Quantum mechanics II

Jaroslav Hamrle & Rudolf Sýkora

jaroslav.hamrle@vsb.cz

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Outline

Classical & quantum description

Classical (Newtonian) mechanics

- each particle has well defined trajectory $\vec{r}(t)$, energy E, momentum $\vec{p}$ and angular momentum $\vec{L}$
- motion of particle, in a given time, described by $\vec{x}(t)$, $\vec{p}(t)$.
- $E = \frac{p^2}{2m}$
- $\vec{p} = m\vec{v}$
- deterministic system

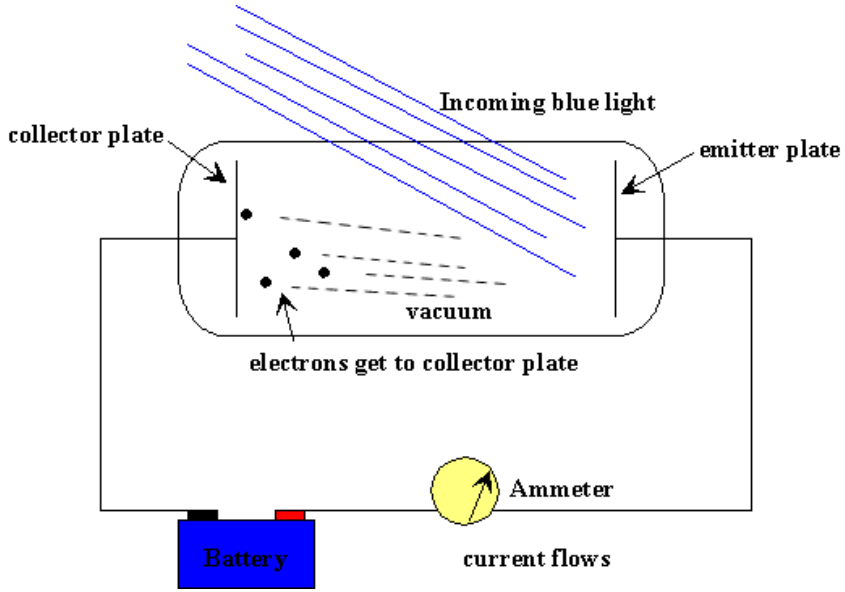
- About 1905, extensions of Newtonian mechanics:
  - for high speeds: special theory of relativity
  - for small object: quantum mechanics
- In 1928, Paul Dirac wrote equation, combining relativistic and quantum mechanics approach.
- Complete quantum relativistic theory missing up-to-date.

Outline

Wave-particle duality I: photons are particles (1)

Photoelectric effect: photons behave as particles:

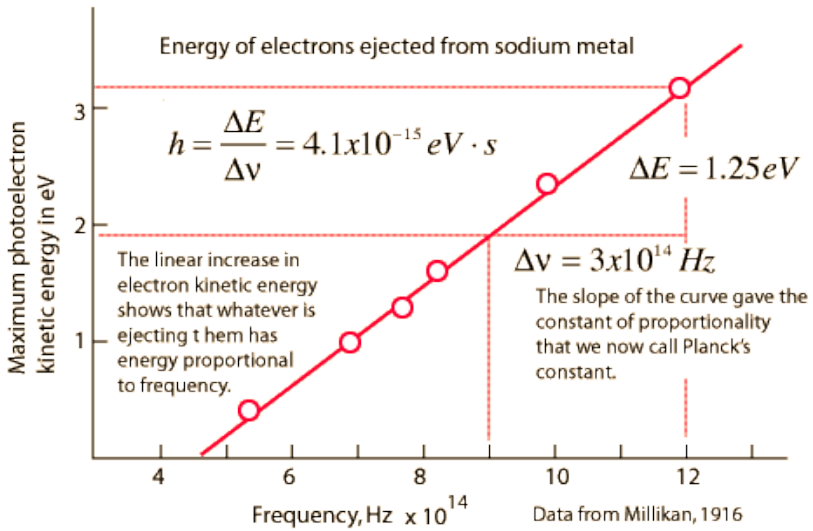
- Monochromatic light falling to metal electrode, knocks out excited electrons (so-called photoelectrons) out of the metal surface.
- The number and energy of the photoelectrons are detected by the volt-ampere characteristic of electric current flowing between both electrodes.



http://galileo.phys.virginia.edu/classes/252/photoelectric_effect.html

Wave-particle duality I: photons are particles (2)

- Energy of photoelectrons given by light frequency, not by beam intensity, as would follow from Maxwell equations
  $E_{\text{photon}} = E_{\text{electron}} + W_{\text{surface\_work}}$
- The light beam intensity determines solely number of photoelectrons, but not their energy!
- Classical (Maxwell) model:
  - $E_{\text{light}} = I = |E_{\text{field}}|^2$
  - E_{light} independent on light frequency



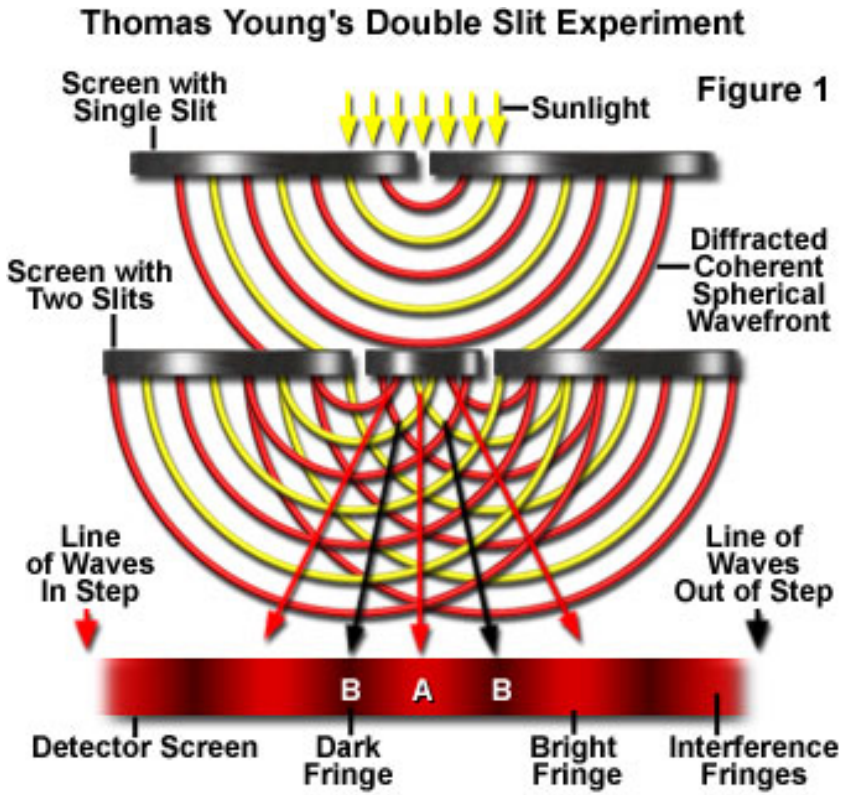
hyperphysics.phy-astr.gsu.edu/hbase/mod2.html

- Quantum model:
  - $E_{\text{photon}} = \hbar\omega = hf$
  - $\vec{p} = \hbar\vec{k}$

Wave-particle duality II: photons are waves

Young (double-slit) experiment: photons (light) behave as waves

- in wave description, two waves originating from each slit interfere each other, providing interference picture on screen, $I(x) = |E_1(x) + E_2(x)|^2$
- when any slit is closed, interference picture disappears, $I(x) = |E_1(x)|^2$ or $I(x) = |E_2(x)|^2$.

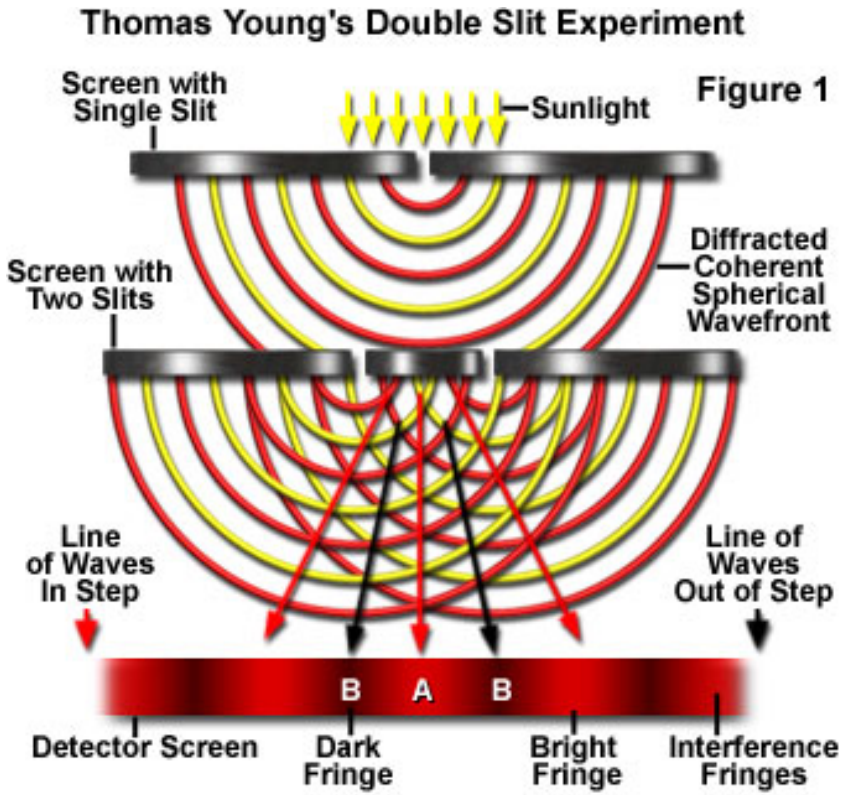


http://micro.magnet.fsu.edu/primer/java/interference/doubleslit/

Wave-particle duality III: photons are waves

However, when any time only one photon is within the setup, both wave and particle theories become invalid:

- when many photons passes, the interference picture appears ⇒ pure particle interpretation based on interaction (interference) between photons is not valid.
- when only few photons detected, their detected position is 'random' ⇒ pure wave interpretation is not valid.
- what was photon trajectory (through which slit the photon passed)?



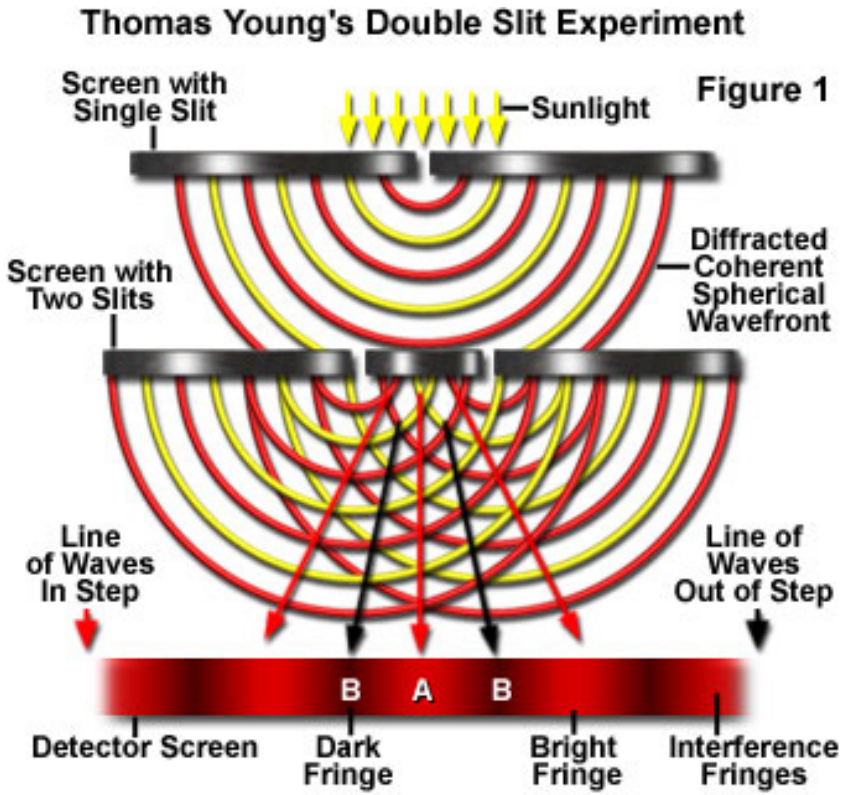
Particle and wave interpretation of light are inseparable. Light behaves at the same time as wave and as flow of particles. Wave nature allows only to calculate probability density of the particle.

Wave-particle duality IV: duality

1) Particle trajectory is wrong concept in quantum mechanics:

- when photon passes just through one slit, why is so important, that both slits are open?
- when we would detect, if photon pass through first or second slit, the interference disappears.

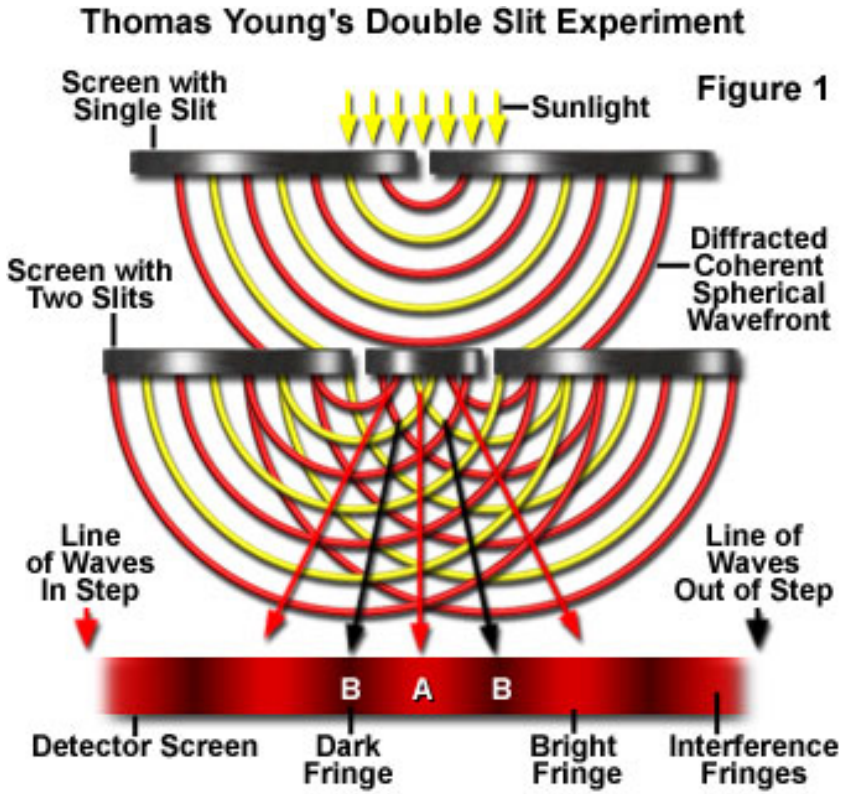
$\Rightarrow$ Trajectory of particle is invalid concept in quantum mechanics (final appearance of photon depends on existence of both splits).



Wave-particle duality V: duality

2) Predictions of photon behaviour has only probability character

- although the individual photons are released under equal circumstances, we can not predict where on the screen they will be detected.
- we can detect and predict only probability of the photon detection in a given position x
- this probability is proportional to the light intensity on the screen $I(x) = |E(x)|^2$, given by wave description.
- later, we show analogy between electric field intensity $E(x)$ and wavefunction $|\psi(x)\rangle$ (But $E(x)$ is not $|\psi(x)\rangle$)



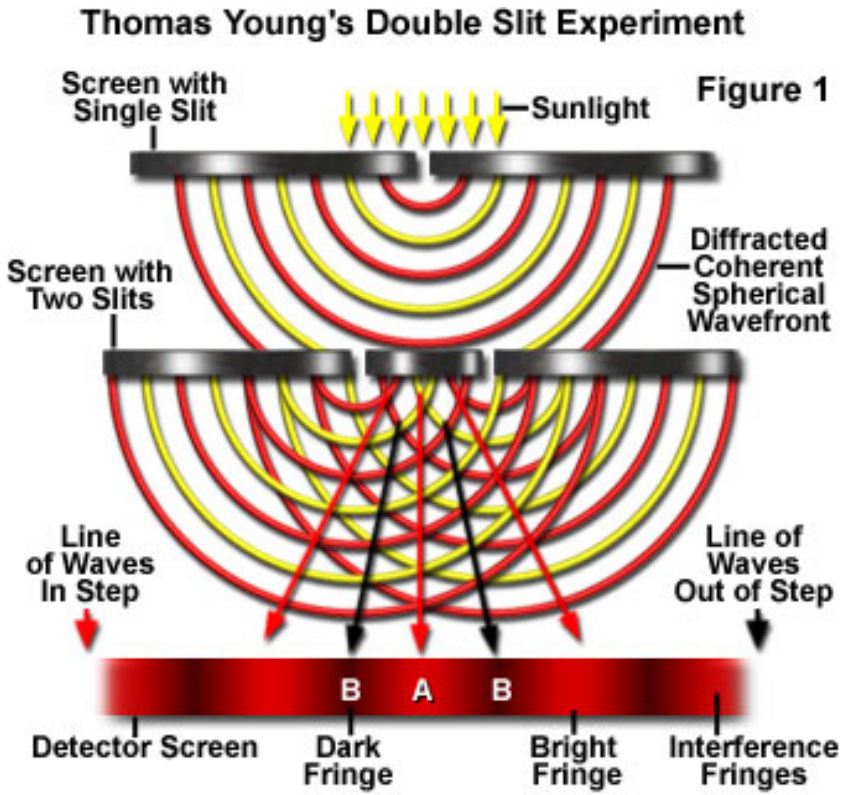
Predictions of photon behaviour have only probability character.

