

Preliminary Syllabus (29nov18)

Professor: Callis

Office: 55 CBB

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Time and place: MWF 1:10-2:00 in Gaines Hall 345

Text: Quantum Chemistry, 7th Edition by Ira N. Levine

Some other reading will be provided.

Prerequisite: Chmy 557 or 371 or equivalent or consent.

Undergraduates are welcome! (even without 557)

Webpage <http://www.chemistry.montana.edu/callis/courses/CHMY564.html>

Note: A strong attempt will be made to build on previous courses students may have had, but at the same time be self-contained and complete. The aim is to impart a maximum of understanding and intuition, in addition to some new skills—all with a minimum of time-consuming homework.

Scope: Applications of quantum mechanics to many-electron atoms and molecules, concentrating on stationary and time-dependent electronic and vibrational states.

Course Outline:

Part I: Time Independent

1. Personalized review of philosophy and foundations, including:

- Scope of theoretical chemistry (starting with the Big Bang)
- Need for quantum mechanics
- Quantum concepts and “understanding” quantum mechanics
- Brief review of operators, wavefunctions, the virial theorem, and the Schrödinger equation with and without time,
- Wavefunction "curvature": relation to kinetic energy and tunneling
- Nodal properties of 3D wavefunctions for various shapes
- Physical relevance and the Rules of Quantum Mechanics
- Comments on Dirac notation

2. Variation principle, linear variation method, and perturbation limit

Theorem and its importance

Examples of non-linear variation

General equations for linear variation method

Diagonalizing the 2 x 2 orthonormal case “at a glance”

Larger matrices: use of simple programs

Non-orthogonal case

3. Born-Oppenheimer approximation,

Franck-Condon factors, and vibrational structure of molecular electronic transitions (including photoelectron spectra)

4. Symmetry and group theory in the context of quantum mechanics

5. Quantum Chemistry, including hands-on ab initio, DFT

Part II: Time dependent quantum mechanics

1. Time dependent Schrödinger Equation

Behavior at a resonance, and non-resonance, weak and strong coupling limits.

General time dependent perturbation theory; “Fermi golden rule” with application to absorption and emission of light, and electron transfer.

2. (a) Time Dependence of Probability Density (Liouville Eq.)

Feynman-Vernon-Hellwarth vector space in the two-state problem

Coherence, dephasing

Applications to magnetic resonance

(b) Atom-centered Density Matrix Propagation (ADMP) i.e., , quantum molecular dynamics computation

This is part of the Gaussian 09 or (Gaussian 16) package and remarkably easy to use; provides insight into mechanisms of simple chemical processes with short computation times (usually several minutes on a desktop computer).

THE WHOLE OF SCIENCE IS NOTHING MORE THAN A
REFINEMENT OF EVERYDAY THINKING.

-- A. EINSTEIN

Thinking does not necessarily mean understanding.
Crucially important facts about our reality are not
possible to “understand” at present.

Today we focus on these facts!

Remarks on Knowledge and Learning:

Quantum Mechanics and why chemistry is difficult to teach

You cannot learn — *if your knowledge is not organized!*

History is not boring — *if it organizes your knowledge.*

Thermodynamics was developed *much* before quantum mechanics (1800-1900)
— *when nobody had a clue about the structure of atoms.*

Quantum ideas—*essential for understanding chemistry*—developed slowly over 25 years (1905-1930 — *beginning while there was still no picture of the atom in 1905 !!*

Only from Rutherford's experiment in **1912**—was it revealed that *electrons do not fall to the nucleus despite enormous electrostatic attraction!!!*

All students of chemistry can easily see—*that Newton's Laws fail for electrons.*

The two most powerful facts for Chemistry cannot be “understood” in the usual sense of the word:

1. 1926: Schrodinger equation—contains Newton’s Laws of Motion and predicts orbitals of electrons, and has NEVER FAILED!

2. THERE ARE ONLY **TWO CLASSES** of PARTICLES KNOWN!
Fermions (*electrons**, *protons**, neutrons, ^3He)—which obey Pauli Exclusion;

Bosons (deuteron, photons, ^4He) -- which obey “INCLUSION”, (identical bosons all want to have the same quantum numbers, leading to phenomena such as lasers, superconductivity, superfluidity, etc.

REALIZE: that these profound facts describe nature perfectly as we now know it.

But no person “understands” *why* they work.

