

**PHY 481/581 Intro
Nano-Materials Science and
–engineering: Some Basics of
Quantum Mechanics**



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Basics of Quantum Mechanics

- Why Quantum Physics? -

Experimental evidence forces conclusions that the concept of classical wave and classical particle are of limited generality, details later on

a beam of light is not only an electromagnetic wave but also a stream of particles, the particles of light are mass less and referred to as photons
Planck's blackbody radiation formulae, Einstein's explanation of the photoelectric effect, Compton's scattering of X-ray photons by electrons (3 Nobel prizes)

a beam of particles with mass or a single particle, e.g. electron, neutron, C_{60} is not only a collection of particles, but also a wave phenomenon is associated with it, by special relativity this collection of particles is moving for some observer while it may be stationary for another observer

Double slit experiment with particles with mass, electron and neutron diffraction

Basics of Quantum Mechanics

- Why Quantum Physics? -

- Classical mechanics (Newton's mechanics) and Maxwell's equations (electromagnetics theory) can explain MACROSCOPIC phenomena such as motion of billiard balls or rockets.
- Quantum mechanics is used to explain microscopic phenomena such as photon-atom scattering and flow of the electrons in a semiconductor.
- QUANTUM MECHANICS is a collection of postulates based on a huge number of experimental observations.
- The differences between the classical and quantum mechanics can be understood by examining both
 - The classical point of view
 - The quantum point of view
 - For large quantum numbers, the predictions of quantum physics match those of classical physics, Niels Bohr's correspondence principle

Basics of Quantum Mechanics

- Classical Point of View -

- In Newtonian mechanics, the laws are written in terms of PARTICLE TRAJECTORIES.
- A PARTICLE is an indivisible mass point object that has a variety of properties that can be measured, which we call observables. The observables specify the state of the particle (position and momentum).
- A SYSTEM is a collection of particles, which interact among themselves via internal forces, and can also interact with the outside world via external forces. The STATE OF A SYSTEM is a collection of the states of the particles that comprise the system.
- All properties of a particle can be known to infinite precision.
- Conclusions:
 - TRAJECTORY → state descriptor of Newtonian physics,
 - EVOLUTION OF THE STATE → Use Newton's second law
 - PRINCIPLE OF CAUSALITY → Two identical systems with the same initial conditions, subject to the same measurement will yield the same result.

Basics of Quantum Mechanics

- Quantum Point of View -

- Quantum particles can act as both particles and waves
→ WAVE-PARTICLE DUALITY
- Quantum state is a conglomeration of several possible outcomes of measurement of physical properties → Quantum mechanics uses the language of PROBABILITY theory
- An observer cannot observe a microscopic system without altering some of its properties. Neither can one predict with certainty how the state of the system will change.
- QUANTIZATION of energy is yet another property of "microscopic" particles.

Basics of Quantum Mechanics

- Heisenberg Uncertainty Principle -

- One cannot unambiguously specify the values of particle's position and its momentum for a microscopic particle, i.e.

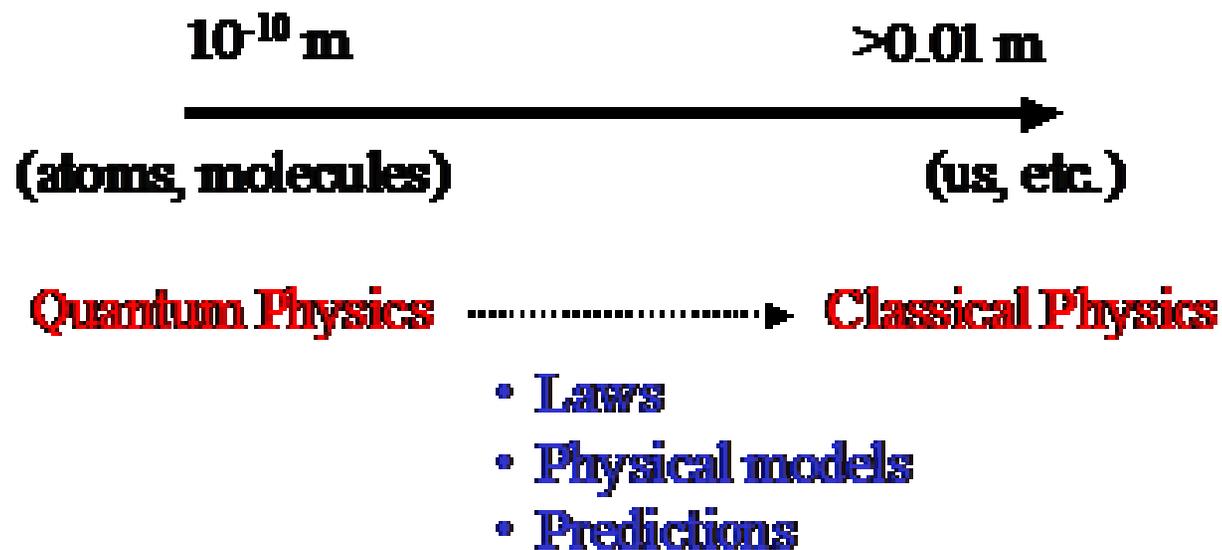
$$\Delta x(t_0) \cdot \Delta p_x(t_0) \geq \frac{1}{2} \frac{h}{2\pi}$$

- Position and momentum are, considered as non-commuting variables (applying the respective operators in different sequences gives different results).
- The Heisenberg uncertainty principle strikes at the very heart of the classical physics => the particle trajectory.
- There is an analogous uncertainty for the product of ΔE and Δt (at the same position).

Basics of Quantum Mechanics

- The Correspondence Principle -

When Quantum physics is applied to macroscopic systems, it must reduce to the classical physics. Therefore, the non-classical phenomena, such as uncertainty and duality, must become undetectable. Niels Bohr codified this requirement into his Correspondence principle:



Basics of Quantum Mechanics

- Particle-Wave Duality -

- The behavior of a "microscopic" particle is very different from that of a classical particle:
 - → in some experiments it resembles the behavior of a classical wave (not localized in space)
 - → in other experiments it behaves as a classical particle (localized in space)
- Corpuscular theories of light treat light as though it were composed of particles, but can not explain **DIFRACTION** and **INTERFERENCE**.
- Interference of light in a double slit experiment was demonstrated as early as 1803 by Thomas Young
- Maxwell's theory of electromagnetic radiation can explain these two phenomena, which was the reason why Newton's corpuscular theory of light was abandoned.

- Particle-Wave Duality -

- **Waves as particles**

- Max Planck work on black-body radiation, in which he assumed that there are resonators/oscillations of charge within the cavity walls that cause light to be emitted and absorbed, described using a simple harmonic oscillator model, can only exchange energy in quantized units.
- 1905 Einstein proposed that the energy in an electromagnetic field is not spread out over a spherical wavefront, but instead is localized in individual clumps - quanta. Each quantum of frequency ν travels through space with speed of light, carrying a discrete amount of energy and momentum = photon => used to explain the photoelectric effect, later to be confirmed by the x-ray experiments of Compton.

- **Particles as waves**

- Double-slit experiment, in which instead of using a light source, one uses the electron gun. The electrons are diffracted by the slit and then interfere in the region between the diaphragm and the detector.

Check this link for Particle-Wave Duality explanation

<http://www.youtube.com/watch?v=DfPeprQ7oGc>

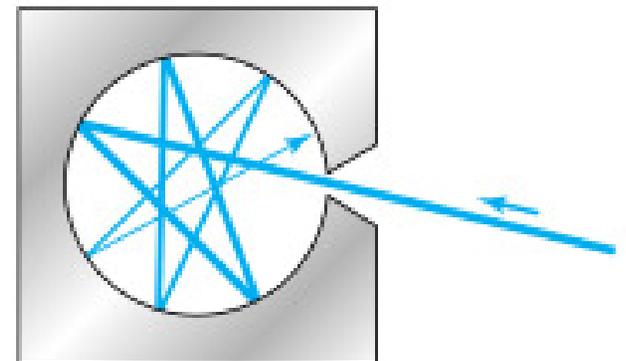
Waves as Particles

Blackbody?