Wave-particle duality VI: detection

3) Detection in quantum system

- imagine, that we put another detector after each slit, detecting by which slit the photon passed.
- then, the interference picture disappears

$\Rightarrow$ unlike in Newtonian systems, the detection changes wavefunction (so-called collapse of wavefunction). Then, the photon behaves as originating from a slit where it is been detected.

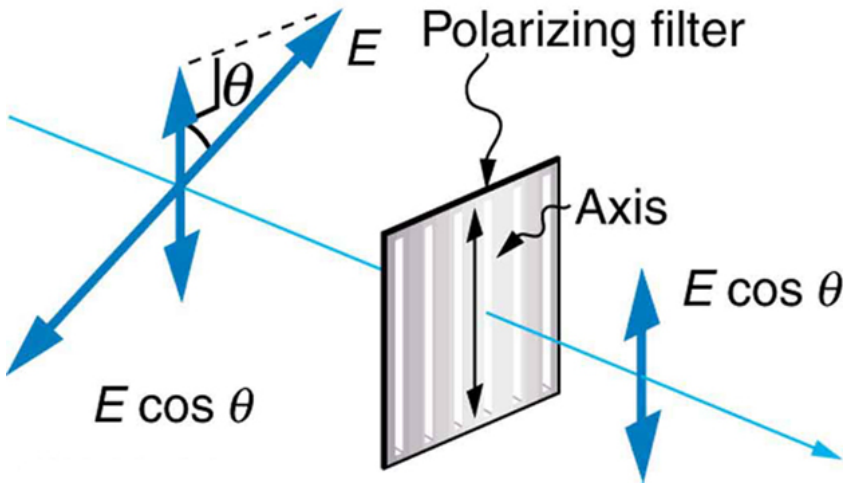


Idea of spectral decomposition I

Linearly polarized wave with orientation θ falls to analyzer with orientation 0 (i.e. along $\hat{x}$).

Classical description:

- incident wave:
  $$E_{\text{in}} = E_0 \begin{bmatrix} \cos\theta \\ \sin\theta \end{bmatrix} \exp[-i\omega t + ikz]$$
- only $\hat{x}$ component of the wave passes:
  $$E_{\text{out}} = E_0 \begin{bmatrix} \cos\theta \\ 0 \end{bmatrix} \exp[-i\omega t + ikz]$$
- detected intensity:
  $$I = |E_{\text{out}}|^2 = |E_0|^2 \cos^2\theta$$

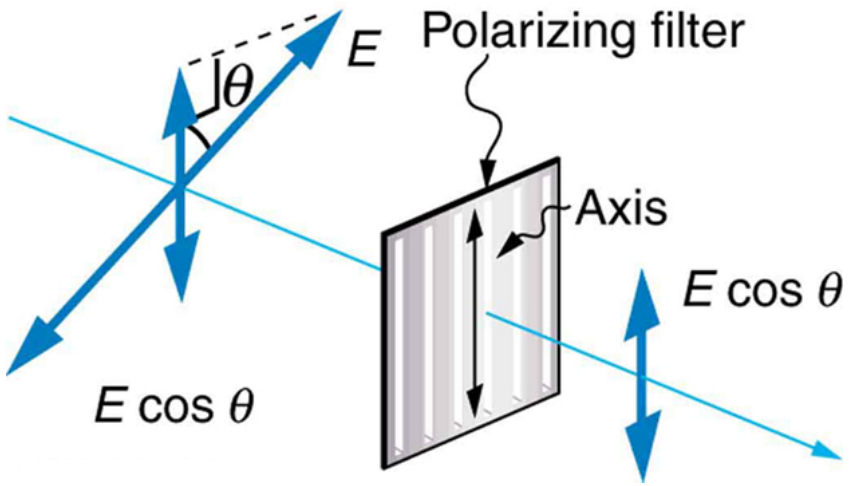


http://cnx.org/content/m42522

Idea of spectral decomposition II

Quantum description:

- for small number of incidence photons, the photon passes polarizer or is absorbed in the polarizer.
- whether the photon passes or is absorbed is a stochastic process.
- when large number of photon passes, the number of passes/absorbed photons must approach classical limit.
- hence, each photon has probability $\cos^2\theta$ to pass and probability $\sin^2\theta$ to be absorbed.



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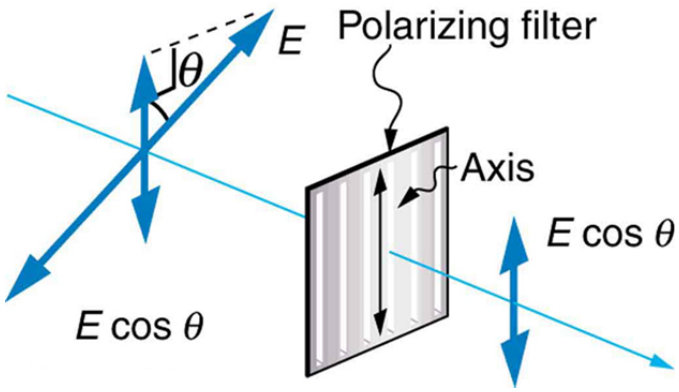
Idea of spectral decomposition III

Quantum description:

- quantum detector (here analyzer) can detect only some privilege states (eigenvalues, *vlastní hodnoty*), providing quantization of detection. Here, there are only two eigenvalues, passed or absorbed. It is different from classical case, where detected intensity continuously moves from I to 0.
- Each eigenvalue corresponds to one eigenstate. Here, two eigenstates are $e_1 = \hat{x}$, $e_2 = \hat{y}$
- after measurement (here after passing analyzer), the quantum state of photon is changed to one of the eigenstates of the detection system. Here, it means that the photon polarization becomes e_1 or e_2.



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Idea of spectral decomposition IV

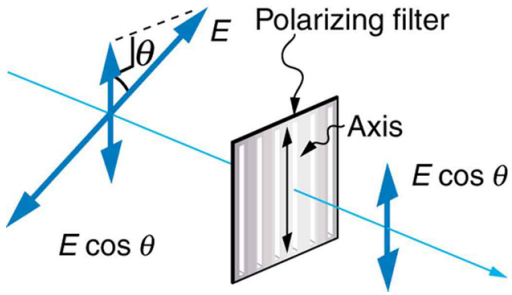
Quantum description:

- if quantum state of the incoming photon is one of the eigenstate of the detection system, then the output is sure, s quantum state will be kept during measurement.
- if quantum state before measurement does not belong to eigenstate, then incoming state must be decomposed as linear combination of detector's eigenstate. Here, it means $e_p = \cos\theta\hat{x} + \sin\theta\hat{y}$. Then , detection probabilities are $\cos^2\theta$ and $\sin^2\theta$. This rule is called spectral decomposition in quantum mechanics.
- after passing polarizer, the light is polarized in $\hat{x}$ direction. It means, that during measurement, the quantum state has changed.
- after measurement (here after passing analyzer), the quantum state of photon is changed to one of the eigenstates of the detection system. Here, it means that the photon polarization becomes e_1 and e_2.

Idea of spectral decomposition V

Quantum description:

- if quantum state of the incoming photon is one of the eigenstate of the detection system, then the output is sure, s quantum state will be kept during measurement.
- if quantum state before measurement does not belong to eigenstate, then incoming state must be decomposed as linear combination of detector's eigenstate. Here, it means $e_p = \cos\theta\hat{x} + \sin\theta\hat{y}$. Then, detection probabilities are $\cos^2\theta$ and $\sin^2\theta$. This rule is called spectral decomposition in quantum mechanics.
- after passing polarizer, the light is polarized in $\hat{x}$ direction. It means, that during measurement, the quantum state has changed.



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Particles and particle's waves

Louis de Broglie (1923): "With every particle of matter with mass m and velocity $\vec{v}$ a real wave must be associated" (valid also for massless particles):

- $E = \hbar\omega$: energy E is the particle energy (rest energy and kinetic energy)
- $\vec{p} = \hbar\vec{k}$: relation between momentum and $\vec{k}$-vector of the particles

Experimentally determined by many means, such as electron diffraction, neutron diffraction, etc.
I just recall:

- $\omega = 2\pi f$ (relation between angular frequency and frequency)
- $k = 2\pi/\lambda$ (relation between wavevector (wavenumber) and wavelength)

Outline

Wavefunction $|\psi(\vec{x},t)\rangle$ I

When generalize conclusion from Young experiment to mass particles:

1. classical description of particle trajectory must be replaced by quantum time-dependent state. Such state is described by wavefunction $|\psi(\vec{x},t)\rangle$, providing all available information about the article.
2. $|\psi(\vec{x},t)\rangle$ is by its nature a complex number (function).
3. interpretation of $|\psi(\vec{x},t)\rangle$ is amplitude of the particle probability appearance (*amplituda pravděpodobnosti výskytu částice*).
4. Probability to find particle in time t in volume d^3r is $\mathrm{d}P(t,r) = |\,|\psi(\vec{x},t)\rangle\,|^2\,\mathrm{d}r^3$, where $|\,|\psi(\vec{x},t)\rangle\,|^2$ is probability density (*hustota pravděpodobnosti*).

Wavefunction $|\psi(\vec{x},t)\rangle$ II

1. idea of spectral decomposition for measurement of physical quantity A follows:
2. (i) the measurement output must belong to eigenvalues a with corresponding eigenstates $|\psi_a(\vec{r})\rangle$.
3. spectral decomposition of wavefunction to eigenstates is $|\psi(\vec{r})\rangle = \sum_a c_a |\psi_a(\vec{r})\rangle$
4. probability that $|\psi(\vec{x},t)\rangle$ is measured in state a is $P_a = \frac{|c_a|^2}{\sum_a |c_a|^2}$
5. after the measurement of the physical quantity A, the eigenstate is $|\psi(\vec{r},t)\rangle = |\psi_a(\vec{r})\rangle$

Wavefunction $|\psi(\vec{x},t)\rangle$ III

1. time evolution of wavefunction of a mass particle is described by Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}|\psi(\vec{r},t)\rangle = -\frac{\hbar^2}{2m}\nabla^2|\psi(\vec{r},t)\rangle + V(\vec{r},t)|\psi(\vec{r},t)\rangle$$

2. $V(\vec{r},t)$: potential energy
3. particle is somewhere in the space, and for mass particle, it can not appeared or disappeared : $\int |\psi(\vec{r},t)|^2 \mathrm{d}^3 r = 1$
4. $|\psi(\vec{x},t)\rangle$ for any time t is determined by $|\psi(\vec{x},t_0)\rangle$
5. Schrödinger equation is not relativistic (different order of derivation for space and time)

Outline

Free particle

potential energy is constant, $V(\vec{r},t)=0$, then

$$i\hbar\frac{\partial}{\partial t}\left|\psi(\vec{r},t)\right\rangle = -\frac{\hbar^2}{2m}\nabla^2\left|\psi(\vec{r},t)\right\rangle$$

- solution is wave equation $\psi(\vec{r},t) = A\exp[i(\vec{k}\cdot\vec{r}-\omega t)]$
- $\vec{k}$ and ω are related by: $\omega = \dfrac{\hbar\vec{k}^2}{2m}$.
- particle energy is: $E = \dfrac{\vec{p}^2}{2m}$, where $\vec{p}=\hbar\vec{k}$

Wave packet I

Any solution is superposition (linear combination) of single wave equation. Three-dimensional wave packet can be written as:

$$\psi(\vec{r},t) = \frac{1}{(2\pi)^{3/2}} \int g(\vec{k}) \exp[i(\vec{k}\cdot\vec{r} - \omega t)] \mathrm{d}^3 k$$

One-dimensional wave packet writes:

$$\psi(x,t) = \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{\infty} g(k) \exp[i(kx - \omega t)] \mathrm{d}k$$

For $t = 0$, wavefunction writes

$$\psi(x,0) = \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{\infty} g(k) \exp[ikx] \mathrm{d}k$$

Hence, $g(k)$ can be determined by inverse Fourier transformation

$$g(k) = \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{\infty} \psi(x,0) \exp[-ikx] \mathrm{d}x$$

Wave packet II: Interpretation of $g(k) = \psi_k(k)$

- $\psi(x)$ (so called x-representation of the wavefunction): $\mathrm{d}\mathcal{P}(x) = |\psi(x)|^2 \mathrm{d}x$: probability to find particle in position x within interval $x + \mathrm{d}x$
- $g(k) = \psi_k(k)$: $\mathrm{d}\mathcal{P}(k) = |\psi_k(k)|^2 \mathrm{d}k$ (so called k-representation of the wavefunction): probability to find particle having momentum $p = \hbar k$ within interval between $\hbar k$ and $\hbar(k + \mathrm{d}k)$
- normalization (general feature for two functions related by FT, so called Bessel–Perseval equality):

$$\int_{-\infty}^{\infty} |\psi(x)|^2 \mathrm{d}x = \int_{-\infty}^{\infty} |\psi_k(p)|^2 \mathrm{d}p$$

Wave packet III: Position of maxima of wavepackets

$$g(k) = |g(k)| \exp(i\alpha(k))$$

Assuming $\alpha(k)$ is slowly changing function around k_0, where k_0 is centre of wavepacket (i.e. maxima for wavepacket in k-representation $|g(k = k_0)| = |\psi_k(k = k_0)|$).

$$\alpha(k) \approx \alpha(k_0) + (k - k_0) \left[\frac{\mathrm{d}\alpha}{\mathrm{d}k}\right]_{k=k_0}$$

Then, whole phase in Fourier transform is:

$$\alpha(k) + kx = k_0 x + \alpha(k_0) + (k - k_0)(x - x_0)$$

where

$$x_0 = -\left[\frac{\mathrm{d}\alpha}{\mathrm{d}k}\right]_{k=k_0}$$

is maxima of wavepacket in x-representation (i.e. maxima for $\psi(x = x_0)$)

Wave packet IV

Then, wavefunction can be written as

$$\psi(x,0) = \frac{\exp[i(k_0 x + \alpha(k_0))]}{(2\pi)^{1/2}} \int_{-\infty}^{\infty} |g(k)| \exp[i(k-k_0)(x-x_0)]$$

- $\psi(x,0)$ is maximal, when $(k-k_0)(x-x_0) = 0$. I.e. it happens at position $x = x_0$ and propagation dominant k-wave is $\psi(x,0) \approx \exp[ik_0 x]$. It means, the central momentum is $p = \hbar k_0$, corresponding to maxima of $|\psi_k(k=k_0)| = |g(k=k_0)|$.

Wave packet V: Heisenberg relation of uncertainty

$$\psi(x,0) = \frac{\exp[i(k_0 x + \alpha(k_0))]}{(2\pi)^{1/2}} \int_{-\infty}^{\infty} |g(k)| \exp[i(k-k_0)(x-x_0)]$$

- Define width of wavefunction in k-representation $\psi_k(k) = g(k)$ is $\Delta k = k - k_0$ and width of the wavefunction in x-representation $\psi(x,0)$ is $\Delta x = x - x_0$. Then, equation above shows, that this happen when $\exp[i(k-k_0)(x-x_0)]$ oscillates roughly once, i.e. when
$$\Delta k \Delta x > 1, \quad \text{and hence} \quad \Delta p \Delta x > \hbar$$
- This is related with wave nature of quantum mechanics and it is a general feature of widths of two functions related by a Fourier transformation.
- So, Heisenberg relation determines minimal width of the wavepackets. There is no limit about maximal width of wavepackets.

