A Crash Course in Quantum Mechanics

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1. Does a quantum state evolve in an indeterministic manner?
2. Why don't electrons fall into the nucleus?
3. Does light travel in straight lines?

Don't ask the wrong question in the quantum world

Richard Feynman

It is my task to convince you not to turn away because you don't understand it. You see, my physics students don't understand it either. That is because I don't understand it. Nobody does.
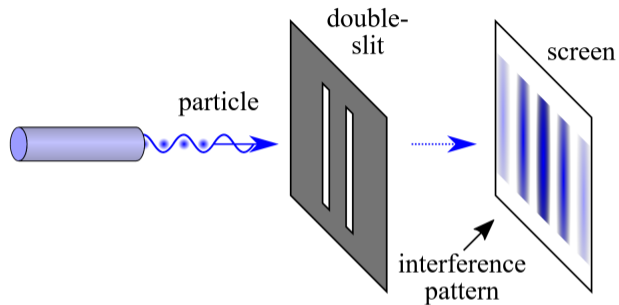
Arthur Eddington

Not only is the universe stranger than we imagine, it is stranger than we can imagine.

Physicists understand the mathematics but not the world! Don't ask why the world works the way it is.

1. Founding experiments of quantum mechanics

Double-slit experiment

The experiment was first performed with light by Thomas Young in 1801. In 1927, Davisson and Germer demonstrated that electrons show the same behavior, which was later extended to atoms and molecules.

# The study of black-body radiation
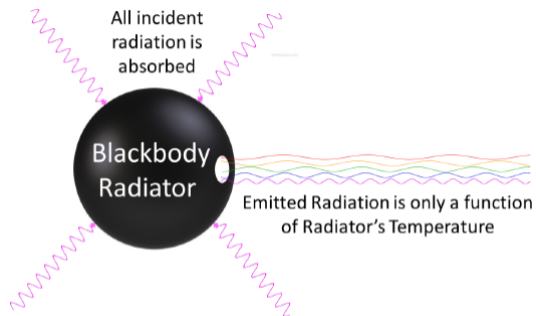
Blackbody radiator is any object that is a perfect emitter and a perfect absorber of radiation. Classical theory failed to model blackbody radiation accurately. Planck postulated that energy can be absorbed or emitted only in discrete units.

Photoelectric effect
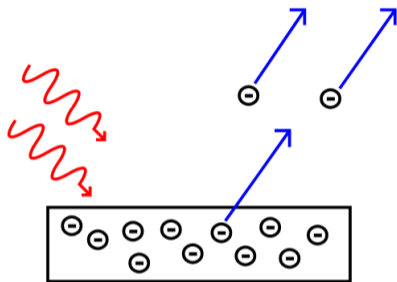
Because a low-frequency beam at a high intensity could not build up the energy required to produce photoelectrons like it would have if light's energy were continuous like a wave, Einstein proposed that a beam of light is not a wave propagating through space, but rather a collection of discrete wave packets (photons).

Bohr's atom model
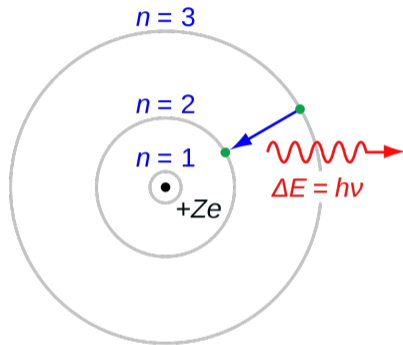
Niels Bohr's 1913 quantum model of the atom.
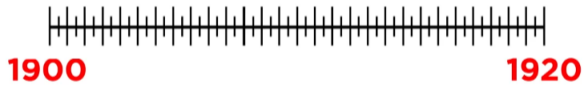
2. Deriving Quantum Mechanical Laws

