. This is still a qualitative introduction.]

Observation of system in state A
result $\alpha$.

Observation on B
result $\beta$.

Observation on a superposition of A and B
Gives either $\alpha$ or $\beta$.
Never gives anything else.
Probability of getting result $\alpha$ or $\beta$ depends on relative weights of A and B in the superposition.
"The intermediate character of the state formed by superposition thus expresses itself through the probability of a particular result for an observation being 'intermediate' between the corresponding probabilities for the original state, not through the result itself being intermediate between the corresponding results for the original states."  

Dirac
Absolute size and Superposition Principle intimately related.

When making a series of observations on identically prepared atomic systems, the result from one observation to the next in general will vary.

If you make enough observations, you will get a probability distribution for the results.

Quantum mechanics calculates these probabilities.