Therefore your job is **NOT to “understand”** these incredible facts.
Just **KNOW** them, marvel at them, and enjoy them.

All of chemistry can be computed (in principle) from these two principles, given enough computer power.

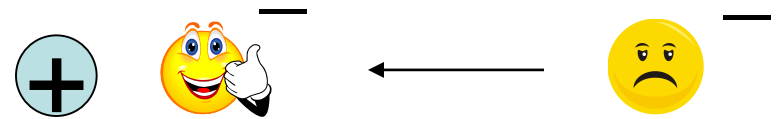
The Working Theory of Chemistry, Biology, and Geology— is simple:

Matter? **Nuclei (+)** and **electrons (-)**

Potential Energy? Electromagnetic --> Coulomb's Law

$$= \text{constant} * \text{charge1} * \text{charge2} / \text{distance}$$

Atoms: electrons seeking a more positive environment



Chemical Energy: electrons getting to a more positive environment by pulling nuclei together



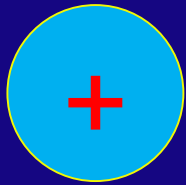
Mechanics: **Quantum** (describes everything; it contains Newtonian mechanics, and “becomes” Newtonian mechanics as the masses and energies become large)


The BIG BANG, 13.8 billion years ago

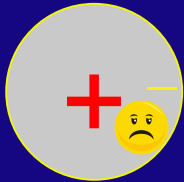


Only Protons & Electrons

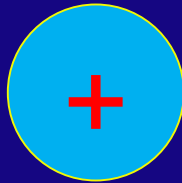
proton



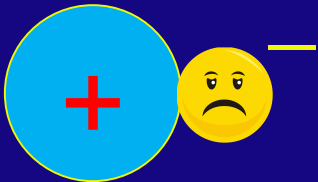
 unhappy electron far from proton
attracted but going too fast to stick



but, a fast electron can get trapped in
the proton = **NEUTRON** (radioactive,
half-life of 15 min.) $n \rightarrow p^+ + e^- + \text{neutrino}$



Cooler Universe: electrons are
caught by protons making
Hydrogen Atoms



But the electron **WILL NOT** “STICK”
TO THE PROTON!

This is **QUANTUM MECHANICAL** behavior
Predicted exactly by Schrodinger’s Equation

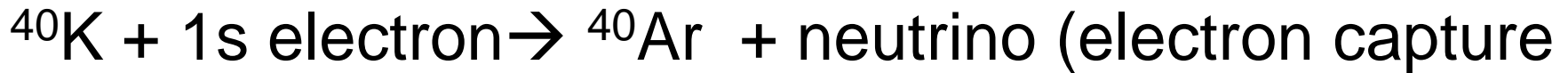
But **NOBODY** understands why this works

Electrostatics in common nuclear physics

Think about radioactive isotopes, e.g. ^{14}C
neutron/proton ratio too high



^{40}K neutron/proton ratio too low



Also, certain NON-radioactive nuclei
become beta emitters if their electron cloud is
removed in a synchrotron.

The only strange thing about quantum mechanics is simple, but I need to be a little silly so it will be remembered. I start with something believable:

A small mouse confined to a small space will become agitated (exhibit frantic motion, or kinetic energy)

A small mass confined to a small space will become agitated (exhibit frantic motion, or **kinetic energy**)

By “small”, we of course mean electrons and protons.

This is the essence of what is strange about Quantum Mechanics:

INTRODUCTION TO QUANTUM MECHANICS

OR

WHY CHEMISTRY IS DIFFICULT TO LEARN

Electrons (and photons) DO NOT behave according to Newton's Laws of Motion

But, Chemistry is all about electrons

Feynman, from *Lectures on Physics III* :

“Quantum Mechanics exactly describes the behavior electrons and light.”

“Electrons and light do not behave like anything we have ever seen.”

“There is one lucky break, however—**electrons behave just like light**”

Understanding Quantum Mechanics?

Richard Feynman lecturing to a lay audience at
Cornell, *circa*. 1965:

“There was a time when the newspapers said that only twelve men understood the theory of relativity.

I do not believe there ever was such a time...