The methodology

Experiments and Observations

The methodology
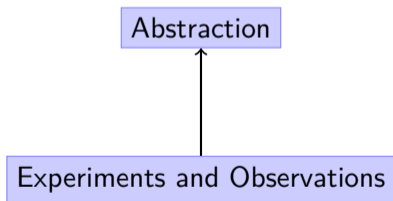
The methodology
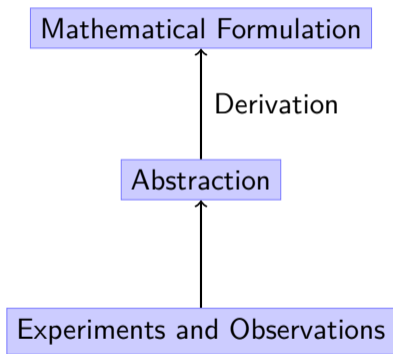
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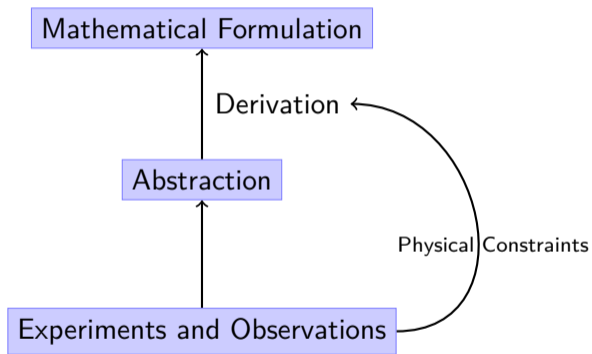
Two questions to answer for a theory describing a physical system:

▶ What are the states of a system?
▶ How do states change with time?

Q1: What are the states of a quantum system?

An example in classical physics
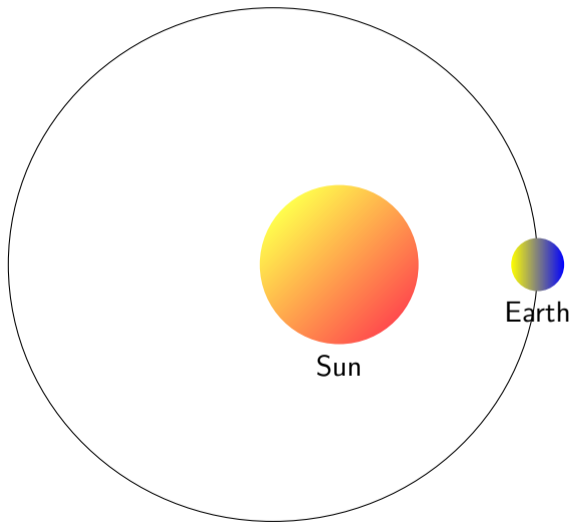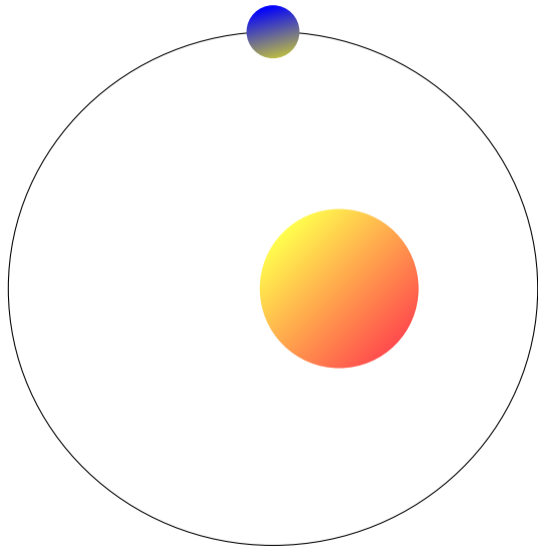
An example in classical physics