- A material is constantly exchanging heat with its surrounding (to remain at a constant temperature):
 - It absorbs and emits radiations
 - Problem: it can reflect incoming radiations, which makes a theoretical description more difficult (depends on the environment)
- A blackbody is a perfect absorber:
 - Incoming radiations is totally absorbed and none is reflected

Blackbody Radiation

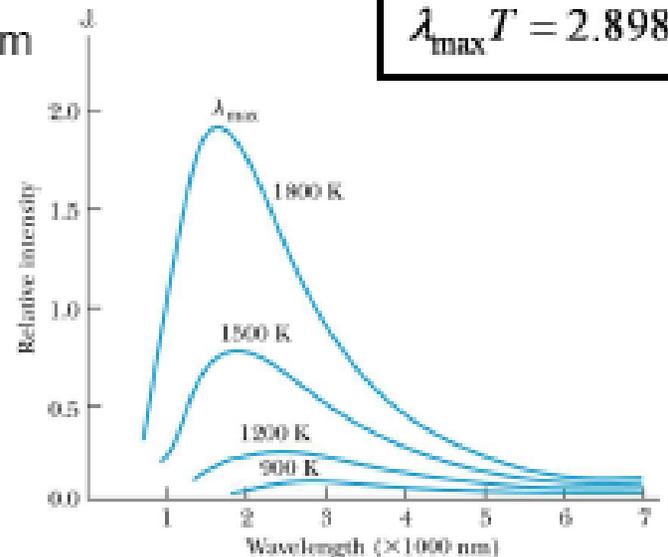
- Blackbody = a cavity in a block of graphite with a small hole connecting the cavity to the outside world.
 - Incoming radiations entering the hole keep bouncing around inside the cavity with a negligible change of escaping again through the hole => Absorbed.
 - The cavity is the perfect absorber, e.g. the blackbody radiation emission does not depend on the material surrounding the cavity => a universal law of nature should be describing this phenomenon



Wien's displacement law

- The intensity $\mathcal{I}(\lambda, T)$ is the total power radiated per unit area per unit wavelength at a given temperature
- **Wien's displacement law:** The maximum of the distribution shifts to smaller wavelengths as the temperature is increased.

Visible light: 400 – 700 nm
UltraViolet: <400 nm
Infrared: >700 nm



$$\lambda_{\max} T = 2.898 \times 10^{-3} \text{ m} \cdot \text{K}$$

Empirical Formula

Wilhem Wien: Nobel Prize 1911

Stefan-Boltzmann Law

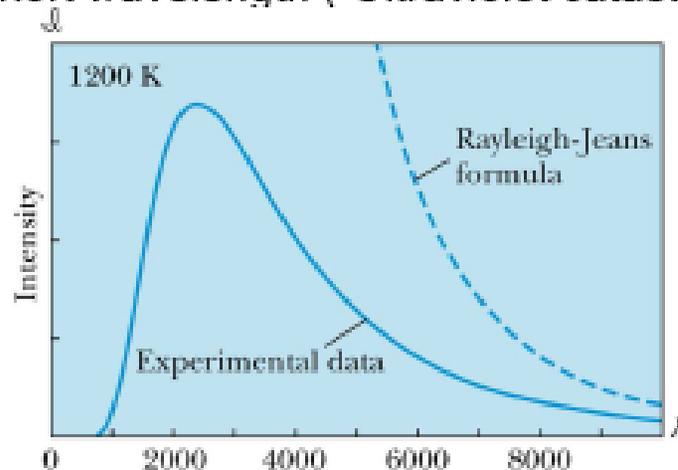
- The total power radiated increases with the temperature:

$$R(T) = \int_0^{\infty} \mathcal{L}(\lambda, T) d\lambda = \epsilon \sigma T^4$$

- This is known as the **Stefan-Boltzmann law**, with the constant σ experimentally measured to be $5.6705 \times 10^{-8} \text{ W / (m}^2 \cdot \text{K}^4)$.
- The **emissivity** ϵ ($\epsilon = 1$ for an idealized blackbody) is simply the ratio of the emissive power of an object to that of an ideal blackbody and is always less than 1.

Understanding the blackbody radiation spectrum

- Attempts to fit the low and high wavelength part of the spectrum
- Using classical theory of electromagnetism and thermodynamics, Lord Rayleigh comes up with:
$$u(\lambda, T) = \frac{2\pi ckT}{\lambda^4}$$
 Rayleigh-Jeans formula
- Major flaw at short wavelength (“Ultraviolet catastrophe”)



In essence the long wavelength part of the blackbody spectrum was derived, the Rayleigh-jeans formulae is what one obtained by Bohr's correspondence principle

[Describing the blackbody emission spectra:](#)
one of the outstanding problems at the beginning of the 20th century

Whenever there is an “infinite result”, some of the physics is wrong

Ultraviolet Catastrophe?

- Classical physics:
 - Emission spectrum of hot body: a superposition of electromagnetic waves of different frequencies (wavelength)
 - Frequencies allowed: standing waves inside the cavity, integral number of wavelengths fit the size of the cavity
- Equipartition of the energy:
 - Every standing wave carries kT of energy
 - Flaw: when $\lambda \rightarrow 0$, the number of standing waves \uparrow , leading to $E \rightarrow \infty$
- [Ultraviolet Catastrophe] Failure of classical theory:
 - The work of Rayleigh-Jeans was considered as state-of-the-art, using well tested theories, which were in very good agreement with experimental results in many other circumstances.
 - ***Need for a new theory...***

**Used in many
application, i.e.
pyrometer**

Planck's radiation law

- Planck assumed that the radiation in the cavity was emitted (and absorbed) by some sort of “oscillators” contained in the walls.

He used statistical physics of arrays of harmonic oscillators under the assumption that their energy is quantized, originally he started with a curve fit and interpreted it physically

$$I(\lambda, T) = \frac{2\pi c^2 h}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}$$

Planck's radiation law

- Planck made two modifications to the classical theory:
 - 1) The oscillators (of electromagnetic origin) can only have certain discrete energies determined by $E_n = nh\nu$, where n is an integer, ν is the frequency, and h is called Planck's constant.

$$h = 6.6261 \times 10^{-34} \text{ J}\cdot\text{s}$$

- 2) The oscillators can absorb or emit energy in discrete multiples of the fundamental quantum of energy given by

$$\Delta E = h\nu$$

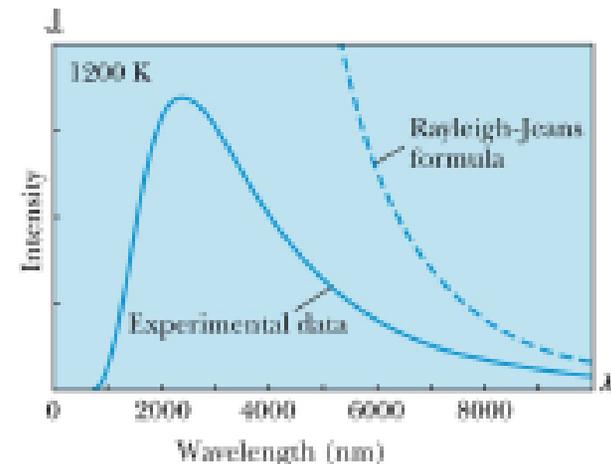
Quantization

of the energy of a harmonic oscillator, never before seen in classical physics

- Blackbody emission spectrum explained by introducing quantization of energy transfers, resolves the ultraviolet catastrophe **from oscillator to light quantum**
 - Low wavelength \leftrightarrow High frequency ($\nu = c/\lambda$)
 - At small λ , the energy $E=h\nu$ needed to fill up the “oscillator” states increases. Their probability to be occupied decreases rapidly, e.g. faster than the rate found in the Rayleigh-Jeans formula: no ultraviolet catastrophe.