After they read the paper, quite a lot of people understood the theory of relativity... On the other hand, I think it is safe to say that

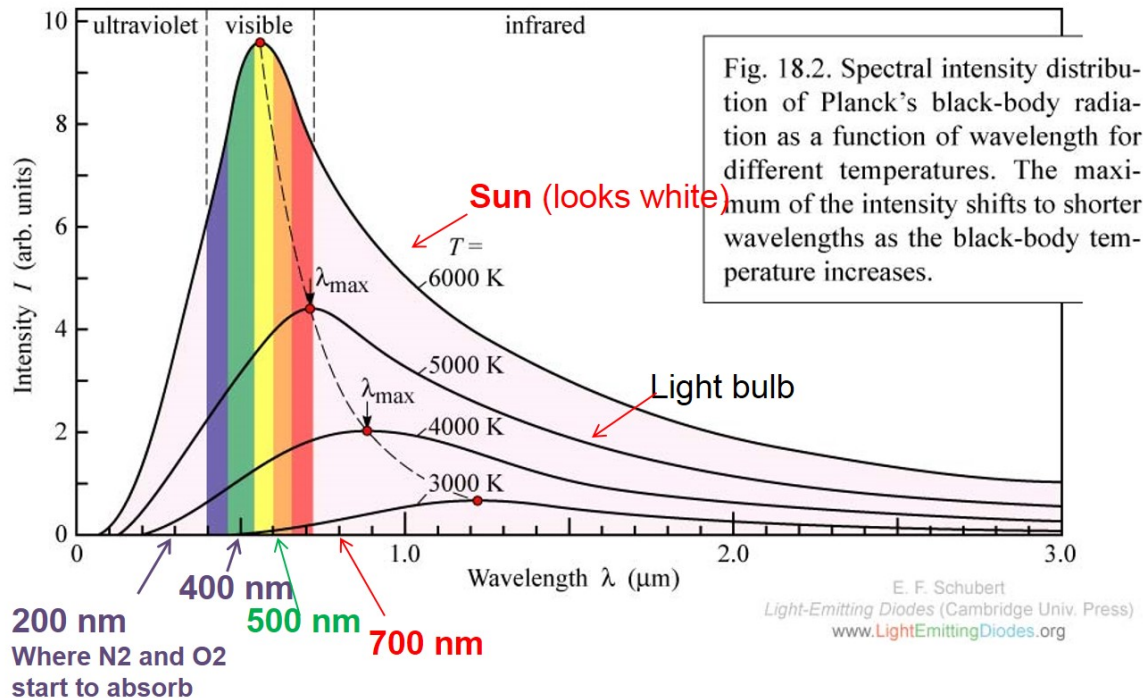
no one “understands” quantum mechanics...

Do not keep saying to your self “But how can it be like that?”, because you will get “down the drain” into a blind alley from which nobody has yet escaped. NOBODY KNOWS HOW IT CAN BE LIKE THAT. “

--Richard P. Feynman

Chapter 6, *The Character of Physical Law*, 23rd Printing, 1998

Light emitted by all objects not at 0 Kelvii.



Around **1905**, Max Planck was working hard on trying to understand this behavior. Classical mechanics **worked fine at the LONG** wavelengths but **NOT** at short wavelengths.

Planck found that if energy of matter was quantized so that $\Delta E = h\nu = hc/\lambda$ then classical mechanics predicted the curves perfectly!!!!

Planck varied h and found that 6.62×10^{-34} gave a perfect match to experiment.

In other words, h is an experimentally derived constant. No theory predicts h

So was born the FIRST QUANTUM CONCEPT: **Energy is quantized!**

Classical thinking does not work for light. $\Delta E = h\nu$

If the structure of the atom were known in 1905 this would have been much more evident.

The mystery could be stated as a very striking problem obvious to chemists.

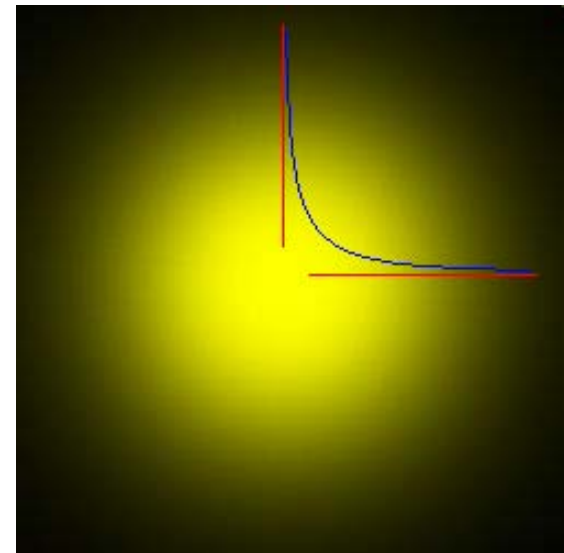
THE ELECTRON WILL NOT FALL TO THE NUCLEUS!!!
despite **ENORMOUS Coulomb force.**

The *lowest* energy state (1s orbital) of the hydrogen atom.