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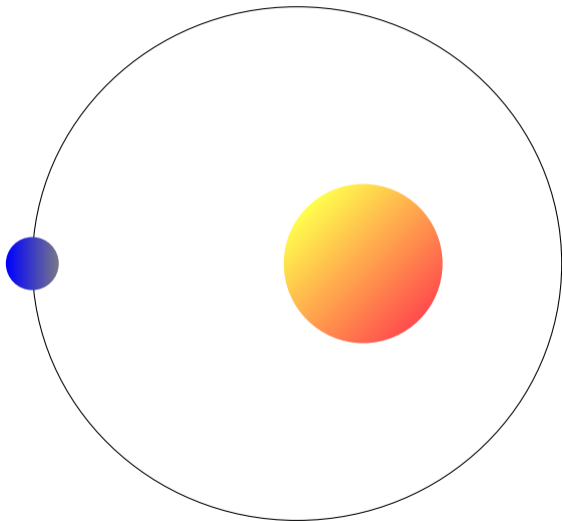
An example in classical physics
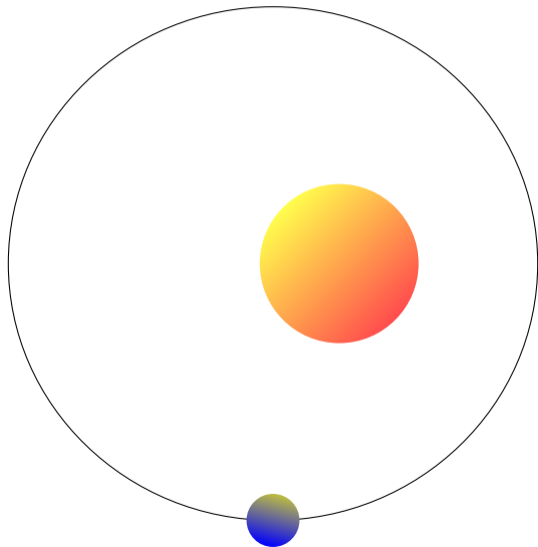
An example in classical physics
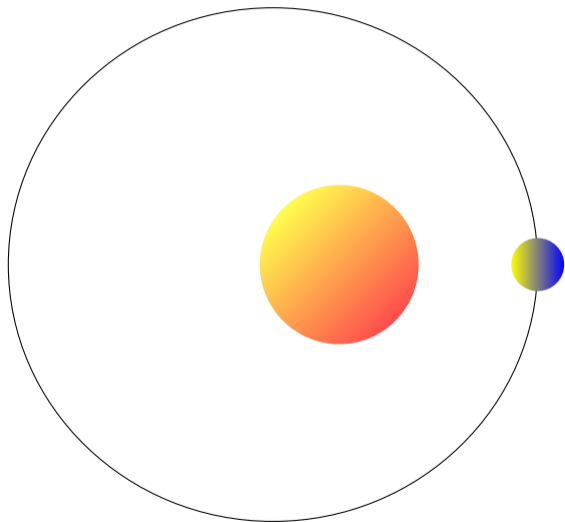
An example in classical physics

For this example, the states of the system: $\{(\overrightarrow{q_{sun}}, \overrightarrow{v_{sun}}), (\overrightarrow{q_{earth}}, \overrightarrow{v_{earth}})\}$, where q denotes coordinate vector and v denotes velocity vector .

The states change with time under the effect of gravitational force.

In quantum mechanics, the *states of a system* correspond to a vector space called *Hilbert Space*. When we come across the term *Hilbert space* in quantum mechanics, it refers to *the space of states*.

Interlude: Hilbert Space and Bra-ket Notation

ket

A ket (e.g. $|A\rangle$) represents a vector in *Hilbert space*.

bra

For every ket-vector $|A\rangle$, there is a "bra" vector in the dual space, denoted by $\langle A|$ which is the *Hermitian conjugate* of the ket with the same label.

Hermitian conjugate is a generalized concept of *conjugate transpose* of matrices, which first transpose a matrix then take the complex conjugate of each entry.

Inner Product

The inner product is the product of a bra and a ket and it is written as $\langle B|A\rangle$.

The following are the axioms that define a Hilbert space of a quantum system (z and w are complex numbers):

1. The sum of any two ket-vectors is also a ket-vector: $|A\rangle + |B\rangle = |C\rangle$.

2. Vector addition is commutative: $|A\rangle + |B\rangle = |B\rangle + |A\rangle$.

3. Vector addition is associative: $\{|A\rangle + |B\rangle\} + |C\rangle = |A\rangle + \{|B\rangle + |C\rangle\}$.

4. There is a unique vector 0 such that when you add it to any ket, it gives the same ket back: $|A\rangle + 0 = |A\rangle$.

5. Given any ket $|A\rangle$, there is a unique ket $-|A\rangle$ such that $|A\rangle + |-A\rangle = 0$.

6. Given any ket $|A\rangle$ and any complex number z, you can multiply them to get a new ket. Also, multiplication by a scalar is linear: $|zA\rangle = z|A\rangle = |B\rangle$.

7. The distributive property holds: $z\{|A\rangle + |B\rangle\} = z|A\rangle + z|B\rangle$, $\{z + w\}|A\rangle = z|A\rangle + w|A\rangle$.

Q2: How do quantum mechnical states change with time?