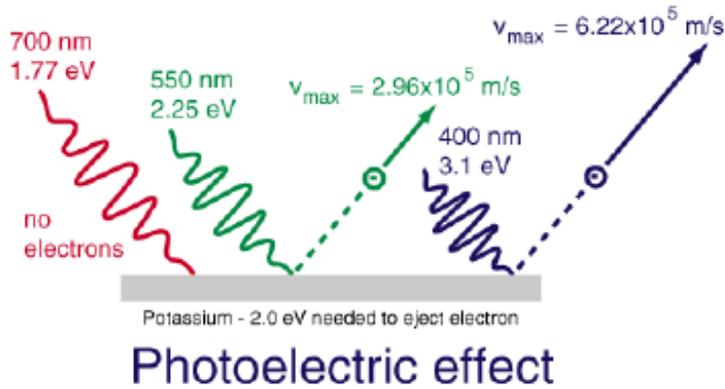
the distribution of energy for different states is different from the classical Maxwell-Boltzmann statistics

- Planck himself looked for a few years in ways to get $h \rightarrow 0$ without success.

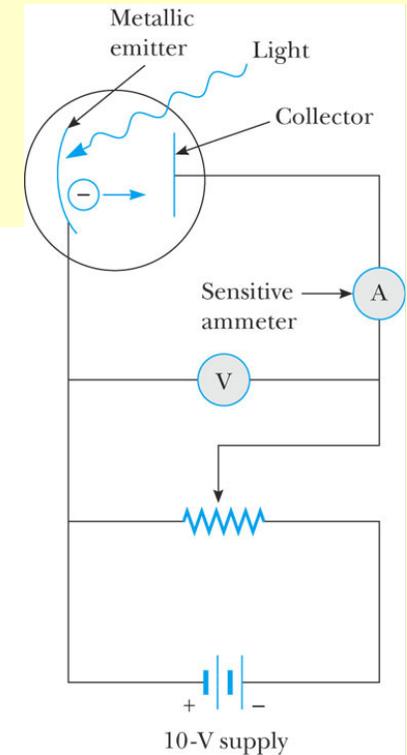


Used in many application, i.e. photocell

Photoelectric Effect



Light can eject electrons from a metal, but only if its frequency is above a threshold frequency (characteristic for each metal).



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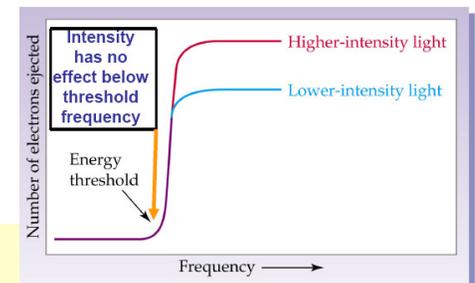
Influence of Light Intensity on the Photoelectric Effect

Classically, for light as a wave, its energy is proportional to the square of its *amplitude*.

For particles, energy is proportional to *frequency*

Einstein (1905) proposed that light has particle nature (as well as wave nature).

light is quantized (photons).



$$KE_{\max} = V_{\text{stop}} = hf - \phi$$

Larger frequency, means smaller wavelength, and larger Energy = hf. 20

Basics of Quantum Mechanics

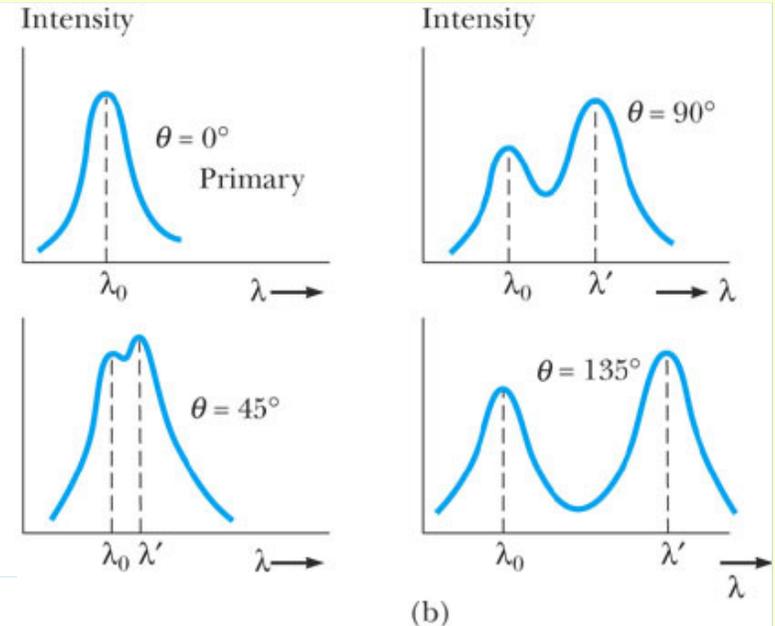
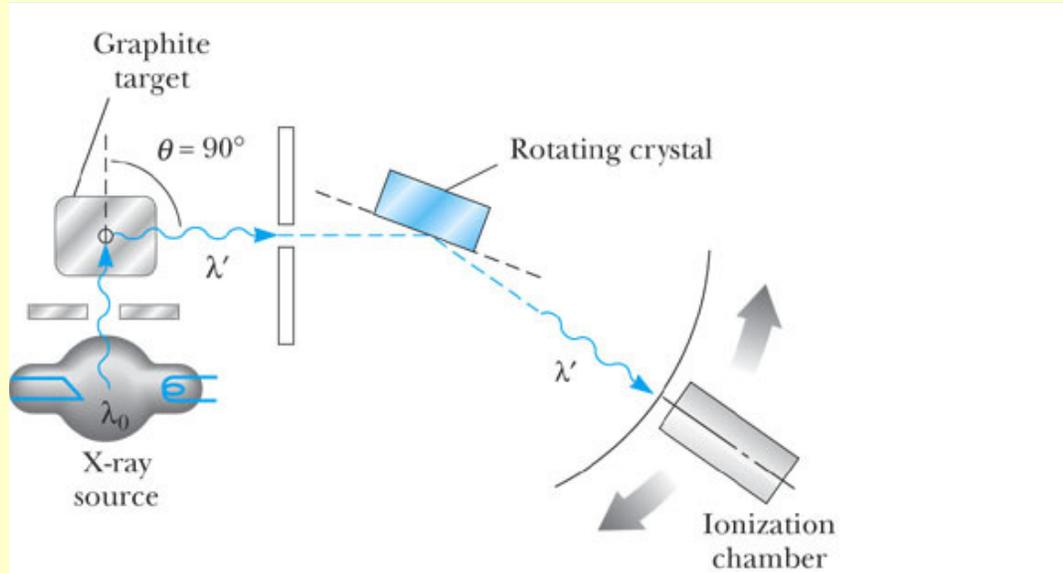
- Photoelectric Effect, summary -

- **The photoelectric effect provides evidence for the particle nature of light.**
- **It also provides evidence for quantization.**
- **The electrons will only be ejected once the threshold frequency is reached .**
- **Below the threshold frequency, no electrons are ejected.**
- **Above the threshold frequency, the number of electrons ejected depend on the intensity of the light.**
- **The effect is almost instantaneous, incompatible with wave explanation**