Wave packet VI: Heisenberg relation of uncertainty

- Heisenberg relation of uncertainty:

$$\Delta p \Delta x > \hbar$$

When e.g. momentum is exacted $p = \hbar k_0$, i.e. $g(k) = \delta(k - k_0)$, then the position of the particle Δx is infinite, i.e. particle is not localized at all. Again, this is consequence of wave nature of quantum mechanics.

Time evolution of wave packet: phase velocity

- Plane wave $\exp[i(kx - \omega t)]$ propagates by phase velocity $v_\phi = \omega/k$.
- As $\omega = \hbar k^2/(2m)$, phase velocity becomes $v_\phi = \hbar k/(2m)$.

Time evolution of wave packet: group velocity

- Let us determine velocity of movement of maxima of the wavepacket (so called group velocity).

$$g(k,t) = |g(k)| \exp(\alpha(k,t))$$

where $\alpha(k,t) = \alpha(k) - \omega(k)t$

- As shown above, position of wavepacket maxima is (derived from $\frac{d}{dk}[kx - \alpha(k) - \omega(k)t]_{k=k_0} = 0$)

$$x_0 = -\left[\frac{\mathrm{d}\alpha(k,t)}{\mathrm{d}k}\right]_{k=k_0} = \left[\frac{\mathrm{d}\omega}{\mathrm{d}k}\right]_{k=k_0}\left[\frac{\mathrm{d}\alpha(k)}{\mathrm{d}k}\right]_{k=k_0}$$

Hence group velocity is

$$V_G(k_0) = \left[\frac{\mathrm{d}\omega(k)}{\mathrm{d}k}\right]_{k=k_0}$$

- Hence, as $\omega = \hbar k^2/(2m)$, group velocity becomes $V_G(k_0) = \hbar k_0/m = 2v_\varphi$. It corresponds to classical particle movement $v = p/m$

Outline

Time-independent potential $V(\vec{r})$: stationary states I

$$i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t) = -\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r},t) + V(\vec{r})\psi(\vec{r},t)$$

Let us separate time and space solutions, $\psi(\vec{r},t) = \psi(\vec{r})\chi(t)$

$$i\hbar\varphi(\vec{r})\frac{\mathrm{d}}{\mathrm{d}t}\chi(t) = \chi(t)\left[-\frac{\hbar^2}{2m}\nabla^2\varphi(\vec{r})\right] + \chi(t)V(\vec{r})\varphi(\vec{r})$$

Which leads to

$$\frac{i\hbar}{\chi(t)}\frac{\mathrm{d}}{\mathrm{d}t}\chi(t) = \frac{1}{\varphi(\vec{r})}\left[-\frac{\hbar^2}{2m}\nabla^2\varphi(\vec{r})\right] + V(\vec{r})$$

As equation must be valid for any time t and any position $\vec{r}$, both sides must be equal to a constant $E = \hbar\omega$

Time-independent potential $V(\vec{r})$: stationary states II

Solution of the left side:

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\chi(t) = \chi(t)\hbar\omega$$

providing solution

$$\chi(t) = A\exp[-i\omega t]$$

Hence, the resulting wavefunction writes:

$$\psi(\vec{r},t) = \varphi(\vec{r})\exp[-i\omega t]$$

Time-independent potential $V(\vec{r})$: stationary states III

Solution of the right side:

$$\left[-\frac{\hbar^2}{2m}\nabla^2\varphi(\vec{r}) + V(\vec{r})\right]\varphi(\vec{r}) = \hbar\omega\varphi(\vec{r}) H\varphi(\vec{r}) \qquad = E\varphi(\vec{r})$$

- This is time-independent form of Schrödinger equation, providing time-independent probability density $|\psi(\vec{r},t)|^2 = |\varphi(\vec{r})|^2$.
- Corresponding particle energy (eigenfrequency) is constant being $E = \hbar\omega$.
- $H\varphi_n(\vec{r}) = E_n\varphi_n(\vec{r})$ can be understood as search of eigenstates $\varphi_n(\vec{r})$ of operator H with eigenvalues E_n. They are also called stationary states.

Time-independent potential $V(\vec{r})$: stationary states IV

Superposition of stationary states:

- As Schrödinger equation is linear, any linear superposition of solutions is also solution, namely

$$\psi(\vec{r},t) = \sum_n c_n \varphi_n(\vec{r}) \exp[-iE_n t/\hbar]$$

  where c_n are some constants, given usually by starting or boundary conditions.
- In general, superposition $|\psi(\vec{r},t)|^2$ depends on time.

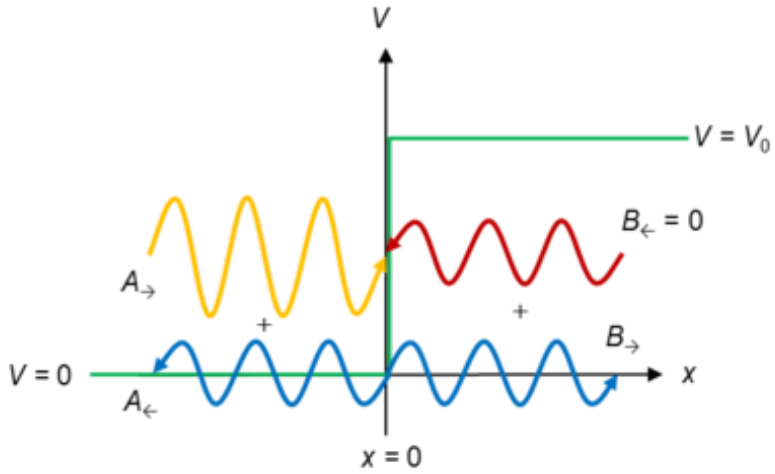
Time-independent potential $V(\vec{r})$: step-like potentials I

- step-like potential,

$$V(x) = \begin{cases} 0 & x < 0 \\ V_0 & x > 0 \end{cases}$$

- Schrödinger equation:

$$\frac{\mathrm{d}^2}{\mathrm{d}x^2}\varphi(x) + \frac{2m}{\hbar^2}(E - V)$$



$E > V$: let us define k being $E - V = \frac{\hbar^2 k^2}{2m}$.
Then, solution has form
$\varphi(x) = A\exp[ikx] + A'\exp[-ikx]$

$E > V$: let us define ρ being $V - E = \frac{\hbar^2 \rho^2}{2m}$.
Then, solution has form
$\varphi(x) = B\exp[\rho x] + B'\exp[-\rho x]$
where A, A', B, B' are unknown complex constants

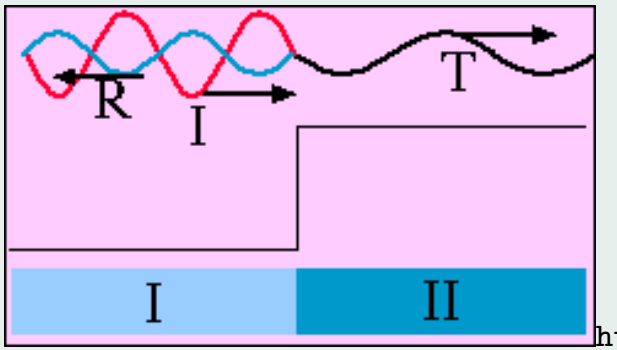
Time-independent potential $V(\vec{r})$: step-like potentials II

Case $E > V_0$

- In case $E > V_0$, the energy is above both potentials. The solution is then partial reflection.
- Solutions in areas I ($V = 0$) and in areas II ($V = V_0$)

$$\varphi_I(x) = A_1 \exp[ik_1 x] + A_1' \exp[-ik_1 x]$$
$$\varphi_{II}(x) = A_2 \exp[ik_2 x] + A_2' \exp[-ik_2 x]$$

  where $k_1 = \sqrt{2mE/\hbar^2}$ and $k_2 = \sqrt{2m(E - V_0)/\hbar^2}$
- let as assume, the wave goes from left, i.e. $A_2' = 0$



http://www.cobalt.chem.ucalgary.ca/ziegler

Time-independent potential $V(\vec{r})$: step-like potentials III

Case $E > V_0$:

- $\varphi(x)$ and $\frac{\mathrm{d}}{\mathrm{d}x}\varphi(x)$ are continuous of potential discontinuity.

(i) $\varphi_I(0) = \varphi_{II}(0)$, leading to $A_1 + A_1' = A_2$

(ii) $\mathrm{d}/\mathrm{d}x\,[\varphi_I(0)]_{x=0} = \mathrm{d}/\mathrm{d}x\,[\varphi_{II}(0)]_{x=0}$, leading to $k_1 A_1 - k_1 A_1' = k_2 A_2$

- this provides

$$\frac{A_1'}{A_1} = \frac{k_1 - k_2}{k_1 + k_2}$$
$$\frac{A_2}{A_1} = 1 + \frac{A_1'}{A_1} = \frac{2k_1}{k_1 + k_2}$$

- Reflection coefficients $R = |\frac{A_1'}{A_1}|^2 = (k_1 - k_2)^2/(k_1 + k_2)^2$
- Transmission coefficients $T = 1 - R = 4k_1 k_2/(k_1 + k_2)^2$

Time-independent potential $V(\vec{r})$: step-like potentials IV

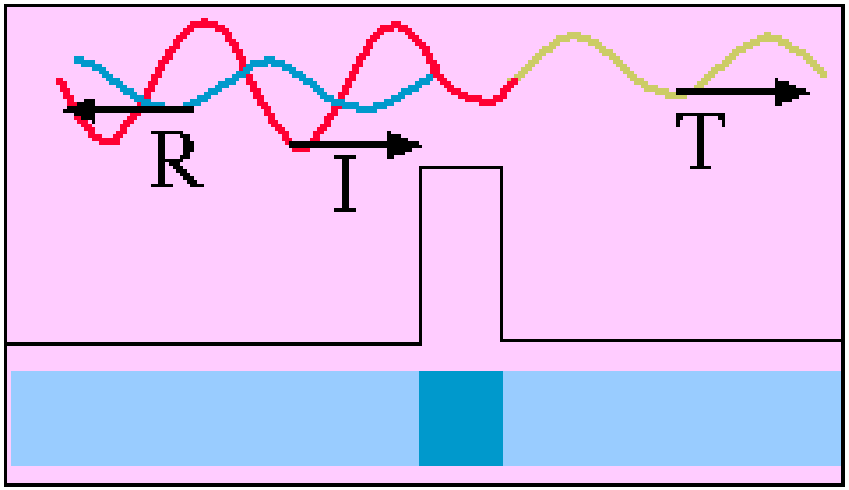
Case $E < V_0$:

- In case $E > V_0$. The solution is total reflection.
- Solutions in areas I ($V = 0$) and in areas II ($V = V_0$)

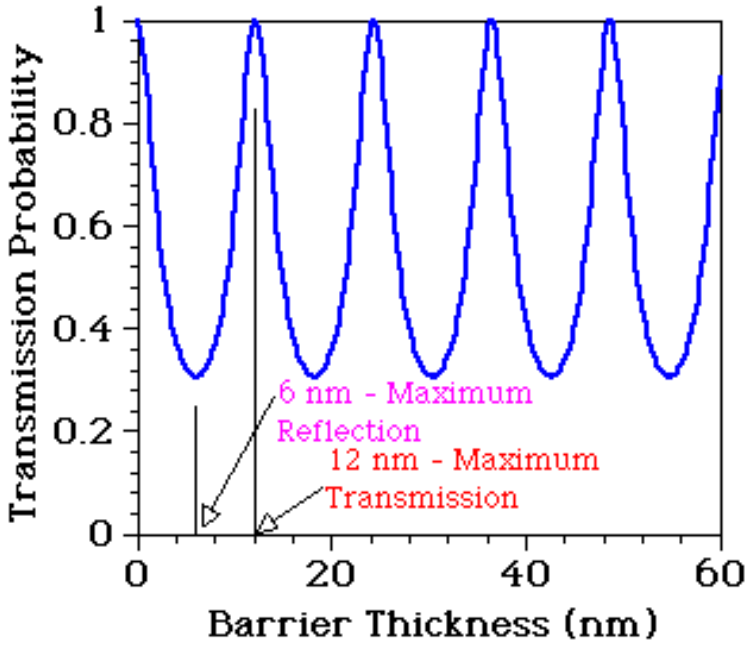
$$\varphi_I(x) = A_1 \exp[ik_1 x] + A_1' \exp[-ik_1 x]$$
$$\varphi_{II}(x) = B_2 \exp[\rho_2 x] + B_2' \exp[-\rho_2 x]$$

  where $k_1 = \sqrt{2mE/\hbar^2}$ and $\rho_2 = \sqrt{2m(V_0 - E)/\hbar^2}$
- let as assume, the wave goes from left, i.e. $B_2' = 0$. Then $\frac{A_1'}{A_1} = \frac{k_1 - i\rho_2}{k_1 + i\rho_2}$ $\quad$ $\frac{B_2}{A_1} = 1 + \frac{A_1'}{A_1} = \frac{2k_1}{k_1 + i\rho_2}$
- Reflection coefficients $R = |\frac{A_1'}{A_1}|^2 = |(k_1 - i\rho_2)/(k_1 + i\rho_2)|^2 = 1$
- Transmission coefficients $T = 1 - R = 0$; just evanescent wave in II exists; $\varphi(x) = B_2 \exp[-\rho_2 t]$

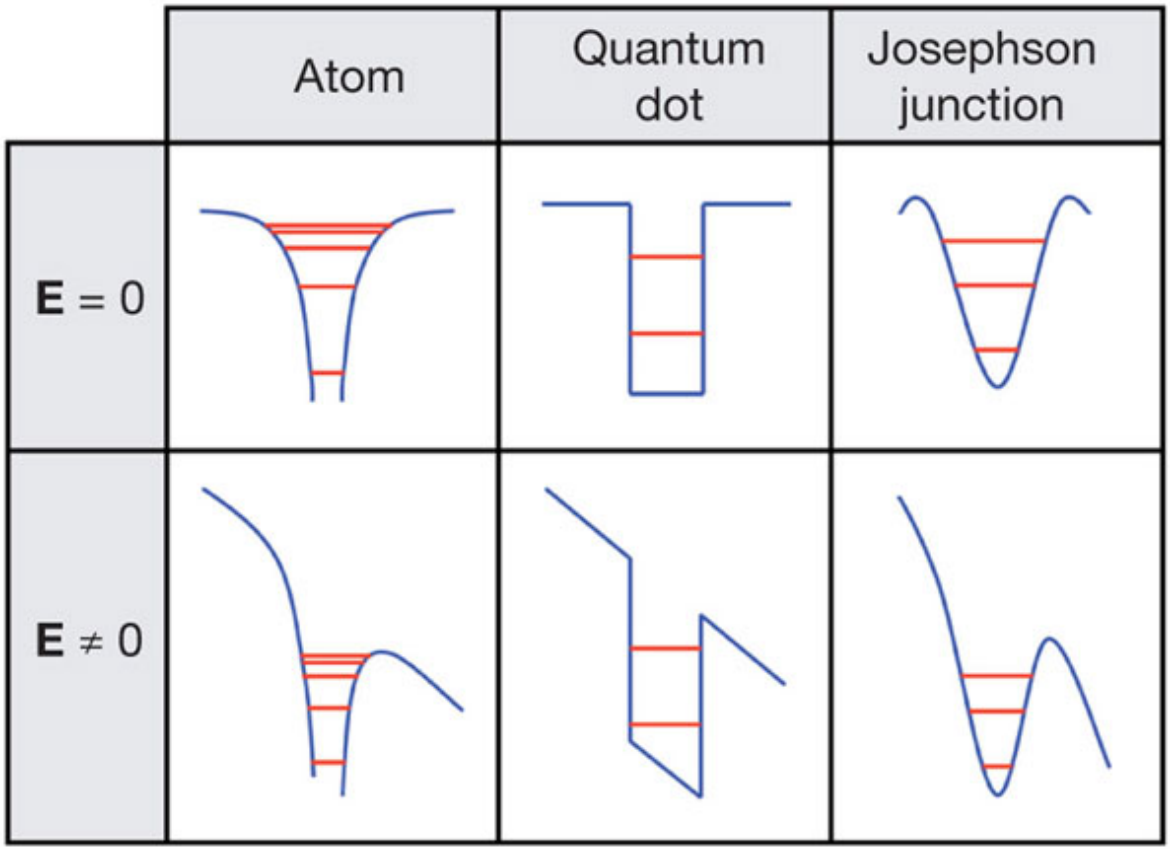
Potential wall



- wavefunction may tunnel through barrier even for $E < V_0$
- In case $E > V_0$ interference between width of the barrier and particle wavelength.