A quantum system evolves in two ways: the system evolves one way between measurements (undisturbed quantum mechanical system) and another way during a measurement.

Let's first derive the laws governing undisturbed quantum mechanical evolution.

What are required to be a properly formulated law?

▶ **Determinism**: wherever you are in the state-space, the next state is completely specified by the law of motion.

▶ **Reversibility**: the law must tell you where you were last.

Suppose state $S_0 \cdots \xrightarrow{\Delta t} \cdots S_t$, we represent this as $\mathbf{U}_{\Delta t}(S_0) = S_t$.

Reversibility requires that $\exists \mathbf{V}_{\Delta t}$ such that $\mathbf{V}_{\Delta t}(S_t) = S_0$. Therefore, $\mathbf{V}_{\Delta t}(\mathbf{U}_{\Delta t}(S_0)) = S_0$.

In other words, the operator $\mathbf{V}_{\Delta t}\mathbf{U}_{\Delta t}$ behaves like the unit operator I, where $I(S) = S$ for any state S. In quantum mechanics, $\mathbf{V}_{\Delta t} = \mathbf{U}_{\Delta t}^{\dagger}$, where the dagger $\dagger$ indicates *Hermitian conjugation*. Thus, $\mathbf{U}_{\Delta t}^{\dagger}\mathbf{U}_{\Delta t} = I$.

An operator $\mathbf{U}$ that satisfies $\mathbf{U}^{\dagger}\mathbf{U} = I$ is called *unitary*.

Now let's consider $\Delta t = \epsilon$, where ϵ is an infinitesimal time interval. When ϵ is zero, $\mathbf{U}_\epsilon = I$.

Continuity of state transition implies that when ϵ is infinitesimal, $\mathbf{U}_\epsilon$ is close to I, differing from it by something of order ϵ.

$$\mathbf{U}_\epsilon = I + \epsilon \mathbf{G}$$

With an eye toward the future, we let $\mathbf{G} = -i\mathbf{H}$. Then, $\mathbf{U}_\epsilon = I - i\epsilon\mathbf{H}$ and $\mathbf{U}_\epsilon^\dagger = I + i\epsilon\mathbf{H}^\dagger$. Thus, $I = \mathbf{U}^\dagger\mathbf{U} = (I + i\epsilon\mathbf{H}^\dagger)(I - i\epsilon\mathbf{H})$.

Expanding to first order in ϵ, we get $\mathbf{H}^\dagger = \mathbf{H}$. This indicates that $\mathbf{H}$ is a unitary operator.

$S_\epsilon = \mathbf{U}_\epsilon(S_0) = S_0 - i\epsilon\mathbf{H}(S_0)$, thus

$$\frac{S_\epsilon - S_0}{\epsilon} = -i\mathbf{H}(S_0).$$

If we take the limit as $\epsilon \to 0$, the left-hand side becomes the time derivative of the state:

$$\frac{\partial S}{\partial t} = -i\mathbf{H}S.$$

Recall that the *state of a system* is a ket vector in a *Hilbert space*. Now we denote the state by $|\Psi\rangle$. With the new symbol, we rewrite the above equation:

$$\frac{\partial |\Psi\rangle}{\partial t} = -i\mathbf{H} |\Psi\rangle .$$

In an abstract way, we have defined an equation to describe a quantum mechanical system with a unitary operator **H**. What is **H**?

It turns out that **H** has real physical meaning. It represents the energy operator and is usually called *Hamiltonian operator*.

Back to physics, the time-dependent Schrödinger equation needs to be polished a little bit to make it actually work for real-world physics.

To make the equation dimensionally consistent, we need to insert a constant with dimension *mass · length²/time*. The constant turns out to be $\hbar$ with value $1.054572 \times 10^{-34} \, m^2 \, kg/s$ when we apply the equation to describe a real quantum system.

$$\hbar \frac{\partial \left| \Psi \right\rangle}{\partial t} = -i\mathbf{H} \left| \Psi \right\rangle$$

or

$$i\hbar \frac{\partial \left| \Psi \right\rangle}{\partial t} = \mathbf{H} \left| \Psi \right\rangle$$

This equation is called *general time-dependent Schrödinger equation*.

Interpretation of Ψ

The Schrödinger equation details the behavior of Ψ but says nothing of its nature.