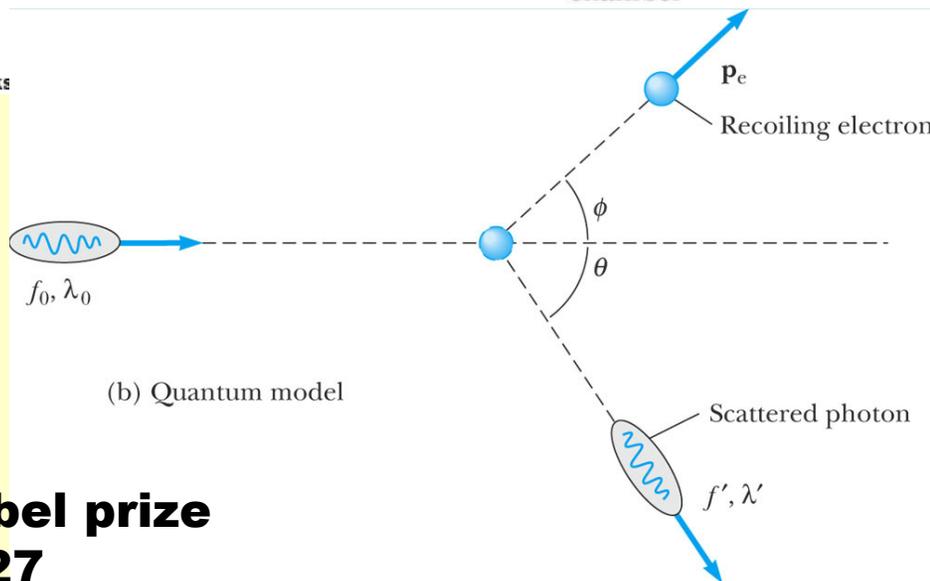
Used in many application, i.e. determining of particle masses

Basics of Quantum Mechanics

- Compton Effect -



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(b) Quantum model

**Nobel prize
1927**

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$$\lambda' - \lambda_0 = \frac{h}{m_e c} (1 - \cos \Theta)$$

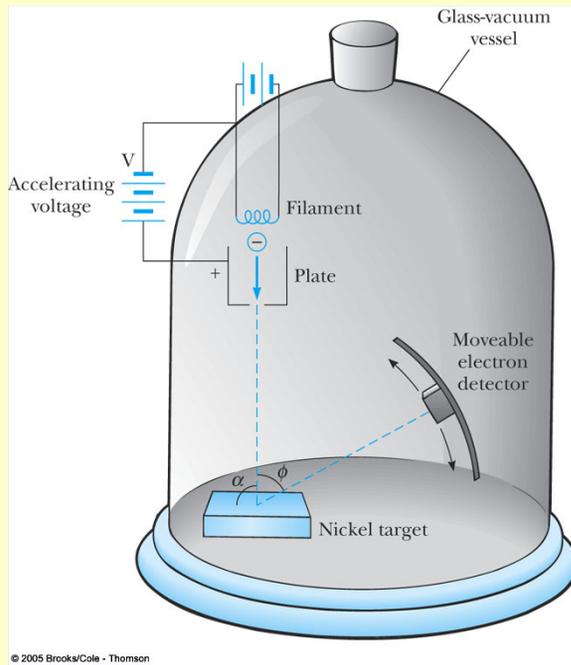
This formula is easily derived by assuming an elastic collision between two particles (energy and momentum is conserved, photon momentum $p = E/c = \frac{h}{\lambda}$)

Particles as waves

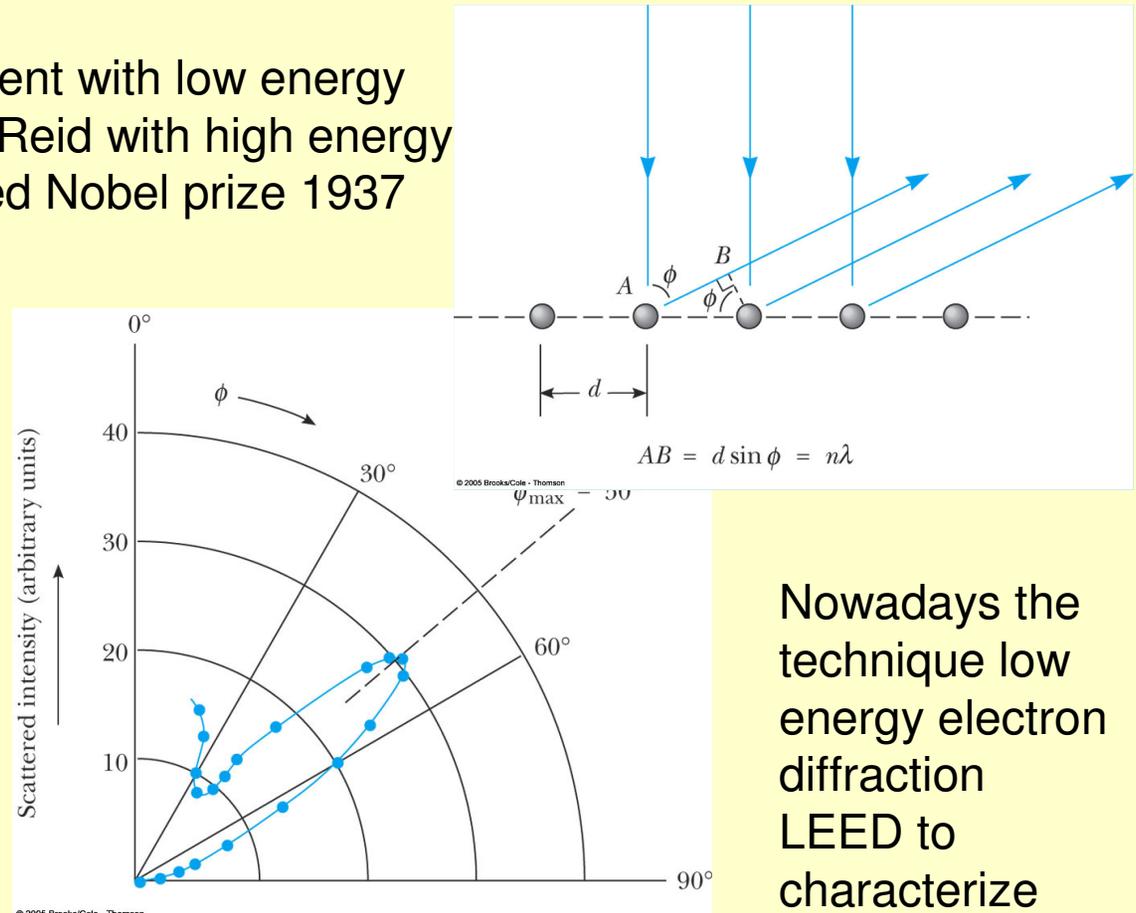
Basics of Quantum Mechanics: electrons as waves

De Broglie hypothesis (1924): Wave properties: $\lambda = h/p$ and $f = E/h$ for moving matter just as for moving particles of light, Nobel prize 1929

Davission and Germer by accident with low energy electrons; G.P. Thompson and Reid with high energy electrons in transmission, shared Nobel prize 1937



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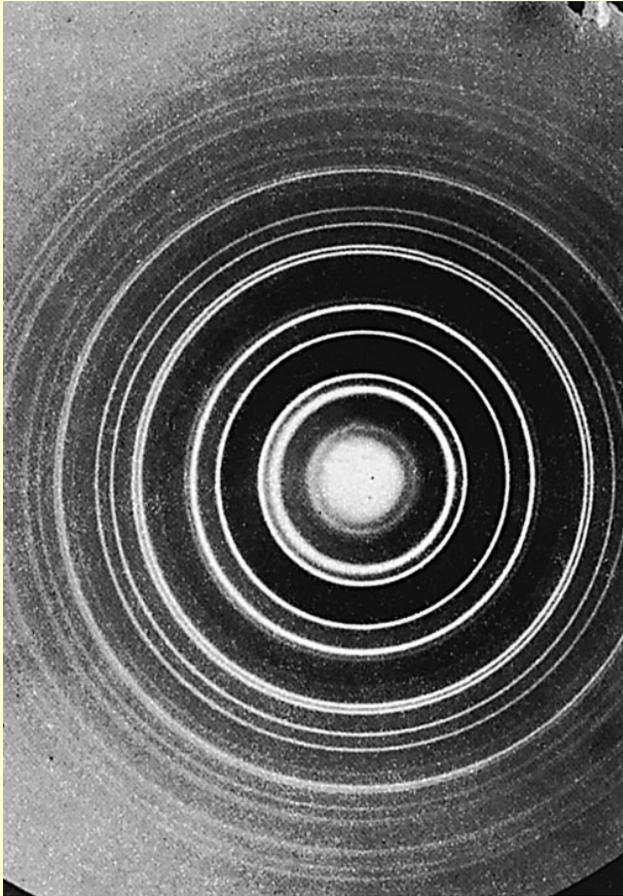