Potential well



- many potential wells exist in nature (single atoms, chemical bonding, etc.)
- for $E < V_0$, V_0 depth of the well, the stationary states with sharp energy exists.

Outline

- Non-relativistic description of angular momentum
- Schrödinger equation
- Addition of angular momentum
- Zeeman effect: angular moment in magnetic field
- Magnetism and relativity: classical picture
- Dirac equation

Dirac approach in quantum mechanics: ket-vector

ket-vector $|\psi(\vec{r})\rangle$: belongs to vector space $\mathcal{E}$ with certain properties, such as integrability $\int |\,|\psi(\vec{r})\rangle\,|^2 \mathrm{d}\vec{r} = 1$. Also, any linear combination of those function belong to $\mathcal{E}$.
Interpretation of ket-vector:

- $|\psi(\vec{r})\rangle$ can be understand as a function of $\vec{r}$ in whole space
- $|\psi(\vec{r})\rangle$ can be understand as a vector in a given (continuous or discrete) base, e.g. in base of $\vec{r}$, $\vec{p}$, $u_i(\vec{r})$

As for ordinary vector, the base of vector is not explicitly given, just $|\psi\rangle$.

Dirac approach in quantum mechanics: bra-vector

Scalar multiplication: $\langle\varphi(\vec{r})|\psi(\vec{r})\rangle = \int \varphi(\vec{r})^*\psi(\vec{r})\mathrm{d}\vec{r}$

- $\langle\varphi|$ is called bra-vector.
- relation between ket-vector and bra-vector is antilinear:
  $(\langle\lambda_1\varphi_1| + \langle\lambda_2\varphi_2|)\,|\psi\rangle = \int[\lambda_1\varphi_1(\vec{r}) + \lambda_2\varphi_2(\vec{r})]^*\psi(\vec{r})\mathrm{d}\vec{r} =$
  $\lambda_1^* \int \varphi_1(\vec{r})^*\psi(\vec{r})\mathrm{d}\vec{r} + \lambda_2^* \int \varphi_2(\vec{r})^*\psi(\vec{r})\mathrm{d}\vec{r} =$
  $\lambda_1^* \langle\varphi_1|\psi\rangle + \lambda_2^* \langle\varphi_2|\psi\rangle$
- Hence, corresponding vector to ket-vektor $\lambda\,|\psi\rangle$ is bra-vektor $\lambda^* \langle\psi| = \langle\lambda\psi|$
- bra-vector $\langle\varphi|$ can be understand as a linear functional, i.e. operator attributing a number to the function.
- Other properties of scalar multiplication
  - $\langle\varphi|\psi\rangle = \langle\psi|\varphi\rangle^*$
  - $\langle\varphi|\lambda_1\psi_1 + \lambda_2\psi_2\rangle = \lambda_1 \langle\varphi|\psi_1\rangle + \lambda_2 \langle\varphi|\psi_2\rangle$
  - $\langle\lambda_1\varphi_1 + \lambda_2\varphi_2|\psi\rangle = \lambda_1^* \langle\varphi_1|\psi\rangle + \lambda_2^* \langle\varphi_2|\psi\rangle$
  - $\langle\psi|\psi\rangle \geq 0$ (and real)
  - $\langle\psi|\psi\rangle = 0$ only when $|\psi\rangle = 0$

Dirac approach in quantum mechanics: linear operators

Linear operators: mathematical entity assigning to each function $|\psi(\vec{r})\rangle \in \mathcal{E}$ another function $|\psi'(\vec{r})\rangle$, $|\psi'(\vec{r})\rangle = \hat{A}\,|\psi(\vec{r})\rangle$

- linearity: $\hat{A}\,|\lambda_1\psi_1 + \lambda_2\psi_2\rangle = \lambda_1\hat{A}\,|\psi_1\rangle + \lambda_2\hat{A}\,|\psi_2\rangle$
- multiplication of two operators: $(\hat{A}\hat{B})\,|\psi\rangle = \hat{A}(\hat{B}\,|\psi\rangle)$.
- However, in general, $\hat{A}\hat{B} \neq \hat{B}\hat{A}$!. Then, we define commutator (*komutátor*): $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$
- as matrix element we call scalar multiplication $\langle\varphi|A|\psi\rangle$
- linear operator $\hat{C} = |\psi\rangle\langle\varphi|$. Prove that $\hat{C}$ is a linear operator: $\hat{C}\,|\chi\rangle = |\psi\rangle\langle\varphi|\chi\rangle$, i.e. application $\hat{C}$ to ket $|\chi\rangle$ makes another ket.
- operator of projection to $|\psi\rangle$: $\hat{P}_\psi = |\psi\rangle\langle\psi|$. Applying to ket $|\chi\rangle$, we get $\hat{P}_\psi\,|\chi\rangle = |\psi\rangle\langle\psi|\chi\rangle$, i.e. ket proportional to ket $|\psi\rangle$.
- similarly, one can define projection to sub-space $|\psi\rangle_i$ $\hat{P} = \sum_i |\psi_i\rangle\langle\psi_i|$

Dirac approach in quantum mechanics: Hermitian conjugate I

Hermitian conjugate *(Hermitovské sdružení)*:
Up to now, operators were acting on ket-vectors. But how do they act on bra-vectors?

- $\langle\varphi|\hat{A}|\psi\rangle = \langle\varphi|(\hat{A}|\psi\rangle) = (\langle\varphi|\hat{A})|\psi\rangle$, i.e. we can define new bra-vector $\langle\varphi|\,\hat{A}$
- let us define Hermitian conjugate operator $A^\dagger$:

$$|\psi'\rangle = A\,|\psi\rangle = |A\psi\rangle \quad \longleftrightarrow \quad \langle\psi'| = \langle\psi|\,A^\dagger = \langle A\psi|$$

- let us prove that $\langle\psi|A^\dagger|\varphi\rangle = \langle\varphi|A|\psi\rangle^*$.
  Proof: $\langle\psi'|\varphi\rangle = \langle\varphi|\psi'\rangle^*$, and then $|\psi\rangle' = A\,|\psi\rangle$
- $(A^\dagger)^\dagger = A$. Proof: $\langle\psi|(A^\dagger)^\dagger|\varphi\rangle = \langle\varphi|A^\dagger|\psi\rangle^* = \langle\psi|A|\varphi\rangle$
- $(\lambda A)^\dagger = \lambda^* A^\dagger$: Proof:
  $\langle\psi|(\lambda A)^\dagger|\varphi\rangle = \langle\varphi|\lambda A|\psi\rangle^* = \lambda^*\,\langle\varphi|A|\psi\rangle^* = \lambda^*\,\langle\psi|A^\dagger|\varphi\rangle$

Dirac approach in quantum mechanics: Hermitian conjugate II

- operation of Hermitian conjugate is also changing order of used objects:

$$(|u\rangle\langle v|)^\dagger = |v\rangle\langle u|$$

  Proof: $\langle\psi|(|u\rangle\langle v|)^\dagger|\varphi\rangle = [\langle\varphi|(|u\rangle\langle v|)|\psi\rangle]^* = \langle\varphi|u\rangle^*\langle v|\psi\rangle^* = \langle\psi|v\rangle\langle u|\varphi\rangle = \langle\psi|(|v\rangle\langle u|)|\varphi\rangle$

- In general, to replace expression by hermitian conjugate one, one has to:
  - constants become complex conjugate
  - ket-vectors becomes bra-vectors
  - bra-vector becomes ket-vectors
  - operators become complex conjugate
  - change order of elements (but for constants, it does not matter)

Dirac approach in quantum mechanics: Hermitian operators I

Hermitian operators: operator is called Hermitian, when

$$A = A^\dagger$$

Then, $\langle\psi|A|\varphi\rangle = \langle\varphi|A|\psi\rangle^*$, i.e. $\langle A\phi|\psi\rangle = \langle\phi|A\psi\rangle$. Notes:

- Hermitian operators are important in quantum mechanics
- Hermitian operators are also called **observables** *(pozorovatelné)*
- note: when A and B are Hermitian, then AB is Hermitian only when $[A, B] = 0$. Proof: $A = A^\dagger$, $B = B^\dagger$; for $(AB)^\dagger = B^\dagger A^\dagger = BA$, which is equal to AB only when $[A, B] = AB - BA = 0$
- eigenvalues of Hermitian operators are real: Proof: $A\psi_\lambda = \lambda\psi_\lambda$; for Hermitian A: $\lambda = \lambda \langle\psi_\lambda|\psi_\lambda\rangle = \langle\psi_\lambda|A|\psi_\lambda\rangle = \langle\psi_\lambda|A^\dagger|\psi_\lambda\rangle = \langle\psi_\lambda|A|\psi_\lambda\rangle^* = \lambda^* \langle\psi_\lambda|\psi_\lambda\rangle = \lambda^*$

Dirac approach in quantum mechanics: Hermitian operators II

Eigenstates of an Hermitian operator corresponding to different eigenvalues are automatically orthogonal.
Proof:

$$A\left|\psi\right\rangle = \lambda\left|\psi\right\rangle \qquad A\left|\phi\right\rangle = \mu\left|\phi\right\rangle$$
$$\left\langle\psi\right| A = \lambda\left\langle\psi\right| \qquad \left\langle\phi\right| A = \mu\left\langle\phi\right|$$

i.e. $|\phi\rangle$, $|\psi\rangle$ are eigenstates with eigenvalues μ, λ, respectively.

$$(\langle\phi|A|)\psi\rangle = \mu\langle\phi|\psi\rangle$$
$$\langle\phi|(A|\psi\rangle) = \lambda\langle\phi|\psi\rangle$$

Hence, difference provides $(\lambda-\mu)\langle\phi|\psi\rangle = 0$. Hence, when $(\lambda-\mu)\neq 0$ then $\langle\phi|\psi\rangle = 0$ and hence $|\phi\rangle$ and $|\psi\rangle$ are orthogonal each other.

Important sentences I

- when $[A, B] = 0$, than eigenvectors of operator A are also eigenvectors of operator B.
  Proof: $A\,|\psi\rangle = a\,|\psi\rangle$. Then
  $BA\,|\psi\rangle = Ba\,|\psi\rangle = A(B\,|\psi\rangle) = a(B\,|\psi\rangle)$

Important sentences II

- when $|\psi_1\rangle$ and $|\psi_2\rangle$ are two eigenvectors of A with different eigenvalues, then matrix elements $\langle\psi_1|A|\psi_2\rangle = 0$ as $|\psi_1\rangle$ and $|\psi_2\rangle$ are orthogonal each other, $\langle\psi_1|\psi_2\rangle = 0$. It means, in bases of its eigenvectors, the operator A is diagonal. When $[A, B] = 0$, then also $\langle\psi_1|B|\psi_2\rangle = 0$.
  Proof 1: as follow from sentence above, when $[A, B] = 0$, then $B\,|\psi_2\rangle$ is eigenvector of A with eigenvalue a_2; $A\,|\psi_2\rangle = a_2\,|\psi_2\rangle$. However, as eigenvalues $a_1 \neq a_2$, hence $|\psi_1\rangle$ is perpendicular to $|\psi_2\rangle$ and hence $\langle\psi_1|B|\psi_2\rangle = 0$.
  Proof 2: $[A, B] = 0$; hence $\langle\psi_1|[AB - BA]|\psi_2\rangle = 0$. As follow for Hermitian operators, we can write

$$\langle\psi_1|AB|\psi_2\rangle = a_1\,\langle\psi_1|B|\psi_2\rangle$$
$$\langle\psi_1|BA|\psi_2\rangle = a_2\,\langle\psi_1|B|\psi_2\rangle$$

  Hence, $(a_1 - a_2)\,\langle\psi_1|B|\psi_2\rangle = 0$. As $a_1 - a_2 \neq 0$ then $\langle\psi_1|B|\psi_2\rangle = 0$.

Dirac approach in quantum mechanics: representation

- To choose representation means to choose orthonormal bases (discrete $|u_i\rangle$ or continuous $|w_\alpha\rangle$).
- When $|\psi\rangle$ is expressed in a given representation, than its meaning is a vector.

$$|\psi\rangle = \sum_i c_i |u_i\rangle \qquad |\psi\rangle = \int \mathrm{d}\alpha c(\alpha) |w_\alpha\rangle$$

- Selection of representation is arbitrary but well chosen representation simplifies calculations.

Dirac approach in quantum mechanics: bases

- Orthonormal relation: set of ket-vectors is orthonormal when $\langle u_i|u_j\rangle = \delta_{ij}$ or $\langle w_\alpha|w_{\alpha'}\rangle = \delta(\alpha - \alpha')$
- Closing relation *(relace uzavření)*: $|u_i\rangle$ or $|w_\alpha\rangle$ makes base when any ket-vector $|\psi\rangle$ belonging to $\mathcal{E}$, i.e.

$$|\psi\rangle = \sum_i c_i |u_i\rangle \qquad |\psi\rangle = \int \mathrm{d}\alpha c(\alpha) |w_\alpha\rangle$$

- Then, the components of vectors are:

$$c_j = \langle u_j|\psi\rangle \qquad c(\alpha) = \langle w_\alpha|\psi\rangle$$

- discrete:

$$|\psi\rangle = \sum_i c_i |u_i\rangle = \sum_i \langle u_i|\psi\rangle |u_i\rangle = \left(\sum_i |u_i\rangle \langle u_i|\right) |\psi\rangle$$

continuous: $|\psi\rangle = \int \langle w_\alpha|\psi\rangle |w_\alpha\rangle = \left(\int \mathrm{d}\alpha |w_\alpha\rangle \langle w_\alpha|\right) |\psi\rangle$

Matrix representation of ket- and bra-vector

- Ket-vector representation

$$|\psi\rangle = \begin{bmatrix} \langle u_1|\psi\rangle \\ \langle u_2|\psi\rangle \\ \vdots \langle u_i|\psi\rangle \\ \vdots \end{bmatrix}$$

- Bra-vector representation

$$\langle\varphi| = \left[\langle\varphi|u_1\rangle, \langle\varphi|u_2\rangle \ldots \langle\varphi|u_i\rangle \ldots\right]$$

- Operator representation is a matrix $A = A_{ij}$, with components $A_{ij} = \langle u_i|A|u_j\rangle$

Properties of representations: change of representation

Change of representation: from old representation $|u_i\rangle$ to new $|t_k\rangle$.