In 1926, Max Born successfully interpreted Ψ as the **probability amplitude**, whose modulus sequared $|\Psi|^2$ is equal to **probability density**.

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$$\int_{-\infty}^{\infty} |\Psi(x)|^2 \, dx = 1.$$

"Concretized" Hamiltonian

The Hamitonian is the sum of the **kinetic energies** plus the **potential energy** for all the particles. Hamitonian **H** is an operator, sometimes denoted by $\hat{\mathbf{H}}$ to highlight its function as an operator.

One Particle

$$\hat{\mathbf{H}} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}, t),$$

Many Particles

$$\hat{\mathbf{H}} = \sum_{n=1}^{N} \hat{T}_n + \hat{V} = -\frac{\hbar^2}{2}\sum_{n=1}^{N}\frac{1}{m_n}\nabla_n^2 + V(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N, t),$$

where $\mathbf{r}$ and $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$ are spatial coordinates.

Schrödinger equation for an *n*-particle system

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N, t) = \left[-\frac{\hbar^2}{2}\sum_{n=1}^{N}\frac{1}{m_n}\nabla_n^2 + V(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N, t) \right]\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N, t)$$

$n = 1$

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r}, t) = \left[\frac{-\hbar^2}{2m}\nabla^2 + V(\mathbf{r}, t) \right]\Psi(\mathbf{r}, t)$$

3. Time-independent Schrödinger Equation

If the Hamiltonian is not an explicit function of time, then

$$\hat{\mathbf{H}} = -\frac{\hbar^2}{2} \sum_{n=1}^{N} \frac{1}{m_n} \nabla_n^2 + V(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N).$$

We now restrict ourselves to looking for the solutions that take the following form:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N, t) = \psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) f(t),$$

where $f(t)$ is a function of time only.

Note: not all solutions have this form.

Letting $\psi = \psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ and $V = V(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ and substituting into the time-dependent equation give

$$i\hbar \frac{\partial}{\partial t} \psi f(t) = \left[-\frac{\hbar^2}{2} \sum_{n=1}^{N} \frac{1}{m_n} \nabla_n^2 + V \right] \psi f(t)$$

$$i\hbar \frac{df(t)}{dt} \psi = -\frac{\hbar^2}{2} f(t) \sum_{n=1}^{N} \frac{1}{m_n} \nabla_n^2 \psi + V f(t) \psi$$

$$i\hbar \frac{1}{f(t)} \frac{df(t)}{dt} = -\frac{\hbar^2}{2} \frac{1}{\psi} \sum_{n=1}^{N} \frac{1}{m_n} \nabla_n^2 \psi + V$$

Since the left side is independent of $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$ and the right side is independent of t, both sides must be equal to a constant, which we call E.

Equating the right side of the blue equation to E, we get

$$-\frac{\hbar^2}{2}\frac{1}{\psi}\sum_{n=1}^{N}\frac{1}{m_n}\nabla_n^2\psi + V = E$$

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This is the **time-independent Schrödinger equation**.

Equating the left side of the blue equation to E, we get

$$i\hbar \frac{1}{f(t)} \frac{df(t)}{dt} = E$$

$$\frac{1}{f(t)} \frac{df(t)}{dt} = -\frac{iE}{\hbar}$$

$$\ln f(t) = -\frac{iE}{\hbar} t + C$$

$$f(t) = e^C e^{-iEt/\hbar}$$

Thus,
$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N, t) = \psi f(t) = e^C \psi e^{-iEt/\hbar} = A\psi e^{-iEt/\hbar},$$
where $A = e^C$.

$$\begin{aligned}
|\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N, t)|^2 &= [A\psi e^{-iEt/\hbar}]^* A\psi e^{-iEt/\hbar} \\
&= A^*\psi^* e^{iEt/\hbar} A\psi e^{-iEt/\hbar} \\
&= A^*\psi^* A\psi \\
&= |A\psi|^2 \\
&= |A\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)|^2
\end{aligned}$$

The probability density is given by $|A\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)|^2$ and does not change with time. Such states are called **stationary states**.

A quantum system evolves in two ways: the system evolves one way between measurements (undisturbed quantum mechanical system) and another way during a measurement.

4. Unsolved Mystery: Measurement

Combining systems and entanglement

Every measurement involves a system and an apparatus. If quantum mechanics is a consistent theory, then it should be possible to combine the system and apparatus into a single bigger system. In this single bigger system, no collapse of the wave function takes place during a measurement. Instead, *entanglement* between the apparatus and the system just happens by unitary evolution of the state-vector.