+ -
proton electron

Probability slice through the 1s orbital. The blue line is the square of the wavefunction (orbital).

Most probable point is AT NUCLEUS.
Most probable DISTANCE is AT Bohr radius



... THIS SEEMS PLAINLY ABSURD;

BUT WHOEVER WISHES TO BECOME A PHILOSOPHER
MUST LEARN NOT TO BE FRIGHTENED BY ABSURDITIES.

-- BERTRAND RUSSELL

Coulomb's Law Force $\oplus \quad \ominus$
 $\leftarrow 1 \text{ \AA} \rightarrow$

$$\frac{(9 \times 10^9) (1.6 \times 10^{-19})^2}{(1 \times 10^{-10} \text{ m})^2} = 2.3 \times 10^{-8} \text{ N}$$

For 2 elementary charges 1 \AA apart.

at 0.01 \AA $2.3 \times 10^{-4} \text{ N}$

FOR ONE proton & ONE e^-

Equivalent to Gravitational
 force of EARTH ON 0.025 gram

But, Experimentally e^- is in the
1s orbital, even at 0 Kelvin!

Striking Example of
Zero point Energy

$$\text{KINETIC } E = 1.3 \times 10^6 \text{ J/mol} \quad u_{\text{rms}} = 2 \times 10^6 \text{ ms}^{-1}$$

YET, IS ABSOLUTELY COLD (& DARK)

Quantum Behavior & Quantum Mechanics Applies to EVERYTHING

But most evident for particles with mass equal or less than proton

Absolutely NECESSARY for electrons and light (photons),

which are neither particles or waves;
there is nothing like them in the macroscopic world !

Thus, Quantum Mechanics cannot be “understood” in the usual sense—***not even by the world’s greatest minds.***

Quantum Mechanics was **discovered**—NOT derived

Newton’s Laws, however, **CAN** be derived from quantum mechanics

Quantum Mechanics has **never failed** to agree with experiment—yet.

Quantum Concepts

<u>Who</u>	<u>When</u>	<u>What</u>	<u>Equation</u>
1. Planck	1905	Quantization of Energy	$\Delta E = h\nu$
2. Einstein	1905	Particle Nature of Light	$p = h/\lambda$
3. DeBroglie	~1920	Wave Nature of Particles	$\lambda = h/p$
4. Bohr	~1920	Quantization of Angular Momentum	$L^2 = l(l+1) (h/2\pi)^2 ;$ $L_z = m (h/2\pi)$ 2L+1 m values from -L to +L
5. Heisenberg	~1925	Uncertainty Principle	$\Delta p_x \Delta x \cong h$ or: “why the electron does not fall into the nucleus” i.e., the concept of <u>ZERO POINT ENERGY</u>

More on **zero point energy** and uncertainty principle

Zero point kinetic energy is $\cong h^2 / (m \Delta x^2)$, where h = Planck's constant, m = mass, and Δx is the length of the region to which the particle is **confined**. For example, as a nucleus pulls an electron close, the zero-point energy increases and **the electron will not fall to the nucleus**. (It is as if the small things like electrons "refuse" to be localized.)

Note: $h^2 = \text{J}^2 \text{s}^2 = \text{kg}^2 \text{m}^4 \text{s}^{-4} \text{s}^2$, so $h^2 / (m \Delta x^2) = \text{kg}^2 \text{m}^4 \text{s}^{-2} / (\text{kgm}^2) = \text{kg m}^2 \text{s}^{-2} = \text{J}$

Heisenberg Uncertainty: $\Delta x \Delta p \cong h$, i.e., product of uncertainty in x and uncertainty in momentum is about $= h$.

ΔH of chemical reactions is equal to the **change in quantum zero point energy** at 0 Kelvin, and is only slightly different at room temperature due to heat capacity differences.

The mysterious "**DARK ENERGY**" that is apparently causing the acceleration of expansion of the Universe is most discussed as **quantum zero point energy** (of gravity, for which there is no quantum theory yet.)