- Then transformation matrix is $S_{ik} = \langle u_i|t_k\rangle$.
- S_{ik} is unitary ($S^\dagger S = SS^\dagger = I$), I being identity matrix (*jednotková matice*): Proof:
  $(SS^\dagger)_{kl} = \sum_i S^\dagger_{ki} S_{il} = \sum_i \langle t_k|u_i\rangle \langle u_i|t_l\rangle = \langle t_k|t_l\rangle = \delta_{kl}$

Transformation of elements of the vector/matrix:

- vector transformation:
  $\langle\psi|t_k\rangle = \langle\psi|I|t_k\rangle = \sum_i \langle\psi|u_i\rangle \langle u_i|t_k\rangle = \sum_i \psi|u_i S_{ik}$
- matrix transformation: $A_{kl} = \langle t_k|A|t_l\rangle =$
  $\sum_{i,j} \langle t_k|u_i\rangle \langle u_i|A|u_j\rangle \langle u_j|t_l\rangle = \sum_{ij} S^\dagger_{ki} A_{ij} S_{jl}$

Properties of representations: eigenstates

Eigenstates $|\psi_n\rangle$ and related eigenvalues λ_n of an operator A are

$$A\,|\psi_n\rangle = \lambda_n\,|\psi_n\rangle$$

- ψ_i, λ_i can be multiplied by any complex constant.
- solution of eigenvectors related with one eigenvalue can be subspace.
- when ket-vectors and operator written as matrix, than eigenvalue equation becomes also matrix one: $\sum_j (A_{ij} - \lambda\delta_{ij})c_j = 0$, where $c_j = \langle u_j|\psi\rangle$ and $A_{ij} = \langle u_i|A|u_j\rangle$

Example of representations: $|\vec{r}\rangle$, $|\vec{p}\rangle$ I

a) bases of representations $|\vec{r}\rangle$, $|\vec{p}\rangle$ are

$$\xi_{\vec{r_0}}(\vec{r}) = \delta(\vec{r} - \vec{r_0})$$

$$\nu_{\vec{p_0}}(\vec{r}) = (2\pi\hbar)^{-3/2} \exp[\frac{i}{\hbar}\vec{p_0} \cdot \vec{r}]$$

b) relation of orthonormalization

Let us calculate scalar multiplication

$$\langle \vec{r_0} | \vec{r_0'} \rangle = \int \mathrm{d}^3\vec{r}\ \xi^*_{\vec{r_0}}(\vec{r}) \xi_{\vec{r_0'}}(\vec{r}) = \delta(\vec{r_0} - \vec{r_0'})$$

$$\langle \vec{p_0} | \vec{p_0'} \rangle = \int \mathrm{d}^3\vec{r}\ \nu^*_{\vec{p_0}}(\vec{r}) \nu_{\vec{p_0'}}(\vec{r}) = \delta(\vec{p_0} - \vec{p_0'})$$

Example of representations: $|\vec{r}\rangle$, $|\vec{p}\rangle$ II

c) elements of ket-vectors Ket-vectors can be written as:

$$|\psi\rangle = \int \mathrm{d}^3\vec{r_0} \;\; |\vec{r_0}\rangle \langle\vec{r_0}|\psi\rangle$$

$$|\psi\rangle = \int \mathrm{d}^3\vec{p_0} \;\; |\vec{p_0}\rangle \langle\vec{p_0}|\psi\rangle$$

And their components are:

$$\langle\vec{r_0}|\psi\rangle = \int \mathrm{d}^3\vec{r}\; \xi^*_{\vec{r_0}}(\vec{r})\psi(\vec{r}) = \int \mathrm{d}^3\vec{r}\delta(\vec{r}-\vec{r_0})\psi(\vec{r}) = \psi(\vec{r_0})$$

$$\begin{aligned}\langle\vec{p_0}|\psi\rangle &= \int \mathrm{d}^3\vec{r}\; \nu^*_{\vec{p_0}}(\vec{r})\psi(\vec{r}) = \int \mathrm{d}^3\vec{r}\; (2\pi\hbar)^{-3/2} \exp[\frac{-i}{\hbar}\vec{p_0}\cdot\vec{r}]\psi(\vec{r}) \\ &= \mathrm{F.T.}(\psi(\vec{r})) = \overline{\psi(\vec{p_0})}\end{aligned}$$

I.e. components $|\psi\rangle$ written in two different representations, $|\vec{r}\rangle$, $|\vec{p}\rangle$.

Example of representations: $|\vec{r}\rangle$, $|\vec{p}\rangle$ III

d) scalar multiplication: example for $|\psi\rangle = |\vec{p_0}\rangle$

$$\langle \vec{r_0}|\vec{p_0}\rangle = \int \mathrm{d}^3\vec{r}\ \delta(\vec{r}-\vec{r_0})(2\pi\hbar)^{-3/2}\exp[\frac{i}{\hbar}\vec{p_0}\cdot\vec{r}]$$
$$= (2\pi\hbar)^{-3/2}\exp[\frac{i}{\hbar}\vec{p_0}\cdot\vec{r_0}]$$

e) transition from representation $|\vec{r}\rangle$ to $|\vec{p}\rangle$:

$$\psi(\vec{r}) = \langle\vec{r}|\psi\rangle = \int \mathrm{d}^3\vec{p}\ \langle\vec{r}|\vec{p}\rangle\langle\vec{p}|\psi\rangle$$
$$= (2\pi\hbar)^{-3/2}\int \mathrm{d}^3\vec{p}\ \exp[\frac{i}{\hbar}\vec{p}\cdot\vec{r}]\overline{\psi(\vec{p})}$$

Similarly for matrix elements of operator A written in $|\vec{p}\rangle$ bases:

$$\langle\vec{p'}|A|\vec{p}\rangle = (2\pi\hbar)^{-3}\int \mathrm{d}^3r\ \int \mathrm{d}^3r'\ \exp[\frac{i}{\hbar}(\vec{p}\cdot\vec{r}-\vec{p'}\cdot\vec{r'})]A(r,r')$$

Wave function as a sum

Note: following cases are used when wavefunction is expressed as sum of other wavefunctions

- evolution of quantum system (such as quantum packet) as a sum of eigenmodes

$$\psi(\vec{r},t) = \sum_i c_i \psi_i(\vec{r}) \exp[-i\omega t]$$

  Here, $\psi_i(\vec{r})$ are different stationary solutions (eigenmodes) with a general different energy

- expressing unknown (*stationary*) solution of Schrodinger equation $\hat{H}\psi_j = E_j\psi_j$, where I search form of ψ as a sum of chosen base-functions ψ_i; $\psi_j(\vec{r}) = \sum_i c_{ji}\psi_i(\vec{r})$

Postulates of quantum system I:

Postulate 1: Description of quantum state:
In a give time t_0, the physical state is described by ket-vector $|\psi(t_0)\rangle$.

Postulate 2: Description of physical variables:
Each measurable physical variable $\mathcal{A}$ is described by operator A. This operator is *observable* (i.e. Hermitian).

- Notice a fundamental difference between quantum and classical system: quantum state of system is described by vector $|\psi\rangle$, and physical variable by an operator A.

Postulates of quantum system II:

Postulate 3: Measurements of physical variables:
Measurement of physical variable $\mathcal{A}$ can give only results being eigenvalues of a given observable (Hermitian) operator A

- measurement of $\mathcal{A}$ provides *always* a real value a, as A (by definition) is Hermitian.
- if spectrum of A is discrete, then results of measurement of $\mathcal{A}$ is quantized, a_n.
- when A is observable, then any wavefunction can be written as sum of eigenstates $|u_n\rangle$ of operator A; $A\,|u_n\rangle = a_n\,|u_n\rangle$

$$|\psi\rangle = \sum_n |u_n\rangle\,\langle u_n|\psi\rangle = \sum_n c_n\,|u_n\rangle$$

Strictly speaking, this defines which Hermitian operators are also observable operators.

Postulates of quantum system III:

Postulate 4: Probability of measurements:
When physical variable $\mathcal{A}$ is measured by (normalized) wavefunction ψ, the probability to obtain non-degenerated eigenvalue a_n of corresponding observable operator A

$$P(a_n) = |c_n|^2 = |\langle u_n|\psi\rangle|^2$$

where u_n is (normalized) eigenvector of of observable operator A corresponding to eigenstate a_n; $A|u_n\rangle = a_n|u_n\rangle$

- in case a_n is degenerate (i.e. several wavefunctions $|u_n^i\rangle$ have equal eigenvalue a_n; $A|u_n^i\rangle = a_n|u_n^i\rangle$), then

$$|\psi\rangle = \sum_n \sum_{i=1}^{g_n} c_n^i |u_n^i\rangle$$

where g_n is degeneration of the eigenvalue a_n. In this case, probability to measure variable $\mathcal{A}$ with value a_n is $P(a_n) = \sum_{i=1}^{g_n} |c_n^i|^2 = \sum_{i=1}^{g_n} |\langle u_n^i|\psi\rangle|^2$

Postulates of quantum system IV:

Postulate 5: Quantum state after the measurement:
When measuring physical variable $\mathcal{A}$ on system in state $|\psi\rangle$. When the measured value is a_n, then the quantum state just after measurement is

$$|\psi_n\rangle = \frac{P_n |\psi\rangle}{\sqrt{\langle\psi|P_n|\psi\rangle}} = \frac{\sum_{i=1}^{g_n} c_n^i |u_n^i\rangle}{\sqrt{\sum_{i=1}^{g_n} |c_n^i|^2}}$$

where P_n is projection to sub-space of wavefunctions, having eigenstates a_n, i.e. $P_n = \sum_{i=1}^{g_n} |u_n^i\rangle \langle u_n^i|$.
Discussion: We want to measure variable $\mathcal{A}$. When quantum state just before measurement is $|\psi\rangle$, then the measurement randomly provides one of the eigenvalues a_n, with probability given by postulate 4. When a_n is undegenerate, than state just after measurement is $|u_n\rangle$. When a_n is degenerate, then the state after the measurements is projection of $|\psi\rangle$ to subspace of eigenfunction having eigenstate a_n; $A|u_n^i\rangle = a_n |u_n^i\rangle$.

Postulates of quantum system V:

Postulate 6: Time evolution of quantum state:
The time evolution of wavefunction is given by Schrödinger equation

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\left|\psi(t)\right\rangle = H(t)\left|\psi(t)\right\rangle$$

where $H(t)$ is an observable operator related with total energy (so called Hamiltonian operator).

Interpretation of postulates I: mean value of observable A

When measuring many times variable $\mathcal{A}$ with incoming state $|\psi\rangle$, then mean value of A is $\langle\psi|A|\psi\rangle = \langle A\rangle_\psi$.

Proof: (for discrete spectrum) Let us make N measurements. Then value a_n is measured $N(a_n) = NP(a_n)$ times.
Mean value of measured value is

$$\langle A\rangle_\psi = \sum_n a_n \frac{N(a_n)}{N} = \sum_n a_n P(a_n) = \sum_n a_n \sum_{i=1}^{g_n} \langle\psi|u_n\rangle \langle u_n|\psi\rangle$$

As $A|u_n^i\rangle = a_n|u_n^i\rangle$, then

$$\begin{aligned}\langle A\rangle_\psi &= \sum_n \sum_{i=1}^{g_n} \langle\psi|A|u_n\rangle \langle u_n|\psi\rangle = \langle\psi|A| \left[\sum_n \sum_{i=1}^{g_n} ||u_n\rangle \langle u_n|\right] |\psi\rangle \\ &= \langle\psi|A|\psi\rangle\end{aligned}$$

as term in square parentheses is unity, as $|u_n^i\rangle$ is complete orthonormal set of bases – closing relations (*relace uzavření*)

Interpretation of postulates II: time evolution of mean value

Time evolution of mean value is

$$\langle A \rangle (t) = \langle \psi(t) | A | \psi(t) \rangle$$

Time derivative $\langle A \rangle (t)$ is:

$$\begin{aligned}
&\frac{\mathrm{d}}{\mathrm{d}t} \langle \psi(t) | A | \psi(t) \rangle \\
&= \left[\frac{\mathrm{d}}{\mathrm{d}t} \langle \psi(t) | \right] |A| \psi(t) \rangle + \langle \psi(t) | A | \left[\frac{\mathrm{d}}{\mathrm{d}t} |\psi(t) \rangle \right] + \langle \psi(t) | \frac{\partial A}{\partial t} | \psi(t) \rangle \\
&= \frac{1}{i\hbar} \langle \psi(t) | AH - HA | \psi(t) \rangle + \langle \psi(t) | \frac{\partial A}{\partial t} | \psi(t) \rangle \\
&= \frac{1}{i\hbar} \langle [A, H] \rangle + \langle \frac{\partial A}{\partial t} \rangle
\end{aligned}$$

I.e. when A commute with Hamiltonian, and both are implicitly independent on time, than mean value of A is not changing with time – so called constants of movement (*konstanty pohybu*).

Ehrenfest theorem

Let us assume spin-less particle, $H = \frac{\mathbf{P}^2}{2m} + V(\mathbf{R})$, where $\mathbf{R}$, $\mathbf{P}$ are operators of momentum and position, respectively. Then,

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\mathbf{R}\rangle = \frac{1}{i\hbar}\langle[\mathbf{R}, H]\rangle = \frac{1}{i\hbar}\langle[\mathbf{R}, \frac{\mathbf{P}^2}{2m}]\rangle = \frac{1}{m}\langle\mathbf{P}\rangle$$
$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\mathbf{P}\rangle = \frac{1}{i\hbar}\langle[\mathbf{P}, H]\rangle = \frac{1}{i\hbar}\langle[\mathbf{P}, V(\mathbf{R})]\rangle = -\langle\nabla V(\mathbf{R})\rangle$$

Which are analogue of classical particle description.
Where commutators writes:

$$\left[\mathbf{R}, \frac{\mathbf{P}^2}{2m}\right] = \frac{i\hbar}{m}\mathbf{P}$$
$$[\mathbf{P}, V(\mathbf{R})] = -i\hbar\nabla V(\mathbf{R})$$

To derive, use entity $[A, BC] = [A, B]C + B[A, C]$

Properties of commutator $[A, B]$

Commutator $[A, B] = AB - BA$

- $[A, B] = -[B, A]$
- $[A, B + C] = [A, B] + [A, C]$
- $[A, BC] = [A, B]C + B[A, C]$
- $[A, B]^\dagger = [B^\dagger, A^\dagger]$
- $[A, [B, C]] + [B, [C, A]] + [C, [A, B]] = 0$

Key commutator relation:

$$[X_i, P_j] = i\hbar\delta_{ij}$$

Outline

- Non-relativistic description of angular momentum
- Schrödinger equation
- Addition of angular momentum
- Zeeman effect: angular moment in magnetic field
- Magnetism and relativity: classical picture
- Dirac equation

Quantum description of electron and its spin

Spin of particles (spin of electron):

- Consequence of relativity, but can be postulated as particle property.
- Electron (and also proton, neutron) has quantized spin $s = \frac{1}{2}$.

In following, we first postulate existence of spin. Then, we show how spin originates from relativistic quantum theory.

Angular momentum I

Total angular momentum = orbital angular momentum + spin angular momentum
Non-relativistic Schrödinger equation does not have spin (only angular momentum) $\Rightarrow$ spin can be included *ad-hoc*.
Definition of angular momentum

$$\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}} = \frac{\hbar}{i} \hat{\mathbf{r}} \times \nabla \tag{1}$$

Commutation relations of angular momentum operator:

$$[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z \qquad [\hat{L}_y, \hat{L}_z] = i\hbar \hat{L}_x \tag{2}$$

$$[\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y \qquad [\hat{\mathbf{L}}^2, \hat{L}_i] = 0 \tag{3}$$

where $L^2 = L_x^2 + L_y^2 + L_z^2$ and

$$[\hat{L}_x, \hat{y}] = -[\hat{L}_y, \hat{x}] = i\hbar \hat{z} \qquad [\hat{L}_x, \hat{p}_y] = -[\hat{L}_y, \hat{p}_x] = i\hbar \hat{p}_z \tag{4}$$

$$[\hat{L}_x, \hat{x}] = [\hat{L}_x, \hat{p}_x] = 0 \tag{5}$$

Example of determining commutators between angular momenta

E.g.

$$[L_x, L_y] = [(YP_z - ZP_y), (ZP_x - XP_Z)] = Y[P_z, Z]P_x + XP_Y[Z, P_Z]$$
$$= i\hbar(-YP_x + XP_y) = i\hbar L_z$$

Angular and spin momentum II

- Spin in non-relativistic description: intrinsic property of the electron

$\Rightarrow$ can not be defined similar to Eq. (1)

$\Rightarrow$ spin is defined as quantity obeying the same commutation equations as $\hat{\mathbf{L}}$.

- Total angular momentum

$$\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}} \tag{6}$$

where $\hat{\mathbf{J}}$ obeys equal commutation relation.

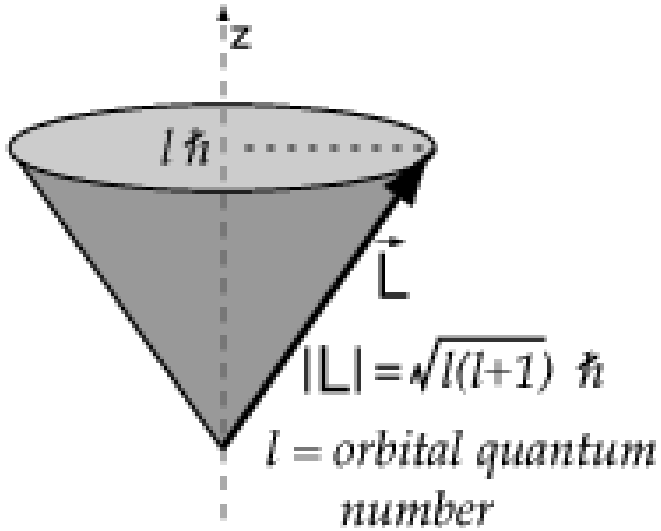
Angular momentum III: eigenvalues

Total angular momentum eigenvalues:

$$|\hat{\mathbf{J}}^2|j, m_j\rangle = j(j+1)\hbar^2 |j, m_j\rangle \quad (7)$$

$$|\hat{J}_z|j, m_j\rangle = m_j\hbar |j, m_j\rangle \quad (8)$$

where $-j \leq m_j \leq j$.