Nowadays the technique low energy electron diffraction LEED to characterize surfaces 24

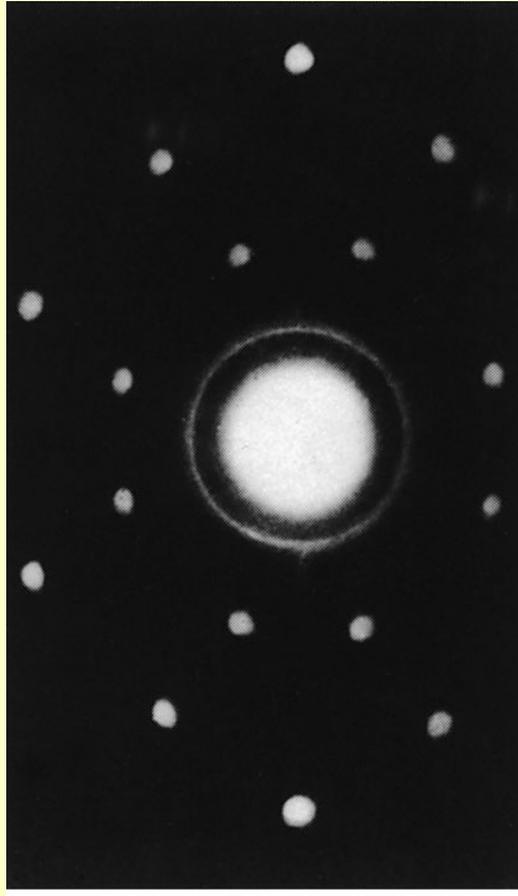
Slow electrons do not need to be treated realistically, λ in a few Å range

$$\lambda = \frac{h}{p} = \frac{h}{m_0 v} = \frac{h}{\sqrt{2m_0 e U}}$$

Basics of Quantum Mechanics: electron diffraction



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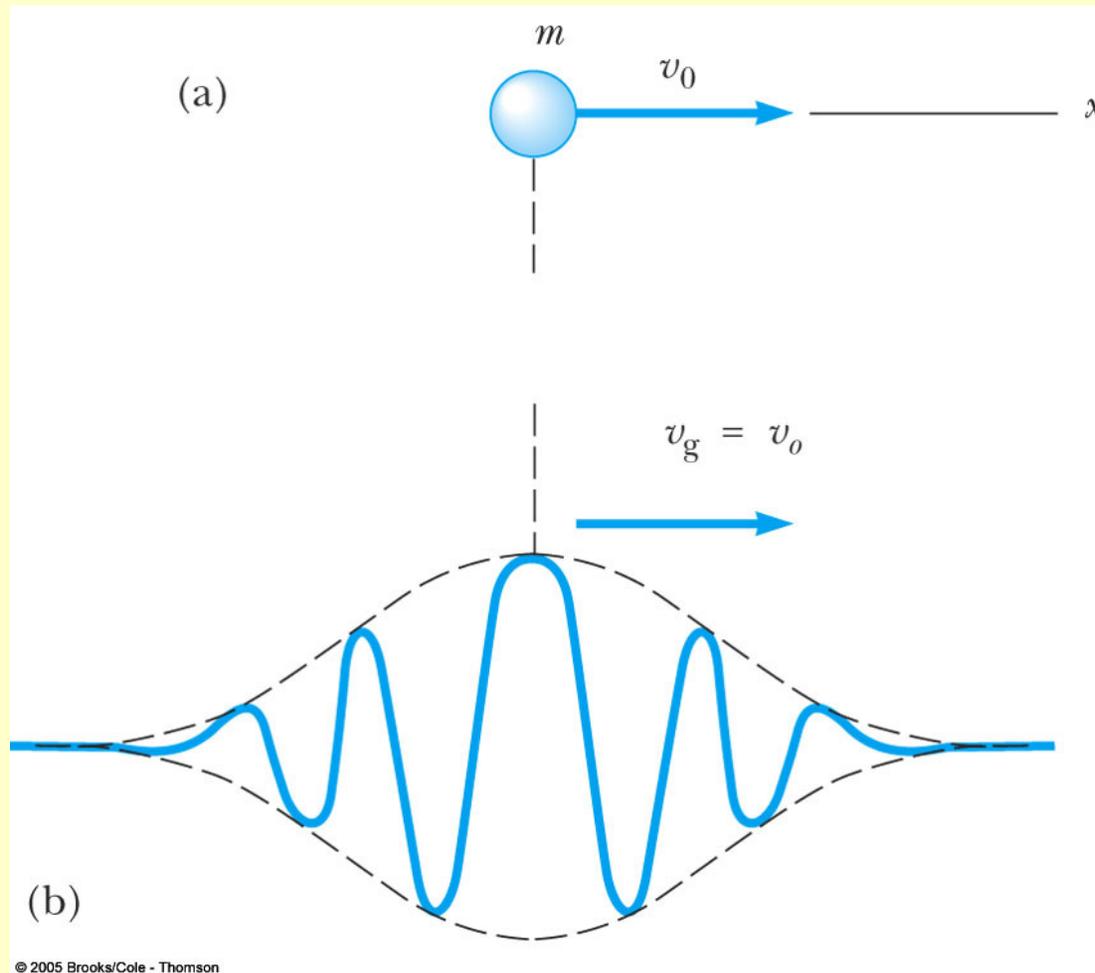
<http://newton.umsl.edu/run//nano/unknown173.html>

$$\lambda = \frac{h}{\sqrt{2m_0eU}} \frac{1}{\sqrt{1 + \frac{eU}{2m_0c^2}}}$$

For TEMs, λ is in the pm range, Acceleration voltage (U) is in the 200 – 300 kV range, velocity: 70 – 80 % speed of light

High energy transmission electron diffraction patterns fine grained polycrystalline material left, one single crystal right

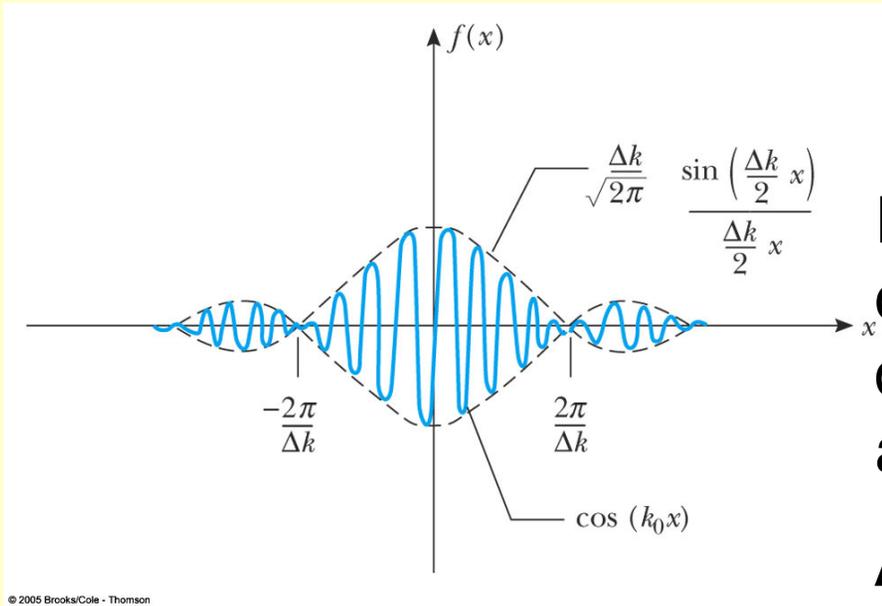
Basics of Quantum Mechanics



Many different waves form together a wave packet,

the group velocity of the packet moves as the same velocity as the particle with which it is associated