Combining systems and entanglement

Does the last entity to look at the system collapse the wave function, or does it just get entangled? Or is there a last looker? We don't know the answers to these questions (yet).

Quantum mechanics is a consistent calculus of probabilities for a certain kind of experiment involving a system and an apparatus. We use it, and it works, but when we try to ask questions about the underlying "reality", we get confused.

Richard Feynman

Nature has got it cooked up so we'll never be able to figure out how She does it: if we put instruments in to find out which way the light goes, we can find out, all right, but the wonderful interference effects disappear. But if we don't have instruments that can tell which way the light goes, the interference effects come back! Very strange, indeed!
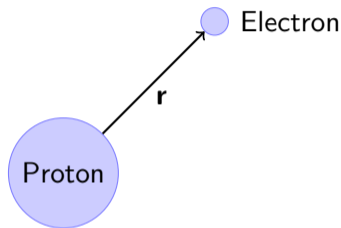
5. Quantum Molecular Dynamics

Interlude

$$F = -\nabla V$$

Coulomb's law for the magnitude of the force between two charges Q_1 and Q_2 separated by a distance r in vacuum is:

$$F = \frac{Q_1 Q_2}{4\pi\epsilon_0 r^2},$$

where ϵ_0 is a constant called the **vacuum permittivity** whose value is $8.8541878 \times 10^{-12} C^2 N^{-1} m^{-2}$.

The "hello world" problem

Simplified Hydrogen Atom

Assume the proton's position is fixed at the origin, **r** is the vector specifying the position of the electron relative to the position of the proton. $|\mathbf{r}| = r$. The mass of the proton is M, the mass of the electron is m.

The "hello world" problem

The Coulomb force on the electron is

$$\mathbf{F} = -\frac{e^2}{4\pi\epsilon_0 r^2}\frac{\mathbf{r}}{r}$$

$$F = -\nabla V \quad \Rightarrow \quad \frac{dV}{dr} = -F = \frac{e^2}{4\pi\epsilon_0 r^2}$$

$$V = \frac{e^2}{4\pi\epsilon_0}\int\frac{1}{r^2} = -\frac{e^2}{4\pi\epsilon_0 r}$$

The "hello world" equation

The Schrödinger equation for the electron

$$\hat{\mathbf{H}}\psi = E\psi$$

$$E\psi = \hat{\mathbf{H}}\psi = \left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r} \right]\psi$$

A more accurate model should replace m with the *reduced mass* μ of the two-particle system.

$$\mu = \frac{mM}{m+M} \approx m \quad \text{when} \quad M \gg m$$

Expanding the Laplacian in spherical coordinates:

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right] - \frac{e^2}{4\pi\epsilon_0 r}\psi = E\psi$$

This is a separable, partial differential equation which can be solved in terms of special functions.

$$\psi_{n\ell m}(r,\theta,\phi) = \sqrt{\left(\frac{2}{na_0}\right)^3\frac{(n-\ell-1)!}{2n[(n+\ell)!]}} \left(\frac{2r}{na_0}\right)^\ell e^{-r/na_0} L_{n-\ell-1}^{2\ell+1}\left(\frac{2r}{na_0}\right) Y_\ell^m(\theta,\phi),$$

where $a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2}$, $L_{n-\ell-1}^{2\ell+1}(\cdots)$ is the generalized Laguerre polynomial of degree $n-\ell-1$, $Y_\ell^m(\theta,\phi)$ is a spherical harmonic function of degree ℓ and order m.

The numbers n, ℓ and m are called quantum numbers. They can take the following values:
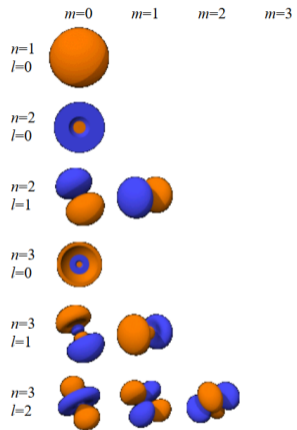
$$n = 1, 2, 3, \ldots$$
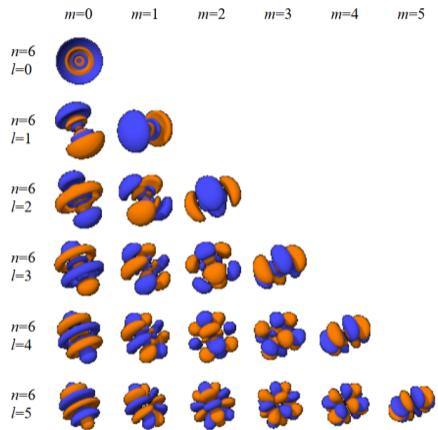$$\ell = 0, 1, 2, \ldots, n-1$$
$$m = -\ell, \ldots, \ell$$