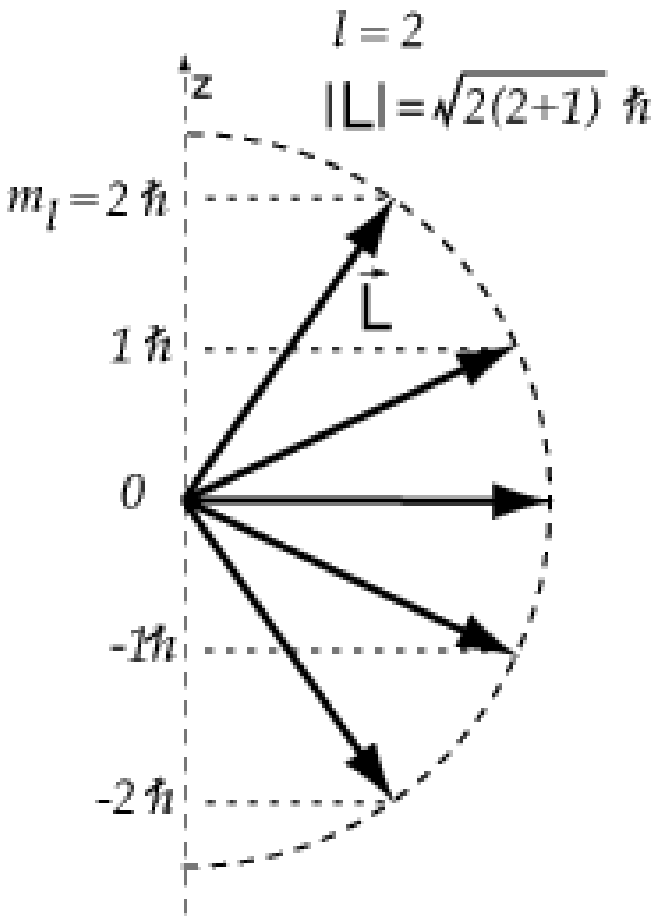
http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/vecmod.html

Angular momentum IV: length of momentum

- Maximum value of J in z-direction is $|m_j| = j$
- However, length of J is $\sqrt{j(j+1)}$

$\Rightarrow$ angular momentum can never points exactly in z (or in any other) direction

- classical limit: $j \to \infty$



http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/vecmod.html

Angular momentum V: raising/lowering operators

Lowering/raising operators:

$$\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y$$

- $J_+J_- = J_x^2 + J_y^2 + \hbar J_z = J^2 - J_z^2 + \hbar J_z$
- $J_-J_+ = J_x^2 + J_y^2 - \hbar J_z = J^2 - J_z^2 - \hbar J_z$
- $[J_z, J_+] = +\hbar J_+$
- $[J_z, J_-] = -\hbar J_-$
- $[J_+, J_-] = 2\hbar J_z$
- $[J^2, J_+] = [J^2, J_-] = [J^2, J_z] = 0$

Angular momentum V: raising/lowering operators

- value of m_j can be increased/decreased by raising/lowering operator $\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y$, working as

$$|\hat{J}_+|j, m_j\rangle = \hbar\sqrt{(j - m_j)(j + m_j + 1)}\,|j, m_j + 1\rangle$$

$$|\hat{J}_-|j, m_j\rangle = \hbar\sqrt{(j + m_j)(j - m_j + 1)}\,|j, m_j - 1\rangle$$

- Can be derived by two steps:
  - Apply $\hat{J}_\pm$ to eigenstate $|j, m_j\rangle$ (by using commutator relations):

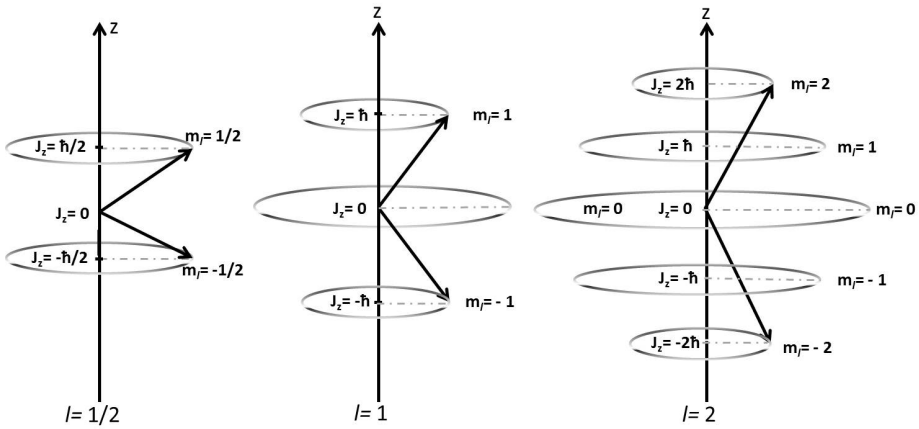
$$|\hat{J}_z\hat{J}_\pm|j, m_j\rangle = |\hat{J}_\pm\hat{J}_z + [\hat{J}_z, \hat{J}_\pm]|j, m_j\rangle = |\hat{J}_\pm\hat{J}_z + \hbar J_\pm|j, m_j\rangle =$$

$$(m_j \pm 1)\hbar\,|\hat{J}_\pm|j, m_j\rangle = (m_j \pm 1)\hbar\,|j, m_j \pm 1\rangle = |\hat{J}_z|j, m_j \pm 1\rangle$$

  - $|\,|J_+|j, m_j\rangle\,|^2 = \langle j, m_j|J_-J_+|j, m_j\rangle =$
    $\langle j, m_j|J^2 - J_z^2 - \hbar J_z|j, m_j\rangle = \hbar^2[j(j+1) - m_j(m_j+1)]$
    $\Rightarrow |J_+|j, m_j\rangle = \hbar\sqrt{j(j+1) - m_j(m_j+1)}\,|j, m_j\rangle =$
    $\hbar\sqrt{(j - m_j)(j + m_j + 1)}\,|j, m_j\rangle$

Angular momentum VI: particles with moment $s = 1/2$

The same valid for spin $j \to s = \frac{1}{2}$, $-s \leq m_s \leq s \Rightarrow m_s = 1/2$: spin-up spin ($\uparrow$); $m_s = -1/2$: spin-down spin ($\downarrow$)



http://chemwiki.ucdavis.edu/Physical_Chemistry/Spectroscopy/

Non-relativistic Schrödinger equation

$$i\hbar\frac{\partial\psi_r(\vec{r},t)}{\partial t} = \frac{1}{2m}\left[\left(\frac{\hbar}{i}\nabla - e\vec{A}(\vec{r},t)\right)^2 + e\Phi(\vec{r},t)\right]\psi_r(\vec{r},t) \quad (9)$$

$$i\hbar\frac{\partial\psi_r(\vec{r},t)}{\partial t} = \hat{H}\psi_r(\vec{r},t) \quad (10)$$

where

- $A(\vec{r},t)$ is the vector potential ($\vec{B} = \nabla \times \vec{A}$)
- $e\Phi(\vec{r},t)$ is the scalar potential ($\vec{E} = -\nabla\Phi - \frac{\partial\vec{A}}{\partial t}$)

Schrödinger equation with spin

Spin can be superimposed into Schödinger equation by product of time-space dependent part $\psi_r(\vec{r},t)$ and spin-dependent part $\chi_s^{m_s}$

$$\psi_s^{m_s} = \psi_r(\vec{r},t)\chi_s^{m_s} \tag{11}$$

However, this is only valid when spin-freedom is strictly independent on its time-space part. This is not valid for e.g. spin-orbit coupling. Then, one can express spin-time-space wavefunction as

$$\psi(\vec{r},t) = c_\uparrow\psi_{r,\uparrow}(\vec{r},t)+c_\downarrow\psi_{r,\downarrow}(\vec{r},t) \equiv \begin{pmatrix} c_\uparrow\psi_{r,\uparrow}(\vec{r},t) \\ c_\downarrow\psi_{r,\downarrow}(\vec{r},t) \end{pmatrix} \approx \begin{pmatrix} c_\uparrow \\ c_\downarrow \end{pmatrix} \psi_r(\vec{r},t) \tag{12}$$

where following eigenvectors were used for definition

$$\chi_\uparrow = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \chi_\downarrow = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{13}$$

Pauli matrices I

Now, we have spin-dependent part of the wavefunction $\chi_{\uparrow/\downarrow}$. The spin operators $\hat{\mathbf{S}}$ (equivalent of angular momentum operators $\hat{\mathbf{L}}$) are

$$\hat{S}_x = \frac{\hbar}{2}\tilde{\sigma}_x \qquad \hat{S}_y = \frac{\hbar}{2}\tilde{\sigma}_y \qquad \hat{S}_z = \frac{\hbar}{2}\tilde{\sigma}_z \tag{14}$$

where $\tilde{\sigma}_{x/y/z}$ are Pauli matrices

$$\tilde{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \tilde{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \tilde{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{15}$$

Pauli matrices: example

- Value of S_x for $\psi = |\uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$:

$$\langle\psi|\hat{S}_x|\psi\rangle = \frac{\hbar}{2}\begin{pmatrix} 1 \\ 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = 0 \tag{16}$$

- Value of S_x for $\psi = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$:

$$\langle\psi|\hat{S}_x|\psi\rangle = \frac{\hbar}{2}\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{\hbar}{2} \tag{17}$$

- Value of S_x for $\psi = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \end{pmatrix}$:

$$\langle\psi|\hat{S}_x|\psi\rangle = \frac{\hbar}{2}\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -i \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ i \end{pmatrix} = 0 \tag{18}$$

Pauli matrices II

Properties of Pauli matrices

- $\tilde{\sigma}_k^2 = \mathbf{1}, \qquad \text{where} \quad k = \{x, y, z\}$
- $\tilde{\sigma}_x \tilde{\sigma}_y + \tilde{\sigma}_y \tilde{\sigma}_x = 0$ etc. for others subscripts
- $\tilde{\sigma}_x \tilde{\sigma}_y - \tilde{\sigma}_y \tilde{\sigma}_x = -2i\tilde{\sigma}_z$ etc. for others subscripts
- raising operator: $\hat{S}_+ = \hat{S}_x + i\hat{S}_y = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$
- lowering operator: $\hat{S}_- = \hat{S}_x - i\hat{S}_y = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$

Pauli matrices III: eigenvalues and eigenvectors

Properties of Pauli matrices

- eigenvector and eigenvalues of $\hat{S}_z$:
  - $\hat{S}_z\chi_\uparrow = \frac{\hbar}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} = \frac{\hbar}{2}\chi_\uparrow$
  - $\hat{S}_z\chi_\downarrow = \frac{\hbar}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix} = -\frac{\hbar}{2}\chi_\downarrow$
  - in another words
    $\langle\chi_{\uparrow/\downarrow}|\hat{\mathbf{S}}_z|\chi_{\uparrow/\downarrow}\rangle = \hbar\langle\chi_{\uparrow/\downarrow}|m_\pm|\chi_{\uparrow/\downarrow}\rangle = \hbar m_\pm = \pm\hbar/2$
- eigenvector and eigenvalue of $\hat{\mathbf{S}}^2$:
  - $\hat{\mathbf{S}}^2\chi_{\uparrow/\downarrow} = (\hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2)\chi_{\uparrow/\downarrow} = \frac{3}{4}\hbar^2\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}\chi_{\uparrow/\downarrow} =$
    $\frac{3}{4}\hbar^2\chi_{\uparrow/\downarrow} = s(s+1)\hbar^2\chi_{\uparrow/\downarrow}$, where $s = 1/2$.
  - in another words:
    $\langle\chi_{\uparrow/\downarrow}|\hat{\mathbf{S}}^2|\chi_{\uparrow/\downarrow}\rangle = \hbar^2\langle\chi_{\uparrow/\downarrow}|s(s+1)|\chi_{\uparrow/\downarrow}\rangle = \hbar^2 s(s+1) = \frac{3\hbar^2}{4}$

Pauli matrices IV: derivation of $\hat{S}_x$, $\hat{S}_y$

- $\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y$
  $\Rightarrow \hat{J}_x = (\hat{J}_+ + \hat{J}_-)/2,\ \hat{J}_y = (\hat{J}_+ - \hat{J}_-)/(2i)$
- $\hat{J}_x \left|\chi_j^m\right\rangle = (\hat{J}_+ + \hat{J}_-) \left|\chi_j^m\right\rangle =$
  $\frac{1}{2}\hbar\sqrt{j(j+1) - m(m+1)}\left|\chi_j^{m+1}\right\rangle +$
  $\frac{1}{2}\hbar\sqrt{j(j+1) - m(m-1)}\left|\chi_j^{m-1}\right\rangle$
- using this equation, the $\hat{S}_x = \frac{\hbar}{2}\tilde{\sigma}_x$ can be constructed

	1/2,1/2>	1/2,-1/2>
<1/2,1/2	0	1/2
<1/2,-1/2	1/2	0

= <Ix>

and hence Pauli matrix $\tilde{\sigma}_x$ derived.

Addition of angular momentum I

Let us assume two angular momenta $\vec{L}$ and $\vec{S}$ (but can be also $\vec{J}_1$ and $\vec{J}_2$). Then, we ask about eigenvector and eigenvalues of summation

$$\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}} \tag{19}$$

Commutation relations:

$$[\hat{\mathbf{J}}^2, \hat{\mathbf{L}}^2] = [\hat{\mathbf{J}}^2, \hat{\mathbf{S}}^2] = 0 \tag{20}$$

$$[\hat{J}_z, \hat{\mathbf{L}}^2] = [\hat{J}_z, \hat{\mathbf{S}}^2] = 0 \tag{21}$$

$$[\hat{S}_z, \hat{J}_z] = [\hat{L}_z, \hat{J}_z] = 0 \tag{22}$$

$$\hat{\mathbf{J}}^2 = \hat{\mathbf{L}}^2 + \hat{\mathbf{S}}^2 + 2\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \tag{23}$$

$$= \hat{\mathbf{L}}^2 + \hat{\mathbf{S}}^2 + 2\hat{L}_z\hat{S}_z + \hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+ \tag{24}$$

Addition of angular momentum II

- Proper vector (from bases of proper vector of $\vec{L}$ and $\vec{S}$):

$$|l, l_z\rangle \oplus |s, s_z\rangle = |l, s, l_z, s_z\rangle \tag{25}$$

  being eigenstates for operators $\hat{\mathbf{L}}^2$, $\hat{\mathbf{S}}^2$, $\hat{L}_z$, $\hat{S}_z$ (with eigenvalues ...$l(l+1)\hbar^2$ etc.); $\oplus$ being tonsorial multiplication.
- However, commutation relations also show, that operators $\hat{\mathbf{J}}^2$, $\hat{\mathbf{J}}_z$, $\hat{\mathbf{L}}^2$, $\hat{\mathbf{S}}^2$ commute with operators $\hat{\mathbf{L}}^2$, $\hat{\mathbf{S}}^2$, $\hat{L}_z$, $\hat{S}_z$ $\Rightarrow$ there must be possibility to write previous eigenvectors in a new base of eigenvectors, being eigenstates of $\hat{\mathbf{J}}^2$, $\hat{\mathbf{J}}_z$, $\hat{\mathbf{L}}^2$, $\hat{\mathbf{S}}^2$ operators, being $|J, M\rangle$.