THEN CAME THE Schrödinger Equation (1926) which says all of the above

This equation was **DISCOVERED**, not derived

Schrodinger **did not know what to make of Ψ** when he published his equation. Everyone knew it was important because the equation gave all the correct energies for the “well behaved” solutions.

Also was immediately shown that Newton's Laws could be derived from the Schrodinger Eq.
(but not the other way around)

1926 Schrodinger's Equation:

A simple equation that was discovered (not derived)

Classical Mechanics

Kinetic Energy + Potential Energy = Total Energy

Quantum Mechanics (Schrodinger's Equation without time) translated into English:

$-\hbar^2/8\pi^2\text{mass} \times \text{Curvature of Wavefunction} + \text{Potential Energy} \times \text{Wavefunction} = \text{Energy} \times \text{Wavefunction}$

curvature operation
(2nd derivative)

$h/2\pi$

$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x)\psi = E\psi$

mass

Kinetic energy

potential energy

Total energy

wavefunction

Time independent Schrodinger Equation :

$$-\frac{\hbar^2}{8\pi^2} \times \sum_{\text{all particles } j} \left(\frac{\partial^2}{\partial x_j^2} + \frac{\partial^2}{\partial y_j^2} + \frac{\partial^2}{\partial z_j^2} \right) \Psi + \text{potential } E \times \Psi = \text{total } E \times \Psi$$

or: kinetic energy operator $\times \Psi$ + classical potential energy $\times \Psi$
 = total energy $\times \Psi$

$H\Psi = E\Psi$, where H = Hamiltonian = total energy operator

$\Psi^* \Psi$ = probability density for finding particle locations

Ψ^* is the complex conjugate. i.e., change all $i \rightarrow -i$

$$i = \sqrt{-1}$$

Potential energy EXACTLY same
 as in Classical mechanics

Three things are different from Classical mechanics:

1) The **wavefunction** (Schrödinger *did not know* what its physical meaning was at the time he published). Later the consensus was reached that the absolute square of the wavefunction gives the **probability density** for finding the particle.)

2) **Kinetic energy** is represented by the **CURVATURE** of the **Wavefunction**.
 In calculus, that is the 2nd derivative (i.e., the slope of the slope of the function)

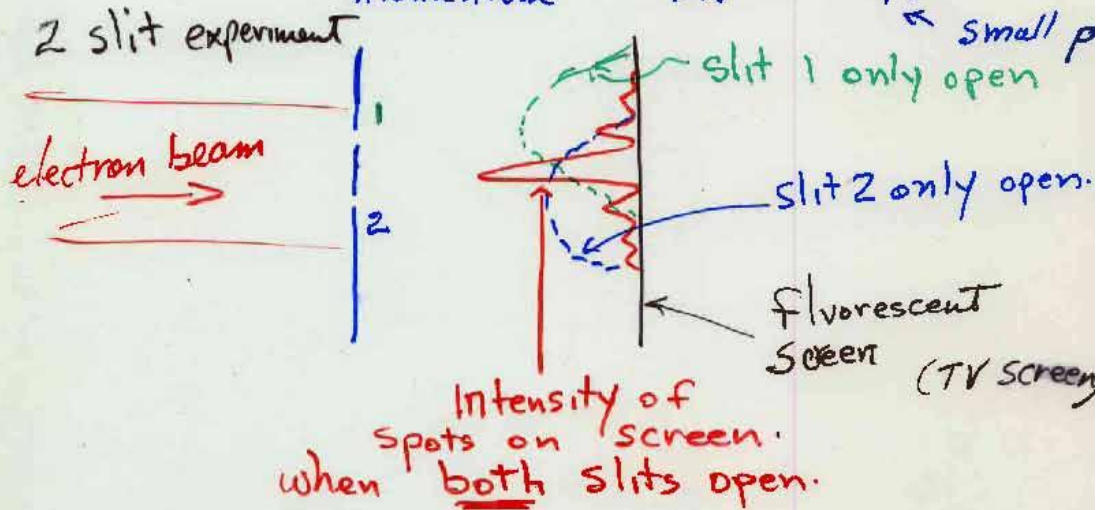
3) **h** , Planck's constant, which was empirically adjusted so that the Schrödinger Equation gives agreement with experiment.