Why don't electrons fall into the nucleus?

The question actually doesn't make sense.

Electrons in the atom do enter the nucleus. All electron states overlap with the nucleus, so the concept of an electron "falling into" or "entering" the nucleus does not really make sense. Electrons are always partially in the nucleus.

	$m=0$	$m=1$	$m=2$	$m=3$	$m=4$	$m=5$
$n=6$ $l=0$						
$n=6$ $l=1$						
$n=6$ $l=2$						
$n=6$ $l=3$						
$n=6$ $l=4$						
$n=6$ $l=5$						

| | $m=0$ | $m=1$ | $m=2$ | $m=3$ | $m=4$ | $m=5$ | $m=6$ | $m=7$ | $m=8$ |
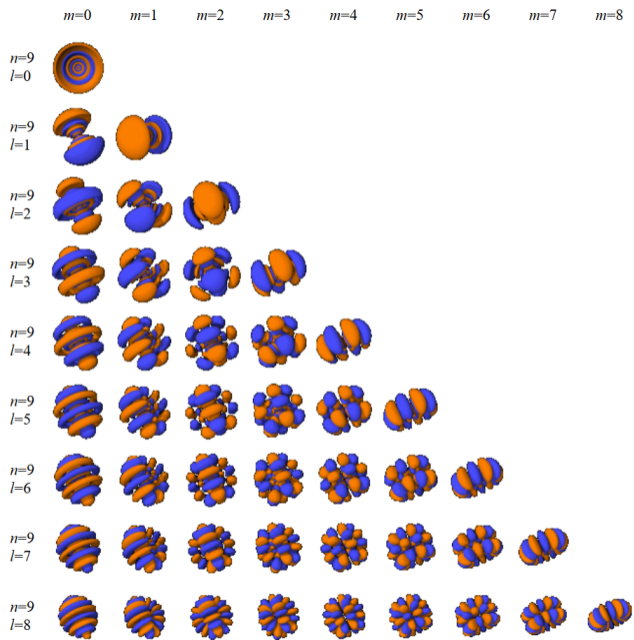
Simulating quantum many-body system

Suppose we have a quantum many-body system with

- N atoms (nuclei) at positions $\mathbf{R} = \{\mathbf{R}_1, \cdots, \mathbf{R}_N\}$ with instantaneous momenta $\mathbf{P} = \{\mathbf{P}_1, \cdots, \mathbf{P}_N\}$ and
- N_e electrons at $\mathbf{r} = \{\mathbf{r}_1, \cdots, \mathbf{r}_{N_e}\}$.

General Molecular System

For a general molecular system consisting of electrons and nuclei, the Hamiltonian can be written as

$$H(\mathbf{r}, \mathbf{R}) = T_N + H_e(\mathbf{r}) + V_{eN}(\mathbf{r}, \mathbf{R}),$$

where T_N represents nuclear kinetic energy operators, H_e is the electronic Hamiltonian and $V_{eN}(\mathbf{r}, \mathbf{R})$ includes all the electron-nuclear and nuclear-nuclear interactions. The electronic Hamiltonian H_e can be written as

$$H_e(\mathbf{r}) = T_e + V_{ee},$$

where T_e represents electron kinetic energy operators and V_{ee} includes all electron-electron interactions. Here, we use $\mathbf{r}$ and $\mathbf{R}$ as collective indexes to denote, respectively, the coordindates of the electrons and nuclei.