Addition of angular momentum III: Clebsch-Gordon coefficients

- So we have two bases of eigenvectors, describing the same wavefunctions $\Rightarrow$ linear relation between them must exist

$$|J, M\rangle = \sum_{s_z=-s}^{s} \sum_{l_z=-l}^{l} |l, s, l_z, s_z\rangle \langle l, s, l_z, s_z|J, M\rangle \tag{26}$$

  where $\langle l, s, l_z, s_z|J, M\rangle$ are called Clebsch-Gordon coefficients. (Note: $|J, M\rangle$ should be named $|J, M, l, s\rangle$).
- Clebsch-Gordon coefficients $\langle l, s, l_z, s_z|J, M\rangle$ are non-zero when

$$M = l_z + s_z \tag{27}$$

$$|l - s| \leq J \leq l + s \tag{28}$$

Clebsch-Gordon coefficients: example I

$l = 1/2$, $s = 1/2$: **two spins**

- $M = 1$, $J = 1$

	$J = 1$
$\|\uparrow,\uparrow\rangle$	1

- $M = 0$, $J = \{1, 0\}$

	$J = 1$	$J = 0$
$\|\uparrow,\downarrow\rangle$	$\sqrt{1/2}$	$\sqrt{1/2}$
$\|\downarrow,\uparrow\rangle$	$\sqrt{1/2}$	$-\sqrt{1/2}$

- $M = -1$, $J = 1$

	$J = 1$
$\|\downarrow,\downarrow\rangle$	1

Clebsch-Gordon coefficients: example II

$l = 1$, $s = 1/2$: **spin + orbital angular momentum** $l = 1$

- $M = 3/2,\ J = 3/2$

	$J = 3/2$
$\|l_z = 1, \uparrow\rangle$	1

- $M = 1/2,\ J = \{3/2, 1/2\}$

	$J = 3/2$	$J = 1/2$
$\|l_z = 1, \downarrow\rangle$	$\sqrt{1/3}$	$\sqrt{2/3}$
$\|l_z = 0, \uparrow\rangle$	$\sqrt{2/3}$	$-\sqrt{1/3}$

- $M = -3/2,\ J = 3/2$

	$J = 3/2$
$\|l_z = -1, \downarrow\rangle$	1

Other symmetric coefficients writes:

$$\langle j_1 j_2; m_1 m_2 | j_1 j_2; j m \rangle = (-1)^{j - j_1 - j_2} \langle j_1 j_2; -m_1, -m_2 | j_1 j_2; j, -m \rangle$$

$$\langle j_1 j_2; m_1 m_2 | j_1 j_2; j m \rangle = (-1)^{j - j_1 - j_2} \langle j_2 j_1; m_2 m_1 | j_1 j_2; j m \rangle$$

Clebsch-Gordon coefficients: example III

$l = 2$, $s = \frac{1}{2}$: **spin + orbital angular momentum** $l = 2$

- $M = \frac{5}{2}$, $J = \frac{5}{2}$

	$J = \frac{5}{2}$
$\lvert l_z = 2, \uparrow\rangle$	1

- $M = \frac{3}{2}$, $J = \{\frac{5}{2}, \frac{3}{2}\}$

	$J = \frac{5}{2}$	$J = \frac{3}{2}$
$\lvert l_z = 2, \downarrow\rangle$	$\sqrt{\frac{1}{5}}$	$\sqrt{\frac{4}{5}}$
$\lvert l_z = 1, \uparrow\rangle$	$\sqrt{\frac{4}{5}}$	$-\sqrt{\frac{1}{5}}$

- $M = \frac{1}{2}$, $J = \{\frac{5}{2}, \frac{3}{2}\}$

	$J = \frac{5}{2}$	$J = \frac{3}{2}$
$\lvert l_z = 1, \downarrow\rangle$	$\sqrt{\frac{2}{5}}$	$\sqrt{\frac{3}{5}}$
$\lvert l_z = 0, \uparrow\rangle$	$\sqrt{\frac{3}{5}}$	$-\sqrt{\frac{2}{5}}$

- and $M = -\frac{1}{2}$, $M = -\frac{3}{2}$, $M = -\frac{5}{2}$ to be added accordingly

Zeeman effect

Splitting of energy levels by (external) magnetic field, due to Hamiltonian term $H_{\text{Zeeman}} = -\vec{\mu}_B \cdot \vec{B}$

1. splitting due to magnetic moment related with orbital angular momentum; odd number of lines, $l(l+1)$

$$\vec{\mu}_L = -\frac{\mu_B}{\hbar}\vec{L} = -g_L\frac{\mu_B}{\hbar}\vec{L} \tag{29}$$

   where $\mu_B = \frac{e\hbar}{2m_e}$ is Bohr magneton

2. splitting due to presence of spin of the electron (non-quantized electromagnetic field), atomic number Z is odd, even number of lines, $\uparrow, \downarrow$

$$\vec{\mu}_S = -2\frac{\mu_B}{\hbar}\vec{S} = -g_e\frac{\mu_B}{\hbar}\vec{S} \tag{30}$$

   (with quantized electromagnetic field, $2 \to 2.0023 = g_e$ for electron, so-called g-factor)

Zeeman effect in weak magnetic field I

Magnetic moment of total angular momentum is

$$\vec{\mu}_J = -g_J \frac{\mu_B}{\hbar} \vec{J} = -\frac{\mu_B}{\hbar}(g_L \vec{L} + g_S \vec{S}) \tag{31}$$

Hamiltonian's form assumes:

1. J commutes with remaining Hamiltonian terms (follows from central symmetry of atomic potential in case of atoms)
2. H_{Zeeman} is small and hence perturbation theory can be used (i.e. solution found in eigenstates of unperturbated Hamiltonian)

Then:

$$H_{\text{Zeeman}} = -\vec{\mu}_J \cdot \vec{B} = g_J \omega_{\text{Larmor}} J_z = \omega_{\text{Larmor}}(L_z + 2S_z) \tag{32}$$

where $\omega_{\text{Larmor}} = -\frac{\mu_B}{\hbar} B$ is the Larmor frequency

Zeeman effect in weak magnetic field II

Eigen-energy is found to be

$$E_{\text{Zeeman}} = g_J M \hbar \omega_{\text{Larmor}} \tag{33}$$

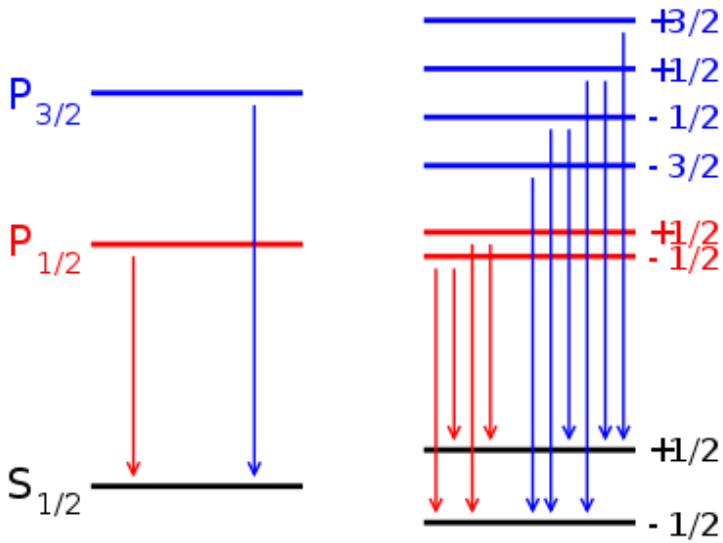
M being magnetic number and g-factor being

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} \tag{34}$$

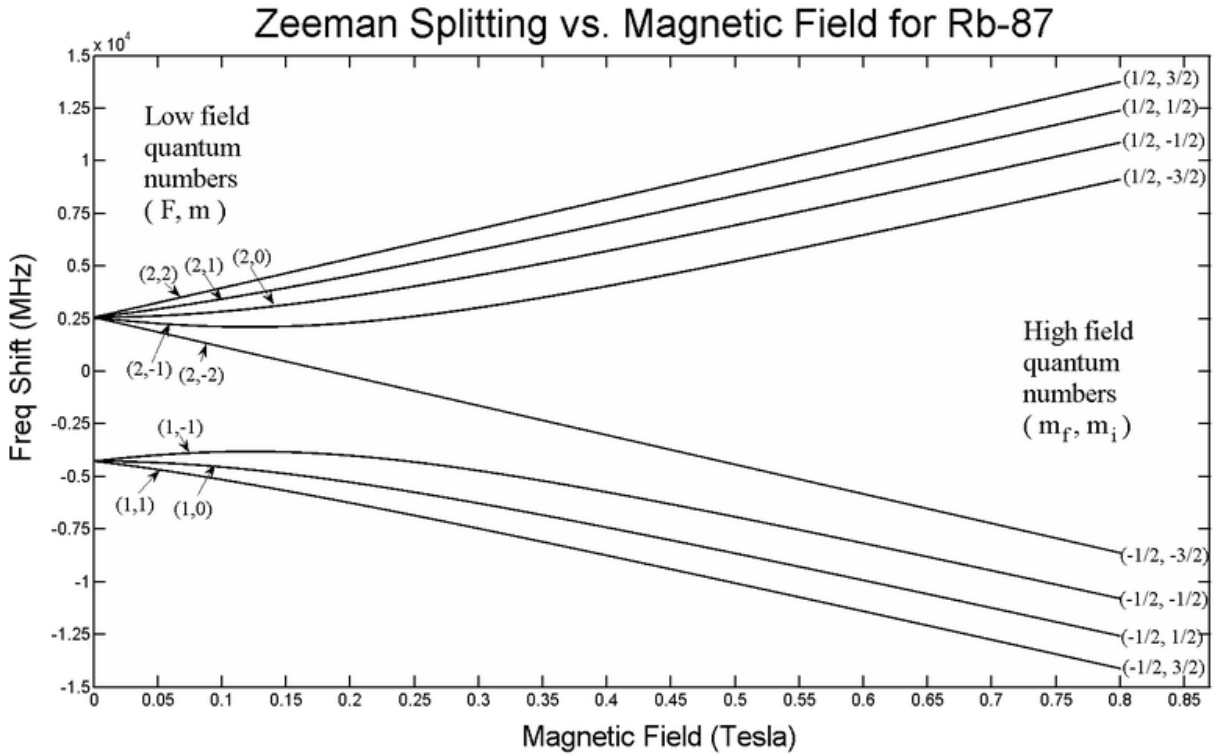
splitting into $2J + 1$ levels.

Zeeman effect: weak magnetic field

$E_{\mathrm{Zeeman}} = g_J M \hbar \omega_{\mathrm{Larmor}} \Rightarrow$
Splitting according total magnetic number M;
$-J \leq M \leq J$



Zeeman effect: strong magnetic field



In this example of Rubidium (^{87}Rb):

without field: splitting by total angular momentum F, where $\vec{F} = \vec{J} + \vec{I}$; I is nucleus momentum

weak field: splitting of F-levels by their magnetic numbers m_F

large field: splitting by magnetic numbers m_F, m_I

http://en.wikipedia.org/wiki/Zeeman_effect

Special relativity I

Postulates of special relativity:

1. No preferential coordinate system exists; there is no absolute speed of translation motion.
2. Speed of light is constant in vacuum, for any observer or any source motion.

Let's assume to have two coordinate systems (x, y, z, ict) and (x', y', z', ict')

1. moving by mutual speed v along x and x' axis
2. in time $t = t' = 0$, both system intersects, $x = x'$, $y = y'$, $z = z'$
3. in time $t = t' = 0$, light pulse is generated

Special relativity II: Lorentz transformation

Then:

- $y = y'$, $z = z'$ as movement only along x, x'
- for $x' = 0$, $x = vt$
- for $x = 0$, $x' = -vt'$
- both systems see light pulse as a ball propagating by speed of light having diameter ct, $ct' \Rightarrow$
  $x^2 + y^2 + z^2 - c^2t^2 = x'^2 + y'^2 + z'^2 - c^2t'^2 \Rightarrow$
  $x^2 - c^2t^2 = x'^2 - c^2t'^2$.

Solutions of those equations:

$$x' = \frac{x - vt}{\sqrt{1 - \frac{v^2}{c^2}}} \qquad x = \frac{x' + vt'}{\sqrt{1 - \frac{v^2}{c^2}}} \tag{35}$$

$$t' = \frac{t - x\frac{v}{c^2}}{\sqrt{1 - \frac{v^2}{c^2}}} \qquad t = \frac{t' + x'\frac{v}{c^2}}{\sqrt{1 - \frac{v^2}{c^2}}} \tag{36}$$

Special relativity III: Lorentz transformation as matrix

This can be written in form of 4-vector (for space-time coordinate) and Lorenz transformation is 4×4 matrix:

$$\begin{bmatrix} x' \\ y' \\ z' \\ ict' \end{bmatrix} = \begin{bmatrix} \frac{1}{\sqrt{1-\frac{v^2}{c^2}}} & 0 & 0 & \frac{i\frac{v}{c}}{\sqrt{1-\frac{v^2}{c^2}}} \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ -\frac{i\frac{v}{c}}{\sqrt{1-\frac{v^2}{c^2}}} & 0 & 0 & \frac{1}{\sqrt{1-\frac{v^2}{c^2}}} \end{bmatrix} \begin{bmatrix} x \\ y \\ z \\ ict \end{bmatrix} \tag{37}$$

Special relativity IV: 4-vectors and invariants I

Let us define a general 4-vector $A_\mu = [A_1, A_2, A_3, A_4]$, which transform under equal Lorentz transformation, $A'_\mu = a_{\mu\nu} A_\nu$. Then, it can be shown that scalar multiplication of two four-vectors, $A_\mu B_\mu$ is invariant, i.e. the same in all cartesian systems related by Lorentz transformations.

$\rightarrow$ **4-vector of space-time:** $x_\mu = [x, y, z, ict]$.

Space-time invariant: $x_\mu x_\mu = s^2 = x^2 + y^2 + z^2 - c^2 t^2$

proper time $\mathrm{d}\tau$ (or proper time interval)

$$\mathrm{d}\tau = \mathrm{d}t \sqrt{1 - \frac{V^2}{c^2}} = \mathrm{d}t' \sqrt{1 - \frac{V'^2}{c^2}} \tag{38}$$

where V, V' is speed of the particle in both coordinate systems.

Special relativity IV: 4-vectors and invariants II

→ **4-vector of speed:**

$$U_\mu = \frac{\mathrm{d}x_\mu}{\mathrm{d}\tau} = \frac{1}{\sqrt{1-\frac{v^2}{c^2}}} \begin{bmatrix} v_x \\ v_y \\ v_z \\ ic \end{bmatrix} \tag{39}$$

Speed invariant: $U_\mu U_\mu = -c^2$

Special relativity V: 4-vectors of linear momentum

$\rightarrow$ **4-vector of linear momentum:**

$$P_\mu = m_0 U_\mu \tag{40}$$

Then, linear momentum has form

$$P_\mu = \begin{bmatrix} \frac{m_0 v_x}{\sqrt{1-\frac{v^2}{c^2}}} \\ \frac{m_0 v_y}{\sqrt{1-\frac{v^2}{c^2}}} \\ \frac{m_0 v_z}{\sqrt{1-\frac{v^2}{c^2}}} \\ \frac{iW}{c} \end{bmatrix} \tag{41}$$

where $W = \frac{m_0 c^2}{\sqrt{1-\frac{v^2}{c^2}}} = m_0 c^2 + \frac{1}{2} m_0 v^2 + \cdots$ is a total particle energy.

Special relativity V: 4-vectors of linear momentum

- Linear momentum and energy of the particle are not independent, but as two pictures of the same quantity, as they are expressed by a components of single 4-vector
- Linear momentum invariant: $P_\mu P_\mu = -m_0^2 c^2 = \vec{p}^2 - W^2/c^2$
- Another expression of the total energy W:

$$W^2 = \vec{p}^2 c^2 + (m_0 c^2)^2 \tag{42}$$

being base of Dirac equation derived later.