uncertainty principle revisited



Results with necessity from the wave particle duality

For a “well defined pulse” composed of many waves with different wave vectors $k = 2\pi/\lambda$ and angular frequencies $\omega = 2\pi f$

$$\Delta k \Delta x \approx 1$$

$$\Delta \omega \Delta t \approx 1$$

$$\Delta x \Delta p \gtrsim h$$

$$\Delta E \Delta t \gtrsim h$$

> $h/4\pi$ if pulse is described by Gaussians

Just multiply both sides by h and use de Broglie/Planck/Einstein relations

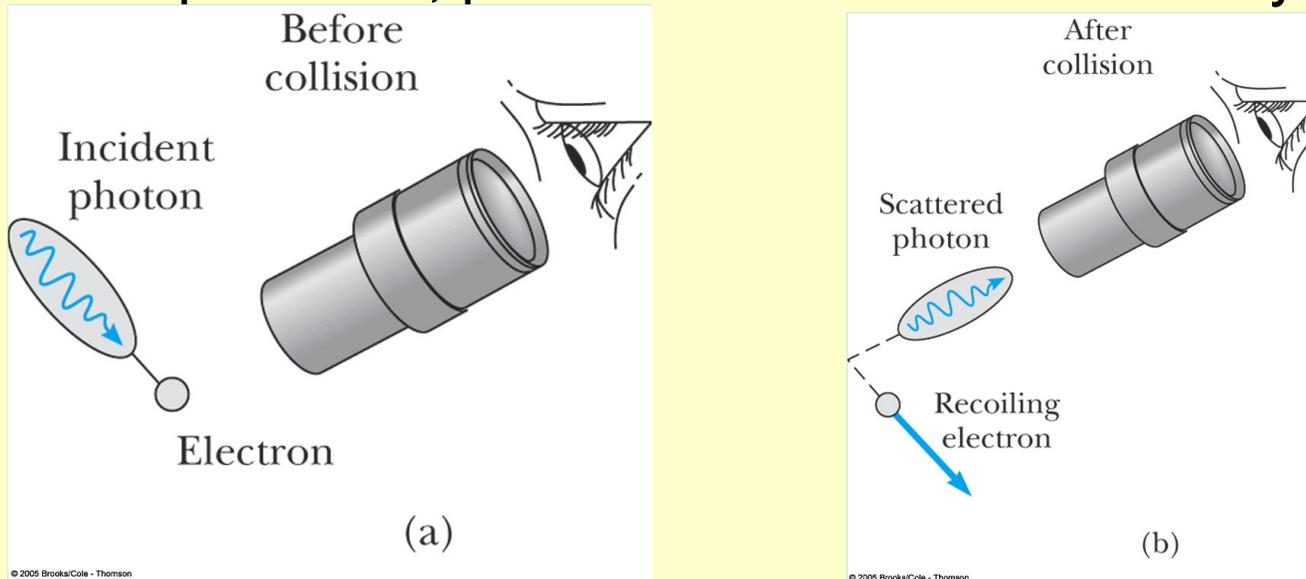
$$E = h f \quad \text{and} \quad p = h/\lambda = h k$$

<http://phys.educ.ksu.edu/vqm/html/wpe.html>

In Heisenberg's non-commuting operator notation

$$[X, P] = XP - PX = i\hbar$$

Basics of Quantum Mechanics: expanding on Compton experiment, precision limit and uncertainty



In order to know something about the electron, (build a theory, use the theory to make predictions,) we need to make a measurement, i.e. we need to interact with it, this however disturbs the electron,

in classical physics the effects of the interaction were negligible, in quantum physics they cannot be neglected, this forces quantum mechanics to use a different logical structure, this in turn leads to probabilistic predictions rather than definitive classical predictions,

It is our classical preconception that makes quantum mechanics not intuitive

Postulates of Quantum Mechanics

Basics of Quantum Mechanics

- The mathematical structure of Quantum Mechanics is just linear algebra and Hilbert spaces
- As most people do not learn about Hilbert space, we will have another set of slides on that
- What makes quantum mechanics a useful physical theory is the physical interpretation of the mathematical results
- As with any mathematical scheme, there are different ways to define the basis postulates, what follows is not particularly strict in the mathematical sense and uses some physical concepts for its justification
- The mathematical structure of classical physics is set theory, because human evolved with the physics of classical objects around, set theory comes natural to us and we have physical intuition even without ever studying classical physics, many animals have something like physical intuition as well, otherwise a carnivore could not successfully hunt an omnivore
- **We did not evolve in an environment where quantum physical effects are directly perceptible by our senses, therefore, we have difficulty understanding it**
- **The only way to do quantum mechanics is to do the mathematics right under the physical boundary conditions that are set by the specifics of the problem, that is all nature allows us to know, but is is enough to build an engineering disciplines and industries on it**

Basics of Quantum Mechanics

- First Postulate of Quantum Mechanics -

Quantum physicists are interested in all kinds of physical systems (photons, conduction electrons in metals and semiconductors, atoms, molecules etc.). States of these rather diverse systems are represented by the same type of functions → STATE FUNCTIONS.

First postulate of Quantum mechanics:

Every physically-realizable state of the system is described in quantum mechanics by a state function ψ that contains all accessible physical information about the system in that state.

- **Physically realizable states** → states that can be studied in laboratory
- **Accesible information** → the information we can extract from the wavefunction
- **State function** → function of position, momentum, energy

Basics of Quantum Mechanics

- First Postulate of Quantum Mechanics -

If ψ_1 and ψ_2 represent two physically-realizable states of the system, then the linear combination

$$\Psi = c_1\Psi_1 + c_2\Psi_2$$

where c_1 and c_2 are arbitrary complex constants, represents a third physically realizable state of the system.

Note:

$$\Psi(x, y, z, t) = \psi(x, y, z) \cdot e^{iEt/\hbar}$$

if the particle finds itself in a potential that does not change over time, e.g. a bound state or a free particle

Wave function $\Psi(x,t)$ \rightarrow position and time probability amplitude

Quantum mechanics describes the outcome of a hypothetical ensemble of measurements, where the ensemble of measurements is very large and has been performed on identical (non-interacting) systems, all of which have been identically prepared so as to be in the same state.

While the wave function is generally complex, all physical observable that are derived from it are real, e.g. probability of finding the particle in region of space dV

$$P \cdot dV \cong \int \Psi^*(x, y, z, t) \cdot \Psi(x, y, z, t) \cdot dV \quad \text{frequently} \quad P \cdot dV \cong \int |\Psi(x, y, z, t)|^2 \cdot dV$$

Basics of Quantum Mechanics

- Second Postulate of Quantum Mechanics -

the normalization condition for the wave function

$$\int P dV = \int |\psi(x, y, z)|^2 dV = \int \psi^*(x, y, z)\psi(x, y, z)dV = 1$$

- Only normalizable functions can represent a quantum state and these are called physically admissible functions. (except for a free particle, which cannot be normalized as it possesses a definitive momentum and is spread out all over space)
- State function must be continuous and single valued function.
- State function must be a smoothly-varying function (continuous first and second derivatives).
- Note that normalization sets a scale, in the formulae above the scale is one full particle per area

Basics of Quantum Mechanics

- Third Postulate of Quantum Mechanics -

Third Postulate:

Every observable in quantum mechanics is represented by an operator which is used to obtain physical information about the observable from the state function. For an observable that is represented in classical physics by a function $Q(x,p)$, the corresponding operator is $Q(\hat{x}, \hat{p})$.