General Molecular System

If all the nuclei were fixed in space ($\mathbf{R}$ fixed), then the motions of electrons would be governed by the following Hamiltonian equation

$$[H_e(\mathbf{r}) + V_{eN}(\mathbf{r}, \mathbf{R})]\,\psi_n(\mathbf{r}, \mathbf{R}) = \epsilon_n(\mathbf{R})\psi_n(\mathbf{r}, \mathbf{R}),$$

where $\psi_n(\mathbf{r}, \mathbf{R})$ and $\epsilon_n(\mathbf{R})$ are called *adiabatic* eigenfunctions and eigenvalues of the electrons with the fixed nuclear coordinates $\mathbf{R}$ as parameters.

Born-Oppenheimer Approximiation

It is the assumption that the motion of atomic nuclei and electrons in a molecule can be treated separately.

The approach is named after Max Born and J. Robert Oppenheimer who proposed it in 1927.

1. First, for fixed nuclear positions $\mathbf{R}(t)$ at a time t, we perform a quantum mechanical calculation for the electrons. From the resulting electronic wave function $\Psi(\mathbf{r}, \mathbf{R})$, which depends only parametrically on the nuclear positions $\mathbf{R}$, we determine a force on each atom.

2. Second, using this quantal force, we advance the nuclei over a short time δt by the classical equations of motion, yielding a new set of positions $\mathbf{R}(t + \delta t)$ and momenta $\mathbf{P}(t + \delta t)$ for the nuclei.

We calculate the electronic many-body wave function $\Psi(\mathbf{r}, \mathbf{R})$ by solving the Schrödinger equation: $\hat{H}\Psi(\mathbf{r}, \mathbf{R}) = E\Psi(\mathbf{r}, \mathbf{R})$, where the Hamiltonian operator $\hat{H}$ has the form $\hat{H} = T_e + V_{ee} + V_{eN} + V_{NN}$. T_e represents the kinetic energy of the electrons. V_{ee}, V_{eN}, and V_{NN} are the potential energy term for the interaction between the electrons, the electrons and the nuclei, and the nuclei.

6. Ending: what is the physics describing reality?

Does light travel in straight line?
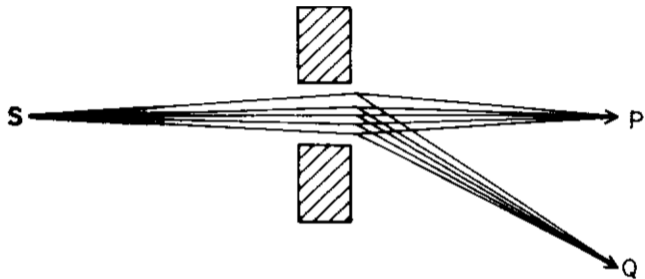
As we push the blocks closer together, at a certain point, the detector at Q starts clicking!

In quantum mechanics the uncertainty principle tells us that the energy can fluctuate wildly over a small interval of time. According to special relativity, energy can be converted into mass and vice versa. With quantum mechanics and special relativity, the wildly fluctuating energy can metamorphose into mass, that is, into new particles not previously present.

Ref: Quantum field theory in a nutshell.

Write down the Schrödinger equation for an electron scattering off a proton. The equation describes the wave function of one electron, and no matter how you shake and bake the mathematics of the partial differential equation, the electron you follow will remain one electron. But special relativity tells us that energy can be converted to matter: If the electron is energetic enough, an electron and a positron ("the antielectron") can be produced. *The Schrödinger equation is simply incapable of describing such a phenomenon*. Nonrelativistic quantum mechanics must break down.

Ref: Quantum field theory in a nutshell.

Casimir effect

Casimir plates
Vacuum fluctuations
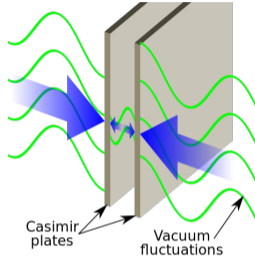
Two uncharged conductive plates are placed a few nanometers apart in a vacuum. In a classical description, the lack of an external field means that there is no field between the plates and no force between them.

When this field is instead studied using the quantum electrodynamic vacuum, it is seen that the plates do affect the virtual photons which constitute the field, and generate a net force.

(As a result), *quantum field theory* was born of the necessity of dealing with the marriage of *special relativity* and *quantum mechanics*, just as the new science of *string theory* is being born of the necessity of dealing with the marriage of *general relativity* and *quantum mechanics*.

Ref: Quantum field theory in a nutshell.

The ultimate theory for the reality? Nobody knows.

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End