Maxwell equations: 4-vector of current I

Conservation of charge: $\nabla \cdot \vec{J} + \frac{\mathrm{d}\rho}{\mathrm{d}t} = 0$
Rewritten into four-vector:

$$J_\mu = \begin{bmatrix} J_x \\ J_y \\ J_z \\ ic\rho \end{bmatrix} = \rho_0 U_\mu \tag{43}$$

where ρ_0 is charge density in rest system and then

$$\Box \cdot J_\mu = 0 \tag{44}$$

where $\Box$ is generalized Nabla operator,

$$\Box = \left[\frac{\mathrm{d}}{\mathrm{d}x}, \frac{\mathrm{d}}{\mathrm{d}y}, \frac{\mathrm{d}}{\mathrm{d}z}, \frac{\mathrm{d}}{\mathrm{d}(ict)} \right]^T \tag{45}$$

Maxwell equations: 4-vector of current II

Then transformation of the current 4-vector leads to (speed v along x-axis)

$$J'_x = \frac{J_x - v\rho}{\sqrt{1 - \frac{v^2}{c^2}}} \qquad J'_y = J_y \tag{46}$$

$$\rho' = \frac{\rho - \frac{v}{c^2} J_x}{\sqrt{1 - \frac{v^2}{c^2}}} \qquad J'_z = J_z \tag{47}$$

- for example, charge is increasing with increasing v
- for small speeds ($v \ll c$), $J'_x = J_x - v\rho$

Maxwell equations: 4-vector of potential I

Maxwell equations expressed by potentials $\vec{A}$ and Φ

$$\nabla^2 \vec{A} - \frac{1}{c^2}\frac{\partial^2 \vec{A}}{\partial^2 t} = -\mu \vec{J} \tag{48}$$

$$\nabla^2 \Phi - \frac{1}{c^2}\frac{\partial^2 \Phi}{\partial^2 t} = -\frac{\rho}{\epsilon} \tag{49}$$

$$\nabla \cdot \vec{A} + \frac{1}{c^2}\frac{\partial \Phi}{\partial t} = 0 \tag{50}$$

where $\vec{B} = \nabla \times \vec{A}$ and $\vec{E} = -\nabla\Phi - \frac{\partial \vec{A}}{\partial t}$

Maxwell equations: 4-vector of potential II

The potential-written Maxwell equations as 4-vector simply writes

$$\Box^2 A_\mu = -\mu J_\mu \tag{51}$$

where 4-vectors A_μ, J_μ are

$$A_\mu = \begin{bmatrix} A_x \\ A_y \\ A_z \\ \frac{i\Phi}{c} \end{bmatrix} \qquad J_\mu = \begin{bmatrix} J_x \\ J_y \\ J_z \\ ic\rho \end{bmatrix} \tag{52}$$

Maxwell equations and special relativity I

Relation between 4-vector potential A_μ and E, B field expressed by antisymmetric tensor $f_{\mu\nu}$

$$f_{\mu\nu} = \frac{\partial A_\nu}{\partial x_\mu} - \frac{\partial A_\mu}{\partial x_\nu} = \begin{bmatrix} 0 & B_z & -B_y & -\frac{iE_x}{c} \\ -B_z & 0 & B_x & -\frac{iE_y}{c} \\ B_y & -B_x & 0 & -\frac{iE_z}{c} \\ \frac{iE_x}{c} & \frac{iE_y}{c} & \frac{iE_z}{c} & 0 \end{bmatrix} \tag{53}$$

Then, using electromagnetic tensor $f_{\mu\nu}$, Maxwell equations are

$$\frac{\partial f_{\lambda\rho}}{\partial x_\nu} + \frac{\partial f_{\rho\nu}}{\partial x_\lambda} + \frac{\partial f_{\nu\lambda}}{\partial x_\rho} = 0 \qquad (\nabla \times \vec{E} = -\partial\vec{B}/\partial t, \quad \nabla \cdot \vec{B} = 0) \tag{54}$$

$$\sum_\nu \frac{\partial f_{\mu\nu}}{\partial x_\nu} = \mu_0 J_\mu \qquad (\nabla \times \vec{B} = \mu_0 \vec{J} + c^{-2}\partial\vec{E}/\partial t, \quad \nabla \cdot \vec{E} = \rho/\epsilon) \tag{55}$$

Maxwell equations and special relativity II

The Lorentz transformation for electromagnetic field are

$$\vec{E}'_{\parallel} = \vec{E}_{\parallel} \qquad \vec{B}'_{\parallel} = \vec{B}_{\parallel} \tag{56}$$

$$\vec{E}'_{\perp} = \frac{(\vec{E} + \vec{v} \times \vec{B})_{\perp}}{\sqrt{1 - \frac{v^2}{c^2}}} \qquad \vec{B}'_{\perp} = \frac{(\vec{B} - \vec{v}/c^2 \times \vec{E})_{\perp}}{\sqrt{1 - \frac{v^2}{c^2}}} \tag{57}$$

i.e. for small speeds, $\vec{E}' = \vec{E} + \vec{v} \times \vec{B}$ and $\vec{B}' = \vec{B}$

Klein-Gordon equation I

Description of relativistic spin-zero particle.
Relativistic theory expresses total energy of the particle as:

$$W^2 = p^2c^2 + m_0^2c^4 \tag{58}$$

Quantum operator substitution: $\vec{p} \to \hat{\mathbf{p}} = -i\hbar\nabla$,
$W \to \hat{W} = i\hbar\partial/\partial t$. It follows in Klein-Gordon equation

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \frac{m_0^2c^2}{\hbar^2}\right)\psi(\vec{r},t) = 0 \tag{59}$$

Derivation: $H = W = \sqrt{p^2c^2 + m_0^2c^4}$ and hence
$i\hbar\frac{\partial\psi}{\partial t} = \left(\sqrt{-\hbar^2c^2\nabla^2 + m^2c^4}\right)\psi$. Then, we make form
$(a + \sqrt{b})\psi = 0$, followed to $(a^2 - b)\psi = 0$

Klein-Gordon equation II

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \frac{m_0^2 c^2}{\hbar^2}\right)\psi(\vec{r},t) = 0 \tag{60}$$

This Eq. reduces to $W^2 = p^2c^2 + m_0^2c^4$ for plane wave (free particle) $\psi(\vec{r},t) = \exp[i(\vec{r}\cdot\vec{p} - Wt)/\hbar]$.

Klein-Gordon equation III

Reduction of Klein-Gordon equation to Schrodinger equation:
Classically, $W = E + m_0c^2$. Hence,
$\psi(\vec{r},t) = \psi(\vec{r},t)\exp[-iWt/\hbar] = \psi_0(\vec{r},t)\exp[-im_0c^2t/\hbar]$
Then, when substituted to Klein-Gordon, and $c \to \infty$, we get Schrodinger equation for free particle,

$$i\hbar\frac{\partial\psi_0(\vec{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi_0(\vec{r},t)$$

Klein-Gordon equation III

Note:
$W = \pm\sqrt{p^2c^2 + m_0^2c^4}$ has two solutions. Those solutions are interpreted as particle and antiparticle, separated by gap $2m_0c^2$

Dirac equation: introduction I

Lorentz transformation unites time and space $\Rightarrow$ relativistic quantum theory must do the same. Schrodinger equation does not fulfils this, as it it has first derivative in time and second in space.

1. Let as ASSUME, the Dirac equation will have first derivative in time. Then, it must be also in first derivative in space.
2. We want linear equations, for the principle of superposition.

Dirac equation: derivation I

As told above, let us assumed for Dirac equation:

1. linear in time and space derivatives
2. wave function is superposition of N base wavefunctions $\psi(\vec{r},t) = \sum \psi_n(\vec{r},t)$

General expression of condition 1:

$$\frac{1}{c}\frac{\partial \psi_i(\vec{r},t)}{\partial t} = -\sum_{d=x,y,z}\sum_{n=1}^{N} \alpha_{i,n}^{d}\frac{\partial \psi_n}{\partial d} - \frac{imc}{\hbar}\sum_{n=1}^{N}\beta_{i,n}\psi_n(\vec{r},t) \quad (61)$$

Dirac equation: II

When expressed in matrix form (ψ is column vector, $\alpha_{i,n}^k$ is $3 \times N \times N$ matrix, $\beta_{i,n}$ is $N \times N$ matrix)

$$\frac{1}{c}\frac{\partial\psi(\vec{r},t)}{\partial t} = -\tilde{\boldsymbol{\alpha}} \cdot \nabla\psi(\vec{r},t) - \frac{imc}{\hbar}\tilde{\beta}\psi(\vec{r},t) \tag{62}$$

Substituting quantum operators $\hat{\mathbf{p}} \to \hbar\nabla/i$, we get Dirac equation

$$i\hbar\frac{\partial\psi(\vec{r},t)}{\partial t} = \hat{H}\psi(\vec{r},t) = (c\tilde{\boldsymbol{\alpha}} \cdot \hat{\mathbf{p}} + \tilde{\beta}mc^2)\psi(\vec{r},t) \tag{63}$$

where matrices $\tilde{\alpha}$, $\tilde{\beta}$ are unknown.

Dirac equation: properties I

Comparing total energy of the particle between relativity and Dirac Hamiltonian

$$W = \sqrt{p^2c^2 + m^2c^4} = \boldsymbol{\alpha} \cdot \vec{p}c + \beta mc^2 \tag{64}$$

Calculating W^2, we obtain conditions on α and β

$$\alpha_x^2 = \alpha_y^2 = \alpha_z^2 = \beta^2 = 1 \tag{65}$$

$$\alpha\beta + \beta\alpha = 0 \tag{66}$$

$$\alpha_x\alpha_y + \alpha_y\alpha_x = \alpha_y\alpha_z + \alpha_z\alpha_y = \alpha_z\alpha_x + \alpha_x\alpha_z = 0 \tag{67}$$

No numbers can fulfils those conditions for α and β; but α, β can be matrices.

Dirac equation: properties II

$$\alpha_x^2 + \alpha_y^2 + \alpha_z^2 = \beta^2 = 1 \tag{68}$$

$$\alpha\beta + \beta\alpha = 0 \tag{69}$$

$$\alpha_x\alpha_y + \alpha_y\alpha_x = \alpha_y\alpha_z + \alpha_z\alpha_y = \alpha_z\alpha_x + \alpha_x\alpha_z = 0 \tag{70}$$

- We need four matrices, with (i) square is identity and (ii) which anti-commute each other.
- Three 2×2 Pauli matrices anticommute each other, but they are only three.

$\Rightarrow$ one must use matrices 4×4.

$\rightarrow$ several sets of those 4×4 can be found.

Dirac equation: Dirac matrices

One of the form of Dirac matrices α and β is

$$\tilde{\alpha}_x = \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} 0 & \tilde{\sigma}_x \\ \tilde{\sigma}_x & 0 \end{bmatrix} \qquad \tilde{\alpha}_y = \begin{bmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} 0 & \tilde{\sigma}_y \\ \tilde{\sigma}_y & 0 \end{bmatrix} \tag{71}$$

$$\tilde{\alpha}_z = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{bmatrix} = \begin{bmatrix} 0 & \tilde{\sigma}_z \\ \tilde{\sigma}_z & 0 \end{bmatrix} \qquad \tilde{\beta} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} \tilde{1} & 0 \\ 0 & \tilde{-1} \end{bmatrix} \tag{72}$$

Note: for any vectors $\vec{A}$ and $\vec{B}$:

$$\tilde{\boldsymbol{\alpha}} \cdot \vec{\boldsymbol{A}} \tilde{\boldsymbol{\alpha}} \cdot \vec{\boldsymbol{B}} = \vec{\boldsymbol{A}} \cdot \vec{\boldsymbol{B}} + i \tilde{\boldsymbol{\alpha}} \cdot (\vec{\boldsymbol{A}} \times \vec{\boldsymbol{B}}) \tag{73}$$

Dirac equation: non-relativistic limit I

Dirac equation in el.-mag. field ($\vec{E} = -\nabla\Phi(\vec{r}) = -\frac{1}{e}\nabla V(\vec{r})$):

$$i\hbar\frac{\partial\psi(\vec{r},t)}{\partial t} = \left(c\tilde{\alpha}\cdot\left(\frac{\hbar}{i}\nabla - e\vec{A}(\vec{r})\right) + \tilde{\beta}mc^2 + V(\vec{r})\right)\psi(\vec{r},t) \tag{74}$$

To take non-relativistic limit, we write

$$\psi(\vec{r},t) = \begin{bmatrix}\phi(\vec{r},t)\\ \chi(\vec{r},t)\end{bmatrix} \tag{75}$$

substituting $\tilde{\alpha}$ and $\tilde{\beta}$ from Eqs. (71-72)

$$i\hbar\frac{\partial}{\partial t}\begin{bmatrix}\phi(\vec{r},t)\\ \chi(\vec{r},t)\end{bmatrix} = \left(\frac{\hbar}{i}\nabla - e\vec{A}(\vec{r})\right)\cdot\tilde{\sigma}\begin{bmatrix}\chi(\vec{r},t)\\ \phi(\vec{r},t)\end{bmatrix} + \left(V(\vec{r}) \pm mc^2\right)\begin{bmatrix}\phi(\vec{r},t)\\ \chi(\vec{r},t)\end{bmatrix} \tag{76}$$

Dirac equation: non-relativistic limit II

Time dependence of $\psi(\vec{r},t)$:

$$\psi(\vec{r},t) = \psi(\vec{r})\exp[-iWt/\hbar] \approx \psi(\vec{r})\exp[-imc^2t/\hbar] \qquad (77)$$

which is valid for both components of $\psi(\vec{r},t)$.
Substituting this time derivative of $\chi(\vec{r},t)$ into lower Eq. (76) and ignoring small terms, we get relation between $\phi(\vec{r},t)$ and $\chi(\vec{r},t)$

$$\chi(\vec{r},t) = \frac{1}{2mc}\left(\frac{\hbar}{i}\nabla - e\vec{A}(\vec{r})\right)\cdot\tilde{\sigma}\phi(\vec{r},t) \qquad (78)$$

Hence, for small speeds ($\vec{p} = m\vec{v}$, and $v \ll c$), $\chi(\vec{r},t)$ is much smaller than $\phi(\vec{r},t)$ by factor about v/c.

Dirac equation: non-relativistic limit III

Substituting $\chi(\vec{r},t)$ from Eq. (78), into upper Eq. (76)

$$i\hbar\frac{\partial}{\partial t}\phi(\vec{r},t)=\frac{1}{2m}\left(\left(\frac{\hbar}{i}\nabla-e\vec{A}(\vec{r})\right)\cdot\tilde{\sigma}\right)^2\phi(\vec{r},t)+\left(V(\vec{r})+mc^2\right)\phi(\vec{r},t) \tag{79}$$

Using $\tilde{\sigma}\cdot\vec{A}\tilde{\sigma}\cdot\vec{B}=\vec{A}\cdot\vec{B}+i\tilde{\sigma}\cdot(\vec{A}\times\vec{B})$

$$\begin{aligned}\left(\left(\frac{\hbar}{i}\nabla-e\vec{A}(\vec{r})\right)\cdot\tilde{\sigma}\right)^2\phi&=\left(\frac{\hbar}{i}\nabla-e\vec{A}(\vec{r})\right)^2\phi-e\hbar\tilde{\sigma}\cdot(\nabla\times\vec{A}+\vec{A}\times\nabla)\phi\\&=\left(\frac{\hbar}{i}\nabla-e\vec{A}(\vec{r})\right)^2\phi-e\hbar\tilde{\sigma}\cdot\vec{B}\phi\end{aligned} \tag{80}$$

And it leads to (see next slide)

Dirac equation: non-relativistic limit IV

$$i\hbar\frac{\partial}{\partial t}\phi(\vec{r},t) = \left(\frac{1}{2m}\left(\frac{\hbar}{i}\nabla - e\vec{A}(\vec{r})\right)^2 - \frac{e\hbar}{2m_0}\tilde{\sigma}\cdot\vec{B} + V(\vec{r}) + mc^2\right)\phi(\vec{r},t \tag{81}$$

- Results is Pauli equation, introducing the spin!
- magnetic moment (of electron) is predicted to be $\mu = e\hbar/(2m)$
- although proton and neutron have also spin $1/2$, it does not predict their magnetic moment $\rightarrow$ problem is that they are composite particles.

Dirac equation: non-relativistic limit V

When Dirac equation is solved up to order $1/c^2$, we get

$$\hat{H} = \frac{1}{2m}\left(\frac{\hbar}{i}\nabla - e\vec{A}(\vec{r})\right)^2 + V(\vec{r}) + mc^2 \tag{82}$$

$$- \frac{e\hbar}{2m}\tilde{\sigma}\cdot\left(\hat{\mathbf{B}} + \frac{\vec{E}\times\hat{\mathbf{p}}}{mc^2}\right) \qquad \text{(Zeeman term in } \bar{e} \text{ rest frame)}$$

$$+ \frac{e}{2mc^2}\hat{\mathbf{S}}\cdot(\vec{E}\times\hat{\mathbf{v}}) \qquad \text{Spin} - \text{orbit coupling}$$

$$- \frac{1}{8m^3c^2}(\vec{p} - e\vec{A})^4 \qquad \text{Special relativity energy correction}$$

$$+ \frac{\hbar^2 e}{8m^2c^2}\nabla^2 V(\vec{r}) \qquad \text{Darwin term}$$

Darwin term: electron is not a point particle, but spread in volume of size of Compton length $\approx \hbar/mc$.

Free particle and antiparticle

Solving Dirac equation for free particle

$$\hat{\boldsymbol{H}} = \boldsymbol{c}\tilde{\boldsymbol{\alpha}} \cdot \hat{\mathbf{p}} + \tilde{\boldsymbol{\beta}}\boldsymbol{mc^2} \tag{83}$$

Solution of free particle ($U(\vec{p}$ has four dimensions)

$$\psi = U(\vec{p}) \exp[i(\vec{p} \cdot \vec{r} - Wt)/\hbar] \tag{84}$$

Substituting in Dirac equation Eq.(83), and assuming motion in xy plane ($p_z = 0$), we get

$$\begin{bmatrix} mc^2 - W & 0 & 0 & cp_- \\ 0 & mc^2 - W & cp_+ & 0 \\ 0 & cp_- & -mc^2 - W & 0 \\ cp_+ & 0 & 0 & -mc^2 - W \end{bmatrix} \begin{bmatrix} U_1 \\ U_2 \\ U_3 \\ U_4 \end{bmatrix} e^{i\vec{p}\cdot\vec{r}/\hbar} = 0 \tag{85}$$