Observable	Operator
Position	\hat{x}
Momentum	$\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x}$
Total Energy, sum of kinetic and potential energy	$E = \frac{\hat{p}^2}{2m} + V(\hat{x}) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$

Basics of Quantum Mechanics

- calculating expectation values -

When we have solved the Schrödinger equation for the correct boundary conditions of our problem, we know that our wave function described the problem correctly,

It contains all we are allowed to know about the system given the constraint of the uncertainty principle

$$\langle p \rangle = \int_{-\infty}^{\infty} \Psi^* \cdot \hat{p} \cdot \Psi \cdot dx \cdot \left\{ \int_{-\infty}^{\infty} \Psi^* \cdot \Psi \cdot dx \right\}^{-1}$$

Generalization to 3D
straightforward

Note that the second factor-integral by which the first factor (with the operator bracketed by the conjugate complex wave function and the wave function) is unity in case the wave function is normalized, this clarifies that normalization sets the scale for all further measurements, calculations

Basics of Quantum Mechanics

- More on Operators -

- An operator is an instruction, a symbol which tells us to perform one or more mathematical acts on a function, say $f(x)$. The essential point is that they act on a function.
- Operators act on everything to the right, unless the action is constrained by brackets.
- Addition and subtraction rule for operators:

$$(\hat{Q}_1 \pm \hat{Q}_2)f(x) = \hat{Q}_1 f(x) \pm \hat{Q}_2 f(x)$$

- The product of two operators implies successive operation:

$$\hat{Q}_1 \hat{Q}_2 f(x) = \hat{Q}_1 [\hat{Q}_2 f(x)]$$

- The product of two operators is a third operator:

$$\hat{Q}_3 = \hat{Q}_1 \hat{Q}_2$$

- Two operators commute if they obey the simple operator expression:

$$[\hat{Q}_1, \hat{Q}_2] = \hat{Q}_1 \hat{Q}_2 - \hat{Q}_2 \hat{Q}_1 = 0 \Rightarrow \hat{Q}_1 \hat{Q}_2 = \hat{Q}_2 \hat{Q}_1$$

Basics of Quantum Mechanics

- More on Operators -

The requirement for two operators to be commuting operators is a very important one in quantum mechanics and it means that we can simultaneously measure the observables represented with these two operators. The non-commutivity of the position and the momentum operators (the inability to simultaneously determine a particle's position and momentum) is represented with the Heisenberg uncertainty principle, which in mathematical form is expressed as:

$$\Delta x \cdot \Delta p \geq \frac{\hbar}{2} = \frac{1}{2} |\langle [\hat{x}, \hat{p}] \rangle|$$

and can be generalized for any pair of non-commuting observables, e.g. time and total energy, spin in two different directions.

Basics of Quantum Mechanics

- Fourth Postulate of Quantum Mechanics -

1926 Erwin Schrödinger proposed an equation that describes the evolution of a quantum-mechanical system → SWE which represents quantum equations of motion, and is of the form:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + U(x,t)\Psi(x,t) = \hat{H}\Psi(x,t) = i\hbar \frac{\partial \Psi(x,t)}{\partial t} = \hat{E}\Psi(x,t)$$

This work of Schrödinger was stimulated by a 1925 paper by Einstein on the quantum theory of ideal gas, and the de Broglie theory of matter waves.

Note: ***i in the total energy operator term, this is a complex equation for complex functions !!***

Examining the time-dependent SWE, one can also define the following operator for the total energy:

$$\hat{H} = K\hat{E} + P\hat{E}$$

$$\hat{E} = i\hbar \frac{\partial}{\partial t}$$

Potential Energy PE typically U or V

Basics of Quantum Mechanics

- Fourth Postulate of Quantum Mechanics -

When potential energy function does not depend on time, one can make a separation of the variables of the wave function and derive the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + U(x)\psi(x) = \hat{H}\psi(x) = E\psi(x)$$

***Note that the i on the total energy side (right hand side) is gone
complex equation for complex functions !!***

After re-arrangements, if three dimensional, one has to go back to partial differentials

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2} \{E - U(x)\}\psi(x) = 0$$

Basics of Quantum Mechanics

- Fourth Postulate of Quantum Mechanics -

- note that it is the potential energy function that sets the physical boundary conditions for the problem, Schrödinger's equation is just an operator statement that energy is conserved multiplied by some wave function
- when Schrödinger's equation is actually fulfilled, we have a wave function that makes sense for the specific problem (so the problem becomes to find a wave function that fulfills this equation)
- from that wave function we can then calculate anything we would like to know and are allowed to know by the Heisenberg uncertainty principle

Basics of Quantum Mechanics

- Fourth Postulate of Quantum Mechanics -

Fourth (Fundamental) postulate of Quantum mechanics:

The time development of the state functions of an isolated quantum system is governed by the time-dependent SWE $\hat{H}\psi = i\hbar\partial\psi/\partial t$, $\hat{H} = K\hat{E} + P\hat{E}$ is the Hamiltonian of the system.

Note on isolated system:

The TDSWE describes the evolution of a state provided that no observations are made. An observation alters the state of the observed system, and as it is, the TDSWE can not describe such changes.

If is said that as soon as a measurement is made, or equivalently as soon as an expectation value is calculated, the wave function collapses into one of the eigenstates of the very operator that has been used for the calculations

Basics of Quantum Mechanics

-meaning of Schrödinger's equation -

Schrödinger's equation is the quantum physics equivalent to both Newton's 2nd law (which deals with classical particles) and the classical wave equation (which deals with classical waves and is sometimes referred to as Helmholtz equation as it can be derive from Newton's law)

So it deals with the wave-particle duality effectively, loosely speaking this is one of the reason that it is complex in its time dependent form

The wave function of the free particle may be considered as being the equivalent of Newton's first law, because its momentum is well defined (not uncertain), the free particle is everywhere with the same probability, in a sense spread out over all space

$$\Psi(x, t) = A e^{-(i/\hbar)(Et - px)} = A e^{(ip/\hbar)x} \cdot e^{-(iE/\hbar)t} = \psi(x) \cdot \phi(t)$$

Heisenberg's law of motion formulated in matrix mechanics is $\frac{d\hat{A}_H}{dt} = \frac{i}{\hbar} [\hat{A}_H, \hat{H}]$ equivalent to Schrödinger equation (Newton's 2nd law, Helmholtz equation), but more general with respect to time dependence

Dirac notation for state vectors, a generalization of wavefunctions to use the mathematical structure of the Hilbert Space

$|a\rangle$ is a ket vector representing quantum state a just as well as a wave function ψ_a
its dual vector $\langle a|$ is a bra vector and represents ψ_a^*

The normalization condition thus becomes $\langle a|a\rangle=1= \langle \psi|\psi\rangle$

A physical quantity or the action to determine a physical quantity, i.e. a measurement is represented by matrix A (instead a linear operator) is written as $A|a\rangle = A|\psi\rangle$

An expectation value thus becomes $\langle A\rangle=\langle \psi|A|\psi\rangle$

Any ket vector can be represented by a linear combination of a complete set of ket basis vectors, these basis vectors are chosen according to the problem to be solved, i.e. for a two state system, there is a two dimensional Hilbert space with two basis vectors, there is also an infinity dimensional Hilbert space with infinitely many basis vectors for certain problems

$$|f\rangle=c_1|\psi_1\rangle+ c_2|\psi_2\rangle + \dots c_i|\psi_i\rangle$$

A measurement changes a quantum state (from a set of probabilities) to a definitively measured state, the probability of observing the eigenvalue of the eigenstate ψ_i is $c_i^*c_i$

The Schrödinger equation becomes $H_{ij}|\psi_j\rangle=E_i|\psi_i\rangle$, instead of solving the differential equation for the wave function for a certain potential energy function, one can diagonalize the matrix that corresponds to the Hamiltonian operator

2.6 Quantum Mechanics Postulates

Here we *summarize* the quantum mechanics postulates arrived at in the previous discussion. They are formulated in the abstract Hilbert space.