This simple equation embodies the 5 seemingly distinct new "quantum concepts"

3. WAVE NATURE OF PARTICLES

de Broglie ~ 1920

$$\lambda = \frac{h}{\text{momentum}} = \frac{h}{mv} \equiv \frac{h}{p} \quad \leftarrow \text{small } p$$



TIME EXPOSURE (1 particle per second)

GIVES EXACTLY SAME RESULT !!!

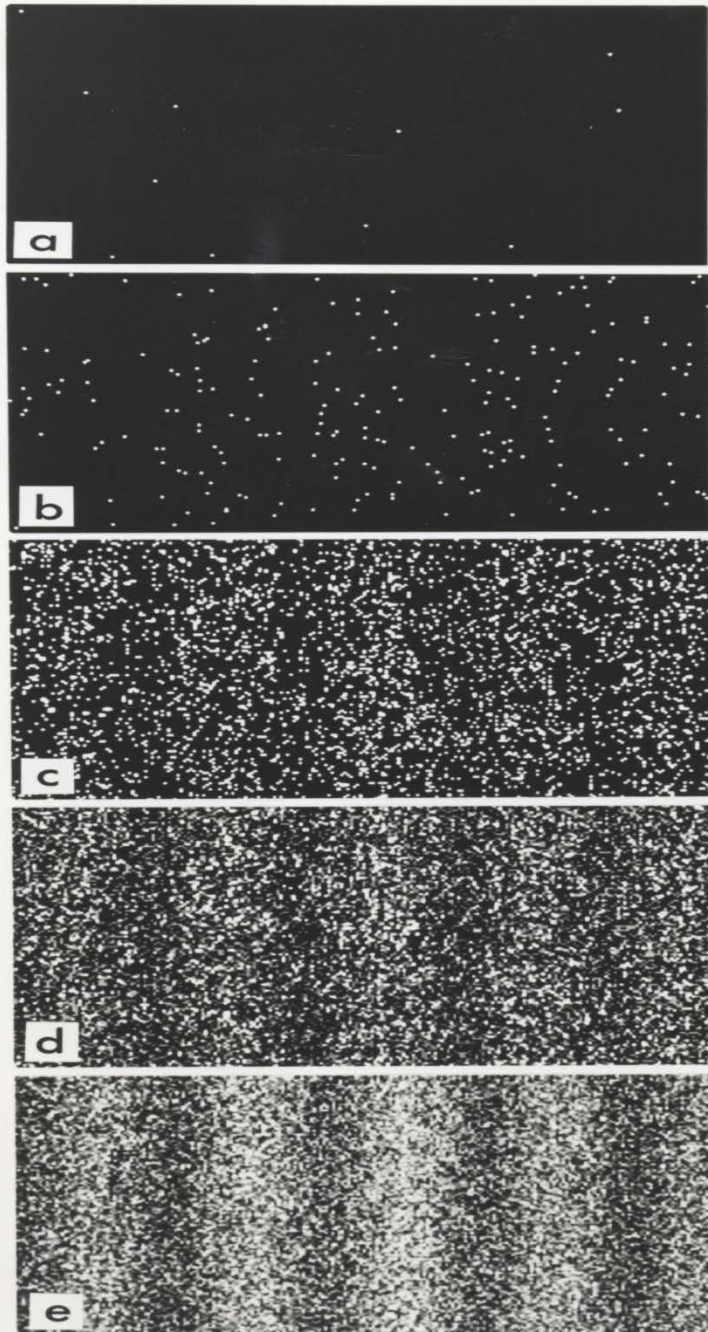
SAME FOR PHOTONS !!!

Interference is a SINGLE PARTICLE phenomenon! (one particle or photon does not interfere with another)

This phenomenon captures the essential mystery of quantum behavior

Results of a [double-slit-experiment](#) performed by Dr. A. Tonomura showing the build-up of an interference pattern of **single electrons**. Numbers of electrons are 10 (a), 200 (b), 6000 (c), 40000 (d), 140000 (e).
(Provided with kind permission of Dr. Akira Tonomura.)





Results of a **double-slit-experiment** performed by Dr. A. Tonomura showing the **build-up** of an interference pattern of **single electrons**. Numbers of electrons are 10 (a), 200 (b), 6000 (c), 40000 (d), 140000 (e). (Provided with kind permission of Dr. Akira Tonomura.)

Electron or photon interference is a single particle phenomenon!

Movies available at:
<http://www.hitachi.com/rd/research/em/movie.html>