- (1) There is a state vector $|\Psi(t)\rangle$ that provides a complete dynamical description of a system;
- (2) An observable F is represented by a linear hermitian operator \hat{F} ;
- (3) The operators obey canonical commutation relations, in particular

$$[\hat{p}, \hat{x}] = \frac{\hbar}{i} \quad (2.95)$$

- (4) The dynamics is given by the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H} |\Psi(t)\rangle \quad (2.96)$$

- (5) The eigenstates of a linear hermitian operator form a complete set

$$\hat{F} |f_n\rangle = f_n |f_n\rangle \quad ; \quad \sum_n |f_n\rangle \langle f_n| = \hat{1} \quad (2.97)$$

- (6) Measurement postulate:

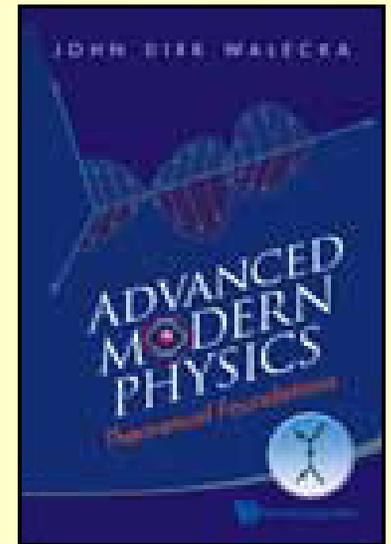
- (a) A precise measurement of F must yield one of the eigenvalues f_n ;
- (b) The probability of observing an eigenvalue f_n at the time t is $|\langle f_n | \Psi(t) \rangle|^2$;
- (c) A measurement $f' \leq f \leq f''$ at time t_0 reduces the state vector to

$$|\Psi(t_0)\rangle' = \frac{\sum'_n a_{f_n}(t_0) |f_n\rangle}{(\sum'_n |a_{f_n}(t_0)|^2)^{1/2}} \quad ; \quad \text{where } f' \leq f_n \leq f'' \quad (2.98)$$

Through his many years in physics, the author has found this to be a complete and essential set of postulates for the implementation of quantum mechanics.

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by John Dirk
Walecka



Basics of Quantum Mechanics

- Only in a few cases can the Schrödinger equation be solved analytically, i.e. square well, simple harmonic oscillator, hydrogen atom, helium 1+ ion, lithium 2+ ion, (key is two- body problem, a three- body problem has no exact solution in classical physics either)
- All other case can be solved by approximations, e.g. WKB as we will see for high n of harmonic oscillator (typically for slowly vary wavelength of standing waves)
- ***A popular approximation method is perturbation theory***
- ***An alternative is density functional theory***

Approximate Methods for solving the Schrödinger equation

- Perturbation theory works when a small perturbing term (\hat{H}') can be added to a known Hamiltonian to set up the unknown problem:

$$\hat{H} = \hat{H}_0 + \lambda\hat{H}'$$

- Then the eigenfunctions and eigenvalues can be approximated by a power series in λ :

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots$$

$$\psi_n = \psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \dots$$

Perturbation theory

- Plugging these expansions into the Schrödinger equation and equating each term in each order in λ
- neglecting all but the first order, quite OK for some problems, the Schrödinger equation becomes

$$E_n^{(1)} \psi_n^{(0)} = \hat{H}' \psi_n^{(0)} + (\hat{H}_0 - E_n^{(0)}) \psi_n^{(1)}$$

Perturbation Theory

- The (infinite series) of eigenstates for the (time independent) Schrödinger equation (SE) form a complete basis set for expanding any other function:

$$\psi_n^{(1)} = \sum_m a_{nm} \psi_m^{(0)}$$

- Substitute this into the first order SE just shown.....

Perturbation theory

- and multiply from the left by $\psi_n^{(0)*}$ and integrate, gives, after using $\langle \psi_n | \psi_m \rangle = \delta_{nm}$

“Correction terms and functions”

$$E_n^{(1)} = \langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle$$

$$\psi_n = \psi_n^{(0)} + \sum_{m \neq n} \frac{H'_{mn} \psi_m^{(0)}}{E_n^{(0)} - E_m^{(0)}} \quad H'_{mn} = \langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle$$

If $E_n^{(0)}$ and $E_m^{(0)}$ are degenerate “by accident” one takes a linear combination of all the degenerate wave functions that solves the perturbing Hamiltonian

Perturbation theory

- The new energy is corrected by the perturbation Hamiltonian evaluated between the unperturbed wavefunctions
- The new wave functions are mixed in using the degree to which the overlap with the perturbation Hamiltonian is significant and by the closeness in energy of the states

Time Dependent Perturbation Theory

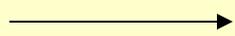
Turning on a perturbing potential at $t = 0$ and applying (something like) the previous procedure to the time dependent Schrödinger equation with P as (time dependent) probability of making a transition from state m to state k :

$$P(k, t) = \left[\frac{1}{i\hbar} \int_0^t \langle \psi_m | \hat{H}' | \psi_k \rangle \exp i \left(\frac{E_m - E_k}{\hbar} t' \right) dt' \right]^2$$

For a cosinusoidal perturbation $H'(t) \propto \cos(\omega t) P$ peaks at $\omega = \frac{E_m - E_k}{\hbar}$ (conservation of energy while uncertainty principle holds), leading to **Fermi's Golden Rule**, that the probability per unit time, dP/dt is

$$\frac{dP(m, k)}{dt} = \frac{2\pi}{\hbar} \left| \langle \psi_m | \hat{H}' | \psi_k \rangle \right|^2 \delta(E_m - E_k + \hbar\omega)$$

Conservation of energy in the transition



For a system with many levels that satisfy energy conservation, many states that are close to E_k the Fermi golden rule becomes

$$\frac{dP(m, k)}{dt} = \frac{2\pi}{\hbar} \left| \langle \psi_m | \hat{H}' | \psi_k \rangle \right|^2 \rho(E_k)$$

Density of States

Many-electron quantum mechanics without wavefunctions?

Density functional theory (DFT)

- Hohenberg and Kohn (Nobel price chemistry 1998 to Kohn): Ground state energy is a unique functional (loosely speaking function of a function) of the electron density distribution, $n(\mathbf{r})$,

$$\frac{\delta E[n(\mathbf{r})]}{\delta n(\mathbf{r})} = 0$$

- Get $n(\mathbf{r})$ by minimizing $E[n(\mathbf{r})]$:
- Δ means varying the function $n(\mathbf{r})$ until minimum is achieved
- Such a functional must exist, but is not known, so approximations are used to derive it

Example of a simple energy functional

$$E[n(\mathbf{r})] = C \int n(\mathbf{r})^{5/3} d\mathbf{r} + \frac{1}{2} \iint \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 + \int n(\mathbf{r})V(\mathbf{r})d\mathbf{r} + XC$$

Kinetic energy

Coulomb energy (e-e
repulsion)

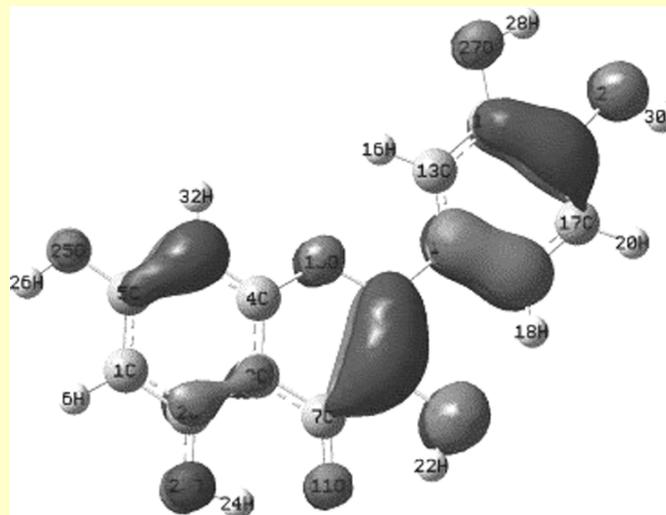
Other potential
(e.g., nuclear)

Exchange and
correlation

In the **Local Density Approximation**, exchange and correlation is modeled simply by $n(\mathbf{r})^{4/3}$

LUMO of quercetin

Lowest unoccupied
molecular orbital =
LUMO



From Stuart Lindsay, Introduction
to Nanoscience, 2010